**ENGINEERING DEVELOPMENT OF
CERAMIC MEMBRANE REACTOR SYSTEM
FOR CONVERTING NATURAL GAS TO HYDROGEN
AND SYNTHESIS GAS FOR
LIQUID TRANSPORTATION FUELS**

FINAL REPORT

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ABSTRACT

An Air Products-led team successfully developed ITM Syngas technology from the concept stage to a stage where a small-scale engineering prototype was about to be built. This technology produces syngas, a gas containing carbon monoxide and hydrogen, by reacting feed gas, primarily methane and steam, with oxygen that is supplied through an ion transport membrane. An ion transport membrane operates at high temperature and oxygen ions are transported through the dense membrane's crystal lattice when an oxygen partial pressure driving force is applied. This development effort solved many significant technical challenges and successfully scaled-up key aspects of the technology to prototype scale. Throughout the project life, the technology showed significant economic benefits over conventional technologies. While there are still on-going technical challenges to overcome, the progress made under the DOE-funded development project proved that the technology was viable and continued development post the DOE agreement would be warranted.

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EXECUTIVE SUMMARY

Ion Transport Membrane (ITM) technology is a new disruptive technology that utilizes the oxygen ion conducting properties of certain mixed metal oxide materials to separate oxygen from an oxygen-containing gas, such as air. These materials operate at high temperature and the oxygen ion is transported through the dense membrane's crystal lattice when a driving force is applied. They have extremely high flux rates with, in theory, 100 percent selectivity.

ITM Syngas is a subset of the broader ITM technology platform and is a disruptive technology for the production of synthesis gas (syngas), a combination of carbon monoxide and hydrogen. ITM Syngas separates oxygen from low pressure air and reacts it on the permeate side of the membrane with methane and steam to generate the syngas. The technology has significant potential to improve the economics for Gas-to-Liquid facilities and hydrogen plants, especially when carbon dioxide capture is required.

In 1997, an Air Products-led team was awarded a competitively bid cooperative agreement with the DOE Federal Energy Technology Center (now the National Energy Technology Laboratory) for a multi-year development project. During the project, the Air Products-led team successfully developed ITM Syngas technology from the concept stage to a stage where a small-scale engineering prototype was about to be built. This effort solved many significant technical challenges and successfully scaled-up key aspects of the technology to prototype scale. Throughout the project life, the technology showed significant economic benefits over conventional technologies. While there are still on-going technical challenges to overcome, the progress made under the DOE-funded development project proved that the technology was viable and continued development post the DOE agreement would be warranted.

The development effort had high technical risk with significant R&D costs, but had a high potential reward when successful. The complexity and long-term nature of the project required significant management effort to ensure successful execution that was focused on commercialization. Many integrated, multi-disciplined problems needed to be solved. Critical attention was focused on materials, ceramic membrane manufacturing, process and reactor design and scale-up, and risk management.

The early phase of the DOE-funded project focused on materials development and successfully identified a class of materials that met commercial targets for oxygen flux, stability, and lifetime. Testing and material composition adjustments continued throughout the project as new insight was attained on material properties, ceramic processing, membrane performance, and process cycles. Today, the chosen material composition has been broadly tested and its properties are well understood.

Ceramic processing development has demonstrated that membranes can be made from the chosen material using conventional ceramic processing technologies. In addition, complex planar membrane structures and membrane modules were designed, fabricated, and tested successfully. A key to this success was new ceramic-to-ceramic joining technology. A ceramic processing infrastructure was developed to fabricate sub-scale and full-size commercial membrane wafers and membrane modules. A key advancement in the infrastructure was the

EXECUTIVE SUMMARY (CONTINUED)

design and fabrication of an automated wafer assembly machine. While fabrication yields have improved during the course of the program, further improvement is required to reach commercial targets.

Commercially relevant oxygen flux was demonstrated and models were developed to predict the observed oxygen flux. The experimental data and models were used to size reactors and develop control schemes. The resulting commercial reactor design had more membrane area than the commercial target. Oxygen flux can be increased by implementing various changes to membrane design parameters and features, and/or reactor operating conditions. This optimization capability should make the commercial target attainable.

One of the major risks identified early in the program was membrane reliability. Significant effort focused on understanding mechanical properties, contaminants, and membrane lifetime. No "show-stoppers" were identified and the results indicated that commercial targets should be attainable, but more work was required to make this a reality. A key aspect of reliability continues to be the ability to operate under transient conditions. Key control strategy advancements were made and are being implemented. Future work in the Process Development Unit (PDU) and Subscale Engineering Prototype (SEP) is planned to demonstrate their effectiveness.

INTRODUCTION

Synthesis gas (syngas), a gas containing carbon monoxide and hydrogen, is a critically important intermediate product required for the generation of multiple end products. Two very important end products are hydrogen and liquid transportation fuels derived through the Fischer-Tropsch process. A preferred feedstock for both these processes is natural gas.

Hydrogen has many applications. One of the earliest large uses of hydrogen was as a rocket fuel, and many additional large hydrogen demands exist today. A very important market is in oil refining, where hydrogen is used to increase product recovery and decrease pollution from the use of refined petroleum-based products. An emerging and important future hydrogen market is the generation of electricity by fuel cells for stationary and vehicular power. Hydrogen is an excellent fuel for these applications, yielding good fuel cell life, high-efficiency power generation, and very low pollution with water as the byproduct.

Syngas can also be used to make very high-purity, low-sulfur liquid transportation fuels. The overall natural gas-to-liquids conversion process, via syngas and the Fischer-Tropsch reaction, is described as gas-to-liquids (GTL) technology. The Fischer-Tropsch process has been used for decades, and today there are a number of large-scale Fischer-Tropsch based GTL plants. There is a great deal of natural gas located in remote regions of the world. In these locations, pipelines do not exist to allow monetization of the natural gas. In some cases, this natural gas is associated with the production of oil. Currently such remote natural gas is released, flared, recompressed and re-injected into the well, or liquefied. GTL technology is a realistic alternative for the monetization of associated natural gas and large-field gas production. Unfortunately, the existing technology choices result in a significant capital cost associated with the GTL process.

*Source: Economics of Alaska North Slope Gas Utilization Options INEL-96/0322

Figure 1-1 Investment Cost Distribution of GTL Using Conventional Technology

INTRODUCTION (CONTINUED)

The syngas production portion of a GTL plant is approximately 60-65% of the total capital cost. The syngas portion of the plant comprises the cryogenic air separation unit (ASU) and the high-temperature syngas generation unit, typically an autothermal reformer (ATR) and its associated high-temperature process equipment. Both of these technologies are relatively mature, so significant technology-based cost reductions are unlikely.

Ion Transport Membranes (ITMs) offer the potential for a substantial reduction in the capital cost associated with syngas production. In this technology, the air separation plant and the high-temperature, partial-oxidation plant are conceptually combined into a single-unit operation. ITMs are non-porous ceramic membranes that, at high temperature, allow the rapid flow of ions through the membrane. Certain materials allow the flow of oxygen ions, and these materials have potentially large application for the production of oxygen or the use of oxygen to make other products.

Figure 1-2 Functions of the ITM Syngas/ITM H₂ Membrane

In the ITM Syngas/ITM H₂ process, oxygen ions from a high-temperature air stream flow through the membrane. The oxygen reacts with natural gas and steam on the high-pressure product side to form syngas. The driving force for oxygen ion transfer across the membrane is based on the partial pressures of oxygen on either side of the membrane. On the air side, the partial pressure of oxygen corresponds to the product of the oxygen concentration and air-side pressure, typically about one atmosphere. On the product side, even though the operating pressure is typically above 30 atmospheres, the oxygen partial pressure is very low, on the order of 10-16 atmospheres, due to the oxidative reforming reactions occurring at the membrane/syngas product interface. The actual driving force is approximately the natural log of the ratio of the air-side oxygen partial pressure and the syngas-side oxygen partial pressure. The ITM solution is elegant and should result in a substantial reduction in capital costs. However, the technical risks are also significant. The composition of the product stream, the membrane temperature, the composition gradient through the membrane, and the very low partial pressure of oxygen at the membrane/product side interface all result in a difficult material development

INTRODUCTION (CONTINUED)

problem. In addition to material challenges, the membrane must mechanically withstand significant pressure differentials and temperature transients. The net result is the need for a carefully-designed membrane contained within a high-pressure and high-temperature reactor.

In 1997, Air Products and Chemicals, Inc. assembled a partnership of key organizations to develop the ITM Syngas process and related technology. The Air Products-led team submitted a competitive bid proposal through a DOE Federal Energy Technology Center solicitation and was awarded this cooperative agreement for a multi-year development project. To be successful, the complex development effort required a mix of closely integrated, unique technical and commercial capabilities. The highly-qualified team from industry, national laboratories, and universities included leading ionic ceramic material scientists; experienced ceramic fabrication technologists; process, design, structural and reaction modeling engineers; and commercial experts. Over the course of the development effort, some team members left and others joined as work scope was completed or added, corporate priorities changed, and new end-users developed interest in the project. Over the course of the project, the team included the following organizations: Air Products and Chemicals, Inc., ARCO Exploration and Production Company, Ceramtec Inc., Chevron, Sasol, Eltron Research Inc., McDermott Technology Incorporated, Norsk Hydro, Pacific Northwest National Laboratory, Pennsylvania State University, the University of Alaska, and the University of Pennsylvania.

The development effort had high technical risk with significant R&D costs, but had a high potential reward when successful. The complexity and long-term nature of the effort required significant management effort to ensure successful execution that was focused on commercialization. Many integrated, multi-disciplined problems needed to be solved. Critical attention was focused on materials, ceramic membrane manufacturing, process and reactor design and scale-up, and risk management.

This report documents the technical progress under this cooperative agreement from its kick-off in 1998 through its conclusion in September 2008. The state of the technology at the conclusion of the contract is also provided.

PHASE 1 RESULTS BY TASK

TASK 1.1 PROCESS DESIGN, ENGINEERING, AND ECONOMIC EVALUATION

Subtask 1.1.1 Process Design and Engineering

During Phase 1, process design proceeded through conceptual to preliminary stages of development. Each successive stage involved a greater level of detail and accuracy, and integrated work from the Materials and Seals Development task and the Reactor Design and Fabrication task. Air Products, Chevron, and McDermott developed ITM Syngas for gas-to-liquids (GTL) applications. Norsk Hydro, with input from Air Products, developed ITM H₂ for large-scale hydrogen applications for power generation with CO₂ sequestration. Air Products developed ITM H₂ for distributed hydrogen applications.

ITM SYNGAS

Conceptual Process Design

The baseline ITM Syngas conceptual process is shown in Figure 1.1.1-1. The hydrocarbon feed is preheated in a flue gas duct system and pre-reformed in an adiabatic pre-reformer. The flue gas duct recovers heat from the O₂-depleted air stream. The CO₂-containing offgas from a downstream Fischer-Tropsch (F-T) GTL plant is recycled to the feed of the ITM Syngas process to adjust the product syngas H₂/CO ratio to 2.03, suitable for F-T GTL. Advantages of the baseline process include the elimination of a separate cryogenic air separation plant, use of conventional processes for gas pretreatment, heating, and heat recovery and the absence of open flames. Process designs and heat and material balances were developed for two ITM Syngas processes that employ different steam-to-carbon (S/C) ratios of 0.6 and 1.5. A baseline S/C ratio of 1.5 was selected based on operating experience with preheating pre-reformed gas to the range of temperatures used for the ITM reactor feed.

The conceptual ITM Syngas plant size is appropriate for an offshore or small land-based GTL facility. The conceptual ITM Syngas process utilizes 50 MMSCFD (60°F standard temperature, dry basis) associated gas feed to the reactor at an upstream supply pressure of 500 psia and produces 163 MMSCFD (60°F) contained H₂ and CO at 350 psia and an H₂/CO ratio of 2.03. Forty-two MMSCFD (60°F) of F-T offgas is recycled to the feed of the ITM Syngas process. Overall thermal efficiency of the ITM Syngas process is 91% (based on HHV) when credit for steam is included. Preliminary equipment specifications were developed to estimate equipment costs for the conceptual-stage economic evaluation.

Figure 1.1.1-1 Baseline ITM Syngas Process for GTL

Preliminary Process Design

The conceptual-stage baseline ITM Syngas process with an adiabatic pre-reformer was refined to develop the preliminary-stage process design for an offshore GTL plant with 55 MMSCFD (60°F) total associated gas feed: 50 MMSCFD (60°F) associated gas for reactor feed and 5 MMSCFD (60°F) associated gas as supplemental fuel for the air preheater, which is also fueled by excess F-T offgas. The offshore GTL plant process design was then scaled up to a land-based GTL plant with 500 MMSCFD (60°F) total associated gas feed. To further evaluate the impact and benefits of GTL integration, the preliminary process study scope was expanded from syngas generation to include F-T GTL and product upgrading (hydrocracking) to produce transportable liquid fuels.

To evaluate process design alternatives and opportunities for integration, process simulation models were developed for ITM Syngas generation, F-T syngas conversion, and product upgrading. These models were integrated for a GTL plant design that included off-site utilities (steam, power, and cooling water). Non-proprietary, public domain information was used to form the basis for the modeling of the Fischer-Tropsch section of the plant. In addition, a process simulation model of an oxygen-blown ATR plant was developed to allow for a comparison of ITM versus ATR.

Unlike the ITM Syngas process, the oxygen-blown ATR process requires a cryogenic air separation plant that uses a large amount of power to compress air to pressures above 100 psig. The ITM Syngas process has much lower power requirements, since the feed air is compressed to only 10 psig. For the 55 MMSCFD (60°F) total associated gas usage case, the overall power demand for the ATR/ASU process is 11 MW greater than for the ITM Syngas process. This shifts the power demand balance from an excess steam situation for ITM Syngas to a steam-deficient situation for O₂-blown ATR. An additional boiler is required to provide the steam for this additional power demand in the ATR process. The expense of this system was identified in the economic evaluation.

The baseline ITM Syngas process uses a S/C ratio of 1.5 based on operating experience with preheating pre-reformed gas to the range of temperatures used for the ITM reactor feed. Commercial ATR processes typically operate with S/C ratios of around 1.4, and ATR suppliers claim that operation is possible at S/C ratios as low 0.6 with pre-reformed feed.

The associated gas and F-T offgas recycle requirements and syngas productions are similar for ITM Syngas and O₂-blown ATR processes with roughly the same S/C ratios. Comparison of the ITM Syngas process with an S/C of 1.5 to an ATR process with an S/C of 0.6 indicates advantages for operation at lower S/C ratios. At higher S/C ratios, the ITM process requires more CO₂ recycle to the syngas generation process in order to achieve the desired 2.03 H₂/CO ratio in the product syngas. This leads to increased F-T offgas recycle compression requirements, increases the volume flow of syngas to the F-T reactors, and leads to larger equipment in the F-T plant. A benefit of higher rates of F-T offgas recycle to the ITM Syngas process is that unreacted syngas and lower hydrocarbons have another opportunity for conversion in the syngas and F-T plants. Work is ongoing to develop ITM processes that can operate with lower S/C ratios.

The reactor design task identified the potential for significant reforming of the non-equilibrium feed gases at the inlet end of the ITM reactor. Cooling due to the endothermic reforming reactions, if not balanced by the exothermic oxidation reactions, may cool the membrane and lead to reductions in oxygen flux. Several methods to mitigate this potential problem were considered: supplemental preheating of the air feed to higher temperatures, additional reforming of the associated gas feed by replacing the adiabatic pre-reformer with a gas heated reformer (GHR), and feed gas oxidation at the inlet section of the ITM reactor. Associated gas usage rates, air feed rates, and oxygen requirements were predicted for these potential solutions. The reactor design task identified ITM reactor inlet oxidation as the preferred approach.

Large-Scale ITM H₂

The large-scale ITM H₂ process is suitable for generating H₂ while facilitating CO₂ sequestration. The partial oxidation-based reforming of hydrocarbon feeds keeps generated CO₂ at process pressures, thereby permitting the use of conventional amine-based acid gas removal (AGR) systems to remove CO₂. The objective of the process was to remove 90% or more of the carbon contained in an associated gas feed. The ITM H₂ process was compared to O₂-blown ATR processes at a plant scale producing 150 MMSCFD (60°F) hydrogen.

The conceptual, large-scale ITM H₂ process is similar to the baseline ITM Syngas process with an adiabatic pre-reformer and flue gas duct heat recovery system. High- and low-temperature shift reactors were added downstream of the waste heat boiler to increase H₂ production, and an amine-based acid gas removal system was added to recover CO₂. A fresh air/O₂-depleted air heat exchanger was added to increase efficiency and CO₂ recovery. Increasing CO₂ recovery from 90 to 95% is possible by using H₂ instead of associated gas as fuel in the direct-fired air preheater. Equipment specifications were developed for cost estimation in the conceptual-stage economic evaluation.

The conceptual, large-scale ITM H₂ process formed the basis for the preliminary-stage process design. Additional ITM H₂ processes that were evaluated included ITM with an adiabatic pre-reformer, ITM with a GHR for pre-reforming, and ITM with a steam methane reformer (SMR) for pre-reforming. These were compared to O₂-blown ATR processes, both with and without a GHR, and to an air-blown ATR process.

The large-scale ITM H₂ processes were optimized to reduce the S/C ratio to 2.0. This increased process efficiency while still providing sufficient steam for the shift reactors. The cost of the gas-to-gas heat exchangers was reduced by optimizing heat exchanger metallurgy and matching heating and cooling streams.

Feed rates, utilities, and efficiencies are compared in Table 1.1.1-1 at 95% CO₂ recovery for ITM and oxygen-blown ATR processes.

Table 1.1.1-1 Comparison of Large-Scale ITM H₂ and ATR-based Hydrogen Processes with 95% CO₂ Recovery

	ITM-AR	ITM-GHR	O₂ ATR	O₂ ATR-GHR
Relative NG consumption	1.027	0.979	1.0	0.968
Steam export MMBtu/MMSCF H ₂	11.18	0	13.13	0
Relative Electric power use	0.257	0.224	1.0	0.798
Delta Fuel efficiency (LHV), % points	+1.4	+4.7	Base	+2.5

ITM-AR: ITM Syngas with adiabatic pre-reformer and AGR.

ITM-GHR: ITM Syngas with GHR and AGR.

O₂ ATR: O₂-blown ATR with cryogenic air separation plant and AGR

O₂ ATR-GHR: O₂-blown ATR and GHR with cryogenic air separation plant and AGR.

Efficiencies are calculated based on an assumed 30% efficiency of fuel to steam to power and an assumed 55% efficiency of fuel to power in a neighboring GTCC power plant.

The ITM H₂ process with a GHR gives the highest efficiency because of its lower airflow and steam production compared to the ITM H₂ process with an adiabatic pre-reformer and because of its much lower electric power consumption compared to ATR-based processes with cryogenic air separation plants.

Distributed-Scale ITM H₂

Process designs and simulations were developed for ITM H₂ processes producing 0.5 MMSCFD (60°F) hydrogen, suitable for Fuel Cell Vehicle distributed refueling applications and for on-site industrial applications. Because product costs are strongly dependent on capital costs at this plant scale, the process was developed with the goal of reducing capital costs by reducing the number and complexity of individual equipment items. The baseline distributed-scale ITM H₂ process shown in Figure 1.1.1-2 has a single high-temperature shift reactor and a H₂ PSA to separate H₂. To reduce natural gas usage, PSA offgas is used as fuel for the air heater, and to simplify the plant design, a steam saturator is employed in place of the waste heat boiler/steam system used in the baseline ITM Syngas process (Figure 1.1.1-1).

The distributed-scale ITM H₂ base case process employs an overall S/C ratio of 3, with all the steam injected into the ITM reactor feed. An alternative process was investigated which maintains the same overall S/C of 3, but reduces steam injection to the ITM feed by injecting the balance of steam into the ITM product syngas upstream of the shift reactor. Preliminary process specifications were developed to estimate equipment costs in the economic evaluation task.

Figure 1.1.1-2 Baseline Distributed-Scale ITM H₂ Process

Subtask 1.1.2

Commercial-Scale Plant Economic Evaluation

Conceptual-stage economics for ITM Syngas were evaluated by Air Products with input from Chevron and McDermott. Preliminary-stage economics for ITM Syngas were evaluated by McDermott with input from Air Products and Chevron. Norsk Hydro, with input from Air Products, evaluated the economics for large-scale ITM H₂ generation, and Air Products evaluated the economics for distributed-scale ITM H₂. In the various areas, costs were compared for ITM processes and current commercial processes.

ITM SYNGAS

Conceptual Economic Evaluation

Preliminary equipment specifications for a 50 MMSCFD (60°F) associated gas feed baseline ITM Syngas plant were developed and used with the ICARUS program to estimate installed equipment costs for the conceptual-stage economic evaluation. To establish a baseline for current syngas generation technology, capital and operating costs were developed for an oxygen-blown ATR syngas process operating with the same feed and product flow rate, pressure, and compositions as the ITM Syngas process. Assumptions include the following: cost of off-sites is 20% of installed equipment cost, owner's cost is 10% of installed equipment cost + off-sites, and the contingency is zero. When compared to an ATR with a cryogenic air separation plant at a plant scale of 50 MMSCFD (60°F) associated gas feed, the ITM Syngas process offers greater than 35% capital cost savings and up to 15% operating costs savings. Operating costs were based on natural gas and steam valued at \$0.50/MMBTU; electric power at \$0.025/KWh; zero cost for FT offgas; annual maintenance, taxes, and insurance of 5% of total investment; excluding depreciation and return on investment.

Preliminary Economic Evaluation

The preliminary ITM Syngas GTL process design with 55 MMSCFD (60°F) total associated gas usage (50 MMSCFD associated gas as ITM reactor feed) produces a nominal 6,000 barrels per day of syncrude. Conceptual-stage economics were evaluated at this plant scale for a land-based plant. The economic analysis at the same plant scale was extended to an offshore basis on a Floating Production, Storage and Offloading (FPSO) ship with a Gulf Coast location.

The preliminary-stage economic evaluation of a 55 MMSCFD (60°F) associated gas offshore GTL plant compared an ITM Syngas process to oxygen-blown ATR processes that included a cryogenic air separation plant. The ITM Syngas process used a S/C ratio of 1.5, and the ATR processes used S/C ratios of 1.4 (the current commercial standard) and 0.6 (the newer lower limit claimed by ATR suppliers). The objectives of the comparison were to identify advantages in capital and operating costs, footprint and weight, and electric power generation costs. As shown in Figures 1.1.2-1 and 1.1.2-2, electric power for the ITM and ATR processes is provided by steam turbines using the high-pressure steam from the ITM process and the low-pressure steam from the F-T process.

McDermott developed a preliminary layout of the ITM and ATR processes on an FPSO with an assumed hull size 100 ft. wide x 690 ft. long. Assuming a usable deck width of 80 ft., the ATR process and cryogenic air separation plant require 385 ft. of deck length, while the ITM Syngas process requires 230 ft. of deck length – a savings of 40%.

McDermott used the conceptual-stage, ICARUS-based cost estimates as a starting point and refined the equipment designs and cost estimates using vendor quotes and an in-house cost database. ATR costs were scaled from various vendor quotes. To account for variability in the quotes, a range for ATR costs was used in the analysis. To determine the impact of ITM reactor costs and to help in setting cost and performance targets, a sensitivity study was performed for ITM reactor installed costs. The cryogenic air separation plant for the FPSO includes additional cost for adaptation to an offshore application. The results of the sensitivity study and comparison of ITM Syngas (at an S/C of 1.5) to oxygen-blown ATR (at S/Cs of 0.6 and 1.4) are shown in Figure 1.1.2-3.

Figure 1.1.2-3 Capital Cost Savings for ITM Syngas Versus Oxygen-blown ATR with Cryogenic Air Separation Plant

Based on current estimated installed costs of a planar membrane ITM Syngas reactor, the expected capital cost savings are 28 to 35% compared to an ATR with cryogenic air separation plant. With further work planned for Phase 2, reactor costs are expected to drop, leading to

expected capital cost savings in the range of 30 to 37%. In addition, the lower power requirement for the ITM Syngas process compared to the ATR/ASU process reduces the capital cost of the power generation equipment by approximately 32%.

The offshore ITM Syngas process was scaled up by a factor of 9 to a land-based ITM Syngas GTL plant that processes 495 MMSCFD (60°F) total associated gas (450 MMSCFD associated gas as ITM reactor feed) and produces a nominal 54,000 BPD of syncrude. The large land-based plant consists of three ITM Syngas trains, each of which is three times the size of the offshore ITM Syngas train. A layout and costs were developed for a Gulf Coast land-based ITM Syngas GTL plant, and are being adjusted for an Alaskan North Slope location.

Large-Scale ITM H₂

Capital and operating costs for ITM H₂ processes and oxygen-blown ATR processes were compared for producing 150 MMSCFD (60°F) H₂ and removing CO₂. Plant scope included the ITM H₂ process, high- and low-temperature shift reactors, and an amine-based CO₂ removal system. Equipment lists and costs from the conceptual-stage evaluation were refined in the preliminary-stage analysis. Particular attention was devoted to the more expensive equipment items with the goal of reducing costs through careful process design and equipment design, including the proper selection of materials of construction. Based on the preliminary economic analysis, the ITM H₂ process with an adiabatic pre-reformer and the ITM H₂ process with a GHR were selected for further evaluation.

Investment costs for the 150 MMSCFD (60°F) hydrogen processes were developed for a land-based site (West Coast Norway) with North Sea natural gas. A sensitivity analysis was performed for installed ITM reactor costs. Investment costs included 20% for contingency and minimal off-sites. ATR costs were based on vendor information and in-house estimates. Equipment costs were estimated using the Icarus "Questimate" program, vendor inquiry, and an in-house cost database.

Figure 1.1.2-4 shows investment cost savings for ITM H₂ with a GHR compared to an oxygen-blown ATR. Based on current estimates of installed costs of a planar membrane ITM Syngas reactor, the expected capital cost savings are 15 to 20% compared to an oxygen-blown ATR, depending on the extent of CO₂ recovery. With further planned work in Phase 2, reactor costs are expected to drop, leading to expected capital cost savings in the range of 17 to 22%. A sensitivity analysis on the ATR installed capital cost showed that a 50 percent change in the installed capital cost would change the savings by 2 percentage points.

Figure 1.1.2-4 Investment Cost Savings for ITM H₂ with Gas-heated Reformer Compared to Oxygen-blown ATR with Cryogenic Air Separation Plant

To evaluate operating costs, a membrane replacement frequency of once every 7.5 years was assumed. Other assumptions included natural gas at \$1/MMBTU, steam at \$0.50/MMBTU, electric power at \$0.025/KWh, annual maintenance equal to 3% of plant investment, 15-year depreciation, and 10% return on investment. The value of recovered CO₂ was assumed to be zero. With these assumptions, production cost savings of up to 16% are possible with an ITM-GHR compared to an oxygen-blown ATR.

Distributed-Scale ITM H₂

Capital and operating costs were evaluated for the distributed-scale ITM H₂ process producing 0.5 MMSCFD (60°F) hydrogen. This size plant is nominally the same size as the Subscale Engineering Prototype (SEP) to be built and operated in Phase 2. Costs were evaluated for two applications: Fuel Cell Vehicle (FCV) refueling applications requiring H₂ compression to 5000 psig, storage and dispensing; and on-site industrial applications that could use H₂ at the produced pressure of 150 psig.

ITM reactor costs were estimated based on current estimates of installed ceramic membranes and seals costs and the vessel cost. Vessel costs were estimated from equivalent small heat exchanger costs. Equipment costs for other items were estimated using the ICARUS program. The cost of H₂ compression, storage, and dispensing for the fuel cell vehicle refueling application were taken from the "Hydrogen Infrastructure Report" by Directed Technologies Inc. for Ford and DOE (DE-AC02-94CE50389), April 1997 draft. Indirect plant costs were estimated following Air Products' experience, and anticipated cost savings from a skidded design

were included. Maintenance, taxes, insurance, operations overhead, general and administrative costs, depreciation, and return on investment were included in calculating the cost of produced H₂. Costs associated with feed, and utilities varied with the application and are shown in Table 1.1.2-1.

The cost of produced hydrogen for ITM H₂ was compared to trucked-in liquid H₂, which is the current commercial benchmark at this scale. Trucked-in liquid H₂ prices range from \$0.60 to \$0.80 per 100 SCF and are dependent on distance from the H₂ plant and transportation costs. Including the cost of H₂ compression, storage, and dispensing for the 5000 psig FCV application adds about \$0.18 per 100 SCF to the cost of trucked-in liquid H₂. As seen in Table 1.1.2-1, distributed-scale ITM H₂ achieves an approximately 8 to 42% reduction in the cost of H₂ compared to trucked-in liquid H₂, depending on the application.

**Table 1.1.2-1 Savings in Cost of H₂ for 0.5 MMSCFD
Distributed-Scale ITM H₂ Compared to Trucked-in Liquid**

	Distributed H ₂ for FCV refueling	On-site industrial H ₂ generator
Cost of utilities		
Natural gas (\$/MMBTU)	4.00	2.50
Electric power (\$/KWh)	0.06	0.05
Cooling water (\$/Kgal)	0.15	0.10
H ₂ delivery pressure (psig)	5000	150
Cost includes compression, storage, dispensing	Yes	No
Cost of ITM H ₂ (\$/100 SCF)	0.72	0.46
Cost of trucked-in liquid H ₂ (\$/100 SCF)	0.78 - 0.98	0.60 - 0.80
% ITM H ₂ cost savings	8 - 27%	23 - 42%

Subtask 1.1.3 PDU Systems Engineering

A nominal 24 MSCFD syngas PDU has been designed and its cost estimated. An initial Design Hazards Review was carried out, and P&IDs have been developed.

The PDU will achieve the first level of scale-up from the laboratory-scale, high-pressure reactors. It will integrate thin-film, sub-scale membranes, manifolds and seals and will simulate the reactor process conditions, including the gas linear velocity of the full-scale process. The PDU will simulate sections of the full-scale reactor, and will be able to use up to four sub-scale membrane stacks. A commercial reforming catalyst will be used between the membrane modules.

The PDU will be used in Phase 2 to validate the engineering and kinetic models of the membrane performance under full-scale reactor conditions. These model parameters include:

- Conversion per unit length of membrane surface
- Thermal profile at the membrane surface
- Thermal and reaction kinetic models
- Reforming catalyst kinetic model
- Mechanical stresses on the membrane and other ceramic components
- Process economics

Figure 1.1.3-1 Conceptual PDU Design

A conceptual illustration of the PDU design is shown in Figure 1.1.3-1. The PDU reactor will be large enough to contain four full-size membranes, up to six inches in width. Each membrane module will have a minimum of three membranes to simulate the gas fluid dynamics of the large-scale process. The reactor vessel will be around 24 inches in diameter, and pressure rated to 500 psig with wall cooling. The process gas and membranes will be contained in an internal enclosure, heated by electrical heaters and surrounded by insulation.

Pre-mixed gases, simulating different stages of the ITM Syngas and ITM H₂ process, will be supplied by tube trailer. Water will be introduced before the mixtures are heated to the operating temperature. In order to simulate an air stream from a direct-fired heater, air supplied by a blower will be mixed with additional nitrogen, CO₂ and water to give a final oxygen concentration of ~15%. The process streams will pass through Alonized Haynes 230 coils placed inside an electric furnace. The Alon coating will reduce chromium vaporization and minimize metal dusting and coking. Before contacting the membranes, the syngas mixture will pass through a Cr removal and additional heating section.

The exit syngas stream will be water quenched to avoid metal dusting and coking. The exhaust gas piping (syngas and non-permeate) will be submerged in a water tank, and heat will be removed by steam generation to maintain a low wall temperature. The quenched exhaust streams will then be flared.

TASK 1.2 MATERIALS AND SEALS DEVELOPMENT

Subtask 1.2.1 Materials Development

Subtask 1.2.1.1 Materials Characterization and Assessment

Development Strategy

The I2 materials originally developed by Eltron Research were found to be unstable or to have too high a chemical expansion strain under the conditions of the high-pressure ITM Syngas process. The development of more stable ITM Syngas material compositions was carried out by Air Products, Ceramtec and Eltron Research, with input on thermodynamics from Norsk Hydro. The initial selection criteria used in the materials development program are listed in Table 1.2.1.1-1.

Thermodynamic predictions of stability under ITM Syngas process conditions were used to make initial selections of the compositions. These predictions were then confirmed by experimental determination of the stability of the compositions under controlled atmospheres simulating the process environment. Selected compositions were synthesized in small batches at Ceramtec to produce tape cast discs and isopressed tubes for the measurements of ionic conductivity by oxygen permeation, syngas generation at atmospheric pressure, mechanical properties, and chemical and thermal expansion. Selected compositions were also scaled up at Ceramtec to produce tubular membranes, sealed into superalloy holders with Air Products proprietary compression seals, to produce samples for syngas generation at high pressure.

Table 1.2.1.1-1 Initial Development of ITM Syngas Materials

Selection Factors	Performance Criteria	Test Methods	Test Location
Stability	Stability at 750°C in high P_{CO_2}/P_{H_2O} , low P_{O_2} atmospheres	Thermodynamic modeling and static atmosphere tests	Air Products and Ceramtec
Chemical expansion	Low strain under large P_{O_2} gradient	Controlled atmosphere dilatometer measurements	Air Products
Oxygen permeance and conductivity	Membrane thickness to obtain oxygen flux target	O_2 permeation tests with He swept permeate, using tape cast discs fabricated by Ceramtec	Air Products

Table 1.2.1.1-1 Initial Development of ITM Syngas Materials (Continued)

Selection Factors	Performance Criteria	Test Methods	Test Location
Fabricability	Membrane fabrication yield	Powder processing, sintering temperature, laminate and tube fabrication	Ceramatec
Mechanical properties	Membrane lifetime, compatibility with process stresses	High temperature strength and creep, Weibull modulus	Penn State University and McDermott
Syngas generation performance	Performance and stability under large P_{O_2} gradient, and under process conditions	1) Atmospheric pressure tests using tubes fabricated by Ceramatec and Eltron 2) High pressure tests with tubes and seals, fabricated by Ceramatec	Air Products and Eltron Research

The application of the series of screening tests listed in Table 1.2.1.1-1 led to the development of the I4 composition series. The progressive improvement in material properties critical for the ITM Syngas reaction that resulted from this development program is illustrated with selected examples in Table 1.2.1.1-2. The approximate membrane thickness required to meet the target flux is calculated assuming bulk ionic conductivity as the controlling resistance to oxygen flux. The values listed in the table are within the range of ceramic membrane thickness achievable using the fabrication process technology developed by Ceramatec and Air Products.

Table 1.2.1.1-2 Results of Initial Screening of I2 and I4 Compositions

Composition	CO₂ stability at 750°C (bar) ⁽¹⁾	σ_{eff} (S/cm) @ 950°C ⁽²⁾ [*1000°C]	Isothermal expansion ppm @ 800°C ⁽³⁾	Isothermal expansion ppm @ 850°C ⁽⁴⁾
I2 (A)	6.3>P>2.1	0.125	> 2000	2811
I2 (B)	P>6.3	0.066, 0.099		2631
I2 (C)	P>6.3	0.044, 0.062		2062
I4 (B)	P>6.3	0.058, 0.063	< 200	764
I4 (C)		0.037, 0.047		1563 ⁽⁵⁾

- (1) Static atmosphere tests, P is the CO₂ pressure for decomposition, $P_{O_2} = 10^{-12}$ bar.
- (2) Atmospheric pressure, He swept permeate, O₂ gradient: 0.21/0.001 atm.
- (3) Isothermal expansion, O₂ partial pressure variation 1.0 to 0.005 atm.
- (4) Isothermal expansion, O₂ partial pressure variation 1.0 to 10^{-10} atm.
- (5) Isothermal expansion at 950°C, O₂ partial pressure variation 1.0 to 10^{-11} atm.

Measurement of the oxygen flux through a series of I2 and I4 compositions determined that I4 (B) has the best ambipolar conductivity among the compositions, with acceptably low chemical expansions. Some I2 compositions have higher conductivity than I4(B), but at the expense of unacceptably high chemical expansion.

Based on these criteria, materials from the I4 composition family were selected for further development. This included the determination of additional thermodynamic and kinetic stability parameters, and is described in the following section.

FURTHER DEVELOPMENT OF CRITICAL PARAMETERS

Phase Stability

A miscibility gap was determined to exist in the I4 system under reducing conditions. Phase stability testing was carried out under simulated reducing conditions at temperatures higher than the predicted maximum reactor temperature, to accelerate any decomposition reactions. The tests identified a compositional range in the I4 series that is stable against decomposition at lower P_{O_2} in the absence of CO_2 . Samples were annealed for periods up to 1 month at 950 and 1050°C in H_2/H_2O mixtures that produce oxygen partial pressures equivalent to those anticipated in the ITM Syngas process. X-ray diffraction was used to detect the presence of any decomposition products. The I4(C) composition was stable at least at 1050°C at a P_{O_2} of 10^{-14} atm. At temperatures lower than 950°C, the kinetics of decomposition in I4(B) were too slow to be observed over 1 month.

Creep

Careful control of cation stoichiometry was found to be necessary to avoid second phase formation in the I4(B) material. Sintered parts of I4(B) with A/B ratios >1.0 do not have detectable amounts of the low melting second phase on their surfaces. Elimination of this second phase reduced the creep rate of I4(B) to levels that are an order of magnitude improvement over earlier generations of this material, and are less than 50% of the maximum allowable creep rate at the given stress level. The creep rate of I4(C) was determined to be fairly close to the creep criteria. Further microstructural development or lowering the design stress should allow the creep criteria to be met.

Development of the I4 composition field is continuing to examine alternate doping on the B-site to further improve high-temperature creep and stability.

Chemical Expansion

The chemical expansion of the I2 compositions was determined to result in a very high probability of failure under the process conditions. The I4 family of materials was developed to have much lower chemical expansions that will result in improved reliability in syngas service.

Table 1.2.1.1-3 lists the measured chemical expansions when porous bars of the indicated compositions were first equilibrated in 1 atm O₂ at the given temperature and then equilibrated in a 30.1% CO₂/40.2 ppm CO/balance N₂ or a 1000 ppm H₂/1.7% H₂O/balance N₂ mixture. The oxygen partial pressures given in Table 1.2.1.1-3 are the equilibrium oxygen partial pressures for that gas mixture at the given temperature. The oxygen partial pressure in the syngas process will be lower, varying from 10⁻²⁰ atm at 750°C to 10⁻¹⁵ atm at 950°C. Expansion on the order of >3000 ppm results in very low predicted reliability in syngas service.

Table 1.2.1.1-3 Chemical Expansion Measured When P_{O2} is Changed from 1 atm to P_{O2} Given in Table

	Chemical Expansion (ppm)				
Temperature (°C)	750	750	850	950	950
P _{O2} (atm)	2.81 x10 ⁻¹³	9.01 x10 ⁻¹⁶	1.03 x10 ⁻¹⁰	1.43x10 ⁻⁰⁸	1.28x10 ⁻¹¹
I4(B)	738	2013	764	496	
I2(A)	3918		2811	1911	
I2(B)	3102		2631	2156	
I2(C)			2062	2201	
I4(C)					1563

Oxygen Flux

The apparent ambipolar conductivity of a selection of the many I2 and I4 compositions measured is listed in Table 1.2.1.1-4. For each composition, the ambipolar conductivity of two samples was measured at 950°C using an air feed and a permeate P_{O2} of 0.001 atm.

**Table 1.2.1.1-4 Apparent Ambipolar Conductivity - 950°C,
Air Feed/Permeate P''_{O2} ~0.001 atm**

Composition	Apparent Ambipolar Conductivity (S/cm)
I2(C)	0.044, 0.062
I2(B)	0.066, 0.099
I4(B)	0.058, 0.063
I4(B')	0.06*
I4(C)	0.04*

* at 1000°C

Other I4 compositions were tested to determine the effect of A-site doping on conductivity. The I4(B) composition performed the best among this group. Other I4 compositions were tested to determine the effect of B-site doping on conductivity. The compositions with only a single B-site substitution performed the best among this group. Adding a second B-site element decreased the apparent ambipolar conductivity measured under these conditions.

Long-term flux testing of the I4(B) composition at high temperatures detected some flux degradation with time. In all cases, the flux decreased with time. The degradation rate of the membrane with an A/B ratio <1 is much higher than that for the membranes with A/B ratios >1. Examination of the membrane surfaces by SEM after flux testing revealed second phases on both the feed and permeate surfaces for all membranes. The phase was very thin making quantitative identification of the composition of the second phase difficult. It is theorized that the second phases appearing on the feed and permeate surface of the membrane partially block the ionic and electronic fluxes, resulting in a lower flux. The amount of the second phase increases with time.

It was found that the degradation rate can be markedly decreased or eliminated by changing the membrane composition. However, increased flux stability comes at the cost of decreased initial performance. Figure 1.2.1.1-5 illustrates that changing from the I4(B) composition to the I4(B') or the I4(C) composition results in a decreased initial flux. However, no flux decline was observed during the first 200 hours on-line for either the I4(B') or the I4(C) composition. This is in marked contrast to the I4(B) composition, for which a flux decrease rate of $\approx 8.3\%/100$ hours was noted. The lower flux of the more stable composition can be offset by using a proportionately thinner membrane layer to achieve the target flux. Longer term testing is necessary to confirm the stability of the various I4 compositions.

Figure 1.2.1.1-1 Illustration Showing that Changing Composition from I4(B) to I4(C) Eliminates Degradation During the First 200 Hours of Operation at the Expense of a Lower Initial Flux (1000°C Air/He Gradient)

Atmospheric Pressure Syngas Tests

Two atmospheric pressure syngas screening reactors were constructed at Air Products and six at Eltron Research.

Air Products

Tubular membranes fabricated by Ceramtec were tested in the Air Products units for up to 35 days, with atmospheric pressure air supplied to the inside of the membrane, and helium, 2% methane in helium, or 4% hydrogen in helium supplied at one atmosphere to the outside of the tubes. The apparent ambipolar conductivity of a number of I4 tubular membranes tested under these conditions is listed in Table 1.2.1.1-5. The tubes were fabricated by Ceramtec and coated with proprietary catalysts. The trend of the apparent conductivity over the length of the test is also given in the table.

**Table 1.2.1.1-5 Apparent Ambipolar Conductivity at
950-960°C - Air Feed/CH₄/He or H₂/He Permeate**

Tube Composition [A/B cation ratio]	Surface Catalyst Layers (OD/ID)	Apparent Ambipolar Conductivity (mS/cm) 2% CH ₄ /He		Apparent Ambipolar Conductivity (mS/cm) 4% H ₂ /He	
		Range	Trend	Range	Trend
I4(B) [0.98]	A/A	31-42	Increasing	55-60	Increasing
I4(B) [0.98]	B/A	30-41	Increasing	47-52	Increasing
I4(B) [1.00]	B/A	23-30	Decreasing	36	Stable
I4(B) [1.01]	B/A	43-69	Dec./Stable	50	Stable

Tests were conducted to determine the ambipolar conductivity of several I4 compositions as a function of temperature with a feed of 2% methane in helium at a flow rate of 100 sccm and an internal air flow rate of 100 sccm. The ambipolar conductivity is calculated using the standard Wagner equation, assuming that the ionic and electronic conductivity are independent of the oxygen concentration. The oxygen flux of I4(B) with an A/B ratio of 1.01 was observed to decrease with time to a steady state at a temperature of 950°C. This performance was consistent with the long-term tests of the I4(B) composition.

Typically it was found that the activation energy for conduction under the methane/helium sweep wash was higher than the activation energy under the hydrogen/helium sweep.

Eltron Research

The atmospheric pressure syngas reactors installed at Eltron Research were used to screen compositions at operating temperature and with feed gas mixtures representative of the ITM Syngas GTL process equilibrated at ambient pressure. The latest efforts concentrated on the I4(B) composition. Techniques were developed for depositing uniform, porous catalyst layers on the tubular membranes via dip coating. The ceramic powders for fabricating the tubes and for use as a catalyst support were produced either at Eltron or provided by Ceramtec.

Methane conversion was observed when sufficient reforming catalyst was present. For example, at 950°C with a total flow rate of 400 ml/min consisting of a 50% GTL equilibrium mixture (20.0% CH₄, 25.4% CO, and 54.6% H₂) and a balance of helium, approximately 50% of the methane content was converted, and both the hydrogen and carbon monoxide flow rates in the product gas increased by around 30%. As the total flow rate was decreased, the conversion increased. At 200 ml/min the methane conversion increased to 75% and at 100 ml/min the methane conversion increased to 85%. When the GTL equilibrium gas mixture was increased to 100%, the methane conversion did not significantly change.

Selection of ITM Syngas Material Compositions

The I4 materials satisfied the initial selection screening tests for stability in CO₂ under low P_{O₂}, reduced chemical expansion, fabricability, creep and ambipolar conductivity. However, tests at temperatures higher than what the material would experience in the ITM reactor (≥1000°C) showed that the oxygen conductivity of the I4(B) material degraded slowly with time. Extrapolation to the predicted membrane temperature range in the reactor (775 - 975°C) indicates that the material would not sustain the target membrane lifetime in the high-temperature regions. In the lower temperature regions of the ITM reactor, the material is predicted to have acceptable stability and creep resistance. For example, a tubular membrane test of I4(B) at Eltron Research in the high-pressure syngas reactor showed stable operation in the oxidation of a reducing gas mixture at 825°C and 250 psig for over 100 days.

I4(C) has given promising results in initial high-temperature stability screening tests under very low P_{O₂}, and high-temperature creep resistance close to the target value. The increase in stability of the I4 appears to correspond to a decrease in conductivity. However, the more stable I4 variation would be used in the higher temperature regions of the reactor, compensating for the conductivity decrease.

Therefore, at the end of Phase 1, the material selection for the ITM Syngas reactor is twofold:

- I4(B) for the lower temperature inlet section
- I4(C) in the higher temperature section

The modular flat-plate membrane ITM reactor design selected in Phase 1 allows a variation in material composition to be made with module location within the reactor. Measurement of the

oxygen flux obtained under syngas process conditions from thin, supported membrane structures of the type described in Subtask 1.3.1 will be carried out in the PDU in Phase 2.

Determination of High-Temperature Mechanical Properties

A testing program was carried out at Pennsylvania State University to determine the mechanical behavior of selected ITM Syngas materials as a function of temperature in both air and non-reactive reducing atmospheres. The bulk of the tests have been performed on segments cut from the isostatically pressed tubes fabricated by Ceramtec for ambient and high-pressure syngas testing. The segments were tested as O-rings in diametrical compression to simulate the behavior of the tubes under hydrostatic external pressurization, as would be expected in service. The strength tests were performed at room temperature and at selected elevated temperatures at a strain rate of $\sim 1.7 \times 10^{-1}/\text{min}$. Strength was also determined as a function of strain rate at the highest test temperature (950°C). These tests provide information on the degree to which subcritical crack growth could lead to premature failure of components. During these tests on materials of the I4(B) composition with an A/B ratio of 0.98, significant plastic deformation was observed at the slowest strain rate ($\sim 1.7 \times 10^{-3}/\text{min}$). This observation is indicative of the tendency for creep to occur and confirms observations of plastic deformation of tubular membrane samples in Eltron's high-pressure test rigs. Further tests on other samples from this compositional family with higher A/B ratios showed that creep resistance improved with increasing A/B ratio. Tests in the non-reactive reducing gas atmosphere (30% CO₂-40 ppm CO-balance N₂) showed a small increase in creep compared to testing in air. In addition, changes in firing procedures for the tubes, which resulted in increased grain size, also resulted in increased creep resistance. Combined, these changes have resulted in a decrease in creep rate of over two orders of magnitude. Assessment of these (and further) changes on the strength and elastic modulus are ongoing.

Subtask 1.2.1.2 Powder Production and Test Sample Fabrication

Ceramtec provided a continuous supply of powders, tapes, tubes and other samples for use by the various members of the syngas program. Approximately 100 isostatically pressed and machined, closed-end tubes and tube assemblies were fabricated for atmospheric and high-pressure testing at Eltron and Air Products. Most of this effort involved fabricating sealed assemblies of I4 materials, primarily I4(B) coated with proprietary catalysts. In the initial stage of Phase 1, difficulty was experienced in maintaining seal integrity during high-pressure syngas testing. Ceramtec made several modifications to the compression seal design and the ITM geometry that lead to the development of a very robust seal for use under conditions with minimal thermal cycling. Consequently, by FY99 Q4, seal performance no longer hindered evaluations of materials performance, and the first long-term testing in realistic, high-pressure, high-temperature syngas environments began.

Figure 1.2.1.2-1 Photograph of an ITM Tube Assembly Used for Evaluating Materials Performance in Simulated, High-pressure, High-temperature Syngas Environments

Ceramatec fabricated tape cast, planar membranes and isostatically pressed tubular specimens of I2, I4, and I5 compositions to determine oxygen flux and stability. In addition, tubular coupons and bend bars were supplied to Penn State University for mechanical testing. During this fabrication development, it was observed that the more refractory ITM compositions toward which the program evolved required both higher processing temperatures and more thorough and intimate mixing of the starting powder components. Consequently, investigations were carried out and are continuing toward optimizing the processing parameters for these new materials. In order to control creep, for example, it became evident that precise control of materials stoichiometry and microstructure is important. The relationship of stoichiometry and material properties and fabricability was demonstrated, and procedures for consistently fabricating the desired materials on a small scale were developed.

Subtask 1.2.1.3 Low ΔP (<300 psig) Testing

Four high-pressure reactors with support hardware and control systems were designed by Air Products and constructed at Eltron Research. Subsequent modifications were made to suit adjusted run requirements.

Tubular membrane/seal assemblies were supplied by Ceramatec. Fifty-one tubes were tested, including 45 ceramic tubes of 8 ceramic compositions and 2 A/B ratios with 5 oxidation catalysts. Of these, 32 tubes reached 250 psig and 825°C, and 22 tubes were tested under methane or syngas. The longest test under syngas was over 2400 hours. The highest measured oxygen flux rate was 1.5 ml/min cm² for an I4(B) material at 900°C. Air flow rates have had a large effect on oxygen flux. At the highest air flow rates, the oxygen flux values are similar to those measured in the ambient pressure reactors at the same temperatures. All values are based on internal active surface areas.

The performance of the longest high-pressure test is illustrated in Figures 1.2.1.3-1 and 1.2.1.3-2. Tube MF Lot 43-3 operated with continuous oxidation of a reducing gas mixture (CO/CH₄/H₂O) for 2407 hours. Series 43-3 was an I4(B) material with an A/B ratio of 1.01, sintered for 12 hours at 1250°C. The test was conducted at 825°C. As shown in Figure 1.2.1.3-1, during each phase of the test, the performance was relatively stable. Large changes in the data during a single phase were due to unplanned events. Several such events occurred when the water flow was stopped for several days around 300 hours, for a 12-hour period near 600 hours and again for periods between 1500 and 1700 hours. At these points, the effect on product distribution was significant due to the reverse water gas shift reaction. Changes in the atmospheric pressure air flow delivered to the inside of the tube (from 100 to 600 sccm) had a dramatic effect on oxygen flux and product composition, as shown in Figure 1.2.1.3-2. Every increase in air flow brought about an increase in product oxidation. The percent of oxygen in the depleted air was never below 16%, so it is not likely that the effect of air flow was due to oxygen concentration in the air, but more likely to the gas flow dynamics inside the tube.

Figure 1.2.1.3-1 Gas Phase Product Distribution in a 100-Day Test of a I4(B) Tube
(The test was run at 825°C and 250 psig.)

Figure 1.2.1.3-2 Oxygen Flux as a Function of Air Flow Rate in a 100-Day Test of a I4(B) Tube
(The test was run at 825°C and 250 psig.)

Subtask 1.2.1.4 High ΔP (<500 psig) Testing

Two cold-wall, high-pressure test reactors were constructed at Air Products, and shakedown of the first reactor has been completed. The reactor system has been demonstrated at full operation temperature and pressure (950°C and 3.1 MPa (450 psig)). These two high-pressure, cold-wall membrane reactor systems permit characterization of membrane performance under process conditions characteristic of anywhere in the proposed membrane reactor vessel designs, albeit at lower space velocities. Temperatures, pressures, and gas compositions representative of both the GTL and H₂ cases are accessible. Tests planned for the reactors involve characterization of the performance of membranes of different material compositions, long-term (lifetime) testing of membranes, and the performance trade-off involved in the use of bulk versus surface syngas partial oxidation catalysts.

Subtask 1.2.2 Seals Development

Subtask 1.2.2.1 Development of Seal Materials and Seal Construction

Compression Seals

As noted in Subtask 1.2.1.2, Ceramatec made a number of modifications to the original seal design in efforts to provide robust tube assemblies for testing in the high-pressure syngas reactors. Figure 1.2.2.1-1 shows the evolution of these modifications as quantified by room temperature pressure testing. Figure 1.2.2.1-2 depicts these changes in a schematic illustration showing the interior parts of the modified assembly. Since making these modifications, it has been found that the primary cause of failure of tube assemblies has been time-dependent deformation (creep) of the ITM materials. However, despite material deformation during testing, significant improvements in tube longevity have been achieved due in part to the high degree of dimensional compliance provided by the modified seals. Eleven of the 12 tube/seal assemblies, tested in FY99 Q4, survived the syngas reactor environment for 20 or more hours, and several survived for 2-4+ weeks without measurable leaks.

Figure 1.2.2.1-1 Room Temperature Leak Rate Measurements Obtained on ITM Tube Assemblies as a Function of Seal Modifications

Figure 1.2.2.1-2 Schematic Illustration of the Basic Components of a Compression Seal Used to Seal ITM Tubes to a Haynes 230 Tube-and-Cup Assembly

Significant emphasis was placed on the optimization of this compression seal. Efforts involved determining appropriate alloy selection, tightening the specifications placed on the fabrication vendor, optimizing the plating thickness, and refining the machining practices and tolerances for machining the end of the ceramic tube elements. Long-term oxidative corrosion tests were performed on plated U-rings to provide input to the alloy selection. Results from these tests in concert with a comprehensive review of the literature values for the high-temperature mechanical properties of these alloys led to the selection of Haynes 230 as the base alloy for the U-ring sealing elements. Gold plating was chosen to provide a soft sealing surface in contact with the surface of the ceramic tube, and to provide a low reactivity interface to the tube. Improvements in the design and configuration led to steady improvement in the success rate of the assembled seals, which now exceeds 90% in high-pressure tests.

Glass-Ceramic Seals

Limited testing at Air Products demonstrated the ability to form a leak-tight, thermally cyclable seal between I4 and 446 stainless steel using a glass ceramic composition developed by Alstom. Leak tests were carried out at room temperature on samples in the as-fabricated condition, as well as on samples cycled up to 25 times between room temperature and 750°C. Application of this composition at higher temperatures is likely to be limited.

Glass-ceramic seal development was conducted by PNNL, with the goal of identifying glass compositions suitable for the desired application. Efforts concentrated on determining effects of

compositional variation on the coefficient of thermal expansion (CTE), bonding characteristics to I4 materials and Haynes 230 alloy, and interface reactions with the ceramic and metal end members. A total of 68 glasses and composite glasses were formulated.

The Sr-Al-Si-O (SAS) series of glass were investigated. Results showed the CTE of the glass increased with increasing SrO content. The highest CTE within SAS family was found to be less than the target necessary to match the I4 materials. In addition, increasing the SrO content clearly increased the glass transition and softening points, which was unfavorable in lowering the processing temperature for sealing.

Next, the addition of B_2O_3 to the SAS system was investigated. The effect of B_2O_3 on CTE was not as strong as that of SrO. The highest measured CTE for these glasses was still below the target. On the other hand, the addition of B_2O_3 can greatly reduce the glass transition and softening points.

The effect of Al_2O_3 on the CTE was also investigated. The CTE of the glass is higher for lower Al_2O_3 content. Again, the highest CTE measured was below the target. It also appeared that more Al_2O_3 resulted in higher glass transition and softening points.

The highest CTE obtained within the addition of Zn was still too low. In several samples, no clear glass was obtained.

Based on these results, composite glasses were investigated. These glasses combined glasses with high-CTE filler materials to obtain the desired CTE. This approach provided acceptable materials, which agreed with the theoretical predictions. The fillers included the I4 material and/or MgO. However, XRD indicated that the composite glass was more reactive.

Alkali-Germanate glasses reportedly have higher CTEs than our target. Several samples were prepared that replaced the alkali element with Sr. The CTEs of these samples were significantly lower than expected and hence lower than the target CTE. No further effort was made to tailor the compositions.

Substituting larger cations (La and/or Y) for the Al was found to be effective to increase the CTE. Five glass compositions were found to meet the target CTE after heat treatment at 1100°C . However, the glass formation region seems to be narrower with substitution of La or Y. The only composition that resulted in clear glass had a TEC below the target value.

Select glasses and composite glasses were used in initial bonding tests. These glasses were tested with ceramic discs, metal discs, and ceramic-metal sandwiches. Some of the glasses formed strong bonding with the ceramic as well as with the metal. Interfacial microstructure characterization depicted the hermetic bonding at the interface. In addition, the ceramic interface is rather straight and the metal interface is more zigzag, which can provide extra mechanical interlocking. Examination of the composite glass showed some glass penetration into the ceramic along the grain boundaries which is undesirable. In addition, the ceramic samples required slow cooling to prevent micro-cracking.

Bonding tests of these select glasses in a sleeve-joining arrangement (ceramic tube in a metal seal cup) resulted in shear fracture along the rim section. Early stress analysis showed high shear and tensile stresses will build up upon cooling from the sealing temperature. The high stress locations were consistent with the actual fracture. For samples that did not fracture, bubble tests were conducted. No seals were hermetic.

Braze Seals

Metallic braze seal development was initiated at PNNL, with a thorough review of commercial braze alloys and vendors. Several nickel-based brazes were selected for evaluation. Results indicated that these brazing filler metals had poor wetting characteristics with the ceramic or resulted in cracking at the ceramic-braze material interface.

A high-temperature vacuum/inert atmosphere brazing furnace has been purchased and installed at Air Products and will also be used to evaluate commercial braze alloys for various seal configurations.

Subtask 1.2.2.2 High ΔP Seal Testing in Inert Atmospheres and Under Process Conditions

The high-pressure syngas generation tests carried out on the isopressed tubular membrane/seal assemblies (Subtask 1.2.1.3) were also a test of the compression seal under reactive conditions. The best performance of this compression seal was 100 days at 250 psig and 825°C. These results suggest that compression seals are the most promising of all the seals considered.

A high-temperature/high-pressure, cold-wall, multi-sample seal test system has been designed and purchased. The unit is being installed at Air Products. The system is capable of testing up to five ceramic to metal seal samples at full process temperatures and pressures in non-reactive reducing, inert, and oxidizing atmospheres. The leak rate of each seal sample will be able to be determined independently.

TASK 1.3 ITM SYNGAS REACTOR DESIGN AND FABRICATION

Subtask 1.3.1 ITM Syngas Reactor Design and Engineering

Subtask 1.3.1.1 Mechanical/Structural Design of Membranes and Seals

Tubular Membrane Geometry

A tubular membrane geometry was investigated to support the reactor design effort. Several design concepts were considered and Figures 1.3.1.1-1 and 1.3.1.1-2 are examples. In Figure 1.3.1.1-2, channel-free porous support layer 522, porous layer 523 and a second porous layer 530 provide an integral support for the dense layer 521. Channels 526 provide the passages for the air supply to the inner membrane surface. The tubular concept in Figure 1.3.1.1-1(b)

allows the use of bayonet elements in a reactor design whereby air flows up through the annulus and back down the center tube. An initial screening criterion for the membrane designs was that they must support the approximately 400-psi pressure differential between the high-pressure syngas and low-pressure air. No design was identified that could withstand the differential pressure stresses without involving very complicated structures or thicker membrane walls that would not achieve the target oxygen fluxes.

Figure 1.3.1.1-1 Conceptual Tubular Membrane Cross Sections
 (a) Bi-ceramic porous over dense layers without internal rib supports.
 (b) Bi-ceramic porous over dense layers with internal rib supports.

Figure 1.3.1.1-2 Conceptual Tubular Membrane Cross Section

Planar Membrane Geometry

A planar membrane geometry was developed to support the reactor design effort. The concept for a planar membrane wafer is shown in Figure 1.3.1.1-3. In Figure 1.3.1.1-3, a dense mixed conducting layer 21 is contiguous to a porous support layer 22, which in turn is adjacent to a

second porous layer 23. Layer 26 contains channels through which the heated air feed stream is passed. The process gas mixture to be oxidized is passed at pressure over the external surface of the mixed conducting layer 21. A partial oxidation catalyst is typically situated contiguous to the dense mixed conducting oxide layer 21. The thickness and spacing of the ribs that separate the air channels are designed so that the membrane can support the 400 psi syngas-to-air pressure differential. Analysis of air-side and syngas-side mass transfer resistances was used to determine the air channel dimensions and wafer-to-wafer spacing. Wafer-scale thermal profiles were used to analyze thermal expansion stresses. It was found that to mitigate thermal stresses, a co-current flow arrangement in which air and syngas flow in the same direction is preferred. The membrane wafer also features a dense rim to manage thermal stresses in the leading and trailing edges.

Figure 1.3.1.1-3 Planar Membrane Wafer Cross Section

Subtask 1.3.1.2 Reaction Engineering and Kinetic Modeling

Reaction and transport models were developed in parallel efforts at different levels of detail. Simpler models were used for initial development of membrane and reactor concepts. More detailed models were used to analyze laboratory-scale experiments, while laying the framework for detailed models to be incorporated into membrane reactor design and analysis.

McDermott developed membrane-scale thermal and reaction models using simplified kinetics for oxidation and equilibrium reforming. Thermal models of tubular and planar membrane elements were used to examine the performance of the membrane, predicting heat transfer and temperature variations across the membrane within the reactor. The effect of membrane temperature on O_2 flux and the resulting oxidation and reforming reactions were integrated into the model. The calculated thermal profiles were used for structural analysis of the membranes.

Air Products, Chevron, and Norsk Hydro developed detailed models of reaction kinetics and membrane-scale transport phenomena to analyze laboratory-scale experimental results and to form the basis for more detailed models to be incorporated into the membrane and reactor design work. The tubular geometry model considered heat transfer, mass transfer, surface and packed-bed reactions, and ionic transport through the membrane. The model was used to evaluate experimental results from the atmospheric pressure reactors at Eltron and Air Products.

Subtask 1.3.1.3 Conceptual Reactor Vessel Engineering

McDermott developed initial tubular and planar membrane and membrane reactor designs, with input from Ceramatec and Air Products. Illustrations of the types of ITM membrane reactor geometries that were considered are shown in Figure 1.3.1.3-1.

Figure 1.3.1.3-1 Potential ITM Membrane Reactor Configurations

Tubular Geometry

A tubular membrane reactor concept was developed for an ITM reactor with 50 MMSCFD (60°F) associated gas feed. The reactor concept incorporates bayonet tubular elements in which air flows up through the annulus and back down the center tube, as shown in Figure 1.3.1.3-2. The outer tube is capped on one end, and the inner tube is open on both ends. Both tubes terminate in air-cooled tube sheets. Active cooling of the tube sheets was needed to reduce metal temperatures and minimize tube-sheet thickness.

Figure 1.3.1.3-2 Bayonet Tube Reactor Concept

Planar Geometry

A potential manifolded planar membrane arrangement is shown in Figure 1.3.1.3-3. In this concept, the feed gas mixture is introduced into the passageways 25, which separate the array of planar membrane units 20. The heated air feed stream is introduced into the interior passages 22 of each planar membrane unit 20 through manifold structure 40 via inlet 50. The oxygen depleted exhaust gas is withdrawn through manifold structure 35 and outlet 45.

Figure 1.3.1.3-3 Conceptual Planar Membrane Stack and Manifolds

A preliminary planar membrane reactor, using this concept was developed for an ITM reactor for processing 50 MMSCFD (60°F) associated gas feed. The wafer element was based on the concept shown in Figure 1.3.1.1-3.

An alternate wafer element that used the concepts of Figure 1.3.1.1-3 with internal air manifolds rather than the external manifolds shown in Figure 1.3.1.3-3 was also considered and ultimately adopted. A wafer stack was built up by using spacers between each wafer to create a syngas flow passage between the wafers. To help manage thermal stresses, a co-current flow arrangement was chosen in which air and syngas flow in the same direction. Figure 1.3.1.3-4 shows this wafer stack arrangement as well as the internal air manifolding concept.

The reactor design considered pressure vessel design, materials of construction, manifolding, insulation, and internal arrangement. Some of the most significant vessel design considerations include minimizing vessel wall penetrations, connecting the wafer stacks on one side for thermal growth considerations, and insulating the air manifold piping.

A potential vessel layout is shown in Figure 1.3.1.3-6. In this design, individual membrane wafers are stacked. These stacks are installed in both a parallel and series arrangement in a refractory-lined syngas duct. This duct ensures that the process gas passes across the membranes. Each stack has an air inlet pipe and an air outlet pipe connected to it. These pipes are then connected to inlet row and outlet row headers, which in turn are connected to main inlet and main outlet headers. The inlet row and main inlet headers direct the incoming hot air into the stacks. The outlet row and main outlet headers direct the oxygen-depleted air (non-permeate) out of the stacks. These header systems are also refractory lined. This entire assembly is installed in a pressure vessel. Since all hot gas streams are in refractory-lined ducts and piping, the pressure vessel can be a "cold-wall" vessel.

Figure 1.3.1.3-6 Planar Membrane Reactor Vessel Layout

Membrane Geometry Selection

The planar membrane geometry was selected for further development and scale-up. A comparison between the planar and tubular membrane geometries is shown in Table 1.3.1.3-1.

Table 1.3.1.3-1 Comparison of Planar and Tubular Membrane Geometries

	Planar	Tubular
Membrane structural requirements	* Able to support 400 psi pressure differential	* Complicated structures and/or thick walls needed to support 400 psi differential
Kinetics and reactor design		
Modularity and flexibility	* Very high degree of flexibility, e.g., in membrane bank height and width, number of banks in a reactor.	* Flexibility limited by anticipated 9 ft maximum length of tubes
Initial reforming endotherm	* Able to process non-equilibrium feed gas and mitigate initial endotherm	* Current concept based on equilibrium feed gas
Reactor layout		
Specific membrane area (ft ² membrane/ft ³ shell)	* 1.3*X to 2*X	* X
Ceramic-Metal seals (ft ² membrane/seal)	* 20*Y	* Y

Subtask 1.3.2 ITM Syngas Membrane Fabrication

Subtask 1.3.2.1 Powder Production, Process Development, and Scale-up

Ceramatec produced intermediate to large batches of I4 powder for membrane sample fabrication. Over 150 kg of I4 powder was produced. Ceramatec recently milled multiple 25+ kg powder batches as part of a feasibility study of a high-energy, dry-grinding method. As a result, a medium-sized attrition mill was purchased.

In addition, aqueous processing routes for scaling up powder production were investigated. Processing ITM powders in aqueous media requires very careful control of the solution chemistry, since the pH quickly rises to ~12, which can lead to problems such as poor dispersion and incongruent powder dissolution. Aqueous passivation systems were investigated to control this. Figure 1.3.2.1-1 illustrates the effect of the passivation systems in controlling the pH as a function of time, agitation or milling conditions. As this figure shows, even during vibratory milling, when powder dissolution processes would be accelerated significantly, the solution pH remained nearly constant and in a manageable range for many hours. Calcined powders are currently being produced for use in a scale-up demonstration for which large batches of I4(B) powder will be wet milled and spray dried.

Figure 1.3.2.1-1 Solution pH as a Function of Time and Agitation or Milling Conditions for I4(B) Powder in Passivated Solutions

Subtask 1.3.2.2 Membrane Fabrication Process Development

Ceramatec provided I4 powder to NGK for use in demonstrating the feasibility of extrusion as a means of fabricating membrane structures. Early efforts to fabricate porous tubular structures, as shown in Figure 1.3.2.2-1, were successful. However, due to decision to use planar structures, the extrusion effort was redirected toward fabrication of planar geometries. Ultimately, the extrusion efforts were abandoned as better fabrication routes to planar components were identified.

Figure 1.3.2.2-1 Photograph of a 1 cm Diameter, Extruded, Porous I4 Tube

Ceramatec investigated other technologies that may be suitable for rapid fabrication of complex planar structures. Scoping efforts evaluated fabrication technologies that included, for example, calendaring, coining, transfer molding, and water-abrasive jet milling. A lamination process was chosen.

Ceramatec successfully fabricated laminate structures incorporating dense, porous, and slotted layers. All layers were fabricated using I4(B) powder. The laminate structure had the configuration BABDD where B was porous layers, A was a dense layer serving as the ITM membrane, and D were dense, slotted layers. Fracture cross sections of a BABDD laminate are shown in Figures 1.3.2.2-2 and 1.3.2.2-3. Fired specimens were hermetic to helium and met the target criteria for specimen geometry and porosity. Model structural elements of these materials were fabricated for mechanical testing purposes. Similar PDS (porous-dense-slotted) specimens were fabricated of more creep-resistant I4 compositions. These PDS structures will be used for flux testing and mechanical testing.

Figure 1.3.2.2-2 Fracture Cross Section of a BABDD ITM Laminate

Figure 1.3.2.2-3 Higher Magnification of a Fractured Cross Section of a BABDD ITM Laminate

PHASE 2 RESULTS

TASK 2.1 COMMERCIAL PLANT ECONOMIC EVALUATION

Subtask 2.1.1 Advanced Process Design and Evaluation

ITM SYNGAS GTL

Air Products investigated process flowsheet improvements to the Phase 1 Baseline ITM Syngas Process for GTL applications. These improvements addressed the potential need to modify the ITM reactor operating conditions to improve membrane material stability. Process simulations and initial cost estimates for these alternative flowsheets were completed to identify the most promising candidates for more detailed evaluation. As in Phase 1, the process simulations and cost estimates were based on a capacity of 50 MMSCFD of associated feed gas.

Some of the alternate processes changed the Fischer-Tropsch (F-T) reactor conditions, such as feed composition and recycle ratios. To allow more accurate simulation of the impact of these changes, Chevron made a number of improvements to the F-T portion of the overall GTL simulation model. To reflect current commercial systems, the F-T facility model was revised from a two-stage reactor system to a single-stage reactor with a recycle loop. A preliminary kinetic equation for CO conversion was added to the F-T reactor model to incorporate the impact of H₂, CO, and water partial pressures on the degree of CO conversion. Equations were also added to the F-T reactor model to estimate the production of CO₂, methane, and ethane depending on syngas composition and pressure. Finally, an equation for the syngas partial pressure-dependency of the F-T product distribution was added to the model.

The first alternate process, Figure 2.1.1-1, added a fired heater to the Phase 1 Base Process to increase the mixed feed temperature to the ITM reactor to 1382°F. The S/C ratio was kept at 1.5. A slip stream of product syngas was fed to a pressure swing adsorption (PSA) unit to provide the necessary H₂ for F-T product upgrading and natural gas hydrogenation. This process still had high CO₂ concentrations in the feed end of the reactor and, hence, the higher mixed feed temperature did not improve the CO₂ stability of the membrane as much as was required.

The second alternate process, Figure 2.1.1-2, made small process improvements for better efficiency over the process in Figure 2.1.1-1, as the ITM mixed feed temperature was raised further. Also, to better match feed temperatures, the air feed temperature was increased. This process still had high CO₂ concentrations in the feed end of the reactor and again the higher temperatures did not provide the required improvement to the CO₂ stability of the membrane. However, this case had a lower O₂ permeation requirement relative to the previous case.

The third case, Figure 2.1.1-3, injected the external F-T recycle into the midpoint of the ITM reactor in order to decrease the equilibrium concentration of CO₂ in the feed end of the reactor. Feed temperatures were the same as those used in the process described in Figure 2.1.1-2. The F-T recycle pre-reformer and the associated preheat coil were added to the flowsheet.

Pre-reformer operating temperatures were optimized for the feed gas conditions. The front end membrane material stability issue was resolved.

The fourth case, Figure 2.1.1-4, added a reverse shift on the external F-T recycle rather than injecting it into ITM reactor. The reverse shift converts the H_2 and CO_2 in the internal F-T recycle to CO and H_2O . This stream is then blended with the syngas product and allows a higher H_2/CO ratio from the ITM reactor. The F-T reactor feed H_2/CO ratio was allowed to increase. The addition of this feature results in numerous other changes to the flowsheet. A significant reduction in O_2 permeation requirement was achieved.

The fifth case, Figure 2.1.1-5, added a Gas Heated Reformer (GHR). The syngas effluent from the ITM reactor was used to provide heat to reform the natural gas feed stream. The midpoint injection of the external F-T recycle stream was still used. The external F-T recycle flowrate increased significantly.

Figure 2.1.1-1 Full F-T Offgas Recycle

Figure 2.1.1-2 Full F-T Offgas Recycle with Higher Reactor Feed Temperature

Figure 2.1.1-3 Mid-point F-T Offgas Injection

Figure 2.1.1-4 F-T Offgas Recycle with Reverse Shift

Figure 2.1.1-5 Gas Heated Reformer and Midpoint F-T Offgas Injection

Table 2.1.1-1 Summary Table of Alternate Process Cycles

Figure	2.1.1.1	2.1.1.2	2.1.1.3	2.1.1.4	2.1.1.5
ITM inlet CO ₂ content, mol%	16.0%	16.3%	3.2%	3.2%	6.3%
ITM feed temperature, F	1382	1472	1472	1472	1472
O ₂ requirement, lb-mol/hr	3678	3267	3436	2731	2896
Carbon efficiency, %	76.4%	77.7%	78.2%	78.1%	78.7%
Thermal efficiency, %	60.2%	61.2%	61.5%	61.5%	62.0%

An updated current technology (ATR with cryogenic air separation plant) case, Figure 2.1.1-6, was also completed for comparison purposes. This case revised the Phase 1 ATR base case to include the PSA unit to make the necessary hydrogen for the facility. The S/C ratio was assumed to be 0.6.

Figure 2.1.1-6 ATR Process Flow Diagram

Costs for these cases were estimated using ICARUS. Offsites and utilities were assumed to be 20 percent of the investment. A 10 percent owner's cost and a 10 percent contingency were also included in the capital cost. The relative capital cost, carbon efficiency, and thermal efficiency for several of the cases are shown in Table 2.1.1-2. This comparison indicated that the F-T recycle mid-point injection flowsheet (Figure 2.1.1-3) was the preferred alternate. The capital cost saving over the conventional ATR case was 25 percent.

**Table 2.1.1-2 Relative Capital Cost, Carbon Efficiency,
and Thermal Efficiency for Various Cases**

	Relative Capital Cost	Carbon Efficiency	Thermal Efficiency
Figure 2.1.1-1	1.03	76.4%	60.2%
Figure 2.1.1-3	1.00	78.2%	61.5%
Figure 2.1.1-4	1.13	78.1%	61.5%
Figure 2.1.1-5	1.33	78.7%	62.0%
Figure 2.1.1-6 (ATR)	1.33	78.6%	61.9%

Additional work on the preferred process (Figure 2.1.1-3) investigated the impact of a reduced ITM reactor outlet temperature (1652°F vs. 1742°F) to improve membrane reliability at the outlet end of the reactor. The lower ITM reactor effluent temperature increases the methane slip from the ITM reactor. To achieve the same H₂/CO ratio in the syngas, the F-T CO₂-rich recycle to the ITM was increased, and the internal F-T recycle was decreased. A slight decrease in ITM O₂ demand was achieved. However, the purge contained 8.4% methane compared to 6.1%. In addition, higher feed/fuel requirements and an additional boiler were needed. Operating at these conditions is a slight penalty (see Table 2.1.1-3), but may be reasonable, if necessary.

The addition of an O₂ secondary reformer was considered to reduce the effects of the lower ITM reactor effluent temperature. The oxygen secondary reformer would raise the syngas process outlet temperature back to 950°C and lower the oxygen demand of the ITM reactor, but would require the use of pure oxygen. As shown in Table 2.1.1-3, the carbon and thermal efficiencies are slightly higher without considering the cost of the pure oxygen. Overall, this process does not appear to provide any significant advantage.

Finally, raising the S/C ratio to 2.0 was also considered to reduce the effects of the lower ITM reactor effluent temperature. While the higher S/C ratio reduces the methane slip, the overall carbon and thermal efficiencies decrease and the oxygen demand of the ITM reactor increases. These results are also shown in Table 2.1.1-3. Overall this process did not appear to provide any significant advantage.

**Table 2.1.1-3 Summary of Process Alternatives for
Lower ITM Reactor Outlet Temperature**

Process	Figure 2.1.1-3	Max F-T Recycle	O ₂ Sec	S/C = 2
ITM exit temperature, °F	1742	1652	1652	1652
S/C ratio	1.5	1.5	1.5	2
O ₂ requirement, lb-mol/hr	3436	3356	3066	3646
O ₂ secondary requirement, lb-mol/hr	---	---	290	---
O ₂ secondary, exit temperature, °F	---	---	1742	---
Carbon efficiency, %	78.2%	77.1%	78.3%	76.4%
Thermal efficiency, %	61.5%	60.7%	61.7%	60.1%

Large-Train, Land-Based GTL

McDermott completed an update of the large-train, land-based reactor design cost estimate. The land-based process design was based on 500 MMSCFD of natural gas using three processing trains, with each train processing approximately 150 MMSCFD of natural gas as process feed, and the balance of the gas used as process fuel. A conceptual design of the large land-based, ITM reactor is shown in Figure 2.1.1-7.

Figure 2.1.1-7 Land-based ITM Reactor (150 MMSCFD Natural Gas Feed Per Train)

The updated estimate, built on work completed during Phase 1, included more detailed evaluation of individual process components, consolidation of multiple systems into a single system per train, and updated material cost data from the McDermott Engineering data base. The current capacity scale-up factor from an offshore size plant (50 MMSCFD natural gas feed per train) to a large land-based plant (150 MMSCFD natural gas feed per train) is 0.75 for the ITM reactor vessel. Results of cost sensitivity evaluations showed that reactor costs can be optimized by reaching a balance between minimizing both the reactor diameter and the number of vessel penetrations.

A schematic side view of the conceptual reactor design is shown in Figure 2.1.1-8. Membrane modules **501**, **503**, **505**, **507**, and **509** are installed in series in flow containment duct **511** within pressure vessel **513**. Inlet **515** directs inlet gas stream **517** to the flow duct and membrane modules **501** to **509**. The inlet gas stream is a reactant feed gas containing one or more components which react with oxygen at elevated temperatures wherein the inlet reactant feed gas is heated by any appropriate method to a temperature of 600°C to 1100°C. An example of a reactant feed gas is a mixture of steam and natural gas wherein the natural gas comprises mostly

methane with smaller amounts of light hydrocarbons. The mixture may be pre-reformed at a temperature below about 800°C to yield a reactant feed gas containing steam, methane, hydrogen, and carbon oxides.

Figure 2.1.1-8 Schematic Side View of Conceptual Reactor Design

The gas pressure in the interior of flow containment duct **511** can be greater than the gas pressure in the interior of pressure vessel **513** between the inner wall of the vessel and the outer wall of flow containment duct **511**. This may be accomplished, for example, by purging the space outside the duct with a gas at lower pressure than the process gas inside the duct; allowing flow communication between the space outside the duct and the process gas in the duct at the process gas outlet, **559**; introducing a purge gas into the space outside the duct, and withdrawing the purge gas through a purge gas outlet while using pressure controllers on a purge gas outlet to maintain a lower pressure in the space outside the duct than inside the duct.

The interior regions of membrane modules **501** to **509** are in flow communication with two manifold systems, one to introduce an oxygen-containing oxidant gas into the modules and the other to withdraw oxygen-depleted oxidant gas from the modules. The first of these manifold systems comprises main inlet manifold **519**, primary inlet manifolds **521**, **523**, **525**, **527**, and **529**, and secondary inlet manifolds **531**, **533**, **535**, **537**, and **539**. The second of these manifold systems comprises main outlet manifold **541** and primary outlet manifolds **543**, **545**, **547**, **549**, and **551**. Alternately, secondary inlet manifolds **531**, **533**, **535**, **537**, and **539** may be combined with primary outlet manifolds **543**, **545**, **547**, **549**, and **551**, respectively, when located within flow containment duct **511**. The two manifolds may be combined by installing a first or inner conduit within a second or outer conduit wherein the first conduit provides a first manifold and the annulus between the conduits provides a second manifold. The conduits may be concentric or coaxial or may have separate parallel or nonparallel axes.

Heated, pressurized oxygen-containing oxidant gas **553**, for example, air that has been heated by any appropriate method to a temperature of 600 to 1100°C, enters main inlet manifold **519** and flows via primary inlet manifolds **521**, **523**, **525**, **527**, and **529** and secondary inlet manifolds

531, 533, 535, 537, and 539 to the inlets of membrane modules **501, 503, 505, 507, and 509**. Oxygen from the oxidant gas in the interior regions of the membrane modules permeates the dense active membrane layers in the wafers of modules **501** to **509** and the permeated oxygen reacts with the reactive components in the exterior regions of the membrane modules. Oxygen-depleted oxidant gas exits the outlets of the interior regions of the membrane modules via primary outlet manifolds **543, 545, 547, 549, and 551** and main outlet manifold **541**, and the final oxygen-depleted oxidant gas is withdrawn as gas stream **555**. Outlet gas stream **557**, which contains reaction products and unreacted feed components, is withdrawn from the reactor system via outlet **559**.

Figure 2.1.1-9 shows a schematic of Section 8-8 of the membrane reactor vessel of Figure 2.1.1-8. In this example, a bank of three membrane modules **503a, 503b, and 503c** are installed in parallel in duct **511**. Oxidant gas flows through main inlet manifold **519**, primary inlet manifold **523**, and secondary inlet manifolds **533a, 533b, and 533c** to the inlets of membrane modules **503a, 503b, and 503c**. Oxygen-depleted oxidant gas exits membrane modules **503a, 503b, and 503c** via primary outlet manifolds **545a, 545b, and 545c**, secondary outlet manifold **561**, and main outlet manifolds **541a and 541b**. Any number of membrane modules can be installed in parallel to accommodate the desired flow capacity of the reaction system.

Figure 2.1.1-9 Schematic View of Section 8-8 of Conceptual Reactor Design Shown in Figure 2.1.1-8

A guard bed may be installed in inlet **515** to pressure vessel **513** to remove trace contaminants from inlet stream **517**. Alternatively, the guard bed may be installed in the interior of the pressure vessel between the inlet and the first membrane module. The contaminants may include, for example, sulfur-, chromium-and/or silicon-containing gaseous species. The guard bed may contain one or more materials selected from the group consisting of magnesium oxide,

calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, strontium oxide, zinc oxide, and alkaline-earth-containing perovskites. These materials react with and remove the contaminants from the inlet stream of reactant gas.

Additional pressure vessels may be installed in series with pressure vessel **513** such that the outlet gas from one vessel feeds the other vessel. Additional pressure vessels may be placed in parallel wherein a plurality of pressure vessels operate in parallel and in series. Guard beds may be placed between any series pressure vessels as desired.

In the embodiments described above, it is desirable to use internal insulation to maintain the walls of pressure vessel **513** at temperatures lower than the temperatures of the respective membrane modules **501** to **509**. The insulation can be installed in a number of different configurations, such as:

- Insulation fills the void between flow containment duct **511** and pressure vessel **503**. The flow containment duct walls could be formed from the insulation or a separate structure made with another material such as metal or ceramic.
- Insulation is placed on the inner wall of pressure vessel **503** and there is a gas void between the insulation and flow containment duct **511**. The manifolds may or may not have external insulation.
- Insulation is placed on the exterior surfaces of flow containment duct **511**. There is a gas void between the insulation and the inner wall of pressure vessel **503**. The flow containment duct walls could be formed from the insulation or a separate structure made with another material such as metal or ceramic. The manifolds may or may not have external insulation.
- Insulation is placed on the interior surfaces of flow containment duct **511**. There is a gas void between flow containment duct **511** and the inner wall of pressure vessel **503**. The manifolds may or may not have external insulation.

Metal-to-ceramic seals are used in primary manifolds **533a**, **533b**, and **533c** to transition from metal manifolds to the ceramic modules. These seals can be located in flow containment duct **511**, in the insulation, or in the gas void of pressure vessel **503** depending on the desired operating temperature of the seal.

The insulation may contain alumina, alumino-silicate, silica, calcium silicate, or other conventional insulation materials suitable for use at elevated temperatures. The insulation may comprise, for example, one or more materials selected from the group consisting of fibrous alumina, fibrous alumino-silicate, porous alumina, and porous alumino-silicate. In the cases where the insulation itself forms a cavity around the membrane modules, the interior walls of the cavity may be coated or covered with a material which prevents volatile components from the insulation from contacting the membrane modules. For example, the cavity may be lined with a foil made of a metal such as Haynes 214 to prevent Si-containing vapor species, which may be generated from insulation material, from contacting the membrane modules.

The insulation may include one or more additional materials selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, strontium carbonate, sodium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites wherein these materials may be applied to the surface of the insulation and/or dispersed throughout the insulation. These additional materials may be used in place of or in addition to the guard bed or beds described above. These materials react with and remove contaminants that may be present in the inlet stream of reactant gas; these contaminants may include, for example, sulfur-, chromium-, silicon-, or oxygen-containing gaseous species.

The series-parallel membrane module arrangement is shown in Figure 2.1.1-10, a sectional plan view of the conceptual reactor design shown in Figure 2.1.1-8. This schematic shows an example arrangement with five banks of three parallel modules that are arranged such that each individual set of series modules lies along a common axis. A potential drawback to this arrangement is that some portion of the total gas flow in the flow containment duct will flow between modules (e.g., between module **501a** and module **501b**) and not react as the gas flowing into the modules (e.g., module **501a** or module **501b**) would react. This bypassing flow may then flow between module **503a** and **503b** and so on down the length of the reactor. Any bypassing will negatively impact the overall efficiency of the reactor. Flow baffles can be used to redirect gas flow bypassing and promote gas mixing.

Figure 2.1.1-10 Schematic Plan View of Conceptual Reactor Design Shown in Figure 2.1.1-8

The module configuration shown in Figure 2.1.1-11 can also minimize the impact of gas flow bypassing. This arrangement has alternate banks of modules offset from the preceding modules such that they no longer lie along a common axis. With proper selection of the spacing between modules in a bank and between banks, the impact of gas flow bypassing can be minimized. Any gas bypassing modules **502a**, **502b**, or **502c**, will contact downstream modules **504a**, **504b**, or **504c**, respectively.

**Figure 2.1.1-11 Schematic Plan View of Conceptual Reactor Design
Shown in Figure 2.1.1-8 Showing an Alternate Membrane Module Arrangement**

Reforming catalyst may be disposed between any series modules, any parallel modules, any series and parallel modules, and/or following the final modules in a vessel. The reforming catalyst promotes the endothermic reactions of water and/or carbon dioxide with hydrocarbons, especially methane, to generate hydrogen and carbon monoxide. The catalyst may be used to complement or balance the exothermic oxidation reactions that occur between permeated oxygen and reactants adjacent to the surfaces of the active membrane material in the modules. By appropriate use of reforming catalyst at strategic locations between the modules in a multiple-module series reactor system, the temperature profiles across the reactor and the product gas composition may be controlled to achieve optimum reactor operation.

In Figure 2.1.1-10, catalyst **501d**, **501e**, and **501f** is placed in series in the space between any modules in the first bank of modules **501a**, **501b**, and **501c** and the second bank of modules **503a**, **503b**, and **503c**. Alternatively, catalyst **501d**, **501e**, and **501f** may extend continuously between the inner walls of flow containment duct **511**. Likewise, catalyst may be placed between any or all of the second and third banks of modules, the third and fourth bank of modules, the fourth and fifth banks of modules, or following the fifth bank. Similarly, catalyst may be placed in series fashion between any or all of the offset banks of modules in the embodiment of Figure 2.1.1-11. For example, catalyst **502d**, **502e**, and **502f** may be placed in series fashion in the space between the first and second banks of modules. Alternatively, catalyst **502d**, **502e**, and **502f** may extend continuously between the inner walls of flow containment duct **511**.

Additionally or alternatively, catalyst may be placed between the modules in a bank of parallel modules to promote reforming reactions in the gas passing between the modules. For example, in Figure 2.1.1-10, catalyst **505d** and **505e** may be placed between modules **505a** and **505b** and between **505b** and **505c**. Alternatively, catalyst **505d**, and **505e** may extend continuously in the axial direction between the first through fifth banks of modules. For example, in Figure 2.1.1-11 catalyst **506d** and **506e** may be placed between modules **506a** and **506b** and between **506b** and **506c**.

The catalyst may be varied in type and/or amount depending on the axial or radial location among the modules in the pressure vessel. In one alternative, for example, the catalyst activity may be varied in the axial direction for optimal control of the module temperatures through the reactor. Catalyst sections near the inlet of the reactor may comprise catalyst which is active at lower temperature (e.g., a high Ni loading), whereas in higher temperature regions of the reactor the optimal catalyst composition may involve lesser activity and greater thermal stability (e.g., a low Ni loading). In this way, optimal catalyst activity can be achieved at every axial location in the reactor, while maintaining thermal stability of the catalyst.

The catalyst for use in this embodiment may include one or more metals or compounds containing metals selected from the group consisting of nickel, cobalt, platinum, gold, palladium, rhodium, ruthenium, and iron. The catalyst may be supported on alumina or other oxide supports and may include additions such as lanthanum or potassium. The catalyst may be placed between modules by any known means including, for example, using monoliths or using granular catalysts in appropriate catalyst holders that fit in the spaces between the modules.

Figure 2.1.1-12 shows an additional module arrangement that reduced the length of the reactor. In this arrangement, there were two sets of membrane modules that were adjacent to each other with a partition between them. The gas flowed along one set, reversed direction, and flowed along the second set. The inlet gas and outlet gas connections are at the same end of the vessel. Vessel **1801** comprises inlet **1803**, outlet **1805**, first wall **1807**, second wall **1809**, end wall **1811**, and internal gas flow control partition **1813**. Inlet gas **1815** flows over two parallel sets of five membrane modules **1817** through **1825** and **1827** through **1835**. Intermediate gas stream **1836** then is diverted 180° by end wall **1811** and flows over two parallel sets of five membrane modules **1837** through **1845** and **1847** through **1855**. Outlet gas stream **1857** exits via outlet **1805**.

Figure 2.1.1-12 Schematic Plan View of Conceptual Reactor Design with Multiple Gas Passes within the Vessel

Distributed Hydrogen Study

The Phase 1 design for a distributed-scale hydrogen generation system was developed further. The process (Figure 2.1.1-13) was sized for a capacity of 860 kg/day of hydrogen. The process was selected to minimize the capital cost since, at this capacity, the capital is the largest component of the hydrogen cost stack. The economic evaluation followed the basis outlined in the 2003 DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The cost of hydrogen from an ITM Syngas reformer coupled with a pressure swing adsorption unit was projected to be \$1.56/kg of hydrogen, which is 25% below the DOE 2005 target of \$2.09 for this scope. Additional cost reductions should be possible with further development.

Figure 2.1.1-13 Distributed Hydrogen Process Flow Diagram

Large-Scale, Fuel-grade ITM Hydrogen Process

Norsk Hydro investigated the feasibility of a large-scale, fuel-grade ITM Hydrogen facility. The hydrogen product could be used for clean power production. The proprietary study compared an oxygen-blown ATR-based process (ATR with a cryogenic ASU) to an ITM Hydrogen process. The design basis was selected to be a remote gas field with only natural gas and seawater available. Products were limited to the fuel-grade hydrogen product at 760 MMSCFD and a carbon dioxide product for potential sequestration; no export power was desired. The fuel-grade

hydrogen was supplied at the battery limits at 1450 psia and the carbon dioxide was supplied at 1160 psia. All utilities other than the natural gas and seawater needed to be supplied by the facility. Steam turbine generators supplied all required power and all large compressors were driven by steam turbines.

The designs for each technology were based on the basic concepts shown in Figure 2.1.1-14. Process flow sheets and mass and energy balances were completed. The process was designed with a steam-to-carbon ratio of 2, suitable for producing fuel-grade hydrogen. Due to its lower power requirements, the ITM Hydrogen process has a higher fuel efficiency than the ATR-based process; 74.3% (based on LHV) versus 71.2%.

Figure 2.1.1-14 Concept Designs for ITM Hydrogen and the Oxygen-blown ATR Technologies

All equipment items, including all the off-site equipment, were sized and preliminary equipment specifications were developed. The initial cost evaluation used factored equipment costs, budget quotes from vendors, or Norsk Hydro internal data. The ITM Hydrogen capital cost savings was 11 to 13 percent for the complete facility, including all off-sites. If off-sites were excluded, the ITM Hydrogen capital cost savings was 14 to 17 percent compared to the ATR-based process.

The ITM Hydrogen process and equipment were optimized further, based on the findings of the initial cost evaluation. Specific high cost equipment was eliminated from the flowsheet and replaced with lower cost alternatives by reconfiguring feed gas preheating methods. In addition, the oxygen recovery was increased. The energy efficiency (LHV basis) for the ITM case increased from 74.3% for the previous process design to 75.3% with this revised design, and is a significant advantage over the 71.2% efficiency for the ATR case.

A revised cost estimate was completed. The resulting capital cost savings were estimated to be 14 to 15 percent for the complete facility, including all off-sites. If the off-sites were excluded, the ITM Hydrogen capital cost savings was 20 to 22 percent compared to the ATR-based process. A sensitivity study on these results to the ITM reactor cost was conducted. The results are shown in Figure 2.1.1-15.

Figure 2.1.1-15 Investment Cost Savings for ITM Hydrogen Compared to Oxygen-Blown ATR with Cryogenic Air Separation Plant (Excludes Off-site Capital)

Large-Scale Methanol Production

Norsk-Hydro initiated a process design study for an ITM syngas-methanol plant having a capacity of 10,000 MT/D. As in the Large-scale, Fuel Grade Hydrogen study, a remote gas field location was considered, where only natural gas and seawater were available as feeds to the facility.

Norsk Hydro used a proprietary study of a 10,000 MT/D, ATR-based methanol plant as the baseline for this study. An ITM Syngas-based process was developed. Various process conditions were investigated, including S/C ratio and syngas delivery pressure. The effort was concluded before the process conditions were optimized and cost estimates started. Initial indications were that the ITM Syngas-based plant had slightly lower energy efficiency. Expectations were that, with further optimization, the energy efficiency of the ITM Syngas-based plant could be improved and that the cost benefits would be similar to those seen in the large-scale GTL studies.

Reactor Control System

Commercial ITM Syngas reactor control concepts were developed to improve steady-state operability of the ITM Syngas reactor, as well as increased ability for process turndown. The control concepts address the issues of heat management within and around the ITM Syngas membranes, by balancing the heat generated by oxidation reactions with the heat removed by methane reforming reactions and by convection.

The basic control concept configures the reactor into sequential stages with each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, and one or more reactant interstage feed gas lines. The interstage reactant gas flows from the outlet of a stage's reactant zone to the inlet of the next stage's reactant zone. Fresh reactant is added to the interstage reactant gas flow through the reactant interstage feed gas lines. Figure 2.1.1-16 illustrates this concept.

Figure 2.1.1-16 Multi-stage Reactor Control Concept

In the example of Figure 2.1.1-16, first stage **1** comprises oxidant side or zone **1a**, membrane **1b**, reactant side or zone **1c**, optional catalyst **1d**, and appropriate gas inlet and outlet regions. Optional catalyst **1d** is shown here as immediately following the module. Alternatively or additionally catalyst may be disposed immediately preceding the module or within or around the module in any desired configuration. Similarly, second stage **3** comprises oxidant side **3a**, membrane **3b**, reactant side **3c**, appropriate gas inlet and outlet regions, and optional catalyst **3d**, which is shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module or within or around the module in any desired configuration. Similarly, third stage **5** comprises oxidant side **5a**, membrane **5b**, reactant side **5c**, appropriate gas inlet and outlet regions, and optional catalyst **5d**. Optional catalyst **5d** is shown here as immediately following the module. Alternatively or additionally catalyst may be disposed immediately preceding the module or within or around the module in any desired configuration. Last or n^{th} stage **7** comprises oxidant side **7a**, membrane **7b**, reactant

side **7c**, appropriate gas inlet and outlet regions, and optional catalyst **7d**, shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module or within or around the module in any desired configuration. Product gas from last stage **7** is withdrawn via product line **7e**.

Interstage reactant gas flows from stage **1** via flow path **1e**, from stage **3** via flow path **3e**, and from stage **5** via flow path **5e**. Stages **1**, **3**, **5**, and **7** may be enclosed in separate pressure vessels or may be enclosed in a single pressure vessel. An oxidant zone (**1a**, **3a**, **5a**, or **7a**) and its corresponding reactant zone (**1c**, **3c**, **5c**, or **7c**) in each stage are isolated from each other so that the bulk flow of oxidant gas through the oxidant zone and the bulk flow of reactant gas through the reactant zone are separate and independent. The membrane or membranes (**1b**, **3b**, **5b**, or **7b**) separating the oxidant zone from the reactant zone prevents any substantial bulk gas flow between the zones and allows the permeation of oxygen through the membrane from the oxidant zone to the reactant zone. An oxidant gas, for example, preheated air or oxygen-containing combustion products from a combustor operated with excess air, is introduced via oxidant inlet line **9** into oxidant zone **1a** of first stage **1** and contacts the oxidant side of membrane **1b**, a portion of the oxygen permeates through membrane **1b**, and oxygen-depleted gas exits first stage **1** via oxygen-depleted oxidant outlet line **11**. Similarly, additional oxidant gas streams may be introduced via lines **13**, **15**, and **19** into stages **3**, **5**, and **7**, respectively, and oxygen-depleted gas may exit the stages via lines **21**, **23**, and **25**, respectively. Alternatively, some or all of the oxidant gas may flow through two or more stages in series via lines **27**, **29**, and **31**. Thus the stages may be operated individually with respect to the flow of oxidant gas, may be operated in series with respect to the flow of oxidant gas, or may utilize any combination of individual and series operation with respect to the flow of oxidant gas. Reactant gas may enter the multi-stage reactor system via manifold **27**, a first portion may be withdrawn via line **29** and combined with another reactant gas (for example, steam) provided in line **31**, and the combined gas may be introduced via reactant gas inlet line **33** into reactant side **1c** of first stage **1**. Additional portions of reactant gas may be withdrawn from manifold **27** via any of reactant interstage feed gas lines **35**, **37**, and **39** and introduced as reactant interstage feed gas into any of interstage reactant gas flow paths **1e**, **3e**, and **5e**, respectively. Alternatively, the reactant interstage feed gas may be introduced directly into the reactant side of any stage and/or upstream of any of the catalysts **1d**, **3d**, **5d**, and **7d**. The reactant gas in manifold **27** may comprise one or more hydrocarbons and also may comprise any of the components water, carbon monoxide, carbon dioxide, and hydrogen. For example, the reactant gas in manifold **27** may be pre-reformed natural gas comprising methane, carbon monoxide, carbon dioxide, hydrogen, and water. The reactant gas provided via line **31** may be, for example, vaporized water (steam). Additional reactant gas may be provided via manifold **41** from a source different than the source of the reactant gas in line **27** and the source of reactant gas provided via line **31**. This additional reactant gas may be introduced via any of lines **29**, **43**, **45**, and **47** into any of first stage **1**, the interstage reactant gas in line **1e**, the interstage reactant gas in line **3e**, and the interstage gas entering last or n^{th} stage **7**. Alternatively, the additional reactant gas may be introduced upstream of any of catalysts **1d**, **3d**, **5d**, and **7d**. This additional reactant gas may be, for example, an oxygen-containing gas comprising carbon dioxide obtained from a downstream process that uses product gas from line **7e**. The additional reactant gas may comprise unreacted offgas from a downstream process that uses product gas from line **7e** and/or may comprise partially-reformed unreacted offgas from a downstream process that uses product gas from line **7e**. Any number of additional stages may be

utilized between stage **5** and last stage **7** as desired. The gas flow rates in any of the lines described above may be regulated by control valves or other flow devices. Alternatively or additionally, the temperatures of any of the gas streams may be controlled by heating and/or cooling by methods known in the art.

Various combinations of reactant gas types may be introduced into the reactant sides of the modules in such a staged membrane oxidation reactor system. For example, pre-reformed natural gas may be introduced into the reactor stages via manifold **27** and lines **29**, **35**, **37**, and **39**, and steam may be introduced via lines **31** and **33** into first stage **1**. No additional reactant gas is provided via manifold **41** and lines **29**, **43**, **45**, and **47**. In another example, pre-reformed natural gas and steam may be introduced into the first stage via lines **31** and **33**, and carbon dioxide-containing gas (for example, a recycle gas from a downstream process) may be introduced into the system via manifold **41** and any of lines **43**, **45**, and **47**. The downstream process may be a hydrocarbon synthesis process (e.g., a Fischer-Tropsch process) or an oxygenated hydrocarbon synthesis process (e.g., an alcohol synthesis process). Manifold **27** and lines **29**, **35**, **37**, and **39** are not used in this example. Yet another example might include pre-reformed natural gas being provided to the staged reactor system via manifold **27** and lines **29**, **35**, **37**, and **39**, steam being introduced into the system via line **31**, and carbon dioxide-containing gas (for example, a recycle gas from a downstream process) being introduced into the system via manifold **41** and any of lines **43**, **45**, and **47**. In another example, a reactant gas comprising pre-reformed natural gas, a carbon dioxide-containing additional reactant gas, and steam are provided to the staged reactor system via manifold **27** and lines **29**, **35**, **37**, and **39**, and steam may be introduced into the system via line **31**. Manifold **41** and lines **43**, **45**, and **47** are not used in this case.

Figure 2.1.1-17 shows a potential control system using the control concepts proposed in Figure 2.1.1-16. In this example, twenty reactor stages are used and are arranged for control purposes into two groups of ten stages each such that stages **301** through **319** are in a first control group and stages **321** through **341** are in a second control group. Pre-reformed natural gas is introduced as a reactant feed gas via line **343**. The reactant feed gas flows via primary manifold **345** and is split to flow through secondary manifolds **347** and **349**. Steam is fed into first stage **301** via line **351**.

The reactant feed gas flows through the reactant side of first stage **301**, and interstage reactant gas flows between successive stages through stage **319**. Interstage reactant gas from the first group of stages **301-319** flows via line **353** and then flows through the reactant sides of the successive stages in the second group of stages **321-341**. Synthesis gas product flows from the system via line **355**. The first group of stages **301-319** may be installed in a single pressure vessel. The reactant feed gas in manifold **347** is divided into ten individual streams, and the first of these streams provides a reactant feed gas in line **357** that is mixed with the steam feed in line **351**. The remaining nine reactant gas streams provide reactant interstage feed gas streams that are mixed with the corresponding interstage reactant gas streams between pairs of adjacent stages **301** through **319** as shown. Manifold **347** may be designed to provide generally equal flow rates of reactive gas into stages **301** to **319**; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages for reaction control purposes.

The second group of stages **321-341** may be installed in a separate pressure vessel or in the same pressure vessel as the first group of stages. The reactant feed gas in manifold **349** is divided into ten individual streams to provide reactant interstage feed gas streams that are mixed with the corresponding interstage reactant gas streams between pairs of adjacent stages **321** through **341**. Manifold **349** may be designed to provide generally equal flow rates of reactive gas into stages **321** to **341**; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages for reaction control purposes.

A first preheated oxidant gas is introduced via line **359** into manifold **361** and is divided into ten portions to provide oxidant gas to the oxidant sides of stages **301** to **319**. A second preheated oxidant gas is introduced via line **363** into manifold **365** and is divided into ten portions to provide oxidant gas to the oxidant sides of stages **321** to **341**. Oxygen permeates through the membranes in the stages and reacts with the reactive components on the reactant sides of the stages. Oxygen-depleted non-permeate gas is withdrawn from stages **301-319** via lines feeding into manifold **367** and the gas is discharged via line **369**. Similarly, oxygen-depleted non-permeate gas is withdrawn from stages **321-341** via lines feeding into manifold **371** and the gas is discharged via line **373**. Manifold **361** may be designed to provide generally equal flow rates of oxidant gas into stages **301** to **319**; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages, for example, for reaction and/or temperature control purposes. Likewise, manifold **365** may be designed to provide generally equal flow rates of oxidant gas into stages **321** to **341**; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages, for example, for reaction and/or temperature control purposes.

Figure 2.1.1-17 Multi-stage Reactor Control System

The temperatures in the stages and the reactions through the stages can be regulated by controlling the flow rates of reactant and oxidant gases to the stages and the operating conditions within the stages. This may be accomplished, for example, by controlling the flow rates of reactant gas into manifolds **347** and **349** by control valves **375** and **377**, respectively, and/or by controlling the flow rates of oxidant gas into manifolds **361** and **365** by control valves **379** and **381**, respectively. For example, control of the reactant gases to the group of stages **301** to **319** may be affected by temperature indicator/controller **383**. Likewise, control of the reactant gases to the group of stages **321** to **341** may be affected by temperature indicator/controller **389**. Typically, flow rates of oxidant gases fed to the stages may be varied to maintain target oxygen concentration in oxygen-depleted non-permeate gas withdrawn from the stages, for example through manifolds **367** and **371**. For example, oxygen concentration may be monitored by an oxygen analyzer/indicator controller (not shown) located on manifold **367** and/or discharge **369**, which may send control signals via a control line (not shown) to control valve **379**. Likewise, oxygen concentration may be monitored by an oxygen analyzer/indicator controller (not shown) located on manifold **371** and/or discharge **373**, which may send control signals via a control line (not shown) to control valve **381**. Flow rate of permeated oxygen through the membranes may also be affected by the operating conditions (e.g., pressure and/or temperature) within the stage, particularly in the vicinity of the membrane permeation surface.

A simulation model was developed using the process simulator Aspen Plus™ from Aspen Technology, Inc. The simulation model was used to understand the operation of the reactor system and control concepts described above. Results from three example simulations are provided below.

Example 1

This simulation utilized 100 membrane reactor stages in series wherein the reactant gas feed is divided into ten portions (not necessarily equal) and each portion is divided into ten equal sub-portions. Each sub-portion is fed to the inlet of a corresponding stage wherein the sub-portion to the first stage is mixed with steam and each of the remaining sub-portions is provided as a reactant interstage feed gas that is mixed with a corresponding interstage reactant gas stream.

The following specific process features and parameters were used in the simulation:

- Total sum of oxygen permeation in all stages is 1000 kg mol/hr, evenly distributed between all stages.
- Overall steam-to-carbon molar ratio is 1.5 in the reactant feed to the system.
- Reactant gas feed is provided by pre-reforming natural gas in an adiabatic pre-reformer to convert hydrocarbons heavier than methane.

- Reactant gas pressure on the reactant sides of all stage membrane modules is 30.3 bara (440 psia) and the oxidant gas pressure on the oxidant sides of all stage membrane modules is 1.7 bara (25 psia).

The pre-reformed mixture is divided into the portions given in Table 2.1.1-4. Each of portions 1-10 in Table 2.1.1-4 is divided into ten equal sub-portions. Steam is mixed with a first sub-portion of portion 1, and the mixture is introduced to the reactant side of the first stage. The other 99 sub-portions (all of the sub-portions except the first sub-portion of portion 1) are provided as reactant interstage feed gas streams, each of which is mixed with a respective interstage reactant gas stream and fed to the inlet of each of the respective 99 stages. Air is provided to the oxidant side of each stage and oxygen-depleted air is withdrawn from the oxidant side of each stage. Sufficient catalyst is provided on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the 100-stage reactor system. A final synthesis gas product is withdrawn from the last stage at 900°C.

Table 2.1.1-4 Reactant Feed Gas Distribution for Example 1

Stage Group	Percent of Flow
1	9.6%
2	9.5%
3	9.9%
4	10.3%
5	10.8%
6	11.2%
7	11.5%
8	11.7%
9	12.0%
10	3.6%
Total	100.0%

The temperature profile of the reactor calculated by the simulation is shown in Figure 2.1.1-18. The temperature of the reactant gas at the inlet and outlet of each stage is plotted as a percentage of the group of 100 reaction stages from the reactant feed inlet (0 percent) to the product outlet (100 percent). These results show that the staged operation of the reactor system controls the reactant gas temperature within a membrane temperature range of 850 to 900°C. The temperature of the reactant gas is generally flat at about 875°C through the first 90 stages and rises to 900°C in the last 10 stages. The saw-tooth temperature profile is attributed to quenching of the interstage reactant gas by the introduction of "cold" pre-reformed reactant feed gas via the reactant interstage feed lines into the interstage reactant gas between each of the 100 stages.

Figure 2.1.1-18 Reactor Temperature Profile of Example 1

Example 2

For this example, Example 1 was modified such that the catalyst is provided at the exit of each stage rather than in the membrane module. The catalyst is used to equilibrate the steam reforming, carbon dioxide reforming, and water-gas shift reactions.

The pre-reformed mixture is divided into the portions given in Table 2.1.1-5. Each of portions 1-10 in Table 2.1.1-5 is divided into ten equal sub-portions. The preheated steam is mixed with a first sub-portion of portion 1, and the mixture is introduced to the reactant side of the first stage. The other 99 sub-portions (all of the sub-portions except the first sub-portion of portion 1) are provided as reactant interstage feed gas streams, each of which is mixed with a respective interstage reactant gas stream and fed to the inlet of each of the respective 99 stages. Air is provided to the oxidant side of each stage and oxygen-depleted air is withdrawn from the oxidant side of each stage. A final synthesis gas product is withdrawn from the last stage at 900°.

Table 2.1.1-5 Reactant Feed Gas Distribution for Example 2

Stage Group	Percent of Flow
1	9.7%
2	9.5%
3	9.8%
4	10.2%
5	10.5%
6	10.8%
7	10.9%
8	11.1%
9	11.3%
10	6.3%
Total	100.0%

The temperature profile of the reactor calculated by the simulation is shown in Figure 2.1.1-19. The temperature of the reactant gas at the inlet and outlet of each stage is plotted as a percentage of the group of 100 reaction stages from the reactant feed inlet (0 percent) to the product outlet (100 percent). These results show that the staged operation of the reactor system controls the reactant gas temperature within a membrane temperature range of 850 to 900°C. The saw-tooth temperature profile is attributed to the exothermic oxidation reactions occurring in each stage followed by the endothermic reforming reactions in each adiabatic catalyst bed following the stage.

Figure 2.1.1-19 Reactor Temperature Profile of Example 2

Example 3

For this example, recycle gas from a Fischer-Tropsch unit is fed to the reactor system in addition to natural gas. The Fischer-Tropsch recycle gas contains hydrogen, methane, carbon dioxide, and carbon monoxide. The total reactant gas flow is the sum of the pre-reformed natural gas feed and the Fischer-Tropsch recycle gas.

The reactant gas is divided into the portions given in Table 2.1.1-6. Each of portions 1-10 in Table 2.1.1-6 is divided into ten equal sub-portions. The preheated steam is mixed with a first sub-portion of portion 1, and the mixture is introduced to the reactant side of the first stage. The other 99 sub-portions (all of the sub-portions except the first sub-portion of portion 1) are provided as reactant interstage feed gas streams, each of which is mixed with a respective interstage reactant gas stream and fed to the inlet of each of the respective 99 stages. Air is provided to the oxidant side of each stage and oxygen-depleted air is withdrawn from the oxidant side of each stage. Sufficient catalyst is provided on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the 100-stage reactor system. A final synthesis gas product is withdrawn from the last stage at 900°C.

Table 2.1.1-6 Reactant Feed Gas Distribution for Example 3

Stage Group	Percent of Flow
1	9.7%
2	9.8%
3	10.3%
4	10.7%
5	11.0%
6	11.2%
7	11.4%
8	11.5%
9	11.5%
10	2.9%
Total	100.0%

The temperature profile of the reactor calculated by the simulation is shown in Figure 2.1.1-20. The temperature of the reactant gas at the inlet and outlet of each stage is plotted as a percentage of the group of 100 reaction stages from the reactant feed inlet (0 percent) to the product outlet (100 percent). These results show that the staged operation of the reactor system controls the reactant gas temperature within a membrane temperature range of 850 to 900°C. The saw-tooth temperature profile is attributed to quenching of the interstage reactant gas upon introduction of "cold" mixed reactant feed gas into the interstage reactant gas between each of the 100 stages.

Figure 2.1.1-20 Reactor Temperature Profile of Example 3

The detailed mixed cell model was used to confirm oxygen flux assumptions in the initial simulations. These comparisons generally showed good agreement. The Aspen Plus™ simulation model was upgraded to include simple correlations for oxygen flux to further optimize the reactor control concepts. Eventually, the detailed mixed cell model was included in a proprietary unit operation block in the simulation model which allowed more detailed calculations of heat and mass transfer in the system in order to predict detailed composition and temperature profiles in the entire reactor without a large number of manual iterations. This upgraded simulation model resulted in better understanding of important design parameters in the reactor system and in more detailed development targets for membrane performance.

Start-up and Shutdown Control Systems

An important aspect of operating an ITM Syngas system is the need to be able to start-up, shutdown, and operate through transients without membrane failure. The ability to operate under these conditions requires an understanding of the membrane material properties. These materials undergo both thermal and chemical expansion. The chemical expansion of these materials is unique (see Subtask 2.2.1.5). Techniques to control differential chemical expansion at or below a maximum value were developed.

One technique, ISO-compositional control, can be applied to an example system shown in Figure 2.1.1-21. This system contains four membrane modules **601**, **603**, **605**, and **607** in series. The modules comprise, respectively, reactant sides **601a**, **603a**, **605a**, and **607a**, membranes **601b**, **603b**, **605b**, and **607b**, and oxygen-containing gas feed sides **601c**, **603c**, **605c**, and **607c**. A heated oxygen-containing gas (for example, air) is introduced to the system via inlet line **409**, manifold **608**, and individual feed lines **609**, **611**, **613**, and **615** into oxygen-containing gas feed sides **601c**, **603c**, **605c**, and **607c**, respectively. Oxygen-depleted non-permeate gas is withdrawn from each module and collected in manifold **616**. Preheated reactant gas (for example, a methane-containing gas such as natural gas or a pre-reformed natural gas/steam/synthesis gas mixture) is introduced via line **617** and flows in series through the reactant sides of modules **601**, **603**, **605**, and **607** while reacting therein with oxygen that has permeated through membranes **601b**, **603b**, **605b**, and **607b**, respectively. Reaction product gas (for example, synthesis gas comprising hydrogen and carbon monoxide) is withdrawn from the system via line **619**.

The oxygen partial pressure in the oxygen-containing gas to each module may be controlled during heating or cooling of modules **601**, **603**, **605**, and **607** by introducing additional gas via lines **621**, **623**, **625**, and **627**, respectively. When the modules are cooled, for example during system shutdown, the oxygen partial pressure in oxygen-containing feed gas sides **601c**, **603c**, **605c**, and **607c** may be reduced by introducing a diluent gas via lines **621**, **623**, **625**, and **627**, respectively. When the modules are heated, for example during system startup, the oxygen partial pressure in oxygen-containing feed gas sides **601c**, **603c**, **605c**, and **607c** may be increased by introducing an O₂-enriched gas via lines **621**, **623**, **625**, and **627**, respectively. Alternatively, during system startup, the oxygen partial pressure in oxygen-containing feed gas sides **601c**, **603c**, **605c**, and **607c** may be controlled by blending an oxygen-containing gas such as air from line **409** with a diluent gas via lines **621**, **623**, **625**, and **627**, respectively. The total pressure of the oxygen-containing gas in oxygen-containing feed gas sides **601c**, **603c**, **605c**, and **607c** may be controlled by known means as necessary during heating, steady state operation, and cooling of the module system.

Figure 2.1.1-21 Example of a Process Including ISO-Compositional Control

Faster start-ups and shutdowns can be attained by controlling the differential strain within the membrane. Control of the differential strain can be attained by adjusting the oxygen partial pressure on both sides of the membrane. As an example, if the mixed conducting metal oxide has a composition of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$, the differential strain can be controlled to be approximately constant if the conditions shown in Figure 2.1.1-22 are followed. On the oxidant feed side of the membrane, nitrogen is blended with air to control the oxygen partial pressure. On the permeate (reaction) side of the membrane, the desired oxygen partial pressure is controlled by passing a mixture of hydrogen and water through the permeate side and varying composition of the gas to achieve the desired P_{O_2} . The oxygen partial pressure is calculated from the equilibrium relation $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$ and the known free energy of formation of the three components. Figure 2.1.1-23 shows the desired molar ratios of H_2 to H_2O as a function of temperature required to achieve the oxygen partial pressures shown for the permeate side in Figure 2.1.1-22.

Figure 2.1.1-22 Example of Oxygen Partial Pressures Required for Maintaining a Constant Differential Strain in the Membrane

Figure 2.1.1-23 Example of Hydrogen: Steam Ratio to Obtain the Permeate Side Oxygen Partial Pressures Shown in Figure 2.1.1-22

Finally, creep relaxation can be incorporated into these techniques to avoid rapid increases in differential strain. By controlling the rate at which the oxygen partial pressure is changed on one or both sides of a membrane, one can control the rate at which the differential strain changes. If the creep rate is greater than the rate of strain creation due to chemical expansion caused by oxygen partial pressure changes, then the differential strain will decrease with time. If the creep rate is less than the rate of strain creation due to chemical expansion caused by oxygen partial pressure changes then the differential strain will increase. The creep rate as a function of stress and temperature for a specific membrane material can be measured experimentally (see Subtask 2.2.1.5).

Updated Large-Scale GTL Economics

Air Products and Chevron updated the process design and economics of an ITM Syngas process integrated into a Gas-to-Liquids (GTL) plant producing ultra-clean transportation fuels. The process and economic evaluation considered the improved concept for control of the ITM Syngas reactor, advances in Fischer-Tropsch technology to convert synthesis gas to liquid hydrocarbons, and advances in conventional technology (Autothermal Reforming with a cryogenic Air Separation Unit for oxygen supply). The basis was an 18,000 barrel/day Gas-to-Liquids (GTL) single-train.

The S/C ratio for the ATR reactor was 0.4 and a sensitivity analysis at 0.6 was considered. The reactor outlet temperature was set at 1050°C. The S/C ratio for the ITM Syngas reactor was 0.8 and sensitivity cases at 0.6 and 1.0 were considered. Overall plant integrations were optimized, using Aspen Plus™ simulations. The syngas H_2/CO ratio was 2.0 and a sensitivity analysis at 1.6 was also considered for both technologies.

The process evaluation shows that the ITM Syngas process has an equivalent thermal efficiency as a comparable ATR/ASU process. The ITM Syngas process would have a higher thermal efficiency compared to a comparable ATR/ASU process if the excess steam being condensed against cooling water was to have value, such as in power production or export.

Equipment specifications were developed for each of the cases. A compact, single train ITM Syngas reactor concept was developed. Processes and equipment to preheat the air feed to the ITM Syngas reactor were identified as areas for future optimization.

Cost estimates were developed based on the equipment specifications. A capital investment analysis for a Mideast site showed that the ITM Syngas process had more than 30% capital cost advantage over an ATR/ASU syngas generation process. Reduced plot area requirements are expected to lead to further cost savings compared to an ATR/ASU process.

TASK 2.2 MATERIALS AND SEALS DEVELOPMENT

Subtask 2.2.1 ITM Syngas Materials

Subtask 2.2.1.1 Materials Characterization and Assessment

A key aspect of the research program was to understand the flux performance of the material compositions under consideration. This information, in combination with material properties, stability, and life that will be discussed in other sections of this report, was critical to the material selection and development of the reactor design, the overall process, and the economic benefits of ITM Syngas. This section discusses examples of specific tests and the resulting data that was collected at Eltron Research and at Air Products.

Laboratory-Scale Test Reactors

High pressure, laboratory scale, test reactors were designed and installed at Eltron Research and Air Products. These are illustrated diagrammatically in Figure 2.2.1.1-1. Air at atmospheric pressure was introduced to the interior of the tubular membrane, while a $\text{CH}_4/\text{H}_2\text{O}/\text{CO}/\text{H}_2/\text{CO}_2$ gas mixture representative of a section of the ITM Syngas reactor was contacted at pressure with the external surface. Oxygen was transported through the tubular membrane to partially oxidize the reducing gas mixture. The oxygen concentration of the exhaust air was measured by an oxygen analyzer and by GC. The exhaust, partially oxidized, high-pressure syngas mixture was analyzed by GC. Carbon, hydrogen and oxygen material balances were obtained for both the process gas and the air streams. Oxygen fluxes were calculated on both the air and process sides of the membrane, and compared for an overall oxygen material balance.

Figure 2.2.1.1-1 Diagram of the High-Pressure ITM Syngas Test Reactors

Tubular Membrane Tests

A series of tests on tubular membranes in the Air Products high-pressure reactors was conducted. These tests had a simulated syngas mixture (approximately 31% hydrogen, 30% steam, 16% methane, 10% carbon monoxide, and 13% carbon dioxide) on the process side. Examples of these tests are provided below and the relative oxygen flux results are provided in Table 2.2.1.1-1.

- An I4(C) tubular membrane and seal fabricated by Ceramtec, was tested in Run HP1-6 for a total of approximately 50 days. For the first 600 hours, the membrane was operated at 250 psia and 825°C. The operating conditions were then changed to 400 psia and 850°C for approximately 500 hours. The temperature was then increased to approximately 950°C. The membrane failed after operating at this temperature for about 50 hours. Leakage across the ceramic/metal seal was continually monitored by GC analysis of the exhaust air stream, and oxygen consumption and process gas loss due to any leakage were accounted for in the overall material balances. Apart from an abnormality occurring when the pressure was raised from 250 to 400 psia, the oxygen flux was constant at constant temperature and showed little or no degradation over time. The oxygen flux measured by the oxygen depletion on the air side of the membrane and by GC analysis of the inlet and exhaust process gas streams were in good agreement. However, the oxygen flux as measured by the oxygen depletion on the air side had much less scatter. Carbon and hydrogen material balances were within $\pm 10\%$.

- Another I4(C) tubular membrane/seal assembly was tested in Run HP1-7. This sample utilized a metallic U- ring at its base in place of the silver foil gasket used in earlier tests. After relatively high leak rates during initial heat up and pressurization, the leakage stabilized at a low rate. The test was conducted at approximately 720°C and 400 psia. The oxygen flux under these conditions remained stable for 500 hours. The membrane failed within four hours of raising the operating temperature to 825°C. The oxygen flux measured by air side oxygen depletion remained constant over the time period. The oxygen flux measured by the process side material balance was inaccurate due to difficulties with measurement of the outlet water concentration.
- Another I4(C) tubular membrane/seal assembly was tested in Run HP1-8. The test was conducted at 775°C and 400 psia. The membrane failed after approximately 200 hours. During that time the oxygen flux remained approximately constant. Problems in obtaining a process gas material balance continued and the oxygen flux measurements based on process side material balance were inaccurate.

Table 2.2.1.1-1 Oxygen Flux Results from Initial High-Pressure Testing at Air Products

Run Number	Membrane Material	Temperature (°C)	Pressure (psia)	Relative O ₂ Flux
HP1-6	I4(C)	825	250	1.00
HP1-6	I4(C)	850	400	1.05
HP1-7	I4(C)	720	400	0.41
HP1-8	I4(C)	775	400	0.94

Eltron Research also conducted early tests of tubular membranes in their high-pressure reactors. The tests were conducted with a simulated syngas mixture on the process side. Results for the tests that were stable over a sufficiently long period are listed in Table 2.2.1.1-2.

Table 2.2.1.1-2 High-Pressure Test Results from Initial Testing at Eltron Research

Tube Number	Membrane Material	Time (hours)	Temperature (°C)	Pressure (psig)	Relative O ₂ Flux
301-3	I4(C)	1386	900	250	n/a
303-18	I4(C)	475	900	250	1.33
303-19	I4(C)	144	900	250	0.89
303-21	I4(C)	144	900	250	1.43
302-8	I4(C)	611	825	250	0.77

Initially, membrane tube sealing was a significant problem in the Eltron Research tests. In addition to seven tubes that did not seal when pressurized, eight tubes that sealed at temperature

and pressure developed leaks after exposure to a reducing gas mix or after several days of operation under the process gas. A number of changes were made to operating procedures in an effort to improve seal rates. These changes included cycling to lower temperature and back to 825°C or 900°C. Although several tubes survived temperature cycling to room temperature and back to test temperature without failing or cracking, attempts to realize consistent seal quality through procedural changes did not succeed. A new seal was successfully developed.

The I4(C) tubular membrane, tested in run 301-3, displayed very low flux in over 1380 hours of exposure to simulated syngas conditions. The tube leaked slightly at the start of the experiment, then sealed and withstood the applied pressure of 250 psi at 900°C for the length of the test. The flux was very low at the outset and gradually decreased to zero. After the experiment was intentionally terminated, the tube was submitted to Air Products for examination. Fragments of the tube were analyzed by SEM/EDS. No evidence could be found in the microstructure to account for the lack of flux through this membrane.

Another tube, an I5 composition tested at Eltron Research, showed very low flux during high-pressure testing for over 400 hours at 250 psi and 900°C. When examined at Air Products, the membrane showed cracking on the inner diameter. Also, decomposition of the outer catalyst layer, a porous Ni/I4 composition, was observed. This decomposition was in agreement with calculations of thermodynamic stability for this composition under the process operating conditions. Analysis showed the formation of Ca-Si-O phases on the syngas surface of the membranes, although this could not be correlated with oxygen flux. There was speculation that alumina liners in the Eltron reactors contributed to silicon contamination of the membrane tubes. The alumina liners on all reactors were subsequently replaced by Inconel 625 tubes. After operation under syngas conditions, there was no evidence that the liners contributed significantly to steam methane reforming or coking.

In another series of tests in the Air Products high-pressure reactors, the membranes were operated in a different syngas mixture to better reflect the current commercial process operating conditions. The composition of this syngas was 44% hydrogen, 26% steam, 16% methane, 9% carbon monoxide, and 5% carbon dioxide. The tests were plagued by premature failures during start-up. These failed tubes showed evidence of cracks forming and propagating approximately half way around the circumference of the tube. The cracks appeared to form primarily toward the closed end of the tubes and to be biased to one side of the tube. The tubes were analyzed at Air Products and Ceramatec but with inconclusive results as to the cause of failure.

A summary of the samples, test conditions, and relative oxygen flux for these tests is given in Table 2.2.1.1-3.

Table 2.2.1.1-3 High-Pressure Test Results from Testing at Air Products

Run Number	Membrane Material	Syngas-side Catalyst	Time (hours)	Temperature (°C)	Pressure (psig)	Relative O ₂ Flux
HP1-14	I4(D)	Ni/I4	2463	817	425	0.31
HP2-13	I4(C)	Ni/I4:LSCO	300	900	250	1.43
				800	425	0.97
HP2-15	I4(D)	Ni/I4	720	800	425	0.41
HP2-16	I4(D)	Ni/I4	625	882	425	0.71
HP1-17	I4(C)	None	448	747	425	0 to 0.51
HP2-18	I4(F)	None	~10	940	425	n/a
HP2-19	I4(F)	None	74	949	425	0.66
HP2-20	I4(D)	None	190	955	425	0.97
HP1-21	I4(D)	None	120	946	425	1.02
HP2-22	I4(D)	None	500	959	425	0.82
HP1-23	I4(D)	None	252	956	425	1.07
HP1-24	I4(D)	None	518	925	425	0.20
HP2-26	I4(D)	None	750	950	425	0.77
HP1-27	I4(D)	None	1130	846 to 950	425	0.10 to 0.41
HP2-28	I4(D)	None	1022	953	425	1.12
HP2-29	I4(D)	None	2010	800	425	0.34
HP1-30	I4(D)	None	1600	950	425	0.07 – 0.96
HP1-31	I4(D)	None	1940	900	425	0.02 – 0.54
HP2-32	I4(D)	None	220	850	425	0.57
HP2-33	I4(D)	None	1000	845	425	0.59
HP2-35	I4(D)	None	1460	850	425	0.47
HP2-36	I4(D)	None	1200	850	425	0.01 – 0.20
HP1-37	I4(D)	None	290	890	425	0.59
HP1-39	I4(D)	None	2090	890	425	0.69 – 0.63
HP1-44	I4(D)	None	1270	890	425	0.67

Details of these runs include:

- The I4(D) tubular membrane tube in Run HP1-14 operated with a stable oxygen flux, as measured by the oxygen depletion on the air side, and with a leak rate of 0 to 2 sccm.
- Run HP2-15 used an I4(D) tubular membrane that was a companion to the one on test in Run HP1-14. This test ran for ~360 hours under syngas conditions before a line blockage led to a reactor shutdown. The reactor was purged with nitrogen, cooled to room temperature, depressurized, and opened to laboratory air. After the blockage was investigated and resolved, the reactor was successfully restarted with the same sample and seal. The test ran for an additional ~360 hours before the sample tube

failed. The oxygen flux, as measured by the oxygen depletion on the air side, was stable and the leak rates were 0 to 2 sccm.

- Run HP2-16 was a third I4(D) tube from the same lot as those tested in HP1-14 and HP2-15. This test ran for ~625 hours before the run was terminated. The oxygen flux, as measured by the oxygen depletion on the air side, was stable and the leak rate was 0 to 2 sccm.
- Run HP1-17 was an I4(C) membrane tube with no catalysts. This tube was on test for ~450 hours under various hydrogen/steam mixtures as part of an oxidation kinetics study. The hydrogen content of the feed stream was too low to generate a meaningful oxygen flux at the beginning of the test. There was no significant leak.
- Runs HP2-18 and HP2-19 were I4(F) membrane tubes with no catalysts. The membranes were exposed to the simulated syngas mixture. There were no significant leaks; however, the tubes failed relatively early in their respective runs.
- Run HP2-20 was an I4(D) membrane tube with no catalysts. The membrane was exposed to the simulated syngas mixture. The tube operated for 190 hours with essentially no leak. There was an indication of oxygen flux decline with time.
- Run HP1-21 was an I4(D) membrane tube with no catalysts. The membrane was on test for ~120 hours under various hydrogen/steam mixtures as part of an oxidation kinetics study. There was no significant leak. The run was terminated in advance of a planned building power outage.
- Run HP2-22 was an I4(D) membrane tube with no catalysts. The membrane was exposed to the simulated syngas mixture. The tube operated for 500 hours with essentially no leak. The oxygen flux declined over the first ~150 hours and then stabilized.
- Run HP1-23 was an I4(D) membrane tube with no catalysts. The membrane was on test for 250 hours under various hydrogen/steam mixtures as part of an oxidation kinetics study. There was no significant leak.
- Run HP1-24 was an I4(D) membrane tube with no catalysts. The membrane was on test for 500 hours under various hydrogen/steam mixtures as part of an oxidation kinetics study. There was no significant leak. The run was terminated for planned sample evaluation.
- The I4(D) membrane tube tested in Run HP2-26 had an A/B ratio of 0.993. The oxygen flux declined significantly during the first 65 hours of operation. There were essentially no leaks. The test ended when the tube failed.

- The I4(D) membrane tube in Run HP1-27 was on test for more than 500 hours under various hydrogen/steam mixtures as part of an oxidation kinetics study. The leak rates varied from no significant leak to a leak of up to 15 sccm.
- The I4(D) membrane tube tested in Run HP2-28 had an A/B ratio of 1.003. The oxygen flux was stable. There were essentially no leaks. The test ended when the tube failed.
- The I4(D) membrane tube tested in Run HP2-29 had an A/B ratio of 1.003. The oxygen flux was stable. There were essentially no leaks.
- The I4(D) membrane tube tested in Run HP1-30 had an A/B ratio of 1.003. The objective of this run was to determine the dependence of oxygen flux on flow rate at constant P_{H_2} and P_{O_2} and on P_{H_2} at constant flow rate and P_{O_2} . The variable of interest in a given series was varied over approximately an order of magnitude. The full results are given in Table 2.2.1.1-4. A repeat test at the end of the testing showed a significantly higher flux than the earlier test.

Table 2.2.1.1-4 Test Results from Run HP1-30 Operating at 950°C and 425 psig

Test Period	P_{H_2} (bar)	Flow (sccm)	Relative O_2 Flux
1	3.32	5000	0.32
2	3.32	3000	0.21
3	3.32	1000	0.14
4	3.32	500	0.13
5	1.14	3000	0.23
6	0.57	3000	0.07
7	5.70	3000	0.96
8	3.32	3000	0.78

- The I4(D) membrane tube tested in Run HP1-31 had an A/B ratio of 1.00. The conditions for this test were 425 psig and 900°C with a range of hydrogen/steam compositions. The tube ran for over 1900 hours. The objective of this run was to determine the dependence of oxygen flux on flow rate at constant P_{H_2} and P_{O_2} and on P_{H_2} at constant flow rate and P_{O_2} . The variable of interest in a given series was varied over approximately an order of magnitude. The full results are given in Table 2.2.1.1-5.

Table 2.2.1.1-5 Test Results from Run HP1-31 Operating at 900°C and 425 psig

Test Period	P_{H2} (bar)	Flow (sccm)	Relative O₂ Flux
1	3.32	3000	0.54
2	1.14	3000	0.08
3	0.57	3000	0.02
4	3.32	3000	0.35
5	5.00	3000	0.48
6	3.32	3000	0.23
7	3.32	500	0.18
8	3.32	3000	0.37

- The I4(D) membrane tube tested in Run HP2-32 had an A/B ratio of 1.00 and no catalysts. The objective of this run was to determine the flux performance of this composition at 850°C, the nominal temperature of most of the process reactor. This run was plagued by a series of equipment and sensor problems which resulted in several restarts until the membrane ultimately failed.
- The I4(D) membrane tube tested in Run HP2-33 had an A/B ratio of 1.00 and no catalysts. The objective of this run was to determine the flux performance of this composition at 850°C, the nominal temperature of most of the process reactor. This was a repeat of Run HP2-32.
- The I4(D) membrane tube tested in Run HP2-35 had an A/B ratio of 1.00 and no catalysts. This run was a repeat of Runs HP2-32 and HP2-33. The oxygen flux was stable at a slightly lower level than observed in HP2-32 or HP2-33 for the first ~1000 hours of operation. Then, the oxygen flux showed a steady decline. The run was ended when a chiller failure led to a partial system shut-down which resulted in either the loss of the seal or the failure of the tube.
- The I4(D) membrane tube tested in Run HP1-36 had an A/B ratio of 1.00 and no catalysts. After an initial decline, the oxygen flux stabilized during the initial 200-hour hold at the baseline conditions of 3.32 bar P_{H2} and 3000 sccm process gas flow rate. The oxygen flux dropped approximately by an order of magnitude when the P_{H2} was reduced to 1.14 bar and by almost another order of magnitude when the P_{H2} was further reduced to 0.57 bar. Upon a return to the baseline conditions, the flux was only about 25 percent of the original value. The flux approximately doubled when the P_{H2} was increased from 3.32 to 5 bar, but returned to the lower value on return to baseline conditions. Table 2.2.1.1-6 lists these results. Leak rates were low. The run was intentionally ended to permit further experiments to determine the causes of the observed flux degradation.

Table 2.2.1.1-6 Test Results from Run HP1-36 Operating at 850°C and 425 psig

Test Period	P _{H2} (bar)	Flow (sccm)	Relative O ₂ Flux
1	3.32	3000	0.20
2	1.14	3000	0.02
3	0.57	3000	0.01
4	3.32	3000	0.04
5	5.00	3000	0.07
6	3.32	3000	0.05

- The I4(D) membrane tube tested in Run HP1-37 had an A/B ratio of 1.00 and no catalysts. The run ended after about 290 hours of operation due to a reactor upset. The oxygen flux was stable over this time period.
- The I4(D) membrane tube tested in Run HP1-39 had an A/B ratio of 1.00 and no catalysts. The oxygen flux was stable for the first 1250 hours of operation. The oxygen flux dropped to a lower, but stable value. The run was purposely ended after the tube had surpassed 2000 hours of operation. The leak rate was low.
- The I4(D) membrane tube tested in Run HP1-44 had an A/B ratio of 1.00 and an outer surface porous layer. The leak rate was low.

In another series of tests in the Eltron Research high-pressure reactors, the membranes were operated in a hydrogen-rich, high steam-to-carbon syngas mixture. The composition of this syngas was 48% hydrogen, 37% steam, 2% methane, 8% carbon monoxide, and 7% carbon dioxide. Changes were made to improve sealing of the tubular membranes and these modifications resulted in an improvement in the number of successful high-pressure tests.

A summary of the samples, test conditions, and relative oxygen flux for these tests is given in Table 2.2.1.1-7.

Table 2.2.1.1-7 High-Pressure Test Results from Testing at Eltron Research

Tube Number	Membrane Material	Syngas-side Catalyst	Time (hours)	Temperature (°C)	Pressure (psig)	Relative O ₂ Flux
303-28	I4(C)	Ni/I4:LSCO	701	825	250	0.87
303-31	I4(C)	Ni/I4:LSCO	4500	825	250	0.46 – 0.66
303-34	I4(C)	Ni/I4	125	825	250	0.97
303-36	I4(C)	Ni/I4	1000	825	250	0.87
			300	900	250	1.43
303-38	I4(C)	None	600	825	250	0.15
303-39	I4(C)	None	240	820	250	0.36

Table 2.2.1.1-7 High-Pressure Test Results from Testing at Eltron Research (Continued)

Tube Number	Membrane Material	Syngas-side Catalyst	Time (hours)	Temperature (°C)	Pressure (psig)	Relative O ₂ Flux
303-42	I4(C)	None	1000	825	250	0.71
			1350	900	250	1.02 – 0.82
306-1	I4(C)	Ni/I4	650	825	250	0.46
306-3	I4(C)	Ni/I4	4435	825	250	0.46 – 0.77
61-15	I4(C)	None	200	900	250	1.32
61-28	I4(C)	None	5590	900	250	0.92 – 0.51
61-30	I4(C)	None	4400	900	250	0.92 – 0.51
02-3	I4(D)	None	4400	825	250	0.31 – 0.56
02-14	I4(D)	None	4270	900	250	0.82 – 0.61
02-19	I4(D)	None	4330	900	250	0.51 – 0.26
000-4	I4(D)	None	2100	900	250	1.12 – 0.82
000-28	I4(D)	None	2700	900	250	0.92 – 0.71
056-16	I4(D)	None	1500	850	250	0.56
056-18	I4(D)	None	1500	900	125	0.46

Details of these runs include:

- Membrane Tube 303-31 was the first to surpass the six-month milestone at high pressure. The oxygen flux declined rapidly during the first 200 to 300 hours of operation and then declined more slowly but steadily over the remainder of the test period. This slow, steady decline amounted to more than a 35 percent reduction in oxygen flux during the remainder of the test period. Figure 2.2.1.1-2 shows the oxygen flux versus time.
- The oxygen flux for Membrane Tube 303-38 was very low, presumably the result of no catalysts on this tube.
- Membrane Tube 303-42 operated for 1000 hours at 825°C and an additional 1350 hours at 900°C. The oxygen flux at 825°C was relatively constant. When the operating temperature was increased to 900°C, the oxygen flux increased by about 85 percent, but then decreased by nearly 40 percent over the remaining period of operation.
- Membrane Tube 306-3 was also operated for more than six months. As shown in Figure 2.2.1.1-3, the oxygen flux was relatively stable after the initial decline in the first 200 to 300 hours of operation. However, the oxygen flux did decline over the last 1500 hours of operation.

- Membrane Tubes 61-28 and 61-30 showed similar declines in oxygen flux over time. Both tubes showed an increase in flux lasting hundreds of hours following a short interruption of the water supply.
- Membrane Tube 61-28 operated for 5590 hours. The membrane failed during a shutdown caused by the failure of a fitting on the product outlet line.
- When Membrane Tube 61-30 was removed, the tube was in good shape with little discoloration and no obvious sign of creep. The support tube for this membrane showed a great deal of deep pitting, which was likely due to "metal dusting." There was also a significant amount of coke in the lower portion of the reactor that could have formed during periods when the water supply was interrupted.
- The oxygen flux for Membrane Tube 02-3 was initially low and gradually increased by more than 60 percent and then stabilized for the last 3500 hours.
- Membrane Tube 02-14 operated for 4270 hours (~ 6 months). The oxygen flux decreased slowly over the period of the test. The tube looked quite clean on removal and subsequent analysis showed little contamination of the surfaces.
- Membrane Tube 02-19 had an A/B ratio of 1.01. The oxygen flux was relatively constant for initial portions of the operating period, then slowly decreased for a portion of the operating period, and finally decreased more rapidly in the latter period.
- Membrane Tube 000-4 operated for 2100 hours. The oxygen flux decreased slowly over the period of the test. The test was halted when an increase in reactor temperature and carbon dioxide in the "air out" line indicated a leak in the tube or seal. On removal, the tube appeared to be very clean and was relatively clean when analyzed.
- Membrane Tube 000-28 had an A/B ratio of 1.01. The oxygen flux was relatively constant for initial portions of the operating period.
- The test of Membrane Tube 056-18 at 125 psig is designed to investigate membrane degradation mechanisms due to different reactivity of carbon dioxide and steam under a low pressure, high temperature condition.

Figure 2.2.1.1-2 Oxygen Flux Degradation for Membrane Tube 303-1

Figure 2.2.1.1-3 Oxygen Flux Degradation for Membrane Tube 303-1

Thin-film Membrane Tests

Ceramatec supplied thin-film membrane disks with a PDS structure for testing. Dense layers were in the range of 100 to 400 microns and porous layers ranged from 300 to 800 microns. The membranes were made with the I4(C) and I4(D) compositions. These membrane tests were generally done at atmospheric pressure. Examples of some of the oxygen flux data collected during these experiments are provided in Tables 2.2.1.1-8 and 2.2.1.1-9. The relative oxygen flux was based on the oxygen flux calculated by the measured oxygen depletion of the air-side gas.

Table 2.2.1.1-8 Relative Oxygen Flux of I4(C) PDS Membrane Disks

Disk Number	Temperature (°C)	Relative O₂ Flux
D12183L	950	0.28 – 0.5
D12193R	950	0.28
D01263R	950	0.61
D01151R1	1000	0.14

Table 2.2.1.1-9 Relative Oxygen Flux of PDS Membrane Disks

Disk Number	Membrane Material	Temperature (°C)	Relative O₂ Flux
1140	I4(D)	950	0.56 – 0.83
1141	I4(C)	925	0.07 – 0.31
1151	I4(C)	975	0.38 – 0.98
1153	I4(D)	975	0.78 – 0.89
1154	I4(C)	925	0.39 – 0.72
D02142L2	I4(D)	950	0.02 – 0.06
D03072R2	I4(D)	950	0.28 – 0.35
D03073R2	I4(D)	925	0.11 – 0.30
D04181R2	I4(D)	925	0.10 – 0.13
D02063R3	I4(D)	825	0.22
D02063L3	I4(D)	825	0.22 – 0.33
D02062R3	I4(D)	825	0.28
D06062R2	I4(D)	950	0.09 – 0.33

Catalyzed I4(D) PDS membranes were tested and had consistently higher oxygen fluxes than the uncatalyzed thin disc membranes. For example, several catalyzed PDS membranes had relative oxygen fluxes of 0.56 to 0.67 while operating at 900°C. These results confirmed that high oxygen fluxes, consistent with commercial requirements, were attainable.

Post Test Analysis

Many of the membrane tubes were examined and analyzed after operation in the test units using SEM and EDS. Table 2.2.1.1-10 provides examples of some of the findings for tubes. Volatile reactor contaminants, such as silicon and chromium, were found on the membrane surfaces. As noted, reactor modifications eventually led to these contaminants being either eliminated or significantly reduced.

Table 2.2.1.1-10 Examples of Post Test Analysis for Membrane Tubes

Tube Number	Examination and Analysis Results
61-30	EDS analyses revealed that the inner surface contained I4 with a Cr impurity, a Ca-Cr-O phase and a Fe-Cr-Ca-La-rich phase. The outer surface had a Ca-Si-O phase and I4 with a Si impurity.
02-3	EDS analyses revealed that the inner surface contained I4 with a Cr impurity, a Ca-Cr-O phase and a Ca-Cr-Fe-La-rich phase. The outer surface had a Ca-Si-rich phase and I4 with an Si impurity.
02-14	EDS analyses revealed that the inner surface contains a Ca-Cr-rich phase, a Cr-Fe-rich phase, CaO and I4 with Cr and Si impurities. The outer surface contains I4, calcium silicate, a Nb impurity and an FeO _x deposit on the membrane tip.
02-19	EDS analyses revealed that inner surface contained a Ca-Cr-rich phase, a Ca-Fe-rich phase and a Cr-Fe-Ca-rich phase. The outer surface contained calcium silicate and mostly I4. The significant Cr contamination on the inner surface may, in part, be the reason for flux degradation.
000-4	EDS analyses revealed that the inner surface contained mostly FeO _x and small areas of exposed I4. The outer surface was primarily stoichiometric I4(D).

Similar post-test analysis was completed for the thin membrane disks. The bulk of these studies were in support of the kinetic demixing studies that are discussed in Subtask 2.2.1.2.

Table 2.2.1.1-11 provides examples of results from post-test analyses.

Table 2.2.1.1-11 Examples of Post-Test Analysis for Thin Membrane Disks

Disk Number	Time on Test (hours)	Examination and Analysis Results
1140	630	Air side primarily stoichiometric I4 with CaFeO _x randomly dispersed along grain boundaries. Syngas side had both stoichiometric I4 and La-rich areas. The La-rich areas were highly porous (i.e., three-dimensional, intergranular surfaces), and the stoichiometric I4 surfaces, which also contained Ni, Cr, Mo, Nb and Si impurities, were etched along grain boundaries.

Table 2.2.1.1-11 Examples of Post-Test Analysis for Thin Membrane Disks (Continued)

Disk Number	Time on Test (hours)	Examination and Analysis Results
1141	1180	Syngas side was stoichiometric I4; air side was mostly CaFeO_x . No impurities observed other than a small amount of carbon on the syngas side.
1151	300	Syngas-side was highly porous and contained La-rich areas; surface of the air side was mostly CaFeO_x . Analyzing a cross-section of the dense layer showed (a) the thickness of porous layer on the syngas side was $\sim 10\text{ }\mu\text{m}$, and (b) thickness of the air-side layer (i.e., CaFeO_x) ranged between 3 to $6\text{ }\mu\text{m}$. No impurities were observed.
1153	288	Syngas side surface was highly porous and contained La-rich areas. Air side surface was mostly CaFeO_x and an Fe-Mg-rich phase. By analyzing a fresh-fracture cross-section of the dense layer, it was found that (a) the thickness of the porous layer on the syngas-side was $\sim 20\text{ }\mu\text{m}$, and that (b) the thickness of the air-side layer was between 2 and $4\text{ }\mu\text{m}$.
D02142L2	300	SEM/EDS revealed that fuel-side surface contained stoichiometric I4(D). Air-side surface had I4 and CaFeO_x of varying thickness; some regions were contaminated with Cr. Secondary phases cover $63.30 \pm 4.03\%$ of the air-side surface, and average thickness is $2.53 \pm 0.39\text{ }\mu\text{m}$ (i.e., $\pm 95\%$ confidence level for the coverage and thickness).
D03072R2	296	SEM/EDS revealed that the fuel-side surface contained stoichiometric I4 and a Si-rich phase. Air-side surface had I4, FeO_x and CaFeO_x with an Mg impurity. The secondary phases cover $68.57 \pm 4.02\%$ of the air-side surface, and the average thickness is $0.94 \pm 0.06\text{ }\mu\text{m}$ (i.e., $\pm 95\%$ confidence level for the coverage and thickness).
D03073R2	800	SEM/EDS revealed that fuel-side surface contained stoichiometric I4 and areas of La enrichment. Air-side surface had I4 and CaFeO_x of varying thickness. The secondary phases cover $68.57 \pm 4.02\%$ of the air-side surface, and the average thickness is $0.45 \pm 0.04\text{ }\mu\text{m}$ (i.e., $\pm 95\%$ confidence level for the coverage and thickness).
D04181R2	300	SEM/EDS analyses revealed that fuel-side surface contained stoichiometric I4 and areas of La enrichment with Si impurity. Air-side surface had I4 and CaFeO_x with Mg impurity. Secondary phases cover $50.78 \pm 4.47\%$ of the air-side surface, and the average thickness is $0.81 \pm 0.05\text{ }\mu\text{m}$ (i.e., $\pm 95\%$ confidence level for the coverage and thickness).

Table 2.2.1.1-11 Examples of Post-Test Analysis for Thin Membrane Disks (Continued)

Disk Number	Time on Test (hours)	Examination and Analysis Results
D02063R3	1000	SEM/EDS analysis revealed that syngas-side (porous layer) surface contains I4 with thin Ca-Si-rich phase and Fe-enriched precious metal particles. Si not found below porous layer outer surface. Number of precious metal particles below the outer surface decreased significantly. The air-side (dense layer) surface contains a variety of Ca- and Fe-rich phases.
D02063L3	1000	SEM/EDS analysis revealed that the syngas-side (porous layer) surface contains I4 with a thin Ca-Si-rich phase and Fe-enriched precious metal particles. Si not found below the outer surface of porous layer, and the number of precious metal particles below the outer surface decreased significantly. Air-side (dense layer) surface contains a variety of Ca- and Fe-rich phases.
D02062R3	1000	SEM/EDS analysis revealed that syngas-side (porous layer) surface contains I4 with a thin Ca-Si-rich phase and Fe-enriched precious metal particles. Si not found below outer surface of porous layer, and the number of Pd particles below outer surface decreased significantly. Air-side (dense layer) surface contains a variety of Ca- and Fe-rich phases, as well as Ca-Si-rich phases.
D06062R2	500	Fuel-side surface contained I4 and Ca-Si-P-rich phase. Air-side surface contained I4, Ca-Si-P-rich phase and CaFeO_x with Mg impurity. Secondary phases covered $28.02 \pm 4.65\%$ of the air-side surface; average thickness was $0.99 \pm 0.14 \mu\text{m}$ (i.e., $\pm 95\%$ confidence level for the coverage and thickness).

Subtask 2.2.1.2 Long-Term Stability and Lifetime Testing

Thermodynamic Stability

One of the critical criteria in selecting the membrane composition is thermodynamic stability. The membrane must be thermodynamically stable in both the syngas environment on the permeate side of the membrane and the oxidizing environment on the air side of the membrane. Many membrane compositions may be kinetically stable in the syngas environment: they do not decompose as long as the membrane is fluxing oxygen. This is because the oxygen flux maintains the membrane in an "oxidized" state such that the metal cations in the membrane cannot be excessively reduced if the membrane would come into chemical equilibrium with the gas on the syngas side of the membrane. However, for some membrane designs, there may be parts of the membrane where the flux is very low, for example the rim of a planar membrane or some of the structural elements at the foot of the membrane. Also, there may be transient or upset conditions in the ITM Syngas reactor where the membrane may be exposed to syngas without any substantial oxygen flux through the membrane. For those parts of the membrane without substantial oxygen flux, and for transient conditions without a substantial oxygen flux,

the membrane composition must be thermodynamically stable to avoid chemical decomposition of the membrane that would damage the membrane. Therefore, the ITM Syngas membrane composition was selected to be thermodynamically stable at the temperature, pressure and gas compositions on both the air side and syngas side of the membrane.

The thermodynamic stability of the membrane composition is a function of the chemical composition of the membrane and the process conditions. The pertinent process conditions are the temperature, pressure and the composition of the gas in contact with the membrane. For the I4 class of membrane materials, the oxygen partial pressure, P_{O_2} , the carbon dioxide partial pressure, P_{CO_2} , and the steam partial pressure P_{H_2O} , are the gas composition variables that affect the stability of the membrane. Of particular concern are the reaction of the metal cations in the membrane material with CO_2 from the syngas atmosphere to form metal carbonates, reaction of the metal cations with steam to form metal hydroxides and the reduction of the metal cations at low oxygen partial pressures to decompose the membrane to form new phases, including lower valent metal oxides or even metal. By carefully choosing the membrane composition and process conditions, these undesired reactions can be avoided.

Thermodynamic Modeling

A thermodynamic model for the reaction of I4 materials with $Si(OH)_4$ was constructed. $Si(OH)_4$ is the dominant Si-containing vapor species in high temperature, moist atmospheres. The model predicted that I4 materials will readily react with partial pressures of $Si(OH)_4$ in equilibrium with SiO_2 at ITM Syngas conditions. The driving force for this reaction was the extreme stability of $CaSiO_3$. Sources for Si in laboratory or commercial ITM syngas reactors include insulation, quartz and glass components, and dense alumina.

A thermodynamic model for the reaction of I4 materials with Cr vapors was constructed. Cr is the dominant vapor species over Cr_2O_3 under reducing conditions. The vapor pressures of CrO and $CrO_2(OH)$ are about an order of magnitude lower. The model predicts that I4 materials will readily react with partial pressures of Cr in equilibrium with Cr_2O_3 at ITM Syngas conditions. The driving force for this reaction is the extreme stability of $CaCr_2O_4$.

Norsk Hydro developed a broader thermodynamic model for I4 and I5 materials. The model allowed the calculation of the stable phase assemblage at any given condition through a free energy minimization. The model was created using literature values of the thermodynamic properties of the parent components of I4, supplemented by thermodynamic properties that were measured as needed.

Model verification of key reactions included the following

- Experiments on $CaFeO_{2.5}$ and $CaFe_2O_4$ confirmed that both powders reacted, as expected, at 900°C , $P_{O_2} = 10^{-16}$ bar, and 10.5 bar CO_2 .
- Experiments on I4 powders confirmed good quantitative agreement between the results and the model at 900°C .

- Experiments on I4(D) samples exposed to high pressure reducing gas atmospheres containing CO₂ remained stable, as predicted, without the development of a surface coating or morphology change after one week of exposure at 750°C with an equilibrium P_{O2}=6.5x10⁻¹³ bar and P_{CO2} = 3.2 and 0.3 bar.
- Other membrane compositions such as I4(B), I4(C), I5(A5) showed some reaction at the P_{CO2}=3 bar condition. These results were in agreement with the thermodynamic model.
- Subsequent experiments on I4 powders under reactor conditions indicated that the I4 powders are more stable than predicted by the model.

The model was used for many purposes, including:

- Investigating the thermodynamic stability of the membrane composition at a large number of process conditions, something that would not be possible to do experimentally in a reasonable time or cost.
- Evaluating the thermodynamic stability of different membrane composition variations.
- Modeling the I4-steam system to determine the degree of Fe(OH)₂ vaporization.
- Investigating potential reactions with atmospheric contaminants.

Figure 2.2.1.2-1 shows the thermodynamic stability of the I4(C) composition at a given process temperature. The black line in the figure denotes the boundary between the process conditions where I4(C) was stable and the conditions where it was unstable. The blue dot represents an example process condition where I4(C) is not stable. Figure 2.2.1.2-2 shows the thermodynamic stability of the I4(D) composition at the same temperature. The I4(D) composition was stable at the process condition represented by the blue dot on the plot. These results showed that the thermodynamic stability of the I4 family of materials can be manipulated through composition variations to meet the requirement of thermodynamic stability at all process conditions.

Figure 2.2.1.2-1 Isothermal Stability Diagram for the I4(C) Composition

Figure 2.2.1.2-2 Isothermal Stability Diagram for the I4(D) Composition

Another example of the membrane composition affecting stability is shown in Figures 2.2.1.2-3 and 2.2.1.2-4. Figure 2.2.1.2-3 shows the stability for the I4(D) composition where the blue dot represents a given set of operating conditions. Figure 2.2.1.2-4 shows the stability diagram for the I5(A5) composition. The blue dot represents the same example process condition shown in Figure 2.2.1.2-3. The I4(D) composition had a wider stability window at this temperature than I5(A5).

Figure 2.2.1.2-3 Isothermal Stability Diagram for the I4(D) Composition

Figure 2.2.1.2-4 Isothermal Stability Diagram for the I5(A5) Composition

Long-term Testing

Long-term testing was conducted at Eltron Research (atmospheric pressure reactors and hot wall reactors) and at Air Products (cold wall reactors). A major issue early in the program's testing was chromium and silicon contamination of the membranes. Each reactor system was reviewed and modifications to the reactors were identified and made to obtain meaningful long-term test results.

A wide range of tests were conducted in these reactors over the course of the program. Examples of early experiments and the results include:

- Experiments were carried out to confirm the stability of selected I4 materials in atmospheres with elevated partial pressures of CO₂ (3 bar), syngas operating temperature (750°C), and relevant partial pressures of oxygen. After one month at these conditions, very little reaction was visible by SEM analysis. This is in contrast to the thermodynamic modeling prediction that certain compositions would not be stable.
- An I4(C) membrane tube was tested at ~720°C and 385 psig for over 500 hours. The oxygen flux under these conditions was stable over the entire test period. The sample failed when the temperature was raised to 825°C. Significant quantities of CaSiO₃ were present over the vast majority of the surface.
- An I4(C) membrane tube was tested at 775°C and 385 psig. After 200 hours of operation, examination of the membrane showed no Si-contamination, confirming that the new Haynes 230 liner was an improvement over the previous alumina liner.
- An I4(C) membrane tube was tested in a hydrogen mixture at low pressure and 825°C for 600 hours. Despite the presence of an Inconel liner, silicon contamination was present on the outer surface, although at significantly reduced levels. CaCO₃ was present on the outer surface and Ca-rich LCF grains and CaO particles were observed on the inner surface.
- An I4(C) membrane tube was tested in a hydrogen mixture at low pressure and 825°C for 650 hours. Despite the presence of an Inconel liner, silicon contamination was present on the outer surface, although at significantly reduced levels. Most of the inner surface was covered with a Ca-rich LCF phase.
- An I4(C) membrane tube was tested at high-pressure in a syngas atmosphere. After operating at 825°C for 1000 hours and at 900°C for 300 hours, the inner surface of the membrane had a significant secondary phase of Ca-rich LCF. CaSiO₃ and CaCO₃ were detected on the outer surface.

- An I4(C) membrane tube with Ni/I4 syngas-side and LSCO air-side catalyst layers was tested under multiple conditions. Initially, the membrane was tested under a low partial pressure hydrogen atmosphere at 235 psig and 900°C for ~100 hours. It was then switched to a GTL inlet feed (low CO₂) at 425 psig and 805°C for ~200 hours. While the Haynes 230 reactor liner had reduced silicon contamination on the outer surface, it was still present and reacting with the calcium in the membrane. Significant quantities of Sr_xCa_{1-x}O were observed on the inner surface.

A series of I4(C) and I4(D) membranes were tested under a syngas/air gradient in Eltron Research's reactors. The membranes were returned to Air Products for analysis of the microstructure using SEM/EDS. These membranes were tested in metal reactors that have successfully reduced silica contamination of the syngas surface. However, occasional membranes are still found with significant Si, Al and/or P contamination.

A number of observations were made from these experiments:

- The oxygen flux through most membranes was stable during the test despite the morphological changes that some of these membranes experienced.
- The syngas surfaces of the I4(C) or I4(D) membranes tested at 950°C were covered or partially covered with a porous layer. On one of the membranes there was evidence that the syngas surface was enriched in La relative to the starting composition.
- The air side surfaces of the membranes tested at 950°C were covered or partially covered with a CaFeO_{2.5} and/or a FeO_x phase. The thickness of the layer increased with length of operation.
- The syngas surfaces of membranes tested at 900°C or 850°C did not have a porous layer. The grain boundaries on the syngas surface were slightly etched.
- There was no difference in the morphology of I4(C) or I4(D) following testing at 950°C. Both compositions showed evidence of Ca and Fe enrichment on the air side and the formation of a porous layer on the syngas side.
- The air side surfaces of membranes tested at 900°C or 850°C do not have any CaFeO_{2.5} and/or a FeO_x second phase. The grain boundaries on the air side surface were slightly etched.

These observations are consistent with kinetic decomposition or demixing, with Ca and Fe being the fastest diffusing cations. A more detailed discussion on kinetic decomposition is provided later in the section.

Additional testing included:

- An I4(D) membrane tube with no air side catalyst and a Ni/I4 syngas side catalyst was tested under a syngas atmosphere. The membrane operated for a total of

700 hours. CaO was prevalent on the inner surface, with small Al- and Si- containing grains. The catalyst layer appeared to be intact on the outer surface, as indicated by the presence of Ni, but had densified considerably due to contamination with silicon. The outer surface was rich in Ca relative to a normal I4(D).

- An I4(C) membrane tube with catalysts on both sides was tested under syngas conditions at 825°C for six months. The oxygen flux was stable over the operating time. The outer surface was very clean, and only small amounts of a Si-containing I4 phase were present. The inner catalyst layer was still intact, with only a small number of gaps in the catalyst coverage.
- An I4(C) membrane tube with no air side catalyst and a Ni/I4 oxidation catalyst was tested under a low hydrogen partial pressure atmosphere at 825°C and for six months. A large amount of chromium was detected on the inner surface. The majority of the outer surface was covered in CaSiO₃, in contrast to the other six-month test which showed very little Si contamination.
- An I4(C) membrane tube without catalysts was tested for 1000 hours at 825°C and for an additional 1350 hours at 900°C. A number of Cr-containing phases were observed on the inner surface. The outer surface was covered with a thin layer of CaSiO₃.

Air Products used SEM/EDS to examine a series of I4(C) and I4(D) membranes that had been tested at ERI in metal reactors having reduced silica contamination on syngas surfaces. However, some membranes are still being contaminated with Si and/or P. The following observations were made:

- The fluxes through most I4(C) membranes have been shown to be stable with time (1200+ hrs) and to increase with temperature, despite morphological changes that occurred. The observed fluxes through the I4(D) membranes were also stable (1200+ hrs), and the magnitude of the fluxes increased with temperature.
- The air side surfaces of the I4(D) membranes tested at 900°C, 925°C and 950°C and I4(C) membranes at 850°C were covered or partially covered with CaFeO_x, FeO_x and/or CaO. The thickness of the air side layer for I4(D) was greatest at 950°C.
- A number of the syngas surfaces were contaminated during testing. These membranes could not be used to evaluate structural degradation phenomena, but the uncontaminated surfaces did reveal grain boundary etching, and, in some cases, severe porosity.
- Where secondary phases formed on the air side during tests at or below 900°C, the observations were inconsistent with previous results. However, subsequent tests for I4(D) revealed no air side, secondary phases at 900°C.

High pressure tests were conducted under a number of different conditions to collect reaction kinetics and oxygen flux data, as well as to assess the performance of ceramic-ceramic joints. Test runs of up to 6000 hours duration were completed. Example test conditions are shown in Table 2.2.1.2-1. The main sources of the observed oxygen flux decline over time in the Eltron Research tests were contaminants from the materials of construction in the reactor system. Starting with tests ER-FY03Q2-2 and ER-FY03Q2-3, the reactor components were modified and improved oxygen flux stability was observed.

Table 2.2.1.2-1 High-Pressure Tubular Membrane Test Conditions

Sample	Material	Temperature (°C)	Pressure (psig)	Duration (hours)
AP-FY02Q4-3	I4(D)	890	425	2094
AP-FY03Q1-1	I4(D)	890	425	1349
AP-FY03Q2-1	I4(D)	900	425	693
AP-FY04Q1-1	I4(E)	900	425	1000
AP-FY04Q3-1	I4(E)	850	425	1500
ER-FY02Q3-1	I4(D)	900	250	4390
ER-FY02Q4-1	I4(D)	850	250	4390
ER-FY02Q4-2	I4(D)	900	125	3140
ER-FY03Q2-1	I4(D)	900	125	4400
ER-FY03Q2-2	I4(E)	900	250	3300
ER-FY03Q2-3	I4(E)	900	250	> 900
ER-FY04Q1-1	I4(E)	850	250	936
ER-FY04Q1-2	I4(E)	850	250	6000

Materials stability tests were conducted at Eltron Research using supported, thin-film membranes to evaluate different membrane compositions within the I4(D) group of materials. Supported, thin-film, catalyzed membranes were tested at 825-900°C and ambient pressure for durations of 1000 hours per membrane. Additional tests at 825°C and 850°C were conducted for periods of operation of 2000 hours. Some degradation by-products were observed in these tests. Performance data and post-test analyses were used to verify model predictions for material stability and to confirm the selection of materials of construction in the ITM Syngas reactor.

Kinetic Decomposition

The large oxygen chemical potential gradient through an ITM Syngas membrane induces an opposing gradient of the metal species through the membrane. As a result, the metal cations diffuse at relatively low rates at process temperatures toward the side of higher oxygen chemical potential, the air-side of the membrane, countercurrent to the oxygen flux. If the cations diffuse at different rates and the cation stoichiometry through the membrane changes, this is referred to as "kinetic demixing." The membrane may also decompose if the membrane is unable to

withstand the change in cation stoichiometry. This phenomenon is called "kinetic decomposition," which reduces membrane performance and lifetime. Secondary phases will form on the outer surfaces of the membrane and possibly within the bulk material, and will potentially reduce membrane performance by affecting surface reactions and/or acting as a resistance barrier for oxygen transport. Similarly, mechanical and bulk ion transport properties may be affected due to changes in the bulk membrane composition as a result of kinetic demixing and/or kinetic decomposition.

Figure 2.2.1.2-5 Kinetic Demixing of an (AB)O Membrane

Since kinetic decomposition is an important lifetime issue, a significant effort during Phase 2 focused on it. Experimental work measured the rates of kinetic demixing/decomposition as a function of temperature and investigated means to reduce the rates.

Experimental results included:

- The rate of decomposition for I4(C) at 1050°C was measured using quantitative EDS. A rate equation was proposed. The rate at 980°C could not be determined due to the large uncertainty of the composition measurement. The rate of decomposition was very slow below this temperature.
- An I4(C) membrane tube tested under syngas conditions with pressures and temperatures ranging from 230 psig at 825°C to 360 psig at 925°C indicated that kinetic demixing had not occurred.
- Estimates of the activation energy were ~450 kJ/mol, although the confidence interval was relatively large (292 to 594 kJ/mol). The high activation energy indicated that the kinetic decomposition reaction will likely be kinetically limited over the projected membrane life at normal operating conditions. Analysis of polished cross sections of

high-pressure test membranes that had been flux tested for 3 to 6 months did not reveal any second phases due to kinetic decomposition.

- Kinetic decomposition rates were measured for a range of I4 compositions, temperatures and annealing times in an atmosphere of 4% H₂ bubbled through water. Analysis of back-scattered electron images was used to determine the composition of the I4 phase. The activation energy was 350 ± 50 kJ/mol, and the pre-exponential was $\exp(30 \pm 5)$ days⁻¹.

A model for kinetic decomposition was formulated for an ideal oxide where the mobilities of its cations have different activation energies. This simplistic model suggested, in a specific temperature range, that the apparent activation energy for kinetic decomposition can far exceed the activation energies for the mobilities of the individual cations.

A comparison between the model and the amount of second phase present on the syngas side of two high-pressure membrane tubes that were in service for more than six months showed good agreement. Cross sectional analysis of the membranes showed a clear trend of increasing second phase from the inner surface of the membrane (air side) to the outer surface of the membrane (syngas side).

Tests on catalyzed PDS membranes at 825°C and 850°C were conducted. These gas phase temperatures may not accurately represent the actual membrane temperature. The "Mixed-Cell" Model was used to predict membrane temperature for each of the cases below and is noted in parentheses next to the gas phase temperature. Test results suggested:

- The rate of kinetic decomposition decreased with time at 825°C (865°C membrane temperature), based on 1000-hour and 2000-hour experiments. The decomposition products had no apparent effect on flux performance under these experimental conditions.
- The rate of kinetic decomposition was greater at 850°C (890°C membrane temperature) and may have increased with time, based on 1000-hour and 2000-hour experiments. Flux degradation was observed during the first 1000 hours.

Theory suggested that grain size may affect the extent of demixing. To evaluate such variables, I4(D) membranes of varying grain size were tested at 950°C for 500 hours.

A membrane disk of I4(D) composition was glassed to an alumina tube. The nominal membrane thickness was 225 microns and the grain size was 4 microns. The membrane assembly was installed in a reactor and was heated to 950°C in helium. The helium was replaced with a mixture of 75% H₂, 17% CO₂ and 8% CH₄ and air was introduced on the opposite side of the membrane. The final flow conditions and temperature were maintained for 500 hrs. The air-side surface of the tested membrane was analyzed to assess kinetic decomposition. The SEM image of the air side surface of the membrane is shown in Figure 2.2.1.2-6 (a). The dark phases are products of kinetic decomposition.

A second disk of I4(D) composition was tested. This specimen was the same in composition and thickness, but the grain size was increased to 8 microns. The experimental procedures and conditions were identical to the previous test. After 500 hours of permeation testing at 950°C, the reactor was cooled, and the air-side surface of the tested membrane was analyzed to assess kinetic decomposition. The SEM image of the air side surface of the membrane is shown in Figure 2.2.1.2-6 (b). The dark phases are products of kinetic decomposition. However, it was noted that the amount of decomposition product in this specimen was significantly less than the previous specimen. These results support the theory that increasing the grain size would reduce the kinetic decomposition rate.

Figure 2.2.1.2-6 SEM Images of the Air-side Surface of Membranes of Differing Grain Size – 4 Micron for (a) and 8 Micron for (b)

The thicknesses of these secondary phases on the air-side surface were determined by analyzing four randomly chosen cross-sections near the air-side surface of the membrane, and the area-percent coverage of secondary phases was determined by analyzing eight randomly chosen areas on the air-side surfaces. The volume of decomposition product on the air-side surface was then determined from the product of the area coverage and thickness of the secondary phases. Roughly four times more kinetic decomposition product was found on the membrane with the smaller grain size.

The oxygen flux through the membranes were effectively the same under identical test conditions at 950°C, demonstrating no oxygen flux dependence on grain size.

Kinetics of Reaction with CO₂

The syngas side of the membranes will be exposed to various partial pressures of carbon dioxide. Studies were conducted to determine under what conditions the carbon dioxide would react with the membrane material. Analysis of specimens from early experiments suggested that carbonate secondary phases could develop under certain operating conditions. For example, a sample of I4(C) operating for two weeks in a CO₂ partial pressure of 83.7 psig at 750°C had a carbonate

layer; albeit a very thin one, since an analysis of a cross section of the sample did not reveal any carbonate layer within the resolution of the SEM.

A literature search of reactions between Ca and CO₂ was conducted. Unfortunately there was very little literature available on reactions with Ca-containing perovskites. However, there was an abundance of references available on the CaO – CO₂ – CaCO₃ system, as well as the decomposition of dolomite. Most of the heterogeneous gas solid reactions were characterized with TGA using powdered solid reactants. Only a few researchers characterized the reaction under high pressures. While a number of models have been proposed to describe the results, the general trend was clear: there was an initial fast reaction-controlled reaction, followed by a slower diffusion-controlled reaction. The initial reaction was surface CaO reacting with CO₂. Once the surface CaO reacted, the CO₂ must diffuse through the CaCO₃ product layer to react further. The rate and activation energy of the diffusion-controlled reaction was characterized by the high-pressure TGA system. This information was used to determine whether or not I4 compositions are kinetically stable in CO₂ containing environments.

Experiments were performed in the high-pressure TGA (HPTGA) unit at a pressure of 500 psig using a N₂/CO/CO₂ gas mixture. Three 4-hour isotherms were chosen so as to span the predicted stability region of I4(C): 1000°C, 900°C, and 800°C. For the 1000°C sample, there was no change in weight after CO₂ was introduced into the reaction tube, which compares favorably with the Norsk Hydro thermodynamic model. The predicted weight change at 900°C was less than the observed weight change, suggesting that the stable I4 composition had a higher La content than predicted. However, the starting powder was not phase-pure, and this may have affected the results. The 4-hour isotherm was not long enough for the 800°C experiment to reach equilibrium.

The accuracy of the HPTGA experiments was checked by reacting CaO with CO₂. The predicted and experimental weight gain matched. In addition, the 800°C and 900°C experiments with I4 powder were repeated using powder that was ground from a sintered block and no weight change was observed in either the 800°C or 900°C experiment.

Further experiments showed that there was no strong correlation between the A/B ratio, surface area, and powder preparation method and the stability of the membrane material. In addition, the weight losses on heat-up and weight gains during exposure to CO₂ were not related.

In general, the experimental data suggested that the thermodynamic model was conservative--that some conditions predicted to be unstable would actually be stable. The model was therefore used to "safely" confirm the viability of proposed membrane operating conditions. When necessary, proposed operating conditions were tested in the HPTGA to determine their viability.

Effect of Fe(OH)₂ Vaporization on Membrane Lifetime

In the syngas environment, the vapor pressure of Fe(OH)₂ might be appreciable and result in loss of iron from the membrane material. For example, at the reactor exit conditions, the vapor pressure of Fe(OH)₂ over I4 may be greater than 10⁻⁵ atm. Studies were conducted to assess Fe(OH)₂ vaporization and its effect on I4 materials.

The weight loss of Fe_2O_3 under 1000 ppm H_2 and ~3% H_2O at 1300°C was compared to that of phase pure I4(C) using TGA. Theoretical predictions were made. Initial results of the tests on Fe_2O_3 (actually Fe_3O_4 under these conditions) were consistent with the theoretical prediction of 0.37 mg/day and ultimately showed $\text{Fe}(\text{OH})_2$ saturation in the flowing gas stream.

Similar experiments were conducted on samples of various I4 compositions. These samples were exposed to a gas mixture of H_2 , H_2O and N_2 at 950°C and 425 psig for 250 hours. The resulting surfaces contained a Ca-Si-rich phase with P and Al impurities, and the thickness of this phase increased with increasing Ca bulk composition. Due to surface contamination, it was difficult to determine if $\text{Fe}(\text{OH})_2$ vaporization caused Fe depletion from the I4 matrix.

Studies on I4(C) revealed that the initial rate of Fe loss from I4 was greater than predicted, however, this rate decreased significantly with time. The decreasing rate may have been due to (a) a gradual loss of surface area, (b) the formation of a secondary phase (e.g., CaO) at the surface and/or (c) the formation of a more stable La-rich I4 phase at the surface. SEM/EDS analyses confirmed the formation of La-rich areas and CaO on the sample that underwent TGA.

A potential engineering solution to this potential problem was developed. A sacrificial bed of FeO_x placed at the reactor inlet was considered. Thermodynamic models were used to confirm that this configuration would inhibit iron loss from I4 materials throughout the reactor with no deposition of iron within the reactor. The model predicted that Fe_3O_4 would produce a higher $P_{\text{Fe}(\text{OH})_2}$ at 800°C than I4(D) at 850°C to 900°C under the most severe process conditions. Further refinement of this concept suggested that three sacrificial beds, two placed at the beginning of the reactor at 800°C and 820°C and one near the injection of the recycle stream at 780°C, would inhibit iron loss from I4(D) throughout a commercial reactor. Similarly, the models predict that two sacrificial beds, both placed at the beginning of the reactor at 800°C and 820°C, would inhibit Fe loss from I4(E). There would be no need to saturate the recycle stream with $\text{Fe}(\text{OH})_2$ when using I4(E) due to its greater stability.

The HPTGA was modified to achieve the necessary experimental conditions to evaluate iron-loss from I4(D) under process conditions due to $\text{Fe}(\text{OH})_2$ vaporization. A few runs were completed; however, SEM analysis revealed that the tested I4 samples were contaminated with silicon. The source of the silicon was the hot metallurgy inside the TGA. The HPTGA was modified to correct this issue. In further experiments, the HPTGA tests showed that the rate of membrane decomposition due to iron loss was at least two orders of magnitude less than that predicted by the thermodynamic model, and would not be a concern at full-scale process conditions.

Subtask 2.2.1.3 Materials Development

Membrane Materials

Two classes of materials were evaluated for use in ITM Syngas membranes: the I4 and I5 families of composition. Evaluation of the I5 class of materials found that these materials had insufficient thermodynamic stability to be used in the ITM Syngas process. The I4 compositions of matter overcame problems associated with many prior art compositions of matter by providing a favorable balance of oxygen permeability, thermodynamic stability, resistance to degradation, favorable sintering properties, and coefficients of thermal expansion which were compatible with other materials used to fabricate solid-state membranes. Thus, the I4 family of materials was particularly well-suited toward use in solid-state membranes suitable for the ITM Syngas process.

The I4 composition, developed and patented during Phase 2 of the research contract, is represented by the formula:

where Ln is La or a mixture of lanthanides comprising La, and "x" is less than 1.0 but greater than 0.5, "y" is less than or equal to 1.1 but greater than 1.0, and δ is a number which renders the composition of matter charge neutral. Of particular interest are the compositions which have "x" less than 0.98 but greater than 0.75 and "y" less than or equal to 1.05 but greater than 1.01.

These compositions were prepared by known powder preparation and tape casting techniques, such as:

- Specified parts by weight of the respective metallic oxides or carbonates were vibratory milled together.
- The mixture of metallic oxides and carbonates was then fired in air at 1200°C.
- The mixture was ground by vibratory milling to yield a milled powder.
- The milled powder was combined with a binder, a plasticizer, and a solvent to form a slip suitable for tape casting.
- The slip was cast into a tape and dried using conventional methods.
- Appropriately-sized sections were cut from the tape using standard methods.
- Where necessary, several sections were laminated together to form a solid-state membrane having sufficient thickness.
- The solid-state membrane was fired in air to remove the plasticizer, binder, and solvent followed by sintering to produce a solid-state membrane.

The A/B ratio ("y" in the above formula) was an important factor in choosing a preferred composition. As noted in other sub-sections of this Task, creep rate was strongly dependent on the value of this ratio with A/B ratios greater than 1.0 having significantly lower creep rates. On the other hand, B-site rich compositions ("y" less than 1.0) sintered more readily and were less reactive than A-site rich compositions ("y" greater than 1.0).

Secondary phases present on surfaces of sintered material were problematic. Subsequent tests confirmed that improved cation mixing can reduce the extent of secondary phase formation. However, the likelihood of secondary phase formation increased dramatically as the A/B ratio deviated from 1.0.

Thus, the final selection of the proprietary composition was the result of balancing and optimizing many different aspects of the composition for manufacturability, performance, and reliability. Since the A/B ratio was such a critical parameter, an analytical method was developed to accurately measure the A/B ratio for I4 powders.

Guard Bed Materials

The structural components of ion transport membrane systems are typically fabricated from metal alloys that may contain chromium, silicon, tungsten, and/or molybdenum; and oxides of each of these elements. Contaminants including vaporized species such as CrO_3 , $\text{CrO}_2(\text{OH})_2$, $\text{Si}(\text{OH})_4$, and $\text{WO}_2(\text{OH})_2$ are known to evolve from hot metallurgy under oxidizing and steam environments at elevated temperatures. These contaminants may adversely react with or deposit onto ion transport membranes. Such species are believed to be generated by the following reactions:

- (a) $\text{Cr}_2\text{O}_3 + 2 \text{H}_2\text{O} (\text{g}) + 3/2 \text{O}_2 (\text{g}) = 2 \text{CrO}_2(\text{OH})_2 (\text{g})$
- (b) $\text{SiO}_2 + 2 \text{H}_2\text{O} (\text{g}) = \text{Si}(\text{OH})_4 (\text{g})$
- (c) $\text{WO}_3 + \text{H}_2\text{O} (\text{g}) = \text{WO}_2(\text{OH})_2 (\text{g})$
- (d) $\text{Cr}_2\text{O}_3 + 3/2 \text{O}_2 (\text{g}) = 2 \text{CrO}_3 (\text{g})$

Reactions (a) and (d) would occur in the feed air circuit of a reactor system. Reactions (b) and (c) would occur in the process circuit of a reactor system. Thermodynamic calculations were used to estimate the volatile species in the feed air and process gases.

Guard beds were developed to protect the membranes from being contaminated. Guard bed materials were chosen such that any residual volatile contaminant in the process gases would be removed before the gases contacted the membrane surfaces. The guard beds may be strategically located in the gas streams prior to or within the ion transport membrane reactor vessel wherein the temperature of the guard beds may be between 600°C and 1100°C; typically, the temperature of the guard beds may be between 700°C and 950°C. The guard beds should be located close to the membrane modules to minimize recontamination of the purified gas stream from the metal in the piping between the guard bed and membrane. A guard bed is defined as any vessel or enclosure which contains reactive solid material and is designed to allow flowing gas to contact

the reactive solid material. A purified gas stream is defined as a process stream in which the concentration of contaminants has been reduced by contacting a contaminant-containing process stream with a reactive solid material in a guard bed.

Figure 2.2.1.3-1 shows the potential locations for guard beds in a typical reactor system. Guard bed 1801 in inlet 515 treats inlet gas stream 517 prior to contact with membrane modules 501, 503

Figure 2.2.1.3-1 Schematic of Guard Bed Locations in Reactor Vessel System

Guard beds can also be placed between the modules of a multiple-module series reactor system to remove volatile contaminants. For example, the reactor, shown in Figure 2.2.1.3-2, includes guard beds 1901, 1903, and 1905 in series fashion in the space between any modules in the first bank of modules 501a, 501b, and 501c and in the second bank of modules 503a, 503b, and 503c. Alternatively, guard beds 1901, 1903, and 1905 may extend continuously between the inner walls of flow containment duct 511. Likewise, guard beds may be placed between any or all of the second and third banks of modules, the third and fourth bank of modules, the fourth and fifth

banks of modules, or following the fifth bank. Additionally or alternatively, guard beds may be placed between the modules in a bank of parallel modules to remove contaminants from the gas passing between the modules. For example, guard beds 1907 and 1909 may be placed between modules 505a and 505b and between 505b and 505c, respectively. Alternatively, guard beds 1907 and 1909 may extend continuously in the axial direction between the first through fifth banks of modules.

Figure 2.2.1.3-2 Schematic of Guard Bed Placement Between Modules in a Reactor Vessel

In addition, when pressure vessel 513 is operated in series with another similar pressure vessel, guard beds may be placed between the vessels such that the effluent gas from one pressure vessel passes through the guard bed before passing into the second pressure vessel.

Each guard bed contains reactive material which reacts with volatile contaminants. The reactive material or materials may be placed in the guard bed in any form selected from porous pellets, beads, rods, extrudates, porous foams, tubes, and solid honeycombs or monoliths. The guard bed may be a typical pressure vessel having an inlet and an outlet wherein the reactive material is supported within the reactor by screens or other porous supports. Alternatively, a disc-shaped or parallelepiped-shaped porous container may be used to hold the reactive material, wherein the porous container may be designed to fit within a length of piping or within the interior of a reactor vessel.

The guard bed may contain, for example, one or more reactive materials selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites. The alkaline-earth-containing perovskites have the general formula $A_x A'_x B_y B'_y O_{3-d}$ where A comprises one or more of lanthanum, yttrium, and one of the lanthanide elements; A' comprises one or more of Ca, Sr, and Ba; B and B' comprise one or more of the first row transition metals Mg, Ga, and Al; where " $x+x$ " is less than 1.1 but greater than 0.9, " $y+y$ " is greater than 0.9 but less than 1.1, " x " is greater than 0, and d is a number that makes the compound charge neutral.

A good example of a reactive material is MgO which may be used in the guard beds to remove these volatile contaminant compounds from the gases prior to contact with the membranes in the membrane modules. MgO is an effective reactive material for this service, and it is safe, easily handled, and inexpensive. The partial pressures of the volatile gas-phase contaminants can be reduced by up to several orders of magnitude, which may significantly reduce or eliminate membrane contamination and damage.

The MgO may be placed in the guard bed in any form selected from porous pellets, beads, rods, extrudates, porous foams, tubes, porous honeycombs, and porous and solid honeycombs or monoliths. The MgO will react with the chromium-, silicon-, and/or tungsten- containing species to form MgCr_2O_4 (magnesium chromite), Mg_2SiO_4 (magnesium silicate), and MgWO_4 (magnesium tungstate), respectively. These reaction products are very stable, safe to handle, and environmentally benign; disposal of spent guard bed material therefore should be simple and inexpensive.

Figure 2.2.1.3-3 shows the equilibrium concentrations of CrO_3 over a Cr-containing alloy and over the MgO guard bed material between 850°C and 900°C at an oxygen partial pressure of 0.25 bara. The difference in partial pressures indicates the potential for an order of magnitude reduction in the gas phase partial pressure of CrO_3 by the guard bed. The calculation of the vapor pressure over the alloy assumes that the surface of the alloy is pure Cr_2O_3 .

Figure 2.2.1.3-3 Guard Bed Performance at Removing CrO_3

Figure 2.2.1.3-4 shows the equilibrium concentrations of Si(OH)_4 over a Si-containing alloy and over the MgO guard bed material between 850°C and 900°C at a water partial pressure of 8.0 bara. The difference in partial pressures indicates the potential for a reduction of nearly three orders of magnitude in the gas phase partial pressure of Si(OH)_4 by the guard bed. The calculation of the vapor pressure over the alloy assumes that the surface of the alloy is pure SiO_2 .

Figure 2.2.1.3-4 Guard Bed Performance at Removing Si(OH)₄

Figure 2.2.1.3-5 shows the equilibrium concentrations of WO₂(OH)₂ over a W-containing alloy and over the MgO guard bed material between 850°C and 900°C at a water partial pressure of 8.0 bara. The difference in partial pressures indicates the potential for a reduction of greater than two orders of magnitude in the gas phase partial pressure of WO₂(OH)₂ by the guard bed. The calculation of the vapor pressure over the alloy assumes that the surface of the alloy is pure WO₃.

Figure 2.2.1.3-5 Guard Bed Performance at Removing WO₂(OH)₂

The MgO in the guard beds may be in the form of porous pellets, beads, or rods to provide high surface area for the reactions and to enhance turbulent flow through the guard bed to minimize any gas phase mass transfer resistances. For example, the guard beds may be filled with MgO rods having a purity of 99.8 wt %, an average diameter of 0.2 cm, an average length of 0.4 cm, and an open porosity of 30%. Other particle shapes, sizes, and porosities may be used as desired.

Alternatively, a honeycomb of porous MgO may be used to provide a lower pressure drop. Other configurations for the guard bed include porous foams, structured packing, and random packing. Magnesium is a relatively small cation and a fast diffuser, and should provide the lowest possible solid phase mass transfer resistance if the MgO surface becomes encased with reaction product. The size of the guard bed will be determined by the rate limiting processes for the transport and reaction of the volatile species with the MgO. These processes include the gas phase diffusion of the volatile species to the surface of the MgO, reaction of MgO with the volatile species, and diffusion of Mg or the volatile species through any reaction product that may form on the MgO.

The examples of volatile contaminants noted above are not the only possibilities that need to be considered. Similar volatile contaminants formed from other oxides of alloying elements or from oxide refractories may also need to be considered. For example, these other alloying elements may include molybdenum and/or vanadium; oxide refractories may include oxides of molybdenum and/or oxides of vanadium.

In addition to the removal of volatile contaminants described above, the guard bed also may be used to remove other volatile contaminants that may be present in the process gases. These may include, for example, any of Cl_2 , Br_2 , I_2 , and compounds containing any of Cl, Br, and I. Guard beds also may be applied to the removal of volatile sulfur-containing contaminants such as sulfur dioxide and/or hydrogen sulfide and to the removal of oxy-hydroxides of molybdenum.

Guard bed materials have been developed and used effectively in the Process Development Unit (PDU) to remove contaminants that are generated from feed air circuit materials of construction. Figure 2.2.1.3-6 shows how air-side contamination by CrO_3 can be nearly eliminated. Figure 2.2.1.3-6(a) shows an SEM image of the air-side surface of a virgin membrane. Figure 2.2.1.3-6(b) shows an SEM image of the air-side surface of a membrane that was exposed to CrO_3 containing gas for only 100 hours. The dark phases are the reaction product, CaCrO_4 , of the reaction between the CrO_3 gas phase contaminant and the membrane material. Figure 2.2.1.3-6(c) shows an SEM image of the air-side surface of a membrane that was exposed to the purified gas stream from a guard bed after 1500 hours of operation. Low pressure drop versions of guard beds have been modeled and have been assembled for testing in the PDU. Models predict that pressure drop through the beds would be acceptable in a full-scale process.

Figure 2.2.1.3-6 SEM images of air-side membrane surfaces for (a) virgin material, (b) material exposed to a contaminated gas after 100 hours of operation, and (c) material exposed to a purified gas from a guard bed after 1500 hours of operation.

Coatings and Liners

Other means of reducing or eliminating potential contamination of the membranes by gas phase contaminants originating from materials of construction in the various piping and equipment were considered. Specific coatings and liners were investigated.

Commercially available coating technologies, such as Alonizing by Alon Processing Inc. of Tarentum, PA or aluminized coatings by Diffusion Alloys Limited of Hatfield, England, were tested and used successfully. Other coating technologies have been proposed. A Chevron coating technology (US Patent 6,803,029) was also tested and used successfully. Some available alloys, such as Haynes 214, are alumina-formers that can generate a protective coating because of their aluminum content. These were also tested and found to reduce contamination of the process gas but to a lesser degree.

Alternately, liners were investigated to reduce or eliminate volatilization of metal alloy species. The term "liner" is defined as a structure disposed within any portion of a system containing a process gas within a conduit, flow direction device, and/or vessel, wherein the process gas comes into contact with one or more ion transport membranes, and wherein the liner provides a barrier adapted to prevent or minimize contact of the process gas with the inner surfaces of the conduit, flow direction device, and/or vessel of the system. Alternatively or additionally, the liner may be adapted to prevent or minimize the diffusion into the process gas of volatile gaseous contaminants formed by reaction between process gas components and the structural metal of the conduit, flow direction device, and/or vessel. In some cases, the liner is disposed adjacent to the surface of the metal that forms a conduit, flow direction device, and/or vessel in the system. In other cases, a flow channel may be formed by insulation material placed within a metal conduit, flow direction device, or vessel; a liner may be disposed adjacent the interior surface of this flow channel to protect membrane modules disposed within this flow channel. A liner is not a coating that adheres to and seals the interior metal surfaces of the conduit, flow direction device, and/or vessel.

The liners may comprise a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, combinations thereof, and mixtures thereof, and the liners may be disposed within one or more portions or segments of any inlet conduit, outlet conduit, interior surface of the gas manifold, and interior surface of the flow duct of such systems. The liners need not cover the entire surface of the inlet conduit, the outlet conduit, the interior surface of the gas manifold, and/or the interior surface of the flow duct. The liners may be disposed within one or more selected portions of the conduits, manifolds, ducts, or vessels wherein process temperatures, alloy compositions, and the processes conducted in the system are likely to generate appreciable amounts of the Si-, Cr-, Mo, and/or W-containing metallic vapor species. The liner may create a diffusion barrier such that the vapor species cannot volatilize into the process gases within the ion transport membrane system and subsequently react with the multi-component metallic oxides of the ion transport membranes to adversely affect process efficiency.

The partial pressures of the volatile contaminant species may be significantly reduced by placing the liners in the flow path of process gases within the ion transport membrane system. The reduction may occur through one or more mechanisms including any of (1) reduction of the temperature of the contaminant source due to the liner insulating the metal surfaces from the hot process gas, (2) a mass transfer barrier provided by the liner where the liner hinders the transport of volatile contaminant species from the metal surfaces into the process stream, and (3) gettering of the volatile contaminants by reaction of the liner material with the volatile contaminant species to produce stable solid phases.

The liners of ion transport membrane systems used to produce syngas or to perform partial oxidations reactions may be advantageously situated within a segment of the inlet conduit and/or a segment of the gas manifold. The liners may be incorporated into any conduit or structure in which process benefits may be obtained by substantially reducing or eliminating volatile species from entering the process gas streams of the ion transport membrane systems.

A duct liner is defined herein as a structure disposed adjacent the inner wall of a duct and comprising a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, combinations thereof, and mixtures thereof. The duct liner composition does not contain compounds used in conventional insulation including but not limited to alumina, alumina-silicate, silica, and calcium silicate. The duct liner has the primary purpose of protecting multi-component metallic oxides of the ion transport membranes from Si-, Cr-, Mo, and/or W-containing vapor species. While the duct liner may affect heat transfer to or from the duct wall to a small degree, it does not have the primary purpose of insulation that significantly reduces heat transfer to or from the duct wall. If a significant reduction of heat transfer to or from the duct wall is needed, conventional insulation may be used in conjunction with the duct liner.

These liners can be formed by conventional methods and may be introduced into a segment or the entire length of desired conduits of the ion transport membrane system. One method of introducing the liner into a conduit is to fabricate the liner in cylindrical sections that fit inside a cylindrical conduit. Linings for conduits with other cross sectional shapes may be similarly

installed. Another method of introducing the lining is to cast the lining on the inside surface of the conduit by coating the inside surface of the conduit with an aqueous slurry comprising calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures or combinations thereof, and drying the applied coating.

These liners may further comprise alumina or zirconia wherein a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures or combinations thereof is deposited by conventional methods onto an alumina or a zirconia substrate. The liners may be composite structures in which the liner material comprises (1) a base liner composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures thereof and (2) materials having other compositions that provide improved mechanical properties of the liners.

One type of liner for use in the ion transport membrane systems consists essentially of magnesium oxide wherein the liner is formed by conventional methods provided that additional additives and materials may be included in the liner that do not contribute or detract from the utility of the liners. Liners comprising magnesium oxide also may include one or more compositions selected from the group consisting of calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, or strontium oxide. A liner may be fabricated from a mixture of magnesium oxide and calcium oxide.

Liners suitable for use as described herein may be formed from dense or porous compositions of matter. Thus the liner may have no connected-through porosity or the liner may have any desired degree of porosity provided that the liner maintains structural integrity during operation of the ion transport membrane system. Moreover, several segments of liner may be placed in desired portions of a conduit wherein each liner is formed of a different composition. Liners may be in the form of bricks which are stacked to line the walls of the conduit. Alternatively, liners may be in the form of rectangular plates.

Any conventional technique suitable for making conduits formed from multi-component metallic oxides, alumina, and the like may be used to fabricate these liners. The liners may be formed in segments of varying length to accommodate their fabrication and installation into the conduits and features of the ion transport membrane system. A cross-section of the liner taken perpendicular to the liner axis may form a concentric circle, a square, or any other shape, and the liner shape may be dictated by fabrication costs and other conventional engineering considerations. Segments of liners may be installed from end to end within the conduits of the system or may be separated by any axial distance depending upon the allowable amount of contaminants that may enter the system during process operation from unlined conduit interior surfaces.

The liners described herein should be fabricated with a thickness having sufficient structural strength for insertion into the desired conduit by pressure fitting or the like and a thickness sufficient to enable operation of the process in the ion transport membrane system, while retaining structural liner integrity during operation. Pressure fitting is an advantageous method

of installing the liners in the conduits and other parts of the ion transport membrane system that may generate contaminants during operation of the system. The required thickness of a liner segment may depend on the diameter of the liner segment, the mechanical properties of the liner segment, the stresses that occur in the liner segment during process operation, and other process parameters. The liner thickness may be, for example, between 0.1 and 6 inches.

Another alternate liner that was especially useful for ITM Syngas applications was the use of copper in reducing gas environments. The copper liner solved two major problems. First, as noted above, it prevented metal alloy species from volatilizing and contaminating the membrane surfaces which degrades the membrane's fluxing capability. Second, it prevented the high-temperature superalloys, particularly alloys containing nickel, from catalyzing the steam reforming of methane. This is an endothermic reaction that can decrease the temperature of the synthesis gas in the reactor, thereby requiring additional preheating of the feed gas to the membrane reactor system. Thus there is a need for reactor designs using metal components that do not promote the steam-methane reforming reaction prior to the membrane system.

Copper liners were an effective solution to these two problems. Copper did not catalyze the steam-methane reforming reaction nearly as much as the nickel present in most high-temperature superalloys. Copper also blocked the transport of volatile silicon and tungsten species from the superalloy into the synthesis gas stream, was relatively inexpensive, and was easy to form into the required shapes.

Lining of the piping and reactor internal surfaces with a copper-containing metal can be achieved by any method known in the vessel and piping metallurgical art. For low-pressure gas flow, alloy piping and vessels subject to low mechanical loads may be lined by electroplating with copper, applying copper foil, or by copper cladding. For high-pressure gas flow, the high-temperature superalloy pipe may be lined by any of these methods or may be lined with copper by hydro-forming copper tubing or pipe to the inside surface of the superalloy pipe and vessels. When the piping, vessels, and/or other parts are subject to low mechanical loads, they may be fabricated directly of copper or copper alloys.

It was not necessary to achieve an entirely seamless lining of copper-containing metal in the gas flow path, and some gaps in the lining could exist. It is only necessary to reduce the amount of exposed non-copper metal or refractory sufficiently to reduce the amount of contaminants emitted by non-copper metal or refractory into the synthesis gas stream to acceptable levels and/or to reduce the amount of reforming that occurs on the exposed non-copper metal to acceptable levels.

The copper-containing metal may be elemental copper metal, which was available in many different grades. It was found that grades with a low oxygen content (i.e., less than about 0.0005 weight % oxygen) were particularly advantageous for surfaces in contact with hot synthesis gas at temperatures above about 374°C. Copper that contains oxygen may blister during high temperature service in synthesis gas, possibly due to diffusion of hydrogen into the copper and reaction with the oxygen to form steam. In some applications, it may be desirable to use a copper-containing alloy instead of elemental copper metal, while in other applications,

elemental copper metal may be preferred. Typically, the copper content of the lining material was greater than about 99 wt %. Exemplary copper-containing alloys that may be used include, for example, Cu-Ag and Cu-Ni alloys.

When the piping, vessels, and/or other parts are subject to low mechanical loads, any of them may be fabricated directly of elemental copper metal or copper-containing alloys having the properties described above for lining applications.

The following examples show the benefits of using copper as a liner:

- Example 1: A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. The piping was heated to 900°C, and 1129 scfh of a feed gas mixture consisting of (in vol %) 21.5% H₂, 24.5% CH₄, 5.1% CO₂, 2.0% CO, and 46.8% H₂O at a pressure of 215 psig (15.8 bara) was fed to the preheater. An ion transport membrane was placed downstream of the preheater. The hot feed gas mixture flowed over the exterior of the membrane while the membrane was held at temperatures between 800 and 900°C and pressure for 20 days. Over the course of the 20 day experiment, the flux through the membrane decreased by 25% from the initial value when measured at the same temperature and gas composition values. At the end of the experiment, the membrane was cooled to room temperature and removed from the reactor. An examination revealed that the surface of the membrane was covered with a Ca-W-O phase. The tungsten contamination likely resulted from the reaction of the steam in the synthesis gas with the tungsten in the Haynes 230 to form the volatile species WO₂(OH)₂ and this contaminant reacted with the Ca in the membrane to form the contaminant phase. The build-up of this contaminant phase on the surface of the membrane resulted in decreasing oxygen flux with time.
- Example 2: A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. A fully-annealed C10100 copper tube with an outer diameter of 0.3125 inch and a wall thickness of 0.017 inch was inserted inside the Haynes tube and hydroformed to the inner surface of the Haynes tube. The copper thickness after hydroforming was 0.015 inch. The piping was heated to 900°C, and 1060 scfh of a feed gas mixture consisting of (in vol %) 25.1% H₂, 25% CH₄, 5.8% CO₂, 0.9% CO, 1% N₂ and 42.2% H₂O at a pressure of 223 psig (16.3 bara) was fed to the preheater. An ion transport membrane was placed downstream of the preheater, and the membrane was housed in a flow duct also lined with copper metal. The membrane was initially maintained at 900°C and a pressure of 215 psig (15.8 bara). The membrane was held at temperature between 800 and 900°C and 215 psia pressure for 50 days. Over the course of the 50-day experiment, the flux through the membrane did not change measurably from the initial value when measured at the same temperature and gas composition values. At the end of the experiment, the membrane was cooled to room temperature and removed from the reactor. Upon examination, no evidence of any tungsten was found on the surface of the membrane. The copper lining of the hot synthesis gas flow path had completely prevented significant quantities of volatile tungsten species from entering the synthesis gas stream and reacting with the membrane.

- Example 3: A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. The piping was heated to 900°C and 1129 scfh of a feed gas mixture consisting of (in vol %) 21.5% H₂, 24.5% CH₄, 5.1% CO₂, 2.0% CO and 46.8% H₂O at a pressure of 215 psig (15.8 bara) was fed to the preheater. On a dry basis the gas composition was (in vol %) 40.5% H₂, 46.2% CH₄, 9.6% CO₂ and 3.8% CO. The composition of the gas exiting the preheater was measured using a gas chromatograph and the exit gas composition on a dry basis was (in vol %) 70% H₂, 6% CH₄, 8.1% CO₂ and 14.9% CO. Most of the methane in the feed had been converted to CO and CO₂ via the steam methane reforming reaction, and the gas had nearly reached reforming equilibrium at the given conditions.
- Example 4: A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. A fully annealed C10100 copper tube with an outer diameter of 0.3125 inch and a wall thickness of 0.017 inch was inserted inside the Haynes tube and hydroformed to the inner surface of the Haynes tube. The copper thickness after hydroforming was 0.015 inch. The piping was heated to 900°C, and 1060 scfh of a gas mixture consisting of (in vol %) 25.1% H₂, 25% CH₄, 5.8% CO₂, 0.9% CO, 1% N₂, and 42.2% H₂O at a pressure of 223 psig (16.3 bara) was fed to the preheater. On a dry basis, the gas composition was (in vol %) 43.4% H₂, 43.2% CH₄, 10.1% CO₂, 1.7% N₂, and 1.6% CO. The composition of the gas exiting the preheater was measured using a gas chromatograph, and the exit gas composition on a dry basis was (in vol %) 43.0% H₂, 43.0% CH₄, 9.1% CO₂, 1.1% N₂, and 3.3% CO. A negligible amount of the methane was consumed by the steam methane reforming reaction. The copper lining effectively stopped the reforming reaction from occurring.

Subtask 2.2.1.4 Catalyst Evaluation and Development

Oxidation and Reduction Catalysts

The early Phase 2 catalyst development work focused on oxidation and reduction catalysts that could enhance membrane oxygen flux. Eltron Research conducted experimental work in their ambient pressure reactors that were installed during Phase 1 of the program.

Tubular I4 membranes were tested with and without catalysts on the fuel and air sides of the membrane. Table 2.2.1.4-1 indicates the configurations of membrane tubes and catalysts that were tested at 950°C with a 50-50 mixture of syngas blend and helium. This table also shows the relative flux range for each sample tested. The flux was the equilibrated flux based on both gain in oxygen content on the fuel side and depletion of oxygen on the air side. The results indicate that the presence of a Ni/porous I4 layer on the syngas side of the membrane results in a higher flux. The results also suggest that a porous layer of the membrane material itself may prove to be a sufficient oxygen reduction catalyst on the air side.

Table 2.2.1.4-1 Relative Oxygen Flux with Different Catalyst Configurations

Oxidation Catalyst	Reduction Catalyst	Relative Flux Range	
		Fuel Side	Air Side
Ni/I4(B)	Type A	0.70 - 0.76	0.94 – 1.00
I4(B)	Type A	0.38 - 0.50	0.60 – 0.70
None	Type A	0.36 – 0.42	0.44 – 0.54
Ni/I4(B)	None	0.46 – 0.64	0.64 – 0.70
I4(B)	None	0.36 – 0.40	0.44 – 0.50
None	None	0.20 – 0.26	0.16 – 0.28
None	I4(B)	0.36 – 0.46	0.56 – 0.62

Subsequently, it was determined that these results were negatively impacted by the effects of silica deposition on the surface of the tubes, where the silica originated from the alumina reactor liner. Modifications were ultimately made, later in Phase 2, to eliminate silicon from the reactor system.

Eltron Research conducted flux experiments, including life tests, on uncatalyzed thin film membranes. The operating temperatures ranged between 850°C and 950°C. A 50% GTL equilibrium mixture (20% methane, 25.4% carbon monoxide, and 54.6% hydrogen), with helium as the carrier gas, was fed to the fuel side of the membrane. Several experiments were operated for over 1000 hours. At 850°C and 900°C, the oxygen flux was generally constant with time. However, in some tests at 950°C the oxygen flux decays over time. As in the previous tests, these results were potentially affected by silicon contamination of the membrane.

Eltron Research initiated experiments to measure the intrinsic catalytic ability of uncatalyzed, thin film membranes for the oxidation of carbon monoxide, hydrogen, and methane. This data was required for the kinetic models that were being developed at the time. Concentrations of the three gases were varied by dilution with helium or argon, and the rate of oxidation was measured as a function of reactant gas concentration at a constant gas flow rate. All measurements were made on a single batch of supported, thin-film I4(C) membranes supplied by Ceramatec.

Carbon monoxide oxidation to carbon dioxide results, at various carbon monoxide concentrations and operating temperatures, are shown in Figure 2.2.1.4-1. The data suggests that the production of carbon dioxide is first order with respect to carbon monoxide concentration. At 950°C (1223°K) and 90% carbon monoxide in the fuel feed, over 10 ml/min of oxygen was transported through the membrane.

Figure 2.2.1.4-1 Production of Carbon Dioxide as a Function of Carbon Monoxide Concentration

Methane oxidization results, at various methane concentrations and operating temperatures, are shown in Figure 2.2.1.4-2. The concentration of methane was varied by dilution with helium. Production of carbon monoxide did not increase with an increase in methane concentration, implying that the reaction is zero order with respect to methane concentration. Production of carbon dioxide was below detection limits at 850°C, and was negligible at 900°C and 950°C. Measurement of methane oxidation was complicated by the fact that methane thermally cracks to carbon and hydrogen on the hot surfaces of the reactor, including the quartz reactor walls and thermocouple. Control experiments were performed to measure the production of hydrogen by thermal cracking of methane in the absence of a membrane.

Figure 2.2.1.4-2 Production of Carbon Monoxide as a Function of Methane Concentration

Hydrogen oxidation results, at various hydrogen concentrations and operating temperatures, are shown in Figure 2.2.1.4-3. The concentration of hydrogen was varied by dilution with argon. At 950°C (1223°K) and 50% hydrogen in the fuel feed, about 4 ml/min of oxygen was transported through the membrane. These results were for relatively low air and fuel flow rates and, hence, gas phase mass transfer resistances probably limited the oxygen flux. Hydrogen oxidation and oxygen flux were expected to increase at higher air and fuel flow rates.

Figure 2.2.1.4-3 Hydrogen Oxidation as a Function of Hydrogen Concentration

Eltron Research investigated the benefits of fuel-side catalysts to enhance carbon monoxide oxidation reactions. Figure 2.2.1.4-4 shows the results of the following tests:

- Carbon monoxide oxidation rates using an uncatalyzed membrane at two different flow rates.
- Carbon monoxide oxidation rates using a fuel-side catalyzed membrane (catalyst was powdered I4 membrane material) at high flow rates.
- Carbon monoxide oxidation rates using an air-side catalyzed membrane (catalyst was palladium) at high flow rates.

Figure 2.2.1.4-4 Production of Carbon Dioxide as a Function of Carbon Monoxide Concentration with Catalyzed and Uncatalyzed Membranes

Eltron Research measured methane partial oxidation rates using palladium fuel-side catalyzed membranes. The methane concentration in the fuel feed was varied by diluting the methane with argon while maintaining a constant total flow. The palladium catalyst had a significant effect on the methane oxidation rate at 950°C, but had a limited effect at 850°C. Figure 2.2.1.4-5 shows the production rates of hydrogen, carbon monoxide, and carbon dioxide at 950°C as a function of methane concentration.

Figure 2.2.1.4-5 Production of H₂, CO, and CO₂ at 950°C as a Function of Methane Concentration with Palladium Fuel-side Catalyzed Membranes

Platinum was the next fuel-side catalyst investigated. The platinum was sputter coated onto the fuel-side of the membrane and annealed at 950°C. Figure 2.2.1.4-6 summarizes oxygen consumption data where the oxygen consumption was calculated by the hydrogen consumption rate. Oxygen consumption rates calculated using the air-side oxygen concentration change were as much as 20% higher. The reason for this large discrepancy was unclear.

Figure 2.2.1.4-6 Oxygen Consumed at 950°C as a Function of Hydrogen Concentration with Platinum Fuel-side Catalyzed Membranes

Further methane oxidation tests on palladium and platinum catalyzed membranes were conducted. The palladium and platinum catalysts were applied to the membrane by ink application followed by sintering or by sputter deposition. The oxygen consumed was calculated based on the amount of carbon monoxide and carbon dioxide in the product gas. As shown in Figure 2.2.1.4-7, platinum-based catalysts had little effect on methane oxidation while palladium-based catalysts had a significant effect.

Figure 2.2.1.4-7 Oxygen Consumption as a Function of Methane Concentration in the Fuel Feed with Catalyzed and Uncatalyzed Membranes

Eltron Research measured the reaction kinetics of methane reforming over uncatalyzed porous-dense-slotted membranes. These experiments determined the intrinsic catalytic ability of the membrane material to set the baseline for determining the contribution of the nickel catalyst. Kinetic measurements were made on the oxidation of H_2 , CO and CH_4 over the porous-dense-slotted (PDS) membrane without catalyst. Examples of the data collected are provided below:

The hydrogen oxidation results at $900^\circ C$ are shown in Figure 2.2.1.4-8. The rates of consumption of both hydrogen and oxygen as a function of the volume percent hydrogen in the fuel are presented. This data was in good agreement since the hydrogen consumption was approximately twice that of the oxygen consumption. Consumption of hydrogen in this concentration range appears to be linear and close to first order.

Figure 2.2.1.4-8 Hydrogen and Oxygen Consumption as a Function of Hydrogen Concentration in the Fuel Feed with Uncatalyzed PDS Membranes

The carbon monoxide oxidation results at three temperatures (850°C, 900°C, and 950°C) are shown in Figure 2.2.1.4-9. The oxygen consumption rate was calculated based on the change in carbon monoxide. The oxygen consumption rate as a function of the volume percent carbon monoxide in the fuel is presented for each temperature. The data is approximately linear and nearly zero order.

Figure 2.2.1.4-9 Oxygen Consumption as a Function of Carbon Monoxide Concentration in the Fuel Feed with Uncatalyzed PDS Membranes

Steam Methane Reforming

Precious Metal Catalysts

Chevron developed methods for catalyst application on supported, thin-film membranes. Chevron focused on precious metal catalysts. Samples were screened in the Chevron labs or provided to Eltron Research for testing in their atmospheric pressure reactors.

Eltron Research conducted steam methane reforming experiments over catalyzed PDS membranes, at a steam-to-methane molar ratio of 1.5 to 1. Helium was used as the diluent gas as the methane concentration was varied in order to maintain a constant total flow rate. Generally, data was collected at reactor temperatures of 850°C, 900°C, and 950°C. Quantities of CO and CO₂ produced in the process were measured. Data accuracy continued to be a significant issue and a considerable effort was made to calibrate all instruments, to check standards, and to gather statistics on the precision of the measurements.

The methane reforming experiments are summarized in Figure 2.2.1.4-10. These results were for different catalysts and catalyst loadings on supported, thin-film membranes of the I4(D) material. Methane conversion rates are significantly enhanced with catalyzed membranes compared to uncatalyzed membranes which have measurable but negligible conversion rates.

Figure 2.2.1.4-10 Methane Consumption Rate for Supported, Thin-film Membranes with Different Catalysts and Catalyst Loadings Tested at 850°C

Chevron's work indicated that that a bimetallic catalyst composition comprising equal parts of two precious metals was considerably more active than either of those elements by itself.

Figure 2.2.1.4-11 summarizes the results from additional steam reforming tests operating at 850°C that used precious metal catalyst on the membrane. The best three catalysts to date for methane consumption were two different bimetallic catalysts and one of the single metal catalysts. Methane consumption was based on measured carbon monoxide and carbon dioxide production rates. Data for net hydrogen production and the air-side oxygen consumption corroborated these methane consumption figures.

Figure 2.2.1.4-11 Methane Consumption Rate for Supported, Thin-film Membranes with Different Catalysts and Catalyst Loadings Tested at 850°C

Experiments were also performed under pure steam reforming conditions with the air flow to the air side of the membranes turned off. The kinetics of methane consumption and hydrogen production were clearly linear with respect to methane concentration and follow first-order kinetics typical for pure steam reforming of methane. The individual kinetics of carbon monoxide and carbon dioxide production was more complex, although the sum of their production (which is used to determine methane consumption) was linear, as expected. For both pure steam reforming (with air flow stopped) and the oxygen fluxing conditions (with air stream applied to the air side of the membrane) the quantity of carbon dioxide exceeded that of carbon monoxide for all temperatures and reaction conditions investigated.

Air Products reviewed the I4 material stability under the pure steam methane reforming conditions and determined the material stability was marginal. The next series of runs had the steam-to-methane ratio raised from 1.5 to 2.0. This change lowered the methane partial pressure by about 20 percent and hence lowered the methane conversion rate by about 20 percent. Data was adjusted to compensate for the change in methane partial pressure and put all data onto a

common basis. Table 2.2.1.4-2 summarizes all the results. The data is listed by descending methane conversion rate. The listed catalyst compositions with the same letter have the same metal composition. Tested metals included bimetallic compositions of rhodium, palladium, platinum, ruthenium, and nickel. Single-component catalysts using palladium, rhodium, platinum, and molybdenum were also tested. Those catalysts with the same metals but prepared with a different method are noted with the same letter but with a different number. The listed conversion rates were measured thirty minutes after the start of the methane flow (TOS = 0.5 hour). The methane conversion activities varied by a factor of forty among the materials tested. Despite the potential for I4 degradation, no weakening of the PDS laminates was noticed at either of the steam-to-methane ratios and none of the laminates broke during these runs.

On-line GC (gas chromatograph) analysis was initiated during these runs, allowing a dozen or more data points to be taken over a period of several hours. This provided information on initial aging rates on the catalyzed PDS laminates. Their aging profiles were not uniform. For most of them, one-third to one-half of the initial activity was lost in 4 to 8 hours, with most of that loss occurring in the first hour or two. Some of the activity loss curves were a logarithmic dependence on time and others were a power law decay. Both catalyst composition and startup procedure were critical variables controlling this behavior.

The bimetallic catalysts generally performed much better than single-metal catalysts. The standard deviation of the reforming activity was about 20% for each class of catalyzed PDS materials. About half of the variation was attributed to differences in preparation variables and about half to experimental error in the test procedure. Various combinations of precious metals had varying degrees of activity. Certain precious metals were dropped from consideration because of their high cost.

Nickel-based bimetallic catalysts had significant reductions in activity compared to the corresponding precious metal bimetallic catalyst.

Molybdenum carbide had been reported in the literature as a good reforming catalyst and was included in this set of experiments. The material was fairly active initially, but it aged extremely rapidly.

Ruthenium-promoted PDS wafers were much less active than those promoted by other precious metals, although the activity of the ruthenium-promoted samples usually increased during a test run. Addition of ruthenium also did not seem detrimental in bimetallic or trimetallic compositions. Since ruthenium was by far the cheapest of the noble metals, it continued to be considered.

Table 2.2.1.4-2 Steam Reforming Over Catalyzed PDS Laminates

Run	Date	Catalyst Composition, Method	CH₄ Rate <i>sccm</i>	Reactor Temp. °C	Inlet Flow <i>sccm</i>	TOS <i>hours</i>
66	15-May-03	Catalyst A	120	900	1250	10
80	3-Jun-03	Catalyst A	99	900	1200	7
69	20-May-03	Catalyst A	91	900	1200	6
68	19-May-03	Catalyst A	90	900	1200	0.5
89	27-Jun-03	Catalyst A1	85	900	1200	8
73	3-Jun-03	Catalyst A	84	900	1200	7
67A	16-May-03	Catalyst A	83	900	1250	5
84	19-Jun-03	Catalyst A2	80	900	1200	1
55	29-Apr-03	Catalyst A3	77	900	1250	4
62	8-May-03	Catalyst A4	76	900	1250	6
67B	16-May-03	Catalyst A	76	900	1200	>5
44	8-Apr-03	Catalyst B	71	900	1250	5
53	25-Apr-03	Catalyst A	69	900	1250	6
63	12-May-03	Catalyst A5	67	900	1250	8
48	16-Apr-03	Catalyst C	62	900	1250	5
49	17-Apr-03	Catalyst D	60	900	1250	5
41	3-Apr-03	Catalyst E	57	900	1250	4
43	7-Apr-03	Catalyst F	54	900	1250	5
45	10-Apr-03	Catalyst G	53	900	1250	4
42	4-Apr-03	Catalyst H	50	900	1250	4
82	17-Jun-03	Catalyst I	42	900	1200	6
46	14-Apr-03	Catalyst J	39	900	1250	5
50	18-Apr-03	Catalyst D	37	900	1250	5
81	16-Jun-03	Catalyst A1	31	900	1200	2
90	30-Jun-03	Catalyst K	29	900	1200	8

Table 2.2.1.4-2 Steam Reforming Over Catalyzed PDS Laminates (Continued)

Run	Date	Catalyst Composition, Method	CH₄ Rate <i>sccm</i>	Reactor Temp. °C	Inlet Flow <i>sccm</i>	TOS <i>hours</i>
88	26-Jun-03	Catalyst L	28	900	1200	8
87	25-Jun-03	Catalyst M	26	900	1200	8
60	5-May-03	Catalyst N	26	900	1250	3
83	18-Jun-03	Catalyst N1	25	900	1200	7
65	14-May-03	Catalyst O	24	900	1250	9
79	3-Jun-03	Catalyst N2	23	900	1200	7
51	21-Apr-03	Catalyst P	22	900	1250	5
85	23-Jun-03	Catalyst A	21	900	1200	8
64	13-May-03	Catalyst N3	21	900	1250	8
39	1-Apr-03	Catalyst Q	21	900	1250	8
61	7-May-03	Catalyst N4	21	900	1250	10
57	1-May-03	Catalyst N	20	900	1250	1
40	2-Apr-03	Catalyst R	18	900	1250	3
75	5-Jun-03	Catalyst S	9	900	1200	7
74	4-Jun-03	Catalyst T	9	900	1200	7
47	15-Apr-03	Catalyst U	9	900	1250	5
76	6-Jun-03	Catalyst V	6	900	1200	7
78	3-Jun-03	Catalyst W	6	900	1200	7
59	5-May-03	Catalyst N5	5	900	1250	1
77	3-Jun-03	Catalyst X	3	900	1200	7
54	28-Apr-03	Catalyst N3	3	900	1250	1

Microprobe measurements of PDS laminates with added precious metals showed a gradient of these metals, with their concentrations decreasing toward the interiors of the porous layers. An example of this is shown in Figure 2.2.1.4-12. The blue curve in the figure shows the variation of the signal for lanthanum as the electron beam passed over a dense part of the slotted layer, then over the dense layer itself, and finally over the porous layer (going from left to right in the figure). The lanthanum signal is fairly constant in the dense regions, as expected. In the porous layer, it decreases wherever void spaces (pores) line up in the electron beam. The decrease in its average value in the porous layer compared with that in the dense layer should be proportional to the porosity. Variations in the lanthanum signal were followed closely by corresponding changes in calcium and iron signals, as expected.

In contrast, signals for the precious metals were highest where the pores were located, since they were deposited from solutions that filled those pores. As shown in Figure 2.2.1.4-12, peaks in the palladium signal were larger toward the outside of the porous layer than they were near the dense layer. The same was true for other precious metal signals. This indicated that the metal distributions are skewed toward higher concentrations at the outer edges of the porous layers.

Figure 2.2.1.4-12 Micro-probe Analysis of Metals Distributions in PDS Laminates

Surface analyses of the porous layer by XPS (X-ray Photoelectron Spectroscopy) showed calcium and lanthanum enrichment relative to iron in freshly promoted PDS laminates, as shown in Table 2.2.1.4-3. After operation at 900°C in steam and methane, the surface concentration of calcium increased significantly. This was accompanied by a corresponding increase in the surface concentration of a silicon impurity. EDAX (Energy Dispersive X-ray analysis)

measurements showed the presence of crystallites at the surfaces that contained mainly calcium and silicon, so it appeared that calcium reacted with impurity silicon to form calcium silicate. Magnesium, used in the setter, was also present at the exterior surface of the porous layers in PDS disks.

Precious metal concentrations were much higher at the exterior surfaces of porous layers in catalyzed PDS laminates than their bulk concentrations would indicate. This is in accord with the gradient in the metal distribution observed by the microprobe. The metals were present initially as oxides, but they became partially reduced to the metallic form during the reforming reaction and they didn't fully reoxidize in air. Their apparent surface concentrations decreased significantly after use. This is consistent with a loss in dispersion to form large metal particles, something that was confirmed by SEM analyses of the used samples.

Table 2.2.1.4-3 Porous Layer Surface Compositions in Catalyzed PDS Laminates

Element	Catalyst A		Catalyst B	
	Fresh	Used	Fresh	Used
C	18.2	22.4	18.0	24.2
% -CO-	25%	24%	22%	30%
O	54.7	50.8	58.6	52.1
La	8.1	6.9	4.9	7.8
Ca	2.5	7.1	1.4	7.8
Fe	4.4	3.4	2.7	3.7
Si	3.4	3.5	0.4	2.4
Mg	1.1	1.2	1.4	1.3
N	0.3	0.7	0.9	0.1
Na	0.2	0.7	2.4	0.1
K	0.8	0.6	0.0	0.0
PM A	<i>None</i>	<i>none</i>	9.1	0.7
PM B	6.3	2.7	<i>none</i>	<i>none</i>
<i>Reduced</i>	<i>0%</i>	25%	<i>0%</i>	48%

Testing at Eltron Research continued to support the conclusion that the most active catalysts were bimetallic precious metal catalysts. Chevron's testing also corroborated these findings. Figure 2.2.1.4-13 shows the catalyst activity for the five best catalysts under methane oxidation conditions. Figure 2.2.1.4-14 shows the catalyst activity for the five best catalysts under pure steam methane reforming conditions (no oxygen flux). The operating temperatures were 850°C and the methane feed concentrations were 25 percent in both sets of data.

Figure 2.2.1.4-13 Catalyst Activity Under Methane Oxidation Conditions

Figure 2.2.1.4-14 Catalyst Activity Under Pure Steam Methane Reforming Conditions (No Oxygen Flux)

Chevron continued testing catalyzed PDS laminates for their steam reforming activity and selectivity under no oxygen flux conditions. The tests focused on the use of promoters and were mainly run at 850°C and atmospheric pressure with the steam-to-methane ratio at 2. Absolute methane conversion rates were about 20 percent lower at this condition, compared with runs at previous test conditions of 900°C and a steam-to-methane ratio of 1.5. Methane conversion rates for various catalyst preparations were determined and are provided in Table 2.2.1.4-4. Catalysts of varying precious metal compositions are noted as A, B, C, etc. The use of a promoter is noted and its concentration level is noted in parentheses. A second type of promoter is noted as "promoted (alt)". The methane conversion rates listed are averages taken over the time on stream (TOS) of the experiments, usually 6-7 hours, and the data are ranked according to average activity. Other catalysts were tested and their methane conversion rates are listed in Table 2.2.1.4-5. These rates were estimated from plots of rate versus TOS and are ranked according to the rate at a TOS of four hours. The nomenclature for this table is similar to Table 2.2.1.4-5.

The most significant finding in these sets of runs was that promotion of the bimetallic catalyst was quite effective in enhancing its activity at low metal loadings. Furthermore, the promoter was most effective when it was added first and the PDS laminates were then calcined before the bimetallic catalyst was added. About half of the precious metals in the "standard" composition could be replaced with promoter without decreasing the activity significantly. This lower precious metal loading makes a large impact on the potential catalyst cost.

Several longer runs were made to see if the activity would line out at a stable value. The aging continued and the activity loss followed linear or near exponential decays with half-lives of 500 to 2000 minutes (10-35 hours). The aging seen in these pure reforming tests was much greater than observed at Eltron Research during tests that included oxygen fluxing, where activities decline slowly over periods of weeks. This difference may be related to processes such as carbon deposition or metal particle sintering that are not as severe when oxygen is supplied to the membrane surface, or when the relative methane pressure is lower, as in Eltron Research's experiments that dilute the methane with helium.

Table 2.2.1.4-4 Steam Reforming Over Catalyzed PDS Laminates

Catalyst	CH ₄ Rate	CO ₂ /CO	TOS
	<i>sccm</i>		<i>hours</i>
Catalyst B – promoted (high)	82.3	3.0	9
Catalyst C – promoted (high)	76.9	3.2	5
Catalyst A	74.2	3.3	6
Catalyst B – promoted (low)	74.0	2.5	5
Catalyst A	70.0	3.4	7
Catalyst A1	68.3	2.7	2
Catalyst C	66.6	3.2	9
Catalyst B – promoted (low)	66.4	3.1	8
Catalyst B – promoted (high)	64.7	3.1	8
Catalyst A2	64.5	3.0	6.5
Catalyst A2 – promoted (very high)	60.3	1.8	11
Catalyst B – promoted (high)	60.1	3.4	8
Catalyst A4	59.5	2.4	5
Catalyst B1 – promoted (high)	58.1	2.2	10
Catalyst A3	57.2	3.1	6
Catalyst A1	53.1	3.4	9
Catalyst F	53.0	3.3	7
Catalyst B1	51.7	3.1	7
Catalyst B1	48.5	3.0	8
Catalyst B – promoted (alt)	48.4	4.4	9
Catalyst A1	48.3	3.4	7
Catalyst B2 – promoted (high)	35.4	4.1	6
Catalyst G - promoted	33.9	4.1	6
Catalyst D	33.1	3.6	7
Catalyst E - promoted	22.5	6.8	6

Table 2.2.1.4-5 Aging of Methane Reforming Rates on Catalyzed PDS Laminates

Catalyst	Rate@30	Rate@240	t_{1/2}
	<i>sccm</i>	<i>sccm</i>	<i>minutes</i>
Catalyst B – promoted (high)	86.8	80.8	2400
Catalyst A	85.0	72.3	930
Catalyst C – promoted	82.9	70.6	950
Catalyst D	87.8	69.6	630
Catalyst A	90.0	69.2	2050
Catalyst A - promoted	87.0	66.4	1000
Catalyst B – promoted (low)	82.0	66.3	700
Catalyst B – promoted (low)	74.9	64.9	1300
Catalyst B – promoted (low)	68.3	59.8	1100
Catalyst B – promoted (high)	80.0	59.5	600
Catalyst B – promoted (high)	75.5	58.6	575
Catalyst A - promoted	63.7	56.7	1100
Catalyst A	66.0	55.3	1400
Catalyst A	57.0	52.7	1900
Catalyst E	55.4	50.0	1430
Catalyst B – promoted (alt)	69.0	49.1	450
Catalyst B	54.0	49.0	1500
Catalyst A	73.9	49.0	1000
Catalyst B	68.5	47.0	1000
Catalyst A	60.0	46.0	1250
Catalyst B – promoted (high)	48.0	30.5	150
Catalyst F	47.0	27.0	600
Catalyst G - promoted	50.0	25.0	300
Catalyst B – promoted (high)	42.0	15.0	260
<i>bare PDS</i>	1.0	1.0	<i>na</i>
Catalyst H - promoted	0.8	0.7	<i>na</i>
promoted	0.8	0.7	2000
<i>none</i>	0.4	0.4	<i>na</i>

Further tests of catalyzed membranes using higher levels of promoter showed continued increases in the reforming activity as the amount of promoter was increased. Activities remained high even with very low levels of precious metals.

Alternate methods of promoter impregnation were explored. Specific preparations were identified that minimized the number of processing steps required for catalyzing the membrane. The resulting catalysts had activities that were as good as or better than those made via the original processing steps.

Alternate promoters with more sintering stability were identified. The best promoter was a dual component composition. Single-step impregnation for this alternate promoter and the bimetallic precious metal catalyst was successful. This catalyst had the highest steam methane reforming activity to date and it was completely stable over a three-day run period. Data (taken at 850°C, atmospheric pressure, and a steam-to-methane ratio of 2) supporting this selection is provided in Table 2.2.1.4-6.

Table 2.2.1.4-6 Effect of Promoters on Catalyzed PDS Laminates

Catalyst		Rates, <i>sccm</i>	
Precious Metal	Promoter	-CH₄	+H₂
Dual – high loading	Dual	122	458
Single – high loading	Single – high loading	104	393
Dual – high loading	Single	83	312
Dual – low loading	Single	82	305
Dual – low loading	Single	69	258
Dual – high loading	None	66	248
Single – high loading	Single	64	241
Dual – high loading	None	60	228
Single – high loading	None	45	172

The process of loading catalyst onto membranes needed further investigation as the ceramic-ceramic joining techniques were developed. Being able to put the catalytic species on the active wafers prior to joining was expected to ensure proper loading of the added metals in the internal porous layers of multi-wafer modules, and greatly simplify quality control measurements on such units. High-temperature calcinations (at 1300°C in air) of PDS laminates impregnated with precious metal catalysts were done to simulate the joining conditions used during assembly of ITM modules. The steam methane reforming (850°C, atmospheric pressure, and steam-to-methane ratio of 2) results, shown in Table 2.2.1.4-7, indicated that after the high-temperature treatment the activity of most catalysts was significantly reduced. These results suggested that adding the precious metal catalyst prior to module assembly would be unacceptable.

Table 2.2.1.4-7 Methane Steam Reforming Over Catalyzed PDS Laminates

Catalyst	CH ₄ Conversion Rate <i>sccm</i>	
	Calcined at 500°C	Calcined at 1310°C
Catalyst A	105	16 (15%)
Catalyst B	45	2 (4%)
Catalyst C	80	37 (46%)
2.8		
13.0		

Methods of loading higher levels of bimetallic precious metal catalysts were investigated. The method chosen was multiple impregnations with intervening calcinations. These highly loaded membranes produced the highest methane conversion rates (i.e., - catalyst activity) seen to date. Table 2.2.1.4-8 shows the test results for three different loadings. At about the same time, flow meter calibration was found to be seriously in error. This error resulted in all the preceding methane conversion rate data to be high by about 35 percent. The flow meter was recalibrated and key operating conditions were redone. These differences are also noted in Table 2.2.1.4-8.

Table 2.2.1.4-8 Methane Steam Reforming Rates at Various Catalyst Loadings

Catalyst	P-methane, atm P-water, atm P-helium, atm Residence time, s steam/C	0.334 0.666 0.000 0.005 2.0	0.161 0.839 0.000 0.006 5.2	0.084 0.168 0.748 0.005 2.0	0.038 0.665 0.296 0.005 17.3	0.048 0.952 0.000 0.007 19.9	Rate as claimed before (Steam/ C = 2.0)	Actual Rate as % of Previous Rate
Bimetallic precious metal catalyst with promoter (base metal loading)	CH ₄ Rate, <i>sccm</i> CO ₂ /CO WGS	45.2 2.2 0.53	26.6 4.2 0.56			4.5 9.1 0.11	69.3	65%
Bimetallic precious metal catalyst with promoter (2x base metal loading)	CH ₄ Rate, <i>sccm</i> CO ₂ /CO WGS	73.9 1.4 0.55	42.0 2.8	33.9 0.8 0.65	--		109.2	68%
Bimetallic precious metal catalyst with promoter (3x base metal loading)	CH ₄ Rate, <i>sccm</i> CO ₂ /CO WGS	95.6 1.3 0.70	51.5 2.3 0.63	39.7 0.7 0.69	14.9 3.3 0.24		133.9	71%

As noted in the above table, the triple-loaded catalyst had nearly twice the methane conversion than the base loading in these non-fluxing experiments. Similar catalyst loadings tested at Eltron

Research under oxygen fluxing conditions and low steam-to-methane ratios showed even higher catalyst activities and the activity declined less than 10 percent during 600 hours of operation. In contrast, under high steam-to-methane ratios and high operating pressure, the same catalyst loading lost 80 percent of its initial activity in a two-month test at APCI.

Surprising results in PDU Runs 10 and 11 suggested that the presence of catalyst in the porous layer of the membrane increased the oxygen flux by as much as 40 percent. The mechanism for this phenomenon was unclear and further investigation was planned.

Catalyzed PDU Modules

Chevron developed methods for impregnating catalyst into the outside porous layers of PDU modules.

The first two PDU modules (PDUM), PDUM-33 and PDUM-34, were impregnated with a bimetallic precious metal catalyst using a one-step aqueous impregnation. The impregnations were done by hand. The PDUMs were held by their seal blocks and dipped into the impregnating solution at a shallow angle so that all of their internal porous layers were covered. The modules were then dried and calcined at 550°C.

The two catalyzed PDU modules were installed in the Air Products PDU during Run 5, along with two uncatalyzed PDU modules. The details of Run 5 are described in Subtask 2.4.3. These catalyzed modules developed massive leaks while being heated with air at 50 psig on the air sides of the membranes and nitrogen on the fuel side of the membrane. The failures occurred slightly above 300°C, well below the calcination temperature. Two uncatalyzed PDUMs remained hermetically sealed, indicating that the catalyst addition procedure may have weakened PDUM-33 and PDUM-34.

A third PDU module, PDUM-27, was catalyzed in the same manner as the two failed modules. PDUM-27 was an off-spec module. This module was tested at 60 psig in a modified seal-test rig at the Air Products labs and failed at about the same temperature as the ones in the PDU.

The potential for the catalyst addition to reduce the strength of the ceramic membrane was investigated as a potential cause of these failures. The strength of porous bend bars catalyzed with different impregnation solutions was determined using four-point bend tests. All of the treatments exhibited the same strength within the resolution of the measurements. In addition, bend bar specimens were designed and fabricated for testing the effect of structure on fracture behavior and reliability. The purpose of fabricating these structures was to examine the interactions among laminate architectures and failure behavior. No effect on the strength of bend bars or active wafers was observed, when compared with no treatment at all, calcination only, or impregnation with solvent only and then calcination.

Other tests that were conducted included thermal cycling of active wafers in air to 550°C and applying multiple stresses to the active wafers rather than a single stress. Neither of these tests resulted in the types of failures that were observed in the testing in the Air Products lab units.

Another hypothesis for the failures was that water used in the catalyst impregnation step or the acidity of the impregnation solutions damaged the I4 membrane structure. Alternate impregnation procedures were developed and investigated. Many of the alternate procedures produced catalysts with lower activities than previously observed. The most promising procedures were used to catalyze PDU modules and tested in the Air Products seal test rig. All of these modules failed in a similar manner, indicating that impregnation was not a major factor in the observed failures.

The calcination step during the preparation of catalyzed membranes had strong exotherms. It was theorized that these exotherms during the calcination step might generate stress cracks in the membrane wafer due to thermal gradients since the exotherm is only present in the porous layer. The calcinations step was modified to eliminate these severe exotherms. This modified process included a thermal treatment in nitrogen to 500°C. Initial results were positive as a dozen catalyzed active wafers using this treatment were fabricated and all survived heating to 380°C with an oxygen gradient (nitrogen outside, air inside) and an applied pressure gradient (60-70 psig outside, ambient pressure inside) across their membrane. Four catalyzed PDUMs given the nitrogen treatment survived heating to 900°C, again with a similar oxygen gradient and with a 220 psi pressure differential across the membranes.

Catalyzed modules for PDU Run 8 were prepared with the new nitrogen calcination treatment. Two modules were catalyzed with promoted, bimetallic precious metal catalysts and the other two modules were catalyzed with promoted, single precious metal catalysts. All modules failed in the same manner as the previous PDU runs with catalyzed modules. Run 8 details are described in Subtask 2.4.3.

Further investigations led to the hypothesis that the catalyst, in the presence of a fuel (such as hydrogen or hydrocarbons) even at trace levels, might combust the fuel with oxygen in the I4 material and hence reduce the I4 material. The reduction of the oxide membrane material would cause the I4 material to expand. Since only the porous layer of the membrane wafer is catalyzed, only the porous layer expands. The differential expansion of the porous layer relative to the uncatalyzed parts of the membrane can cause the membrane to break. Experiments showed that this reduction would occur at temperatures between 300°C and 400°C, the same failure temperatures for the modules in the PDU. Since these fuels, especially trace amounts of hydrocarbon fuels, may be unavoidable in large-scale, commercial reactors, a method of avoiding this uncontrolled I4 reduction was needed. Preconditioning the module was the chosen route. This preconditioning consisted of:

1. Fabricating the membrane module using the existing procedures.
2. Heating the module in the same atmosphere in which it was cooled during the standard fabrication procedure to a sufficiently high temperature to allow oxygen anion mobility in the membrane material.
3. Changing the gas composition that the module is exposed to from the gas used in Step 2 to a gas with a sufficiently low oxygen partial pressure to reduce the oxygen stoichiometry of the module. Examples of these low oxygen partial pressure gases would

be hydrogen/steam/nitrogen blends. The rate of change of the oxygen partial pressure is controlled to prevent excessively large gradients in oxygen stoichiometry from developing in the solid parts of the module while the oxygen anions are diffusing out of I4 material. The gas must not reduce the oxygen partial pressure too much as to cause the chemical decomposition of the phase of the membrane material.

4. Cooling the module to room temperature in a gas with a sufficiently low oxygen partial pressure to maintain a reduced oxygen stoichiometry in the module.

Specimens were fabricated to test. These specimens included bars that were catalyzed but not preconditioned, bars that were catalyzed and preconditioned, bars that were preconditioned but not catalyzed, and bars that were neither preconditioned nor catalyzed. The strength of these bars was measured using a standard 4-point flexure geometry. The catalyzed but not preconditioned bars, the preconditioned catalyzed bars, and preconditioned but not catalyzed bars were heated to 450°C in an atmosphere of 2.5% H₂O, 5% H₂, balance Ar. The strength was measured at 450°C after holding each bar in this atmosphere. The strength of the bars that were neither catalyzed nor preconditioned was measured at room temperature. The average strength is given in the Table 2.2.1.4-9. The bars that were catalyzed but not pretreated had strengths below the resolution of the measuring device, which was approximately 20 MPa. The catalyzed bars that were preconditioned had a strength equal to within 1 standard deviation of the room temperature strength of the bars that were neither catalyzed nor pretreated. Therefore, preconditioning catalyzed bars of I4 preserved the strength of the material when the strength was measured in the presence of a dilute fuel.

Table 2.2.1.4-9 Strength of Bars That Underwent Different Treatments

Type	Average Strength (MPa)	Std Dev (MPa)	# Specimens
Room temperature	201	26	21
Not catalyzed and not pretreated	139	27	3
Catalyzed but not pretreated	untestable		10
Catalyzed and pretreated	191	20	5

Catalyzed PDU modules were fabricated using this new preconditioning procedure and supplied to Air Products for installation and testing in the PDU (Run 9). These were the first catalyzed modules to be successfully operated in the PDU. Run 9 details are described in Subtask 2.4.3.

Catalyst Impregnation of Preconditioned Modules

Preconditioning modules was implemented to resolve module failures in the PDU when initially exposed to reducing conditions. This process was designed to very slowly change the Fe(IV) in the I4 lattice to Fe(III) by exposing the module to oxidizing conditions and changing from the

oxidizing condition to mildly reducing conditions (*air to 0.5% hydrogen/2.5% water/97% nitrogen*) while the modules were held at 900°C. With the advent of this process, the process of impregnating the catalyst onto the membrane needed to be re-investigated.

If the bimetallic precious metal catalyst was added before the reduction treatment, the catalyst activity was very low. Techniques were developed to add the catalyst after the treatment. Experiments showed that this impregnation route resulted in excellent activity, consistent with past experience with catalyst impregnated on unconditioned membranes. Figure 2.2.1.4-15 shows relative methane conversion rates for various preparation methods. The labels 1X, 2X, etc. in this figure refer to the metal loading level as compared to the base loading. Some of the catalysts that were added post preconditioning were more active than the baseline catalyst. A doubly-loaded sample made in this way was about 30 percent more active than the standard catalyst and was the most stable ever tested (less than 0.2% variation in activity over 7 hours). Reoxidation of the catalysts in air increased their initial activities by 4-5 times but they rapidly lost about half of the increase before the activity stabilized. Reversibility of the activity upon oxidation indicated that the negative effect of high-temperature preconditioning may have been caused by a "skin" of the reduced support material growing over the active metal surfaces.

These data showed that catalyst preparations were possible that are compatible with the preconditioning treatment, needed to prevent mechanical damage during PDU startup. Unfortunately, catalyst compositions and preparations needed to be re-optimized, since it wasn't certain that relative activities would remain the same when the process steps were changed. Chevron purchased and installed new equipment for loading catalyst on the preconditioned membranes.

Figure 2.2.1.4-15 Preconditioning Method Effect on Catalyst Activity

Start-up, Shutdown, and Regenerating Catalyzed Membranes

Runs were normally started by heating the PDS laminates rapidly (5-10°C/min.) in helium to the run temperature. Steam generation was initiated by introducing water into the steam generator and the resulting steam was added to the helium feed to the reactor. The water flow was increased in increments until the steam flow reached the desired level. Methane was introduced into the feed gas in increments with a corresponding decrease in the helium flow to maintain a constant total flow to the reactor.

The shutdown procedure that seemed to work the best was simply the reverse of the startup steps: replacing methane flow with helium, then shutting off the water flow, then cooling to room temperature. Cooling is slower than the heat-up step because of the large mass of the furnace. To ensure that this shutdown procedure preserves the state of the catalyst, a test specimen was restarted after a successful test period and a normal shutdown. Figure 2.1.4-16 shows the activity, as hydrogen production, of the initial run and the restarted run. While the initial activity in the second run was slightly above the value at the finish of the first run, the activity declined within a couple of hours and reached the same aging curve that had been established in the first run. This confirms that the normal shutdown procedure preserves the state of the catalyst.

Figure 2.2.1.4-16 Catalyst Activity Changes as a Result of a Restart

Regeneration of the catalyzed membrane was investigated. After running in the reforming reactor for 30 hours, a test specimen was shut down normally. The sample was then removed from the reactor tube and transferred to a treater where it was calcined in air (1°C/min. to 550°C, as in the initial calcination). The sample was then placed back in the reactor and restarted. Figure 2.4.1-17 shows the catalyst activity, as hydrogen production rate, for the two runs, with the latter plotted as if it had been started about an hour after the first. The activity of the recalcined sample was about 20% higher than the activity at the end of the first run. It would have had to increase by 100% to be equal to the activity of the fresh catalyst. This result indicates that most of the activity decline is caused by sintering of the active phase, not by carbon deposition.

Figure 2.2.1.4-17 Catalyst Activity Changes as a Result of Recalcination

Experiments at Air Products investigated the catalyst reactivity with the I4 membrane material. Several catalyst metals that have little or no reactivity with the membrane material under process conditions were identified.

Nickel-based Catalysts

As precious metal costs escalated significantly, a renewed effort on nickel catalysts was initiated to determine the potential for a lower cost catalyst. Past investigation showed that nickel catalysts had very low activity, especially under the high steam-to-methane conditions at the inlet

of the reactor in the new process cycle. The use of a bimetallic nickel-based catalyst was investigated and found to have activities that were an order of magnitude greater than nickel alone. Even at these activity levels, the bimetallic nickel-based catalysts were still only half as active as the best bimetallic precious metal catalysts. However, the metal costs were two orders of magnitude lower, thus making the nickel-based catalyst attractive.

When tested, the stability of the nickel-based bimetallic catalysts was significantly greater than for a nickel-only catalyst. In one experiment, a nickel-only catalyst and a nickel-based bimetallic catalyst had similar initial activity but the nickel-only catalyst retained only about 10 percent of its initial activity after three hours of operation, while the comparable bimetallic nickel-based catalyst retained 60-65 percent. The rapid initial deactivation of the nickel-only material was thought to be due to carbon deposition, and that second metal inhibits coke formation. Literature references claimed improved stability (higher coking resistance) or better selectivity with certain bimetallic nickel-based catalysts, but none indicated such a large activity increase. The strong effect of the additional metal species may be specific to the I4 support or the improvement may only be in a narrow range of metal ratios leading the effect to be overlooked in previous work.

The best nickel-based catalyst was promoted with two additional metals and had a methane conversion rate of about 28 sccm using PDS laminate discs operating at 850°C, atmospheric pressure, and a steam-to-methane ratio of 5.2. Nickel-based catalysts with a single metal promoter and high metal loadings had methane conversion rates of about 24 sccm. These catalyst activities are lower than those of the pre-reduced, promoted bimetallic precious metal catalysts where the methane conversion rates approached 54 sccm at the same operating conditions.

Further investigation of the use of promoters indicated that small additions of precious metals to catalysts with low nickel loading could significantly improve catalyst activity and stability. A single-promoted, nickel-based catalyst with low metal loadings would typically have a methane conversion rate of about 16 sccm. With the addition of a small quantity of precious metal, the methane conversion rate was increased to 25 to 35 sccm, depending on the precious metal that was used. These catalyst activities, however, were still well below the activities of the bimetallic precious metal catalysts.

Interbank Methane Reforming Catalysts

Given the current membrane design, process operating conditions, and the identified catalyst activities, it became evident that the sole use of on-membrane catalysts would not provide the steam methane reforming endotherms required to balance the oxidation exotherms. Thus, the concept of interbank catalyst was developed (see Subtask 2.1.1) and the catalyst development efforts began to investigate these catalyst requirements. These catalysts had to have very low pressure-drops to accommodate the high gas flows. They also needed to be placed onto supports that had material components that were compatible with the membranes.

The process operating conditions of the new process cycles required the catalyst to operate under very high steam-to-methane ratio conditions. These conditions had two major impacts. First

was that the methane or hydrogen partial pressures were significantly reduced and hence the conversion rates for a given amount of catalyst were significantly lower. Second was the potential for the high steam conditions to negatively impact the long-term stability of the catalyst. These issues were the major focus of the initial investigations.

The best nickel-based catalyst was impregnated onto an alumina support and tested under steam-to-methane ratios between 6 and 100. The feed gas was an argon-methane-steam blend and the test conditions were 850°C and atmospheric pressure. Table 2.2.1.4-10 shows the results. The methane conversion rate decreased significantly as the steam-to-methane ratio increased. The conditions could be cycled between high steam-to-methane ratios and the standard ratio with no change in activity at the standard condition. Thus, the activity was quite stable and any changes caused by high steam partial pressures were readily reversed.

Table 2.2.1.4-10 Methane Conversion Rate Versus Steam-to-Methane Ratio for a Nickel-Based Catalyst on an Alumina Support

P_{CH4} (atm)	Steam-to-Methane Ratio	Methane Conversion Rate (sccm)
0.113	6.9	45.4
0.030	28.1	8.1
0.009	105.3	1.1

Further tests with different supports showed a methane conversion ratio dependence on the support material. For example, with the above catalyst at a steam-to-methane ratio of 6.9, the methane conversion rate with a MgO support was 65 sccm compared to the 45 sccm noted in Table 2.2.1.4-10.

For brief exposures, operation at a steam-to-methane ratio of 100 caused no permanent deactivation of these catalysts. However, the decrease in methane conversion rate in going to that ratio was 2 to 3 times larger than the decrease in methane partial pressure. This indicated either a very strong inhibition by water or a change in the catalyst surfaces at the high steam pressure.

Atmospheric pressure tests of nickel-based reforming catalysts on various refractory supports showed that all were highly active. As shown in Table 2.2.1.4-11, their reforming rates at a steam-to-methane ratio of 6 varied from 20 to 50 sccm/gramcat at 850°C. During brief exposures to steam-to-methane ratios of 100, the reforming rates declined to 0.5 to 2.5 sccm/gramcat. Operation for less than a day at the high steam-to-methane condition caused no permanent deactivation of any of the catalysts. However, some of them deactivated and reactivated slowly, so lined out conversions at the high steam condition were never reached. Interestingly, Catalyst A had decreased activity as the catalyst loading increased. This indicated that loss in dispersion far exceeded the increase in metal content at the higher loadings and indicates that either the surface area or pore volume (or both) must be quite low for that material.

Table 2.2.1.4-11 Methane Conversion Rate Versus Steam-to-Methane Ratio for Nickel-Based Catalysts on Various Supports

Steam/CH ₄ Ratio =		6	30	100
Support	Catalyst	Rate, <i>sccm/g_{cat}</i>		
MgO	Catalyst A – low loading	49.6	...	2.0
MgO	Catalyst B – low loading	46.5	5.9	1.2
Alumina	Catalyst B – high loading	45.2	...	2.5
Alumina foam	Catalyst A – high loading	44.2	...	1.0
MgO	Catalyst A – med loading	30.0	...	...
Fused alumina	Catalyst A – very low loading	24.8	...	0.8
MgO	Catalyst A – high loading	22.1	...	0.5

Atmospheric pressure tests were conducted with commercial rhodium/alumina and nickel/alumina with high external metal concentrations and compared to the best nickel-based catalysts developed to date. All catalysts were highly active. Their reforming rates at a steam-to-methane ratio of 6 varied from 20 to 110 sccm/gramcat at 850°C. The highest activity was that for the commercial rhodium/alumina catalyst. During daylong exposures to a steam/methane ratio of 100, the reforming rates declined 20 to 40 times, to rates of 0.5 to 4.0 sccm/gramcat. For commercial catalysts with high external concentrations of metals (edge loading), the decrease was only slightly faster than the decrease in methane pressure. This bodes well for the activity of monolith or foam catalysts, since the active metals for those materials will also be readily available (i.e., close to the surface). All the catalysts returned to their initial activities when a steam-to-methane ratio of 6 was restored. Addition of hydrogen to the feed improved the activity at all conditions.

Among supports potentially satisfying the requirements for interbank catalysts (i.e., stability in high steam-to-methane environments and availability of low pressure-drop formulations, such as monoliths), the most prominent candidates are α -Al₂O₃, MgAl₂O₄, and CaAl₂O₄. Use of washcoats with these supports was investigated. Available surface areas were increased by a factor of 20 with certain washcoats. Reforming tests on nickel-based catalysts on an α -alumina support were conducted at 850°C, atmospheric pressure, and steam-to-methane ratios of 6 and 100. Results are shown in Table 2.2.1.4-12. There was very little variation in absolute rate with catalyst composition at either condition. Rates at the high steam condition were 14 to 17 times lower than at moderate steam/methane ratios for most catalysts; close to the difference in methane partial pressure. The small effect of catalyst composition on methane conversion rate suggested that the reaction may be diffusion limited in these experiments.

**Table 2.2.1.4-12. Methane Conversion Rate Versus Steam-to-Methane Ratio
for Nickel-Based Catalysts on an α -Alumina Support**

Catalyst	CH ₄ Rate (sccm/gram _{cat})		Ratio
	Steam/Methane = 6	Steam/Methane = 100	
Catalyst A	78		
Catalyst B	96	6.8	14
Catalyst B + precious metal (low loading)	82	5.5	14
Catalyst B + precious metal (medium loading)	80	4.9	17
Catalyst B + precious metal (high loading)	112	6.7	17
Catalyst C	102	4.9	21
Catalyst C + precious metal (medium loading)	115	6.7	17

Unlike the case of nickel-based catalysts impregnated into porous I4 layer, these promoted nickel catalysts on alumina supports did not lead to significant increases in methane conversion over nickel-only catalysts. In contrast, precious metal promotion of nickel on alumina led to an increase in activity when high loadings were used. Catalyst C, an unpromoted nickel catalyst, lost more activity when operated at the high steam-to-methane conditions. Thus, the promoters seemed to inhibit nickel oxidation in steam. Over time, Catalysts A and B were more stable than Catalyst B with precious metal added or Catalyst C.

Long-term (50 hours) tests of promoted nickel catalysts on α -alumina foams at atmospheric pressure and 850°C showed that they suffered irreversible deactivation after treatment with feeds having steam-to-methane ratios of 100. Bimetallic precious metal catalysts on the same support did not lose their activity after the same treatment. Thus, precious metal catalysts may be preferred for operation near the front of the ITM reactor system. Methane conversion rates in the atmospheric pressure reactor were limited to about 100 sccm over foams with thicknesses of 7.0 mm - 12.7 mm.

Discussions with catalyst vendors were initiated in order to determine what commercial catalysts were available for interbank catalyst. In particular, catalyst vendors with monolith supports were of the greatest interest.

Subtask 2.2.1.5 High-Temperature Material Properties

Creep Rate Measurements

I4(C) Materials

During Phase 2, Penn State University continued their Phase 1 efforts to measure creep rates of various ITM Syngas materials. Ceramtec provided the specimens for this testing. In general these specimens were rectangular bars of specific compositions. Each bar was individually tested in an apparatus using a four point bend arrangement to measure the creep rate. A description of a suitable technique for this measurement can be found in Chapter 5 of "Mechanical Testing Methodology for Ceramic Design and Reliability," edited by David C. Cramer and David W. Richerson and published by Marcel Decker, Inc., 1998. Each individual test specimen was heated to desired temperature and known stresses were applied to the bars. The deflection of the respective specimen was measured as a function of time, from which the strain rate, or creep rate, was calculated.

Early testing determined the reproducibility of the creep rate between batches of I4(C) material. The results, shown in Table 2.2.1.5-1, indicated that there was no significant difference between the two batches (see Table 2.2.1.5-1).

Table 2.2.1.5-1 Creep Strain Rates (min^{-1}) for I4(C) Flexural Bars Tested at 950°C

Applied Stress (psi)	Batch/Sample Number			
	1/1	1/2	2/13	2/15
1000	4.49×10^{-08}	1.16×10^{-07}	1.14×10^{-07}	1.81×10^{-07}
2000	1.33×10^{-07}	3.33×10^{-07}	4.38×10^{-08}	3.52×10^{-07}
4000	5.37×10^{-07}	1.22×10^{-06}	1.89×10^{-07}	6.05×10^{-07}
6000	1.09×10^{-06}			

Additional testing was completed on a number of specimens of I4(C). Table 2.2.1.5-2 lists the creep strain rates obtained for these samples as a function of the applied stress and temperature. Measuring reliable creep rates at 850°C proved difficult. At 850°C, the creep rates for the lower applied stresses of 1000 and 2000 psi are too low for the measurement capability of the test stand transducers. Thus, testing at 850°C was discontinued, and the focus became testing at 900°C and 975°C in an effort to obtain reliable creep rate data at temperatures below and above 950°C.

Table 2.2.1.5-2 Creep Rates (min⁻¹) for I4(C) Flexural Bars

Temperature	850°C		900°C		950°C		975°C
Sample No.	2/20	2/22	2/24	2/15	2/16	2/26	
Applied Stress (psi)							
1000	--	1.74x10 ⁻⁰⁸	1.66x10 ⁻⁰⁸	1.81x10 ⁻⁰⁷	6.55x10 ⁻⁰⁸	1.36x10 ⁻⁰⁷	
2000	1.30x10 ⁻⁰⁸	5.11x10 ⁻⁰⁸	4.61x10 ⁻⁰⁸	3.52x10 ⁻⁰⁷	1.27x10 ⁻⁰⁷	3.74x10 ⁻⁰⁷	
3000	2.83x10 ⁻⁰⁸	--	--	--	--	--	
4000	--	6.32x10 ⁻⁰⁸	6.51x10 ⁻⁰⁸	6.05x10 ⁻⁰⁷	2.41x10 ⁻⁰⁷	7.48x10 ⁻⁰⁷	

A creep model was developed using the following form

$$\dot{\epsilon}_{ss} = A \sigma^n \exp(E_a / RT)$$

where the steady-state secondary creep strain rate ($\dot{\epsilon}_{ss}$) is related to the applied stress (σ) raised to the creep stress exponent (n); E_a is the creep activation energy; R is the gas constant; T is the temperature; and A is the pre-exponential term. Figure 2.2.1.5-1 shows the fit and the experimental data for I4(C) bars creep tested at Penn State.

Figure 2.2.1.5-1 Creep Data and Creep Model Prediction for I4(C)

Creep rates for two I4(C) compositions with varying A/B ratio were measured and are presented in Figure 2.2.1.5-2. The creep rates for the specimen formed from the composition having an A/B ratio of 1.01 were nearly an order of magnitude lower than the creep rates of the specimen formed from composition having an A/B ratio of 0.98. These results suggested that compositions with an A/B ratio greater than 1.0 have significantly lower creep rates than membranes with an A/B ratio less than 1.0. Thus, membranes with A/B ratios greater than 1.0 are more desirable and were chosen.

Figure 2.2.1.5-2 Creep Rates of I4(C) Specimens with Different A/B Ratios

Creep rate as a function of A/B ratio was investigated in more detail. Data for I4(C) specimens operating at 900°C are shown in Figure 2.2.1.5-3. These results showed that the A/B ratio had a large effect on the observed creep rates. Figure 2.2.1.5-3 also provides the grain size of the samples. The creep rate decreased by factor of 2 as the A/B ratio increased from less than 1.0 to greater than 1.0. This was even more impressive considering that the creep rate can increase significantly with decreasing grain size, as shown in Figure 2.2.1.5-4 where the grain size is varied at a constant A/B ratio.

Figure 2.2.1.5-3 Creep Rate as a Function of A/B Ratio

Figure 2.2.1.5-4 Creep Rate as a Function of Grain Size

I4(D) Materials

Penn State measured creep rates of I4(D) compositions. An example of initial data is provided in Table 2.2.1.5-3. The creep rate of I4(D) specimens operating at 950°C was typically a factor of 3 to 5 lower than the equivalent I4(C) specimen. These differences were attributed to the fact that the I4(D) material had ~50% larger grains than the I4(C) material.

Table 2.2.1.5-3 Creep Rates (1/min) of I4(D) Specimens at 950°C

Temperature	950°C				900°C
Sample No.	1	2	3		4
Applied stress (psi)				Average Strain Rate/ Std. Dev.	
1000	5.08×10^{-8}	3.75×10^{-8}	1.33×10^{-8}	$3.39 \times 10^{-8}/$ 1.90×10^{-8}	2.52×10^{-8}
2000	7.32×10^{-8}	5.42×10^{-8}	2.32×10^{-8}	$5.02 \times 10^{-8}/$ 2.52×10^{-8}	?
4000	1.13×10^{-7}	9.93×10^{-8}	7.05×10^{-8}	$9.43 \times 10^{-8}/$ 2.17×10^{-8}	7.36×10^{-8}

As shown in Figure 2.2.1.5-5, the I4(D) materials had creep rates that were less than 25% of the creep rates of I4(C). This improvement was a significant advancement for membrane life and was a major driver to the decision to use the I4(D) materials rather than the I4(C) materials.

Figure 2.2.1.5-5 Creep Rates of the I4(C) and I4(D) Materials

The tensile creep data for the I4(D) samples tested in air at 925-975°C was regressed using a multi-variable regression package. The results are summarized in Figure 2.2.1.5-6 which compares the data to the model predictions.

Figure 2.2.1.5-6 Comparison of Data with Model Predictions for the Tensile Creep of I4(D) Materials

Penn State measured the compressive creep rates for an I4(D) material. Examples of this data are shown in Table 2.2.1.5-4. Samples tested at 4000 psi for several days resulted in diffusion bonding of the individual discs.

Table 2.2.1.5-4 Compressive Creep Data for Dense I4(D) Discs

Sample #	Temp (°C)	Stress (psi)	Strain Rate (1/s)
1	950	4000	3.32E-08
2	950	4000	1.33E-08
3	950	4000	2.16E-08
4	950	2000	9.43E-09
		1000	3.90E-09
5	950	2000	1.36E-08
		1000	3.03E-09

Chemical Expansion Measurements

Under typical syngas process conditions, the solid-state membrane will be subjected to mechanical stresses arising from the oxygen partial pressure gradient across the solid-state membrane. Solid-state membranes comprising a dense layer formed from a composition having a lower expansion when the gas composition is switched from air to a reducing gas mixture will be subjected to less mechanical stress than solid-state membranes formed from a composition having a relatively higher expansion.

A chemical expansion verification test unit was built by Air Products and installed at Penn State University. The apparatus characterizes and models the mechanical behavior of ITM materials under PO_2 and total pressure gradients. A thin disk sealed on top of an alumina tube is subjected to either a total pressure gradient or an oxygen chemical potential gradient. The flexure of the disk is measured using silica push rods attached to length transducers.

The apparatus was initially tested by measuring the flexure of alumina disks under a pressure gradient over a range of temperatures. There was a good match between the experimental data and model predictions at room temperature. At high temperatures, it was expected that the glass used to seal the disc would act like a simple support, but the experimental data was between two extreme models for support (bounded and simply supported). This suggested that the viscosity and surface tension of the glass have an important effect on the flexure of the disk that must be included in the flexure model.

Test specimens formed from the I4(B), I4(C) and I2(B) compositions were prepared. The specimens were tested under the following specified conditions for their expansion upon changing P_{O_2} . The specimen was placed in a dilatometer and heated to 750°C in pure oxygen. After equilibrating at 750°C , the atmosphere inside the dilatometer was switched to a $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ mixture having oxygen partial pressure given in Table 2.2.1.5-5. The dilatometer recorded the change in length of the specimen with the change in oxygen partial pressure. The results, shown in Table 2.2.1.5-5, demonstrated that I4(C) had much lower expansion when switched from oxygen to the $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ mixture than the I4(B) or I2(B) compositions.

Table 2.2.1.5-5 Expansion Measurements of ITM Syngas Membranes Materials

Composition	Final P_{O_2} (atm)	Expansion (ppm)
I4(C)	5.5×10^{-21}	1820
I4(B)	5.5×10^{-21}	4060
I2(B)	2.8×10^{-13}	3918

Table 2.2.1.5-6 shows the chemical expansion of the I4 and I5 compositions when switched from pure oxygen at the given temperature to the oxygen partial pressure given in the table. These results showed that the chemical expansion could be tailored by changing the composition. However, compositions with lower expansion tended to have lower fluxes.

Table 2.2.1.5-6 Expansion Data for I4 and I5 Compositions

Material	Expansion (ppm) at Given Temperature and P _{O2}		
	750°C/5.53E-21 atm	850°C/1.00E-18 atm	950°C/7.85E-17 atm
I4(C)	1430	1200	940
I5(A1)	1010	911	739
I5(A2)	1930	1380	1130
I5(A3)	458	369	260
I5(A4)	-	560	540
I5(A5)	700	530	383
I5(A6)	1860	1780	1820
I5(A7)	1150	1050	1000

Data was collected on the chemical expansion of the I4(D) material, which was chosen as the desired material based on creep rate and flux capabilities. This data was used to determine the strains that would occur under start-up conditions in the PDU. Ramp rates and hold times were determined to minimize the peak chemical expansion strain.

Elastic Properties

Penn State measured the elastic properties of porous and dense I4(C) as a function of temperature. Room temperature properties were measured using acoustic resonance. Table 2.2.1.5-7 shows the elastic modulus of specimens of varying A/B ratio. The 30% porous sample had a Young's modulus of 55 GPa (giga Pascals) at room temperature which decreased to 40 GPa at 1000°C. Elastic modulus data for dense and porous I4(C) as a function of temperature is shown in Table 2.2.1.5-8. The shear modulus decreased from 22 GPa to 16 GPa over the same temperature range. The room temperature Poisson's ratio was 0.262.

Table 2.2.1.5-7 Room Temperature Elastic Modulus (E) Data for Dense I4(C) at Various A/B Ratios

A/B Ratio	E (GPa)
1.01	197±3
1.005	194±3
1.00	193±3
0.995	196±7
0.990	184±3

Table 2.2.1.5-8 Elastic Modulus (E) Data for I4(C) at Various Temperatures

Temperature (°C)	E (GPa)	
	Dense	30% Porous
25	218	55
400	201	49
600	189	47
750	137	37
850	143	37
950	156	39
1000	159	40

The elastic modulus measurements as a function of temperature revealed a significant decrease between 600°C and 850°C for both dense and 30% porous I4(C) materials. This unexpected behavior prompted further investigations, which revealed an endothermic transition at approximately 815°C on heating and a corresponding exothermic at approximately 815°C on cooling.

The Young's modulus of I4(D) material was measured as a function of temperature. Like the I4(C), the I4(D) also exhibited similar Young's modulus behavior as function of temperature. Results of tests of both I4(D) and I4(C) appear in Figure 2.2.1.5-7. While the phase transformation for the I4(C) materials seemed to occur slightly above 800°C, the phase transformation for the I4(D) material appeared to occur at or near 850°C according to measured minima in the Young's modulus.

Figure 2.2.1.5-7 Comparative Measurements of Young's Modulus for I4(D) and I4(C)

Slow Crack Growth

Dynamic fatigue testing of I4(D) samples in air at 800°C showed that no significant slow crack growth occurred. Additional tests showed that the I4(D) material is not very susceptible to slow crack growth at room temperature in air. Slow crack growth testing of I4(D) ceramic samples in a reducing atmosphere at 750°C continued to suggest that the I4(D) material does not undergo slow crack growth.

Strength Measurements

Penn State conducted strength and fracture toughness testing of I4(D) bend bars over a range of temperatures. Tests conducted at different stressing rates showed no significant effect of stressing rate on strength. Test specimens were exposed to a syngas mixture at commercial operating temperature and pressure for three months. Mechanical strength of the specimens was measured to evaluate any potential impact of syngas exposure on material strength. A slight decrease in strength was observed in the aged samples, compared to un-aged samples. The tests confirmed the importance of using methods to control residual stresses that can be generated as membranes are cycled through different temperature and gas composition conditions.

Penn State also conducted biaxial flexure strength tests of dense and porous I4(D) material.

Subtask 2.2.2 Seals Development

Ceramic-to-Ceramic Seals

Pacific Northwest National Labs (PNNL) continued their Phase 1 investigation of glass seals for ceramic-to-ceramic joining. New glass compositions were developed with the goal of minimizing glass penetration into the I4(C) material. The softening temperatures of many of the new glass compositions were too low to be considered. Optimization of heat treatment conditions yielded a glass that matched the thermal expansion of the I4(C) material.

Long-term stability tests were conducted at 750 and 950°C for 20 days in a humid and simulated syngas environment. Microstructure and crystalline phases were characterized using SEM, EDS, and XRD for a sample tested at 950°C. SEM showed that the long-term exposure had changed the surface features, while XRD showed that a new crystalline phase on the exposed outer surface (expected to be $(\text{Ca,Sr})_2\text{SiO}_4$) was formed.

Thermal cycling (950°C/0.5 hour) tests were conducted. After 21 thermal cycles, the joined I4(C)/I4(C) coupons were leak tested with helium at room temperature. The leak test results are listed in Table 2.2.2-1, together with leak rates before the thermal cycling tests. The two tested glasses showed excellent thermal cycle stability. The measured leak rates were at the detection limit of the helium leak detector, $1\sim 2 \times 10^{-9}$ atm.cc/s. This rate was equivalent to a leak rate of

0.63~1.3 cc/year at 300 psi. In addition, these two glasses demonstrated a wide processing (sealing) temperature window for joining the ceramic components.

Table 2.2.2-1 Room Temperature Leak Rates of Thermally Cycled Glass Seals

Glass	Heat Treatment Condition	Leak Rate Before Cycling (atm-cc/sec)	Leak Rate After 6 Cycles (atm-cc/sec)	Leak Rate After 21 Cycles (atm-cc/sec)
Blank		1×10^{-9}	2×10^{-9}	2×10^{-9}
A	1100°C/0.2h+ 1000°C/2h	1×10^{-9}	2×10^{-9}	2×10^{-9}
A	1000°C/2h	1×10^{-9}	2×10^{-9}	2×10^{-9}
B	1200°C/0.2h+ 1100°C/1h	2×10^{-9}	Not tested	2×10^{-9}
B	1150°C/0.2h+ 1100°C/1h	2×10^{-9}	Not tested	2×10^{-9}
B	1100°C/2h	2×10^{-9}	Not tested	2×10^{-9}
B	1050°C/2h	Too high to be measured	Too high to be measured	Too high to be measured

Microstructural characterization of the sealed couples after thermal cycling was conducted using SEM/EDS. The results revealed limited (less than 5 microns) or no glass penetration into the I4(C) matrix.

A stability test of the joined I4(C)/I4(C) couples was conducted for 500 hrs at 950°C. Room temperature leak test results, shown in Table 2.2.2-2, were very promising, as all of the joined couples had leak rates below the detectable limit of the test (1×10^{-9} atm-cc/sec). SEM analysis showed no distinct glass penetration of the I4 matrix, or glass degradation for either glass.

Table 2.2.2-2 Room Temperature Leak Rates of Glass Seals After Stability Test

Glass	Heat Treatment Condition	Leak Rate Before Stability Test (atm-cc/sec)	Leak Rate After Stability Test (atm-cc/sec)
Blank		1×10^{-9}	1×10^{-9}
A	1100°C/0.2h+ 1000°C/1h	1×10^{-9}	1×10^{-9}
A	1100°C/0.2h+ 1000°C/1h	1×10^{-9}	1×10^{-9}
B	1150°C/0.2h+ 1100°C/1h	1×10^{-9}	1×10^{-9}
B	1150°C/0.2h+ 1100°C/1h	1×10^{-9}	1×10^{-9}

Similar stability tests were conducted on various glass compositions to determine if the materials change enough to impact the CTE of the glass. These glasses showed very consistent and matching CTE with the base I4(C) material, suggesting very good long-term stability in the harsh oxidizing and reducing environments. The measured CTE values of these glasses before and after the long-term stability tests are listed in Table 2.2.2-3.

Table 2.2.2-3 Average CTE for Various Glasses After Stability Tests

Glass	Heat Treatment Condition	CTE Before Stability Test (ppm/°C)	CTE After Stability Test (ppm/°C)
C	1150°C/0.2h+ 1100°C/1h	11.39	11.15 (RT to ~963°C) 11.10 (RT to ~972°C)
C	1150°C/0.2h+ 1000°C/1h	11.39	11.05 (RT to ~950°C) 11.07 (RT to ~950°C) 11.08 (RT to ~950°C)
B	1150°C/0.2h+ 1050°C/1h	11.29	11.00 10.93 11.07
B	1150°C/0.2h+ 1100°C/1h	11.29	11.12
D	1150°C/0.2h+ 1100°C/1h	11.37	11.15 11.15

Further optimization of sealing glass microstructures was conducted with the goal of eliminating large pores (~50 μm) that were observed after the sealing and crystallization processes. This effort focused on the impact of different temperature, time, and stress variables and glasses in both powder and tape forms. It was found that much larger pores (~100 μm) were present when using glass tapes made by conventional tape casting of organic slurry. Neither applying higher sealing stresses of up to 4 psi nor lengthening the sealing time at the highest temperature would eliminate these large pores. The large pores were likely caused by trapped gaseous species, since the coupon rim sections tended to sinter/seal first, trapping the gases.

Composite glass compositions were considered because they might provide better thermal stability in harsh environments, since the composite was made of sealing glass and the I4 material. In addition, with the composite, the CTE had the potential to be tailored to a wider range of values. These composite glass compositions showed an excellent CTE match with the I4(C) material. A typical linear thermal expansion curve is shown in Figure 2.2.2-1 for a sample that was heat treated at 1100°C for two hours. Figure 2.2.2-2 shows the linear thermal expansion curve for the same sample after an additional 24 hours of heat treatment. The consistency of the CTE for these tests suggested long-term stability. In addition, these composite glass compositions showed no softening at temperatures up to 1000°C.

Figure 2.2.2-1 Linear Thermal Expansion of a Composite Glass Composition After Heat Treatment at 1100°C for 2 Hours

Figure 2.2.2-2 Linear Thermal Expansion of a Composite Glass Composition After Heat Treatment at 1100°C for 2 Hours Followed by an Additional 24 Hours at 1100°C

Room temperature helium leak tests of I4(C)/I4(C) couples joined by these composite glass compositions also showed very promising results, as shown in Table 2.2.2-4, in that the leak rates were all below the detection limit of the test (1×10^{-9} atm-cc/sec).

Table 2.2.2-4 Room Temperature Leak Rates of Glass Seals

Glass	Form of Glass	Heat Treatment	Leak Rate (atm.cc/sec)
Blank			1×10^{-9}
E	tape	1150°C/0.5hr+1000°C/2hr	1×10^{-9}
E	tape	1150°C/0.5hr+1000°C/2hr	1×10^{-9}
F	tape	1150°C/0.5hr+1000°C/2hr	1×10^{-9}
F	tape	1150°C/0.5hr+1000°C/2hr	1×10^{-9}

The porous nature of the microstructure of the glass seals continued to be problematic. Ultimately, the best candidate glass composition (composition B) was used to fabricate joined tubes for evaluation in the Eltron test reactors. Results were disappointing in that the joined tubes failed shortly after the introduction of process gases. Similar results were observed in the Air Products test reactors. These results, in combination with concerns over the use of materials containing silicon (potential contamination issues) and the positive results from Ceramatec's efforts to develop ceramic-ceramic joining techniques (Subtask 2.3.3-2), led the team to decide to abandon glass for the ceramic-to-ceramic seals.

Ceramic-to-Metal Seals

Work in Phase 1 identified three general seal technologies and investigated their use on tubular membranes. Successful ceramic-to-metal seals for tubular membranes were made using a double U-ring design. Early in Phase 2, the identified seal technologies (compression seals, glass seals, and brazed seals) continued to be investigated and refined. Specific ceramic-to-metal seal designs for the PDU modules were developed.

Braze Seals

Several brazes were selected by PNNL for evaluation based on the requirements of a thermal expansion match to the I4 materials and to superalloys and a sufficiently high melting point to withstand the ITM Syngas process conditions. Tests of the selected brazes showed good wetting and adhesion to the superalloy surfaces. However, the brazes either did not wet the I4 ceramic surface, or showed substantial reaction and cracking at the braze/ceramic interface. PNNL investigated alternate ceramic interfacial coatings and deposition of thin layers to promote wetting and adhesion of the brazes to I4 substrates. These techniques did not promote wetting of the I4 surface.

Experiments were conducted to investigate sleeve seals of sputter coated I4(C) with SS446. The sample showed no leakage or very low leak rates at room temperature. Initial characterization of the joined cups by optical microscopy showed complete wetting of the metal cup by the braze,

but only partial coverage of the coated I4 tube. Optical microscopy revealed no gross reaction between the braze alloy and the I4 material.

Without reasonable indication of a potential solution to this wetting issue, the investigation of brazed ceramic-to-metal seals was abandoned.

Glass Seals

PNNL investigated glass-ceramic seal compositions for ceramic-to-metal seals. Sealed cup assemblies (a tube made of an early I4 composition and a cup made of SS346) were prepared and tested using various substituted yttria borosilicate glass compositions. The sealed cup assemblies were subjected to helium leak tests at room temperature and found to be hermetic. Thermal cycle tests were then carried out in an environment of 40 ppm CO/30% CO₂/ 70%N₂ containing 20 torr H₂O at atmospheric pressure. The thermal cycle was set from 200 to 950oC at a heating and cooling rate of 1oC/min. Tests showed that the samples maintained a very low leak rate after nine thermal cycles.

To approximate syngas operating conditions more closely, the water vapor pressure was increased to 525 torr in subsequent tests of the chemical stability of the sealing materials. After exposure to this gas mixture at temperatures of 750 and 950oC for 24 hours, samples of the glasses were characterized using SEM/EDS to identify morphology and composition changes. One of the three samples tested showed a sufficiently low reactivity under these simulated syngas process conditions.

PNNL updated the tests with tubes made of the I4(C) material and sealed with the same glass. Initial tests showed that the leak rates of the seals were measurable but probably acceptable. However, other samples had high leak rates that were clearly not acceptable. This decreased performance was believed to be due in part to a larger expansion mismatch between the I4(C) and the SS346.

Further investigation of glass seals for ceramic-to-metal seals was abandoned.

Compression Seals

The ceramic-to-metal compression seals used in high-pressure/high-temperature syngas tests of tubular membranes showed good performance during Phase 1. This double U-ring seal concept was used to mate the air inlet and outlet tubes to the PDU module seal block that is described in Subtask 2.3.1. The major change in using this concept for this application was that a metal tube was mated to a ceramic seal block (Figure 2.2.2-4) rather than a ceramic tube being mated to a metal seal block (Figure 2.2.2-3).

Figure 2.2.2-3 Cross Section of a U-ring Compression Seal Mating a Ceramic Tube (35) with a Metal Seal Block (33).

Figure 2.2.2-4 Cross Section of a U-ring Compression Seal Mating a Metal Tube (1) with a Ceramic Seal Block (2)

The first test of a high-pressure compression seal, utilizing a double U-ring, demonstrated good sealing behavior. However, preliminary examination of the sample after ~500 hr at 715°C and 400 psia indicated that significant deformation of the U-rings had occurred.

A series of tests was conducted to investigate design parameters of the double U-ring seals. These design parameters included the thickness of the gold foil at the base of the seal and the interference fit of the U-ring. Unfortunately, the samples leaked at temperature and pressure and were found to have cracked seal blocks. McDermott provided structural analysis support on the PDU seal block to help identify the cause of the seal block failures. The modeling showed that loads due to U-ring seal installation and thermal expansion were likely not responsible for the failures. In addition, further analyses showed that reaction forces on the seal block due to the air tubes were small and did not warrant redesign of the shape of the air tubes. Further analysis and testing determined that the most likely cause of the failures in these tests was parasitic stress set up during attachment of the assemblies in the seal rig. A series of measures was put in place to minimize all parasitic stresses.

The results of the next test are shown in Figure 2.2.2-5. This I4(C) seal block had two blind holes that acted as independent seals. The seal configuration (Figure 2.2.2-4), consisted of two 0.010" gold foil washers in the base of the hole, a machined Haynes 230 tube stub, a 0.020" gold wire ring at the outer edge of the tube stub flange, and two U-rings with a spacer. The seal in "Hole 1" was significantly better than the seal in "Hole 2". The leak rate of the "Hole 1" seal was less than 10 sccm throughout the test and less than 1 sccm at the final temperature and pressure (~775°C/425 psig). This low leak rate was confirmed by doing a pressure rise leak measurement in which the pressure in the 1-liter ballast rose 0.2 psi in 60 minutes. The leak rate of the "Hole 2" seal was off scale (>100 sccm) through several portions of the test, although the leak rate did decay to ~55 sccm at the final test conditions. Upon examination of the sample after the test, it was determined that the block was intact. After the seals were removed from the block, it was discovered that the gold wire ring had been pulled over the bottom U-ring on one side. The wire was flattened between the U-ring and the wall of the hole in the block, still permitting a modest seal to form.

Figure 2.2.2-5 Results From Seal Tests on a PDU Module Seal Block

A repeat test was successful, as shown in Figure 2.2.2-6. Although the test was interrupted by chiller equipment problems, which resulted in additional thermal cycles, both seals exhibited leak rates of less than 10 sccm at target temperature and pressure conditions.

Figure 2.2.2-6 Results From Repeat Seal Tests on a PDU Module Seal Block

These compression seals were then demonstrated for over 500 hr of static exposure at 425 psig and 780°C and through 18 thermal cycles. This test involved seals with three design variants. Four of the five seal samples and two of the three design variants remained leak tight throughout the test. The results are shown in Figure 2.2.2-7.

Figure 2.2.2-7 Results From Long-term and Thermal Cycling Seal Tests on a PDU Module Seal Block

Proposed PDU start-up conditions were simulated in the Air Products Seal Test Rig to test the seal design under these conditions. Modifications to the start-up procedures were identified and translated into actual PDU runs. Additional testing also identified minor improvements to the double U-ring design and the seal block.

SEP Module Seals

As discussed in Subtask 2.3.1, the SEP modules used full-size, commercial membrane wafers. As noted in Subtask 2.5.1, these modules were envisioned to have up to five membrane wafers to meet the capacity requirements of the planned SEP. Thus, the seal development for the SEP modules focused on developing a smaller scale, commercial-like seal design to be mated to full-size commercial membrane wafer sub-modules. The expectation was that this small-scale seal design would then be scaled up to full size to accommodate modules containing many more membrane wafers.

The PDU module seal design experience was used to generate a new design concept for the SEP module. The concept incorporated an air manifold, replacing the PDU module seal block, to mate the two seals (air inlet seal and non-permeate outlet seal) with the multi-wafer membrane sub-module described in Subtask 2.3.1. The air manifold used a concentric tube design, as shown in Figure 2.2.2-8. This design had incoming air in the center tube and non-permeate in the annulus between the inner and outer tubes. The outer tube required a high differential pressure ceramic-to-metal seal between the syngas and the non-permeate, and the inner tube required a low differential pressure ceramic-to-metal seal between the inlet air and the outlet air.

Figure 2.2.2-8 Cross Section of the Air Manifold of the SEP Membrane Module

High Differential Pressure Seal

The high differential pressure seal required two main features – a face seal between the end of the ceramic tube and the metal seal cup and a seal assembly which houses the face seal and applies a force on the face seal. Several options for each main feature were investigated, and resulting designs were developed. The chosen face seal was a composite washer seal. The chosen seal assembly included a matched-CTE design.

Composite Washer Seal

The composite washer seal **10**, as shown in Figure 2.2.2-9, comprised a first metal layer **12** having an outer perimeter **14** and an inner perimeter **16** defining an aperture **18** through the metal layer. A second metal layer **20** was positioned in spaced relation overlying the first metal layer. The second metal layer also had an outer perimeter **22**, as well as an inner perimeter **24** that defines an aperture **26** through the second metal layer.

Figure 2.2.2-9 Exploded View of Composite Seal Washer

The metal layers were foils having a thickness between about 0.002 inches and about 0.020 inches. Metal foils were preferred for their toughness and flexibility, advantageous qualities for seals that must accommodate significant stresses and strains when used in the desired service. Although any metals may be used, for high-temperature applications it was advantageous to employ metals such as gold, silver, platinum, alloys containing gold, silver or platinum, stainless steels, or nickel superalloys which would not melt or oxidize in the high-temperature, oxygen-rich environments typical of ion transport membranes, for example.

A mineral layer **28** was positioned between the first and second metal layers **12** and **22**. The mineral layer **28** also had an aperture **30**. Preferred minerals included mica, vermiculite, and other similar materials. The mineral layer was chosen based on its ability to withstand high temperatures and its ability to accommodate in-plane displacements of the metal layers that were the result of the different CTEs of the materials. The mineral layer may have a thickness between about 0.001 inches to about 0.1 inches, with a preferred thickness between about 0.002 inches to about 0.05 inches. Practical mineral layers formed of mica were used in a composite seal having a thickness of about 0.005 inches. Layers of other similar materials having a thickness between about 0.017 inches and about 0.034 inches were also used in trial seals.

When assembled, as shown in Figure 2.2.2-10, the apertures **18**, **26** and **30** in the metal layers **12** and **20** and the mineral layer **28**, respectively, overlap one another and are preferably coaxially aligned so as to form an aperture **32** in the seal assembly comprising the various layers. Although the layers are illustrated as being round, it is understood that they could be any shape as required to perform the interfacing and sealing function for a particular application.

Figure 2.2.2-10 Composite Washer Seal with Outer Perimeter of Washer Sealed

In order to facilitate assembly of the seal **10**, it was advantageous to form at least one of the metal layers (in this example layer **20**) to have a recess **34** defined by a surrounding sidewall **36**, which receives the mineral layer **28**. This configuration allowed the layer's outer perimeter **22** to come into contact with the outer perimeter **14** of metal layer **12** when the metal layers are positioned in overlying relation. With the recess and sidewall formed in the metal layer **20**, the outer perimeters of the metal layers may be readily joined, as shown in the seal embodiment **10a** illustrated in Figure 2.2.2-10.

In the seal embodiment **10a**, the outer perimeters **14** and **22** were preferably joined by welding. Orbital welding, using a gas tungsten arc, was advantageous to form the joint **38** at the outer perimeters of the metal layers **12** and **22**. The arc generated intense heat, which melted the base metal in the region of the joint. The molten metal was allowed to cool and fuse in the presence of an argon purge gas to form a fluid-tight joint around the entire perimeter of the seal. No filler metal was used to form the weld. Other techniques for joining the perimeters, including brazing, electron beam welding, crimping, staking, folding, rolling and explosive bonding, were also feasible.

In operation, the outside diameter of metal tube **40** was exposed to high-pressure gas, while a low-pressure gas at high temperature flowed through the bore **44** of metal tube **40**, through the seal aperture **32** and into the ceramic component **42**. As the device depicted in Figure 2.2.2-10 heats up during operation, the metal tube **40** will expand radially outwardly to a different extent than the portion of the ceramic component **42** to which it is attached due to the difference in the thermal expansion coefficients between the two components. The difference in expansion between the metal tube **40** and the ceramic component **42** induces shear stress in the seal **10a** as the metal layer **20** of the seal, in contact with the metal tube **40**, expands with the tube to a different extent than the metal layer **12**, in contact with the ceramic component **42**, expands. This shear stress is accommodated by flexure of the metal layer's sidewall **36** which defines the recess **34** formed to receive the mineral layer **28**. The shear is also accommodated by the mineral layer **28**. The lamina forming this layer separate in plane and allow the metal layer **20** in

contact with the metal tube **40** to expand to a different extent than the metal layer **12** in contact with the ceramic component **42**. The fluid-tight weld of joint **38** ensures hermetic integrity of the joint, preventing any gas within or without the tube bore **44** from finding a leak path through the mineral layer.

Figure 2.2.2-11 illustrates another seal embodiment **10b**, wherein the inner perimeters **16** and **24** of the metal layers **12** and **20** are joined, again, preferably by a welded joint **38** which extends continuously around the inner perimeters. Once again, metal layer **20** was deformed to form a recess **34** defined by a sidewall **36** which helps to accommodate shear forces induced by differential expansion on opposite sides of the seal **10b**. Figure 2.2.2-12 shows another seal embodiment **10c**, wherein both the inner (**16**, **24**) and outer (**14**, **22**) perimeters on each metal layer **12** and **20** are joined, preferably by welded joints **38**.

Figure 2.2.2-11 Composite Washer Seal with Inner Perimeter of Washer Sealed

Figure 2.2.2-12 Composite Washer Seal with Inner and Outer Perimeters of Washer Sealed

The efficacy of these types of seals was borne out in testing. In a first test, a composite washer seal was formed from two layers of silver foil (each 0.025 cm thick) with an inner diameter of 2.223 cm and an outer diameter of 3.493 cm. One of the foil layers was formed to provide a recess 3.251 cm in diameter and 0.013 cm deep. A mineral layer of muscovite mica having a thickness of 0.010 cm, an inner diameter of 2.223 cm and an outer diameter of 3.239 cm was positioned within the recess, and the metal layers were joined at their outer perimeter by welding. The composite seal was placed in facing contact with the open end of a closed end tube made of $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-x}$ ceramic, where x is a number that makes the compound charge neutral. The opposite face of the seal was engaged with a cup formed of Haynes 230 alloy, the cup having an opening aligned with the aperture of the seal. The tube and seal assembly was placed in a pressure vessel and heated to 875°C, and the outside of the assembly was pressurized to 200 psig. The leak rate was below detection limits. The outside of the assembly was then depressurized and cooled to room temperature. The assembly was then heated to 875°C, and the outside of the assembly was again pressurized to 200 psig. The leak rate was again below detection limits. The heating/pressurization/depressurization/cooling cycles were repeated 10 times, and the maximum leak rate observed at the peak temperature and pressure for any of the cycles was 160 sccm. The leak rate did not increase with the number of cycles.

In a second example, composite washer seals were formed from two layers of gold foil (each 0.025 cm thick) with an inner diameter of 0.475 cm and an outer diameter of 1.054 cm. One of the foil layers was formed to provide a recess 0.901 cm in diameter and 0.013 cm deep. A mineral layer of muscovite mica having a thickness of 0.010 cm, an inner diameter of 0.475 cm and an outer diameter of 0.889 cm was positioned within the recess, and the metal layers were joined at their outer perimeter by welding. Two of the seals were then placed in the base of each of two holes machined into a block of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-x}$ ceramic, where x is a number that makes the compound charge neutral. The two holes were in fluid communication. A tube stub fabricated from Haynes 230 alloy was then inserted into each hole such that a composite seal was between the flat end of each tube stub and the flat base of each hole in the ceramic block. The open ends of the tube stubs were welded to inlet and outlet tubing, and the assembly was then mounted in a pressure vessel. The outside of the assembly was pressurized to 60 psig, the assembly was heated to 900°C, and air flow was initiated through the inlet tube. While at 900°C, the pressure outside the assembly was increased, first to 100 psig and then to 215 psig. The difference in outlet and inlet air flow was monitored to assess seal leakage. The assembly was held at 215 psig and 900°C for about 70 hours and then cooled to room temperature and depressurized. The flow difference was below detection limits throughout the test.

Seal Assembly

The basic design concept for the seal assembly was to apply a nearly constant force on the sealing elements over a wide range of temperatures when the materials of the two parts being sealed, including a ceramic part and a metal part, had different CTEs.

A schematic of such a seal assembly concept is shown in Figure 2.2.2-13. Seal assembly **1** comprises a clamping element having first segment **3**, connecting segment **5**, and second segment **7**; first seal element or compensating spacer element **9**; and second seal element **11**.

First segment **3**, connecting segment **5**, and second segment **7** of the clamping element may be the same materials or may be different materials. First segment **3** may be attached to connecting segment **5** by a bolt or other fastening device (not shown) at interfacial zone **13**. Alternatively, first segment **3** and connecting segment **5** may be a single piece of a common material. Alternatively or additionally, second segment **7** may be attached to connecting segment **5** by a bolt or other fastening device (not shown) at interfacial zone **15**. Alternatively, second segment **7** and connecting segment **5** may be a single piece of a common material.

First seal element or compensating spacer element **9** typically is a separate piece as shown. Second seal element **11** may be a part of and connected to a first vessel or piping system, and either or both of segments **3** and **7** of the clamping element may be part of a second vessel or piping system that is being sealed to the first vessel or piping system.

Figure 2.2.2-13 Schematic of the Matched-CTE Seal Assembly

The clamping element engages first segment **3** into forcible contact with compensating spacer element **9** at interfacial zone **17** and second segment **7** into forcible contact with second seal element **11** at interfacial zone **19**. As a result, compensating spacer element **9** and second seal element **11** are engaged into forcible contact at interfacial zone **21**.

Compensating spacer element **9** is characterized by dimension B, which is the orthogonal or axial distance between the plane formed by the surface of the compensating spacer element at interfacial zone **17** and the plane formed by the surface of the compensating spacer element at interfacial zone **21**. Second seal element **11** is characterized by dimension C, which is the orthogonal or axial distance between the plane formed by the surface of second seal element **11** at interfacial zone **21** and the plane formed by the surface of the second seal element at interfacial zone **19**. The dimension A is defined as the sum of dimensions B and C. Dimension A is equivalent to the portion of connecting segment **5** that lies between the plane formed by the surface of compensating spacer element **9** at interfacial zone **17** and the plane formed by the surface of second seal element **11** at interfacial zone **19**. Connecting segment **5** is characterized

by dimension **D**, which lies between the plane formed by the surface of first segment **3** at interfacial zone **17** and the plane formed by the surface of second segment **7** at interfacial zone **19**, i.e., **D** is the distance between the faces of the clamping element.

Interfacial zone **17** may be an interface formed by contact between flat surfaces on first segment **3** and compensating spacer element **9**. Alternatively, interfacial zone **17** may include an intermediate member (not shown) such as a compliant sealing member. Interfacial zone **19** may be an interface formed by contact between flat surfaces on second segment **7** and second seal element **11**. Alternatively, interfacial zone **19** may include an intermediate member (not shown) such as a compliant sealing member. Typically, interfacial zone **21** is an interface formed by direct contact between flat surfaces on compensating spacer element **9** and second seal element **11**. Alternatively, interfacial zone **21** may include an intermediate member (not shown) such as a compliant sealing member.

The term "forcible contact" as applied at the interfacial zone of two parts means that both parts on either side of the interfacial zone are forced together by axial compressive forces applied by the clamping element. For example, at interfacial zone **17**, the forcible contact may be formed directly by actual contact between flat surfaces on first segment **3** and compensating spacer element **9**. Alternatively, if interfacial zone **17** includes an intermediate seal member, the forcible contact between first segment **3** and compensating spacer element **9** will occur via the intermediate member, i.e., the axial compressive force will be transmitted from first segment **3** to the intermediate member and from the intermediate member to compensating spacer element **9**. In another example, at interfacial zone **19**, the forcible contact may be formed directly by actual contact between flat surfaces on second segment **7** and second seal element **11**. Alternatively, if interfacial zone **19** includes an intermediate member as discussed above, the forcible contact between second segment **7** and second seal element **11** will occur via the intermediate member. In yet another example, at interfacial zone **21**, the forcible contact may be formed directly by actual contact between flat surfaces on compensating spacer element **9** and second seal element **11**. Alternatively, if interfacial zone **21** includes an intermediate member as discussed above, the forcible contact between compensating spacer element **9** and second seal element **11** will occur via the intermediate member. Thus the term "forcible contact" at an interfacial zone includes either (1) actual contact between two surfaces or (2) contact of a first surface with a surface of an intermediate member and contact of a second surface with another surface of the intermediate member, wherein all surfaces and, if present, the surfaces of the intermediate member, are forced together by compressive axial forces applied by the clamping element.

First segment **3**, connecting segment **5**, and second segment **7** of the clamping element may be the same materials or may be different materials. Compensating spacer element **9** is made of a first material having a first coefficient of thermal expansion, second seal element **11** is made of a second material having a second coefficient of thermal expansion, and connecting segment **5** is made of a third material having a third coefficient of thermal expansion. The third coefficient of thermal expansion is intermediate to the first and second coefficients of thermal expansion.

First seal element or compensating spacer element **9** has a reference thickness or dimension defined by a reference dimension B_R at a reference temperature, second seal element **11** has a reference thickness or dimension defined by the dimension C_R at the reference temperature, and

dimension A_R at the reference temperature is the sum of reference dimensions B_R and C_R at the reference temperature. The reference temperature may be any temperature, but advantageously the reference temperature is an ambient temperature between about 15 and 35°C. When the seal assembly is at the reference temperature, the clamping element applies an initial axial compressive force that presses compensating spacer element **9** and second seal element **11** together in forcible contact.

The reference dimensions of compensating spacer element **9** (B_R) and seal element **11** (C_R), and the materials of compensating spacer element **9**, second seal element **11**, and connecting segment **5**, are initially selected when the seal assembly is designed. The proper selection of these parameters is made so that, at any selected temperature, a temperature-compensated dimension, A_T , differs from the sum of temperature-compensated dimensions B_T and C_T at the selected temperature by an absolute value of less than about 0.002 inch. Typically, this difference is within the compliance tolerance that can be achieved by commercially-available compliant sealing elements such as C-rings and O-rings.

The temperature-compensated dimensions A_T , B_T , and C_T at any selected temperature are defined by the equations:

$$A_T = A_R(\alpha_A)(T - T_R) \quad (\text{Eq. 1})$$

$$B_T = B_R(\alpha_B)(T - T_R) \quad (\text{Eq. 2})$$

$$C_T = C_R(\alpha_C)(T - T_R) \quad (\text{Eq. 3})$$

where T is the selected temperature, T_R is the reference temperature, α_A is the coefficient of thermal expansion of the material of connecting segment **5** of the clamping element, α_B is the coefficient of thermal expansion of the material of compensating spacer element **9**, α_C is the coefficient of thermal expansion of the material of second seal element **11**, and $A_R = B_R + C_R$.

The reference dimensions of compensating spacer element **9** (B_R) and seal element **11** (C_R), and the materials of compensating spacer element **9**, second seal element **11**, and connecting segment **5**, are initially selected when the seal assembly is designed such that, at any selected temperature, dimensions of the seal assembly are described by the equation:

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch} \quad (\text{Eq. 4})$$

The seal assembly components are assembled at the reference temperature (typically ambient temperature), and an initial axial loading is placed on compensating spacer element **9**, second seal element **11**, and compliant sealing member(s) or spring-type member(s), if used, by the clamping element. This initial clamping force may be provided, for example, by set screws or threaded studs and bolts for attaching segment **3** and/or second segment **7** to connecting segment **5**. Other known methods of generating axial clamping or compression forces may be used. When the coefficients and initial dimensions of the seal components are properly selected, the initial axial loading of the seal assembly will be sufficient after heating such that sealing is maintained by the components of the sealing assembly at elevated temperatures.

The working seal or seals of the seal assembly may be provided at any of interfacial zones **17**, **19**, and **21**. A working seal is an element that provides the actual sealing contact between the two adjacent surfaces to minimize or eliminate gas leakage across the seal assembly. A working seal may be formed by an interface between carefully machined mating surfaces or at an interfacial zone by commercially-available compliant sealing elements such as C-rings and O-rings. The location of the working seal or seals will depend on the actual configuration of the seal assembly and the relative pressure differential across the seal assembly. The seal assembly may be attached to the piping or vessel systems that are being connected in any desired configuration. In Figure 2.2.2-13, any of first segment **3**, second segment **7**, and second seal element **11** may be attached to the piping or vessel systems being connected by the seal assembly. Typically, compensating spacer element **9** is independent of and not attached to the piping or vessel systems being connected.

Figure 2.2.2-14 is an example of this concept used in conjunction with the SEP air manifold and the composite washer seal. Seal assembly **201** was a torroidal assembly comprising a clamping element having first clamp segment or ring **203**, clamp connecting segment **205**, and second clamp segment **207**; first seal element or compensating spacer element **209**; and intermediate seal element **211**. The clamp connecting segment **205** and second clamp segment **207** composed a single piece of material forming a second ring of the clamping element. Intermediate seal element **211** formed a flange portion of cylindrical pipe **213** and was made of the same ceramic material. Clamp connecting segment **205**, first seal element or compensating spacer element **209**, and intermediate seal element **211** were made of different materials.

Figure 2.2.2-14 Cross Sectional View of Seal Assembly

First clamp segment or ring **203** was attached to clamp connecting segment **205** by set screws **215**. The set screws typically were made of the same material as clamp connecting segment **205**, and ring **203** may be made of the same material as set screws **215** and clamp connecting segment **205**. Alternatively, any other known type of fastening devices may be used. For example,

threaded studs may be screwed into clamp connecting segment **205** and extend through stud holes in first clamp segment or ring **203**, and bolts may be placed on the studs and tightened to connect first clamp segment or ring **203** to clamp connecting segment **205** and generate axial clamping forces on the seal assembly.

Hole **219** extended through second clamp segment **207** and may be utilized to connect a second pipe (not shown) via a threaded or welded connection so that seal element **201** provides an operating seal between the second pipe and pipe **213**.

The clamping element applied a compressive axial load to the seal assembly. The first clamp segment or ring **203** was in forcible contact with compliant seal member **221**, thereby applying the compressive axial load through the following members – compliant seal member **221**, compensating spacer element **209**, intermediate seal element **211**, and second clamp segment **207**. Compliant seal member **221** may be, for example, a suitable commercially-available compliant gasket, O-ring, C-ring, or other sealing device. The composite washer seal was placed between intermediate seal element **211** and second clamp segment **207**.

Clamp connecting segment **205** was characterized by dimension D, which lies between the plane formed by the surface of first clamp segment or ring **203** at interfacial zone **217** and the plane formed by the surface of second clamp segment **207** at interfacial zone **223**. Compensating spacer element **209** was characterized by dimension B, which is the orthogonal or axial distance between the plane formed by the surface of the compensating spacer element at interfacial zone **217** and the plane formed by the surface of the compensating spacer element at interfacial zone **225**. Second seal element **211** was characterized by dimension C, which is the orthogonal or axial distance between the plane formed by the surface of second seal element **211** at interfacial zone **225** and the plane formed by the surface of the second seal element at interfacial zone **223**.

Interfacial zone **217** included compliant sealing member **221** to provide sealing force for seal assembly **201**. Alternatively, interfacial zone **217** may be an interface formed by contact between flat surfaces on first segment **203** and compensating spacer element **209**. Interfacial zone **223** may be an interface formed by contact between flat surfaces on second segment **207** and second seal element **211**. Alternatively, interfacial zone **223** may contain an intermediate member (not shown) such as a compliant sealing member (composite washer). Interfacial zone **225** is an interface formed by contact between flat surfaces on compensating spacer element **209** and second seal element **211**.

Dimension A was the sum of dimensions B and C. Dimension A was equivalent to the portion of connecting segment **205** that lies between the plane formed by the surface of compensating spacer element **209** at interfacial zone **217** and the plane formed by the surface of second seal element **211** at interfacial zone **223**. Dimension D was the distance between the faces of the clamping element at interfaces **217** and **223**. In this embodiment, dimension D differed from dimension A by the height of compliant sealing member **221**.

Seal assembly **201** was designed by selecting the materials and reference dimensions of the components of the assembly. In particular, the reference dimensions of compensating spacer element **209** (B_R) and seal element **211** (C_R), and the materials of compensating spacer element

209, second seal element **211**, and connecting segment **205**, were properly selected. The coefficient of thermal expansion of connecting segment **205** was between the coefficients of thermal expansion of compensating spacer element **209** and second seal element **211**. The seal components were assembled at ambient conditions, and an initial axial compressive force was applied by the clamping element. The completed seal assembly then is changed, for example by heating, to a selected temperature, T. As a result of the proper selection of the parameters defined above, the temperature-compensated dimension A_T differed from the sum of the temperature-compensated dimensions B_T and C_T at the selected temperature by an absolute value of less than about 0.002 inch as defined in Equation (4) above.

In the above design, pipe **213** had a composition of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-z}$ and the metallic clamping element was Haynes 230. The compensating metallic spacer element was chosen to be Incoloy 800H. The seal utilized a compliant gasket (composite washer) at interface **223** and a compressive compliant ring at interface **217** in a circular groove in the first clamp segment or ring **203**. The thermal expansion behavior on a unit length basis as a function of temperature for the three materials is given in Table 2.2.2-5.

Table 2.2.2-5 Thermal Expansion of Seal Assembly Elements

Temperature (°C)	Thermal Expansion (ppm)		
	Clamping Element (Haynes 230)	Compensating Element (Incoloy 800H)	Ceramic Element ($\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-z}$)
0	0	0	0
100	982.5	1152	671
200	2327.5	2862	1638
300	3740	4536	2720
400	5287.5	6270	3891
500	6935	8064	5031
600	8740	9918	6151
700	10665	11900	7298

Using these expansion characteristics, the reference dimensions A_R , B_R , and C_R were selected so that the temperature-compensated dimensions satisfied Equation (4). The results are given in Table 2.2.2-6. The values of A, B, and C at ambient temperature are the reference dimensions A_R , B_R , and C_R , respectively. The values of A, B, and C at above-ambient temperature are the temperature-compensated dimensions A_T , B_T , and C_T , respectively. The net differential displacement, as defined by Equation (4), never exceeds one ten thousandth of an inch, which is well within the dimensional compensating ability of commercial compliant elements such as metallic C-rings or O-rings.

Table 2.2.2-6 Net Differential Displacement of Seal Assembly Elements

Temperature (°C)	Clamping Element Length (A) (inches)	Ceramic Element Length (B) (inches)	Compensating Element Length (C) (inches)	Net differential displacement (inches)
Ambient	1.035	0.45	0.585	0
100	1.03598584	0.450302	0.58567392	9.9×10^{-6}
200	1.03735463	0.450737	0.58667427	-5.7×10^{-5}
300	1.03878551	0.451224	0.58765356	-9.2×10^{-5}
400	1.04031731	0.451751	0.58866795	-1.0×10^{-4}
500	1.04188275	0.452264	0.58971744	-9.9×10^{-5}
600	1.0435698	0.452768	0.59080203	-2.3×10^{-7}
700	1.04533965	0.453284	0.5919615	9.4×10^{-5}

Low Differential Pressure Seal

The low differential pressure seal was designed to mate a ceramic tube to a metal tube. This seal did not require the same leak-tightness required by the high differential pressure seal. The design concept for this seal was a clip seal. The initial design (Figure 2.2.2-15) was completed by Advanced Products Company.

Figure 2.2.2-15 Schematic View of a Clip Seal for the Low Differential Pressure Seal

A prototype was tested at room temperature to validate the design concept. The interference between the seal and ceramic test plug was 0.000 to 0.001 inches. With this low interference, a slip fit was feasible. The single seal with a pressure differential of 25 psi had a leak rate of only 90 cc/min. Additional testing at operating temperature and through thermal cycles was successful when measured leak rates remained below 1% of the allowable limit. The design concept was implemented in the SEP Module.

TASK 2.3 MEMBRANE AND MODULE DESIGN AND FABRICATION

Subtask 2.3.1 Membrane and Module Design and Engineering

Membrane Active Wafer Design

Initial planar geometries were developed in Phase 1. The planar geometry required the thin active membrane to be incorporated into a multi-layer wafer to provide the necessary support and to provide other functional layers necessary in the application.

Figure 2.3.1-1 is an example of such a membrane and its supporting layers. Active membrane layer **1** is a dense layer of mixed-conducting multi-component metal oxide material and may have a thickness in the range of about 10 μm to about 500 μm . One side of the active membrane layer, which may be defined as the outer side, is in contact with and preferably bonded to porous support layer **3**. The other side of the active membrane layer, which may be defined as the inner side, is in contact with and preferably bonded to channeled layer or channeled support layer **5**, which comprises ceramic support ribs **7** interspersed with oxidant flow channels **9** that extend through the layer. One side of porous support layer **3**, which may be defined as the inner side, is in contact with the outer side of active membrane layer **1**. The other side of porous support layer **3**, which may be defined as the outer side, is exposed to the reacting gases. Channeled support layer **5** may be made of mixed-conducting, multi-component metal oxide material and may have a typical thickness in the range of about 100 μm to about 4 mm. Porous support layer **3** may have a thickness in the range of about 50 μm to about 1 mm, a porosity, defined as the volume fraction of pores, between about 10% and about 40%, and a tortuosity, between about 3 and 10. The tortuosity is defined as the ratio of the gas phase diffusivity multiplied by the porosity divided by the measured effective diffusivity through the porous layer. Porous support layer **3** optionally may include one or more catalysts to promote reactions that occur in the porous layer. The catalyst or catalysts may be disposed on either or both surfaces of porous support layer **3**, or alternatively may be dispersed throughout the layer. The catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof. If desired for structural and/or process reasons, an additional porous layer may be disposed between active membrane layer **1** and channeled support layer **5**.

Figure 2.3.1-1 Schematic View of Planar Membrane Wafer

A wafer assembly which incorporates the basic structure of Figure 2.3.1-1 is shown in Figure 2.3.1-2. This wafer assembly includes a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the second side of the ceramic channeled layer, and a second porous layer of mixed-conducting, multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the outer side of the second dense layer. The wafer assembly thus has a central channeled layer sandwiched between two active membrane layers, and the two active membrane layers are sandwiched between two outer porous support layers.

Figure 2.3.1-2 3-D View of the Internals of a Planar Membrane Wafer

Figure 2.3.1-3 shows the same wafer structure in more detail, with the two cross-sectional views being taken at right angles within the structure. Outer porous support layers **701** and **703** are equivalent to the porous support layer **3** of Figure 2.3.1-1. Active dense membrane layers **705** and **707** are equivalent to the active membrane layer **1** in Figure 2.3.1-1. Slotted support layers **715** and **717** are equivalent to the channeled support layer in Figure 2.3.1-1. Slotted support layer **709** has been added to permit flow communication between the various internal flow channels, as shown in Figure 2.3.1-2. Representative open slots **713** are wider than intermediate supporting ribs **721**, **723**, **727**, and **729**, so that open channels **719** and **725** are in flow communication via open slots **713**. Portions of dense layer **705** are in contact with alternating supporting ribs **303**, and other portions are not in contact with these ribs. Also, portions of dense layer **707** are in contact with alternating supporting ribs **303**, and other portions are not in contact with these ribs.

A SEM image of such a wafer structure cross-section is shown in Figure 2.3.1-4.

Figure 2.3.1-3 Cross-sectional views of membrane wafer assembly.
The two cross-sectional views are at right angles with each other.

Figure 2.3.1-4 SEM Image of an Actual Membrane Wafer

PDU Membrane and Module Design

A membrane wafer assembly was designed for testing in the Process Development Unit (PDU). This assembly incorporated an active membrane sized to provide enough oxygen to match the desired syngas flow capacity of the PDU. In addition, air and non-permeate (oxygen-depleted air) manifolds and ports were included in the membrane wafer assembly (active wafer). A PDU module was designed to include the active wafer and the necessary parts (a flow transition wafer and a seal block) to enable the air to be fed to the active wafer and to enable the non-permeate (oxygen-depleted air) to be collected. The flow transition wafer directs the air and non-permeate flows between the active wafer and the seal block. The seal block is the ceramic portion of the ceramic-to-metal seals. Figure 2.3.1-5 shows a schematic of the PDU module's main components and Figure 2.3.1-6 shows a photo of a PDU module.

Figure 2.3.1-5 Schematic of PDU Module Showing its Main Components

Figure 2.3.1-6 Photo of a PDU Module

Engineering analysis was conducted to understand the temperature profiles and stresses within the ceramic components during operation.

A detailed two-dimensional thermal analysis of the PDU wafer design was performed. The thermal model included all thermal boundary conditions of the PDU reactor vessel. The model geometry represents the active wafer surrounded by two boundary wafers. The syngas flow passes from left to right over the top and bottom of the active wafer. Air flows through the flow transition wafer, from left to right through the active wafer, and back through the flow transition wafer. A sample temperature profile result of the model is shown in Figure 2.3.1-7. The thin slice in the middle is the active wafer. The expanded view of the active wafer shows the temperature gradients developed in both the flow direction and through wafer direction. These types of temperature profiles were used in the structural analysis to confirm and optimize the design of the PDU wafer and module.

Figure 2.3.1-7 Thermal Profile of PDU Module

A finite element structural model of the PDU module was constructed. The model included the seal block, the flow transition wafer and the active wafer. Each of the layers in the active wafer and the flow transition wafer were modeled. The model was used to evaluate thermal stress profiles. The structural model of the PDU module is shown in Figure 2.3.1-8. An example of thermal stress profiles calculated using the global structural model is shown in Figure 2.3.1-9. Modifications to the PDU module were made, as necessary, based on these models.

Figure 2.3.1-8 Structural Model of the PDU Module

Figure 2.3.1-9 Maximum Principal Stress Due to Thermal Profiles at Operating Conditions

The flow resistances through the air-side passages of a series of Plexiglas models of the PDU wafer were measured, with the goal of understanding the locations of flow resistance inside the wafer and lowering the overall flow resistance of the wafer. Testing included both overall flow resistance of the model wafer and measuring the pressure drop in different parts of the wafer using pressure taps. Testing allowed the rapid prototyping of improved designs. A design capable of providing sufficiently low flow resistance and sufficient active area flow distribution was identified and adopted. These modifications included modifying the slotted layers in the active wafer and the side and end manifolds for the air and non-permeate flows.

The pressure drops through the air side of modified ITM Syngas PDU active wafers were measured. The pressure drops through the active wafers were lower than observed for earlier versions of the PDU active wafers, but not nearly low enough. Dissection of one of the active wafers revealed that the slotted layers were thinner than design and the channel widths were narrower than design.

Several revisions on the active and flow transition wafers' internal design were made before the air-flow pressure drop was within specifications. The pressure drop through the airside of two ceramic ITM Syngas PDU modules were measured. The pressure drops of the modules were well below the maximum allowable pressure drop.

Detailed three-dimensional stress analysis was performed for a PDU module, considering stresses due to chemical expansion. The regions of high stress are shown in Figure 2.3.1-10. The crack locations observed in actual PDU modules that had operated were generally consistent with these regions of high stress. Further membrane design modifications were made, as required, to reduce stresses in key areas.

Figure 2.3.1.10 PDU Module Principal Stresses Due to Chemical Expansion

SEP Membrane and Module Design

The next level of scale-up for the planar membrane wafer was to a size that was considered commercial and that could be tested in the existing PDU and the planned Sub-scale Engineering Prototype (SEP). The basic PDU membrane wafer was the starting point. Numerous options were considered for this larger size, and engineering analysis was used to evaluate key aspects of

the design. Air-side pressure drop and flow distribution were key considerations, given the challenges experienced in the PDU membrane module design. The learnings from these challenges directed the path to solutions for the full-size membrane wafer. Plexiglas models were used to confirm that the air-side pressure drop and the flow distribution were within specification. Analysis of thermal gradients and their associated stresses and chemical expansion stresses were completed in a manner similar to those analyses completed on the PDU membrane wafer design. Again, learnings from the experiences designing the PDU membrane wafer were instrumental in ensuring a proper design for the full-size membrane wafer. The chosen design is shown in Figure 2.3.1-11.

Figure 2.3.1-11 Cut-away View of the ITM Syngas Membrane Wafer Design

The internal structure of the full-size membrane wafer was similar to the general structure shown in Figure 2.3.1-3. The multi-layer membrane wafer structure consists of the following layers:

- A flow channel layer (Figure 2.3.1-12) was formed from planar dense green ceramic material having a selected composition. Flow channel layer **201** was rectangular and had two rectangular channeled regions **203** and **205** formed therein. Each channeled region had a pattern of through channels passing through the layer with a lattice of solid ribs formed between the channels. This pattern is better illustrated in Figure 2.3.1-12(b), which is a magnified plan view (not necessarily to scale) of the channels in regions **203** and **205** of Figure 2.3.1-12, showing a pattern of alternating open channels **301** formed by representative alternating supporting ribs **303** that were parallel to through channels **301** and intermediate supporting ribs **305** that were perpendicular to through channels **301**.

Figure 2.3.1-12 Flow Channel Layer (a) Plan View and (b) Detail of Slots

- A slotted support layer (Figure 2.3.1-13) was formed from planar dense green ceramic material having a selected composition and typically having a similar shape and outer perimeter dimensions as the flow channel layer. Slotted support layer **401** had a first generally rectangular region containing parallel slots **403** passing through the layer between support ribs **405** and a second generally rectangular region containing parallel slots **407** passing through the layer between support ribs **409**. Typically, the width of support ribs **405** and **409** (or the distance between slots **403** and **407**) was between about 0.2 and 4 mm, and the width of slots **403** and **407** was between about 0.2 and 2 mm. Slotted support layer **401** also had a plurality of parallel slots **411** passing through the layer that are perpendicular to parallel slots **403** and disposed between one side of the first generally rectangular region and outer periphery **413**. Slotted support layer **401** also had a plurality of parallel slots **415** passing through the layer that were perpendicular to parallel slots **403** and disposed between an opposite side of the first generally rectangular region and outer periphery **417**. Slotted support layer **401** also had a plurality of parallel slots **419** passing through the layer that were perpendicular to parallel slots **407** and disposed between one side of the second generally rectangular region and outer periphery **419**. Slotted support layer **401** also had a plurality of parallel slots **423** passing through the layer that were perpendicular to parallel slots **407** and disposed between the opposite side of the second generally rectangular region and outer periphery **425**.

Figure 2.3.1-13 Slotted Support Layer Plan View

- An intermediate channeled support layer assembly was fabricated by sandwiching a slotted support layer, such as slotted support layer **401**, between two flow channel layers, such as flow channel layer **201**. In this intermediate channeled support layer assembly, alternating supporting ribs **303** of flow channel layer **201** were supported by support ribs **405** and **409**. Intermediate supporting ribs **305** were superimposed on slots **403** and **407** and were narrower than the width of parallel slots **403** and **407**, such that neighboring channels **301** in the lengthwise direction could be in flow communication, i.e., intermediate supporting ribs **305** did not block or bridge slots **403** and **407**.
- The completed channeled support layer assembly **501** (Figure 2.3.1-14) was fabricated by modifying the intermediate channeled support layer assembly. The modification comprised cutting parallel slots **503** and **505** on either side of rectangular channeled region **507**, wherein these slots were parallel to slots **403** and **407** in the slotted support layer. These slots passed completely through channeled support layer **501**, and therefore cut through and intersected slots **411** and **415** in the slotted support layer. The modification also included cutting parallel slots **509** and **511** on either side of rectangular channeled region **513**. These slots passed completely through channeled support layer **501** and therefore cut through and intersected slots **419** and **423** in the slotted support layer. Slots **503** and **505** therefore were in flow communication with slots **403** and with the slots in rectangular channeled region **507**, and also with the other rectangular channeled region on the opposite side of channeled support layer **501**. In addition, slots **509** and **511** therefore were in flow communication with slots **407** and with the slots in rectangular channeled region **513**, and also with the other rectangular channeled region on the opposite side of channeled support layer **501**.

Figure 2.3.1-14 Completed Channeled Support Layer Assembly Plan View

- A composite support layer of green ceramic material was placed in contact with a thin layer of the green ceramic material that is the precursor of the active membrane material. The composite support layer was formed by featuring a green ceramic tape that was a precursor of a dense ceramic material to form a frame defining two windows that approximately matched the dimensions of rectangular channeled regions **507** and **513**.
- A green membrane wafer was assembled by placing a composite support layer in contact with each side of the completed channeled support layer assembly **501**. Green ceramic material that was a precursor of the porous support material was applied within the windows of the composite support layer in contact with the green ceramic material that was a precursor of the active membrane material on each side of completed channeled support layer assembly **501**.
- The green membrane wafer assembly was completed by cutting holes, for example, four holes **609**, **611**, **613**, and **615**, completely through the center region of the green membrane wafer assembly, as shown in Figure 2.3.1-15. More than four holes may be used if desired. Hole **609** intersected and was in flow communication with slots **503** and **509**. Likewise, hole **615** intersected and was in flow communication with slots **505** and **511**. Holes **609** and **615** thus provided internal manifolds in flow communication with slots **403** and **407** and with the slots in rectangular channeled regions **507** and **513**. Regions **617** and **619** of the composite support layer contained the green ceramic material that was a precursor of the porous support material. The remaining region of the support layer, i.e., the region surrounding holes **609-615**, region **617**, and region **619**, contained the green ceramic tape described above that was a precursor of a dense ceramic material.

Figure 2.3.1-15 Completed Green Membrane Wafer Plan View

- These completed green membrane wafers were then fired to sinter all ceramic material in the assemblies. After firing, the internal configurations of the completed membrane wafer allowed gas to flow through hole **609**, through slots **503** and **509**, and distributed into the slots in regions **507** and **513**, thereby contacting the gas with the surfaces of the two active dense membrane layers on either side of central channeled support layer **501**. After contact with the two active dense membrane layers, the gas was collected in slots **505** and **511** and directed into hole **615**. Holes **611** and **613** were not in direct flow communication with the internal slots and channels in channeled support layer **501**, since these holes passed through the middle region of the support layer between slotted regions **507** and **513**. Holes **611** and **613**, may serve as part of a stack flow manifold. The completed membrane wafers may have a width between 5 and 40 cm, a length of between 5 and 40 cm, and a thickness between 1.5 and 8 mm.

The sintered membrane wafer formed one of the basic repeating elements for a multi-wafer membrane module. The other repeating element was the ceramic spacer shown in the views of Figure 2.3.1-16. The ceramic spacer was made of a selected ceramic material, had openings **801** and **803** separated by rib **805**, and had a width similar to the width of the membrane wafer. Opening **801** was sized to fit over holes **609** and **611** of the membrane wafer assembly. Opening **803** was sized to fit over holes **613** and **615**. The height of the spacer (the vertical dimension) was in the range of 0.5 to 5 mm.

Figure 2.3.1-16 Spacer Top and Side Views

A membrane sub-module was assembled from a plurality of membrane wafers and spacers where the wafers and spacers were alternately stacked, as shown in Figure 2.3.1-17. These parts were joined using the techniques described in Subtask 2.3.3-2. The membrane wafers were supported in the center of the stack by the spacers and were cantilevered out to the edges of the stack. Optionally, spacers **907** could be placed between the wafers on opposite sides of the stack, as shown, to provide support and reduce the bending moment on the wafers near the central spacers. These spacers may extend across the full width of the stack. Cap **909** was placed on the top wafer of the stack to close holes **609**, **611**, **613**, and **615**. Openings **911** and holes **609** and **611** formed an internal manifold extending through the length of the stack. Likewise, openings **913** and holes **613** and **615** formed an internal manifold extending through the length of the stack. These two internal manifolds were in flow communication through the wafers via the internal slots and channels in the channel support layer. A membrane sub-module might contain between 1 and 200 wafers and might have a height of 2.5 mm to 2.6 m.

Figure 2.3.1-17 Multi-wafer Membrane Sub-module (a) Side View and (b) End View

A membrane module was assembled by joining an air manifold to one or more stacked sub-modules. The air manifold for the SEP membrane module, as described in Subtask 2.2.2, was designed to accommodate air flow rates consistent with one to five membrane wafers per membrane module. The air manifold was joined to the membrane sub-module using the techniques described in Subtask 2.3.3-2. Figure 2.3.1-18 shows a photo of a single-wafer SEP membrane module.

Figure 2.3.1-18 Photo of a Single Wafer SEP Membrane Module

Subtask 2.3.2 Reaction Engineering and Kinetic Modeling

The tubular geometry model, developed under Phase 1 work, was used to evaluate experimental data from testing at both high and atmospheric pressures. Developed by Air Products, Chevron, and Norsk Hydro, this model considered heat transfer, mass transfer, surface and packed bed-reactions, and ionic transport through the membrane. The reaction and transport model also incorporated the oxygen vacancy correlation and empirical flux model developed earlier.

A consistent set of parameters was developed fitting early experimental results, all of which used tubes with the I4(C) composition. A correlating parameter, $\sigma_{i,Xv}$, was defined as:

$$\sigma_{i,xv} = \frac{c_{mc} D_v z_i^2 F^2}{RT}$$

where $z_i = 2$, $F = 96,500$ coulomb/mole, and $R = 8.314$ J/mole-K. The fit of $\sigma_{i,Xv}$ is shown in Figure 2.3.2.-1.

Figure 2.3.2-1 Correlating Parameter $\sigma_{i,xv}$ for Data from Experiments Using I4(C) Tubular Membranes

Air Products completed the formulation of a simplified one-dimensional reaction and transport model of the planar membrane. Mass transport and heat fluxes were calculated for the air channel, the dense membrane layer, the syngas-side catalytic porous layer, and the syngas channel. Combustion reactions were considered at the interface of the dense and porous membrane layers, and steam-methane reforming and water-gas shift reactions were considered in the porous layer. Oxygen ion transport through the dense membrane layer was modeled using the correlation and parameters previously developed. Simplifying assumptions were made for transport and kinetic parameters to allow a more rapid solution of the model's equations during the preliminary analyses. Placeholder values for reaction rate parameters were used for model testing.

Figures 2.3.2-2 and 2.3.2-3 show sample test profiles for a membrane with a reactive (catalyzed) porous layer operating at a pressure of 10 atmospheres of syngas and a temperature of 900°C. Hydrogen and water fluxes dominated the mass transport. For the chosen parameter values, steam-methane reforming occurred near the porous layer surface.

Figure 2.3.2-2 Sample Component Flux Profiles - Reactive Porous Membrane Layer

Figure 2.3.3 Sample Concentration Profiles - Reactive Porous Membrane Layer

A detailed one-dimensional model was developed for the planar membrane incorporating the porous layer, the dense layer, and bulk gas transport resistances. Chevron completed the portion of this model relating to kinetic and transport phenomenon for the porous layer. Testing of the model demonstrated that the numerical shooting method could be used to successfully solve the boundary value problem to model the porous layer. Initial test results for the one-dimensional model were consistent with the simplified model.

Subsequently, a two-dimensional model was developed for the planar membrane. This model considered the dimensions in the direction of the membrane thickness (same as the one-dimensional model) and in the direction of the bulk gas flow. Because of problematic convergence issues, significant work was required to find the best numerical techniques to solve the model's equations describing gas flows, compositions, temperatures, and flux. Engineering approximations were used in the model to allow integration along the length of the membrane. Model parameters were estimated, calculated, or measured as appropriate.

Two numerical methods were developed to solve the simultaneous equations of the basic two-dimensional model. The Mixed-Cell model used the first numerical method which incorporated an approximation to solve the equations in the porous layer. The Collocation model used the second numerical method which solved the porous layer equations rigorously. The Mixed-Cell model was faster and produced essentially the same results as the Collocation model. On this basis, the Mixed-Cell model was adopted for membrane and reactor design.

The Mixed-Cell model for a planar ITM-syngas membrane reactor solved the transport and reaction equations for a slice of the membrane and porous layer at a given position in an ITM-syngas reactor. The overall concept of the model, which allowed for nine gas components (He, N₂, O₂, Ar, CH₄, H₂, CO, H₂O, and CO₂), is shown schematically in Figure 2.3.2-4.

Planar Model

Figure 2.3.2-4 Schematic Showing Membrane Layers in the Planar Model

The membrane has a porous support layer, potentially containing catalyst, on the syngas side. Combustion reactions are assumed to occur on the syngas-side surface of the dense membrane. The membrane is divided into named and numbered regions as shown in Figure 2.3.2-5. The equations used to model the mechanisms occurring in each region are discussed in the following sections.

Definition of Regions

Figure 2.3.2-5 Schematic Showing Regions of Membrane Used in Planar Model

Region I - Air Channel

The air was assumed to be confined in tiny rectangular channels and was assumed to be laminar flow. The model's equations for air-side mass and heat transfer, including the effect of the net mass flux towards the membrane, were:

$$N_{O_2}^I = \frac{P^I k_M^I}{RT^I} \ln \left(\frac{1 - y_{O_2, z_0}^I}{1 - y_{O_2}^I} \right) \quad [I-1]$$

$$q^I = h_{O_2}^I N_{O_2}^I + \frac{\beta^I \alpha_I^o}{\exp(\beta^I) - 1} (T^I - T_{z_0}^I) = h_{O_2, z_0}^I N_{O_2}^I + \frac{\beta^I \alpha_I^o}{1 - \exp(-\beta^I)} (T^I - T_{z_0}^I) \quad [I-2]$$

where

- $N_{O_2}^I$ = oxygen flux towards the surface in Region I, moles/cm²-s
- P^I = air-side pressure, atm
- T^I = air-side bulk temperature, K
- k_M^I = air-side mass transfer coefficient, cm/s
- $y_{O_2}^I$ = bulk mole fraction oxygen
- y_{O_2, z_0}^I = mole fraction of oxygen at the surface of the porous layer (i.e., @ $z = z_0$)
- q^I = total enthalpy flux towards the surface in Region I, J/cm²-s

$$\begin{aligned}
h_{O_2}^I &= \text{molar enthalpy of oxygen in (bulk) Region I, J/mol} \\
h_{O_2,z0}^I &= \text{molar enthalpy of oxygen at the surface of the porous layer, J/mol} \\
T_{z0}^I &= \text{temperature at the surface, K} \\
\alpha_I^0 &= \text{gas-to-surface heat transfer coefficient, calculated in the absence of net mass flux at the wall, J/cm}^2\text{-s-K,} \\
C_{p,O_2} &= \text{heat capacity of oxygen, J/mol-K} \\
\beta^I &\equiv C_{p,O_2} N_{O_2}^I / \alpha_I^0
\end{aligned}$$

The mass transfer equation was based on the transport of oxygen through a stagnant film of the other components of the air-side mixture. For reference, the Nusselt number (and also the Sherwood number) for fully-developed laminar flow in the air channels was taken as $Nu_\infty = \alpha_I^0 d_h / \lambda \sim 3.2$.

Region II - Dense Membrane (Including Reduction Catalyst)

The flow of oxygen ions across the membrane was calculated using the oxygen vacancy model:

$$N_{O_2} = \frac{c_{mc} D_v}{4L} \int_{P_{O_2}^{permeate}}^{P_{O_2}^{airfeed}} x_v \frac{dP}{P} \quad [\text{II-1}]$$

where

$$\begin{aligned}
P &= \text{oxygen pressure, atm} \\
X_v &= \text{oxygen vacancy fraction} \\
C_{mc} &= \text{concentration of oxygen sites, mol/cm}^3 \\
D_v &= \text{oxygen ion diffusion coefficient, cm}^2\text{/s} \\
L &= \text{membrane thickness, cm}
\end{aligned}$$

For each ITM material, correlations of X_v were obtained from experimental data in a form amenable to analytical integration. The usual integrated form was:

$$N_{O_2} = \frac{c_{mc} D_v}{4L} \left[\left(\frac{C}{D} \right) (P_{O_2,1}^D - P_b^D) + \left(\frac{A}{B} \right) (P_b^B - P_{O_2,2}^B) \right] \quad [\text{II-2}]$$

where A, B, C, D, and P_b are correlating parameters. A, B, C, and D are all temperature dependent.

The membrane surface was assumed not to be in equilibrium with the gas phase at the surface because the surface oxygen has finite resistance to ionization. The rate for this reaction was assumed to be given by:

$$2N_{O_2} = I_{O=} = k_{ion,A} (P_{O_2,A}^H)^{1/2} - k_{S,A} c_{O=,A} \quad [\text{II-3}]$$

where $c_{O=}$ is the concentration of oxygen ions at the membrane surface.

This reaction rate equation can be modified by replacing $k_{ScO=}$ using the following thermodynamic equilibrium relationship

$$k_S c_{O=} = k_{ion} (p_{eq,O2})^{1/2} \quad [II-4]$$

Therefore, equation II-3 can be re-written as:

$$2N_{O2} = I_{O=} = k_{ion,A} \left[(p_{O2,A}^{II})^{1/2} - (p_{eq,O2})^{1/2} \right] \quad [II-5]$$

In equation II-5, $p_{O2,A}$ was the partial pressure of oxygen in the gas phase at the air-side surface of the membrane, and $p_{eq,O2}$ was the partial pressure of oxygen to be used as the value of $p_{O2,1}$ in equation II-2. There were no data to establish values for k_{ion} . Consequently, the value for k_{ion} used in the model was usually large, which corresponds to a negligible kinetic resistance to ionization ($p_{O2,1} \cong p_{O2,A}$).

Since the dense (non-porous) membrane thickness was expected to be very small, the membrane was assumed to be at a constant temperature, T^{II} . At the boundary between Regions I and II, $T_{z1}^I = T_{z1}^{II}$, $p_{O2,z1}^I = p_{O2,z1}^{II}$, $N_{O2}^I = N_{O2}^{II}$, $q^I = q^{II}$, and $h_{O2,z1}^I = h_{O2,z1}^{II}$.

Region III - Porous Layer (Including Combustion Catalyst at the Syngas-side Surface of the Membrane and Reforming Catalyst in the Porous Layer)

The two equations governing the porous layer in Region III were:

$$\frac{dN_i}{dz} = \sum_j v_{ij}^{III} R_j^{III} \quad [III-1]$$

and

$$q^{III} = constant = \sum_{i=1}^n h_i^{III} N_i^{III} - k_{eff}^{III} \frac{dT^{III}}{dz} \quad [III-2]$$

where R_j^{III} = volumetric rate for reaction j in the porous layer, mol/cm³-s
 v_{ij} = stoichiometric constant for component i in reaction j

The fluxes of the components varied because of the reactions in the porous layer. Any species participating in the reactions was assumed to have a non-zero net flux. This description of the effect of the reactions applied regardless which form of kinetic expression was used to calculate reaction rates. Steam reforming and water-gas shift reactions were allowed in Region III. Because combustion was assumed to occur at the dense membrane-porous layer boundary, it therefore enters into the boundary conditions describing the transition between Regions II and III.

The description of the component fluxes in the porous layer was given by the following Stefan-Maxwell equations:

$$N_i^{III} = y_i^{III} \sum_j N_j^{III} - c^{III} D_{eff,i-m}^{III} \frac{dy_i^{III}}{dz} \quad [III-3]$$

$$\frac{1}{D_{eff,i-m}^{III}} = \frac{\sum_{j=1}^n (1/D_{eff,ij}^{III})(y_j^{III} N_i^{III} - y_i^{III} N_j^{III})}{N_i^{III} - y_i^{III} \sum_{j=1}^n N_j^{III}} \quad [III-4]$$

The effective binary diffusion coefficients, $D_{eff,ij}$, were the binary bulk gas diffusion coefficients multiplied by ε/τ , the porosity:tortuosity ratio for the porous layer. The binary diffusion coefficients were estimated from standard correlations. The binary coefficients were calculated using the same composition and temperature as the bulk syngas. Although in principle they should be recalculated at each point inside the porous layer, the variation in diffusion coefficients was much less than the uncertainty in ε/τ .

Equations III-1 through III-3 must be integrated numerically across the porous layer. Solving this boundary-value problem was the challenging part of the model development.

At the boundary between Regions II and III, $T_{z2}^{II} = T_{z2}^{III}$, $p_{O2,z2}^{II} = p_{O2,z2}^{III}$, $q^{II} = q^{III}$ and $h_{O2,z2}^{II} = h_{O2,z2}^{III}$.

Surface reactions were introduced as part of the boundary conditions. In general, equation III-7 applied for the mass fluxes:

$$N_i^{III} = N_i^{II} + \sum_j \nu_{s,ij} \mathfrak{R}_{s,j} \quad [III-7]$$

where $\mathfrak{R}_{s,j}$ = rate of surface reaction j in the porous layer, $\text{mol}/\text{cm}^2\text{-s}$
 $\nu_{s,ij}$ = stoichiometric factor for component i in surface reaction j

In the current model, methane, hydrogen, and CO combustion were the only reactions at the surface. A simplification, supported by experimental data, was that the combustion reaction rates were zero-order in oxygen. The partial pressure of oxygen, $p_{O2,z2}^{II}$, was the value needed to supply the oxygen for combustion. It normally had a very low value, which allowed the additional assumption that $N_{O2}^{III} = 0$. Since $N_i^{II} = 0$ for all components other than oxygen, the reaction rates at the surface of the dense membrane determined the values of N_i^{III} at this boundary. The reaction rates were functions of the partial pressures and temperature at the surface of the dense membrane. In the current model, which used the shooting method for solving the boundary-condition problem, the initial guesses were the gas composition and

temperature at the ITM/porous layer boundary and the conditions to be matched were the compositions and temperature at the boundary between the porous layer and the syngas.

The net enthalpy flux across the membrane and the porous layer was assumed to be constant. The overall system was assumed to be adiabatic and the enthalpy gain (or loss) of the syngas was forced to equal the enthalpy loss (or gain) of the air.

Region IV - Syngas Channel

The syngas flowed in a gap between the membrane wafers. Although the gap was small, the flow was expected to be high enough to be turbulent, or at least in the transition-flow region.

The equation for heat transfer in Region IV was analogous to that of Region I,

$$q^{IV} = \sum_{i=1}^n h_{i,z2}^{IV} N_i^{IV} + \frac{\beta^{IV} \alpha_v^o}{\exp(\beta^{IV}) - 1} (T_{z2}^{IV} - T^{IV}) \quad [IV-1]$$

where $\beta^{IV} \equiv \sum C_{p,i} N_i^{IV} / \alpha_v^o$

The equations for mass transfer were analogous to the Stefan-Maxwell equations in Region III, with dz replaced by a boundary layer thickness estimated from a turbulent-flow mass transfer correlation.

At the boundary between Regions III and IV, $T_{z3}^{III} = T_{z3}^{IV}$, $N_{i,z3}^{III} = N_i^{IV}$, $p_{i,z3}^{III} = p_{i,z3}^{IV}$, $q^{III} = q^{IV}$ and $h_{i,z3}^{III} = h_{i,z3}^{IV}$. The pressure, temperature, and mole fractions in the bulk gas in Region IV were determined from the numerical integration in the direction of the syngas flow.

Experimental data from the Process Development Unit (PDU) was used for parameter estimation and validation of the Mixed-Cell model. Model predictions of PDU Run 12 data (sub-scale PDU module) prior to parameter fitting are shown in Figure 2.3.2-6. Parameter fitting significantly improved the model predictions (Figure 2.3.2-7) and highlighted several areas for future work including: independent tests to verify activation energy for oxygen vacancy coefficient, independent tests to verify the porous layer tortuosity factor, and improved modeling of syngas-side heat transfer.

Model Prediction of Oxygen Flux

Figure 2.3.2-6 Model Prediction of Experimental Data for PDU Run 12 Without Parameter Fitting

Model Prediction of Oxygen Flux

Figure 2.3.2-7 Model Prediction of Experimental Data for PDU Run 12 With Parameter Fitting

The model predictions also showed reasonable agreement with experimental data for a commercial scale wafer module (PDU Run 15) as shown in Figures 2.3.2-8.

Figure 2.3.2-8 Model Prediction of Experimental Data for PDU Run 15 With Parameter Fitting

Validation of the Mixed-Cell model over a wider range of gas compositions is required to better understand the effects of each component. Improved syngas-side heat transfer models were incorporated into the model, but were not validated.

The Mixed-Cell model was the primary modeling tool for the ITM Syngas program since 2001. However, the approach of slicing the porous layer into several "mixed cells" continued to have issues with both its speed and accuracy. More recently a new numerical approach, the Galerkin method, was investigated. With the Galerkin method, the concentrations and temperatures of each region and, perhaps eventually, the oxygen activity in the solid fraction can be described by a series of continuous functions. Initial indications were that the model using the Galerkin method produced equivalent results at a faster speed than the Mixed-Cell model. More validation work is required before this approach can be fully implemented.

ITM Syngas modeling was also extended to the Aspen platform. ITM Syngas membrane models were developed using both Aspen Custom Modeler® and Aspen Plus®. The goal was to provide model access in a platform that is more widely supported and to have the ability to incorporate the ITM unit operation into a larger simulation flowsheet. The Aspen models have been validated by comparison to the Mixed-Cell model.

Subtask 2.3.3 Membrane and Module Fabrication

Subtask 2.3.3.1 Powder Synthesis and Scale-up

In general, powders were prepared using conventional ceramic methods. Such methods included mixing respective amounts of metal oxides, carbonates, hydroxides, nitrates, or oxalates to achieve the desired cation fraction of each of the metal cations, mixing the components in any suitable conventional means, such as attrition milling, vibratory milling, ball milling and high sheer mixing, and calcining the mixture to achieve a homogenous single phase, or nearly single phase, ceramic powder. More specifically, an example powder preparation method would mill the components in a vibratory mill for 72 hours, calcine the mixture in air at 1200°C for 10 hours, and grind the mixture by vibratory milling for 72 hours.

Ceramatec produced various I4 ceramic powders for the production of membrane test samples, PDU membranes, commercial-size SEP membranes, and membrane module components. Early in Phase 2, production of the I4(C) powder was the major focus. Later in the program, the I4(D) powder dominated the production, as it became the baseline powder composition. Other powder variants were produced throughout the Phase 2 effort, as required by the program.

Ceramic processing improvements were tested and, if appropriate, qualified to improve the quality or the capacity of the powder production process. Examples of these types of improvements included the following:

- The milling media was changed from carbon steel to zirconia to eliminate contamination of the powder with excessive amounts of iron.
- Attrition milling capacity was increased 20-fold through the use of larger capacity equipment and a reduction in the required milling time.
- New powder calcining kilns were installed to increase production capacity.
- Alternative processes were evaluated for producing powder used to manufacture ceramic manifold components.

Subtask 2.3.3.2 Membrane and Module Fabrication Development

Ceramatec developed fabrication processes for components of the membrane modules intended for testing in the Process Development Unit (PDU). The basis for the membrane was the planar design, identified during Phase 1. The membrane module, shown in Figure 2.3.3.2-1, comprised membrane wafers, flow transition (FT) wafers, and seal blocks. The membrane wafer design utilized a laminate structure incorporating dense, porous, and slotted layers, as described in Subtask 2.3.1.1. The FT wafer was also a laminate structure incorporating dense and slotted layers. Finally, the seal block was fabricated by iso-pressing the powder. Thus, fabrication

development focused on two key areas: ceramic processing equipment and procedures, associated with laminate structures and pressed components, and ceramic-to-ceramic joining techniques.

Figure 2.3.3.2-1 PDU Module

Ceramic Processing – Laminate Structures

Development of the required ceramic processes to make the laminate structures proceeded through phases that included identifying the required process to make a particular ceramic part, implementing the process with small-scale equipment, and automating and scaling up the capacity of the qualified process. The use of commercial ceramic processing equipment was maximized.

The fabrication techniques for the laminate structures were developed. The processing steps included tape casting the required layers to generate "green" tapes, featuring the "green" tape for specific layers, laminating the various layers into a "green" wafer, and sintering the "green" wafer to make the final ceramic part. Figure 2.3.3.2-2 shows the general ceramic processing steps. Numerous details for these steps were developed and optimized. Often, unexpected results drove further investigation and refinement or complete revamping of the details. It was often observed that small changes in such variables as environmental conditions, powder composition or morphology, or binder or solvent compositions could significantly alter the fabricated part and ceramic processing yields. These issues were also investigated and corrected, but more important, they drove the development of stringent specifications and quality control.

Figure 2.3.3.2-2 Ceramic Processing Steps

Ceramic processing tooling and equipment to conduct the desired fabrication techniques were identified and purchased. Each new piece of equipment required qualification, a process that ensured proper operation and product consistency, before being put into service. Tape-casting equipment was initially purchased at a small capacity and, as confidence in the process and demand increased, larger commercial continuous tape casters were installed. Associated tape-casting slip preparation processes and equipment were developed and installed for each tape-casting scale-up. High-speed laser cutters were installed to efficiently and accurately feature the "green" tape for the slotted layers. The lamination process initially stacked the layers manually and then used a lamination press to ensure bonding of the assembled layers. Later in the program, automated wafer assembly was investigated, and a proprietary assembly machine was designed and built. At the time of this report, the wafer assembly machine was being qualified. The capacity of this machine significantly increases the production capabilities of the ceramic processing facility. Finally, sintering furnaces were purchased to match the increased production capabilities of the facility.

Ceramic Processing – ISO-pressed Components

The fabrication techniques for the seal block were developed. The processing steps included iso-pressing powder to form a "green" body, sintering, and machining. Numerous details for these steps were developed and optimized. As with laminate structure, often, unexpected results

drove further investigation and refinement or complete revamping of the details. It was often observed that small changes in variables such as powder composition or morphology, or binder or solvent compositions could significantly alter the fabricated part and ceramic processing yields. These issues were also investigated and corrected, but more important, they drove the development of stringent specifications and quality control. Standard commercial equipment was used for these processing steps.

Ceramic-to-Ceramic Joining Techniques

Ceramic-to-ceramic joints between sintered bodies have historically been formed by using metallic brazes, nanocrystalline oxides, oxide-metal eutectics, glasses and ceramic-glass composites. These types of joints could not provide the desired reliability for the membrane module fabrication where the membrane wafer, the FT wafer, and the seal block are joined. Therefore, an improved method of forming a ceramic-to-ceramic joint between two sintered ceramic bodies was developed. Specifically, the first sintered body was a multicomponent metallic oxide having a crystal structure of the perovskitic or the fluorite type, and the second sintered body was either the same multicomponent metallic oxide or a different multicomponent metallic oxide having a crystal structure of the same type as the first multicomponent metallic oxide.

This improved method entails (i) providing at the interface of the sintered bodies, where the joint is to be formed, a joint material comprising a metal oxide or mixture of metal oxides, (ii) heating the sintered bodies and the joint material, and (iii) holding the assembled part at the heating temperature to react the metal oxide or mixture of metal oxides, or part thereof, to form the joint. This reaction may result in a third multicomponent metallic oxide having a crystal structure of the same type as the first and the second multicomponent metallic oxide. This reaction may also result in formation of a joint without any noticeable phase being formed at the interface.

Upon heating in step (ii) a liquid phase is provided by the joint material. This liquid phase then reacts in step (iii) to form the joint, and may hence be called a transient liquid phase. This method relies on this transient liquid phase and sintering for formation of the joint. Upon heating in step (ii) a liquid phase and one or two solid phases are created. Reaction of the liquid phase in step (iii) may be with one of the solid phases and/or with the first and/or second multicomponent metallic oxide. In the course of the reaction, a third multicomponent metallic oxide may be formed at the interface.

The joint material may comprise a single metal oxide, a mixture of metal oxides, a single multicomponent metallic oxide, a mixture of multicomponent metallic oxides or mixtures. In any case, the joint material forms a liquid phase, which reacts to form the joint in step (iii). The liquid phase forms from the joint material by melting, phase segregation into a liquid and a solid phase, or the like. The metallic oxide or mixture of metallic oxides can be combined with conventional binders and/or solvents to provide an ink, paste or tape. This ink, paste or tape is then provided as the joint material at the interface. Using the tape form of the joint material is preferred, since the "green tape" has sufficient plasticity (even prior to heating) to conform to a shape of the interface between the first sintered body and the second sintered body.

Since formation of the joint should typically not deteriorate the structural integrity of the sintered bodies to be joined, joining is carried out at temperatures below the sintering temperature of these sintered bodies. During heating and/or holding in steps (ii) and (iii), respectively, a pressure can be applied to the sintered bodies to be joined to promote joint formation. Generally, such pressure may be in the range of up to 1 MPa.

Upon heating, the liquid phase is provided in a quantity sufficient to allow the seal to form. The liquid phase then reacts with any remaining solid phase(s) of the joint material and/or the first and/or second multicomponent metallic oxide of the first and second sintered body, respectively. During the reaction a third multicomponent metallic oxide may be formed at the interface. This is especially advantageous in the case of uneven surfaces, since formation of the third oxide allows for filling voids during joining. As the reaction proceeds, the liquid phase is consumed and finally vanishes. The sufficient amount of liquid phase is typically obtained by choosing a low melting point composition within a phase diagram of the oxides contained in the joint material. The low melting point composition may comprise additional metals not contained in the first and second multicomponent metallic oxides.

An example of such a joint is shown in Figure 2.3.3.2-3. This joint was made using a joining tape of 80 percent Fe_2O_3 and 20 percent CaO . The composition of the sintered bodies (discs) was $(\text{La}_{0.75}\text{Ca}_{0.25})_{1.01}\text{FeO}_{3-x}$. The joining tape was placed between the sintered discs, heated to 1250°C , held at this temperature for one hour, and cooled to room temperature. The dark phase at the interfaces and in nearby regions was identified by Energy Dispersive Spectroscopy (EDS) as containing a calcium ferrite phase. A helium leak check indicated that the joint was hermetic.

Figure 2.3.3.2-3 A SEM Image of an Improved Ceramic-to-Ceramic Joint

This joining method was qualified and implemented for membrane module fabrication. An example of a PDU module that was fabricated using this joining method is shown in Figure 2.3.3.2-4.

Figure 2.3.3.2-4 Three-wafer PDU Module

Further development resulted in another ceramic-to-ceramic joining technique that was superior to the previously developed technique. This superior technique forms a joint between previously sintered ceramic bodies, so as to provide a substantially seamless (or monolithic) structure using green ceramic joint material of the same composition as the sintered bodies. A "ceramic joint material" (sometimes referred to as "joint material" or "joining material") is defined herein as a composite mixture of ceramic particle and organic components. The organic components can include, for example, polymeric binders, plasticizers, dispersants and/or solvents. The term "green" denotes that the joint material is unsintered.

The green joint material comprised tightly-packed ceramic particles held together by a plasticized polymeric binder. The polymeric component of the green joint material allowed the ceramic particles to rearrange under the application of pressure and temperature, conforming to the joining surfaces of the sintered ceramic bodies. Once the polymers were removed during joining, only ceramic particles remained. No liquid phase was formed at any point of the joining process. Typically, the binders were removed by heating the joint material in air, whereupon the binders decompose and diffuse out of the joint as vapor or combustion products. The ceramic joint material was densified by solid state sintering under the application of load and pressure. Initially, the particles necked together and formed a bond with the joining surfaces of the previously sintered ceramic. Once a continuous network of bonded ceramic particles was formed between the joining surfaces, the application of pressure was no longer required. Although pressure was advantageous in lowering the sintering temperature, it was only required in order to allow constrained sintering. Necking of particles and partial sintering, however, were adequate to form enough constraint so that sintering can proceed in the absence of applied pressure, if this was desired.

When joining flat surfaces there was great flexibility in the joining process since constraint on the joint was easily achieved. The green joint material could therefore be formed with little polymer by processes such as dry pressing, isostatic pressing, roll compaction, gel casting, slip casting, centrifugal casting, extrusion or other methods known to the art, as well as by methods which require more polymeric material such as tape casting or injection molding. While methods which result in lower packing densities, such as screen or ink-jet printing, could also be used, it was desired to increase the packing density in the green state in order to limit z-direction shrinkage during firing.

Constraint was preferred during the initial stages of joining in order to allow bonding as solid state sintering progresses. Constraint was preferably applied as a pressure normal to the joining surfaces. Pressure could also be applied from more than one direction. However, there was no need in this process for any constraint on the joint in the x-y direction since nearly all of the densification occurred in the z-direction.

The amount of pressure was preferably at least 1 kPa but less than 5 MPa, and more preferably less than 2 MPa. Too high a joining pressure caused cracking in the green state prior to the necking of ceramic particles in the joint material as solid state sintering initiated. The green joint material was especially susceptible to cracking after the removal of the binder and prior to the onset of sintering. Excessively high pressures also damaged the sintered bodies to be joined, either by causing creep of those bodies or by breaking those bodies.

When joining surfaces with local or global out-of-flatness it was important to balance high green density with the ability of the green ceramic to conform to the surfaces to be bonded under the application of low pressure and low temperature (the temperature at which 90% by weight of the polymers are removed by processes such as wicking, capillary flow, volatilization, and/or decomposition). The application of pressure must remain until the ceramic joint had sufficient strength to apply constraint due to the stability of the previously sintered ceramic surrounding the joint. These requirements typically required a high volume of organic material, such that the green joint material contains 20-50 vol. % organic material.

While it was possible to allow the green joint material to conform at room temperature, this was not necessary since the application of temperature permitted plastic flow of polymeric components of the joint material under stress. Creep of the polymer allowed the surfaces of the green joint material to conform to the joining surfaces of the sintered bodies to be joined. Too much elongation resulted in rupture of the green tape. Cracks originated during low-temperature plastic flow and were difficult to detect until sintering allowed the cracks to open. Therefore, the flatness of the surfaces to be joined and the elongation at rupture of the joint material needed to be matched such that the joint material did not crack during the thermal treatment. Any cracks originating from rupture during plastic flow were easy to distinguish from cooling cracks not only due to their crack opening displacement but also because of the thermal etching of the surfaces compared to cracking that occurred upon cooling. Cracking can also occur at the onset of sintering, if constraint was not present, since only the joint material densified and stresses can only be relaxed through diffusion and creep. During the onset of sintering, the creep rate is low.

Means for forming the green joint material were not limited. Tape casting was the preferred method, since it was simple and easy to tailor the properties of the green tape by choosing the appropriate binder and plasticizer in combination with the selection of the ceramic particle size distribution and solids loading.

In order to minimize z-direction shrinkage and to enhance densification of the joint material, it was desirable to achieve a high packing density in the green ceramic joint material. One method of obtaining high packing density was to attain a high solid fraction of ceramic particles in the green joint. Processing methods such as tape casting, uniaxial pressing, isostatic pressing,

extrusion, roll compaction, gel casting, slip casting, centrifugal casting, and injection molding were common methods for obtaining high packing densities of the ceramic particles. Packing, however, needed to be tempered with sintering activity. It was not uncommon to use bimodal or trimodal size distributions, where particles were chosen such that the smaller particles fit into the interstices of the larger particles. High packing density was only desirable if it allowed for high sinterability. Since larger particles dictated the sintering rate, higher packing density was not desired if it hindered the sintering activity. Similarly, while nanoparticles enhanced sinterability, a joint material made entirely of nanoparticles typically did not allow high packing density due to their high surface area. Therefore an optimum amount of sintering activity was desired. The joint material had a green density of at least 40% of theoretical after binder removal and preferably above 50% of theoretical, so that the maximum z-direction shrinkage was less than 60% of the initial gasket thickness. With proper packing it was possible to get green densities above 60% of theoretical, thereby limiting the z-direction shrinkage to less than 40%.

The particle size distribution and surface area of the ceramic particles in the green seal were dictated by the desired joining conditions. Surface areas could be as low as $2 \text{ m}^2/\text{g}$ and particle size distributions could range from $0.1 \text{ }\mu\text{m}$ to $3 \text{ }\mu\text{m}$, with a d_{50} of $1 \text{ }\mu\text{m}$. Particles having surface areas as high as $25 \text{ m}^2/\text{g}$ can be employed, but small particles limited plastic flow in the green state and resulted in poor particle packing. The preferred surface area ranged from 2 to $10 \text{ m}^2/\text{g}$ and was more preferably from 3 to $8 \text{ m}^2/\text{g}$. The mean particle size was preferably from 0.1 to $1.0 \text{ }\mu\text{m}$.

A variety of aqueous and nonaqueous solvent systems could be used in the green joint material, based on the selection of binder and plasticizer. Solids content, once the solvent had been fully evaporated, was preferably range from 40 to 75 vol. % and more preferably from 50 to 65 vol. % for joining nonplanar surfaces. Solids content was defined as the volume fraction of ceramic particle in the joint material after the evaporation of the solvent. When joining surfaces, the binder was plasticized such that it was above its glass transition temperature at room temperature. The choice of plasticizers depended on the binder choice. For example, butyl benzyl phthalate will plasticize polyvinyl butyral binder.

Suitable binders included but were not limited to polyvinyl butyral, polypropylene carbonate, polyvinyl alcohol, polyvinyl chloride, polyacrylate esters, polymethyl methacrylate, polyisobutylene, polyurethane, methyl cellulose, and latex.

Suitable plasticizers included but were not limited to butyl benzyl phthalate, dimethyl phthalate, polyethylene glycol, polyalkylene glycol, triethylene glycol, glycerol, butyl stearate, propylene carbonate, and butyl stearate.

The ultimate tensile strength of the joining tape was preferably above 1 MPa and more preferably above 2 MPa, with a yield strength, which was preferably at least 0.1 MPa and more preferably above 0.2 MPa. The percent elongation of the green tape under tension preferably exceeded 5% when joining unground surfaces and more preferably was in excess of 10%.

The surfaces to be joined were as flat as possible, with ground or creep-flattened surfaces preferred over unground or as-fired surfaces. The maximum out-of-flatness of the sintered parts

being joined was less than 500 μm and preferably less than 250 μm . Most preferably, the maximum out-of-flatness was less than 100 μm . Maximum out of flatness was measured using laser profilometry or using a drop gage. Out of flatness was the difference between the minimum and maximum heights on a surface.

When joining surfaces that were not lapped to make them flat and parallel, it was desirable to conform the ceramic joint material to the surfaces to be joined while the ceramic joint material was in the green state. Ceramics were typically loaded with polymeric materials in order to give them strength in the green state. Prior to removal of the polymeric materials it was possible to allow the green ceramic joint material to conform to the rigid surfaces of the material being joined. Preferably, the surfaces to be joined were flat and parallel. However, this method was suitable for joining surfaces that were out-of-flat. The maximum degree of out-of-flatness was dictated by both the local and global conformity of the surfaces joined.

One way to control ductility of the green ceramic joint material was to add plasticizers or select binders that allow the green ceramic joint material to conform to the surfaces to be joined. Surfaces with global out-of-flatness of up to 250 μm over 25 mm were joined successfully using this new joining technique. The green ceramic joint material was thick enough to allow plastic flow in the plane parallel to the surfaces to be joined, called the x-y plane, in order to allow the joining tape to conform to both rigid surfaces. The green ceramic joint material was thin enough to prevent x-y shrinkage from initiating cracking during sintering. Preferred thicknesses for the green joint material were on the order of 5 μm to 1 mm.

Prior to the joining step, the surfaces were cleaned by firing, grit blasting, ultrasonic cleaning, or standard laboratory practices. No special treatment was necessary to roughen the surfaces and cleaning was only for the purpose of removing unwanted impurities which might be entrained in the part as part of the high-temperature joining process.

The joint material was placed between the two joining surfaces of the sintered bodies to be joined. Aligning fixtures were used, if necessary or desired. When using green ceramic tapes, it was very easy to shear the gasket to the size desired. A solvent was applied in a thin coating to both surfaces of the tape prior to placing the gasket in the desired location on the sintered samples.

Pressure was then applied during the initial stages of heating in order to allow the binder to flow and the gasket to conform to the surfaces to be joined. The pressure was at least 10 kPa and preferably between 100 kPa and 700 kPa. The pressure was less than 5 MPa and preferably less than 2 MPa. The purpose of the pressure was to plastically deform the joint material to the contour of the sintered joining surfaces, if needed, as well as keeping the joint material in contact with the sintered surfaces until bonding had occurred by the initiation of solid state sintering, and to enhance the sintering kinetics. Pressure aided in densification at elevated temperatures and was increased once necking has occurred, if desired. Alternatively, the pressure was after necking, when increased pressure results in unwanted reaction between the sintered surfaces and the setter material or if the strength of the sintered ceramics decreases at elevated temperature. The pressure was applied statically or was controlled with a load cell or displacement gauge.

The increase in temperature should be dictated by knowledge of how the binder was removed from the polymer so as not to damage the joint material. Joining temperature was dependent on the thickness of the joint material, the width of the joint and the removal characteristics of the polymer in the green joint material. Since the sintered surfaces will often be sintered to a state of closed porosity, it was desirable to remove the binder in the x-y plane. Thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA) was the method used for tailoring a binder removal cycle. As was common with ceramic processing, the control of the partial pressure of oxygen or air flow was used.

The joining temperature did not exceed the sintering temperature used to manufacture the sintered bodies being joined and was preferably below that sintering temperature. The reason for limiting the joining temperature was to control the grain size in the sintered bodies, since grain growth occurs at elevated temperatures and to limit the amount of creep deformation that could occur in the sintered bodies. For some applications, it was preferred to maintain the joining temperature at least 100°C below the minimum sintering temperature (i.e., the lowest temperature at which at least one of the sintered bodies sinters) of the sintered bodies so that the grain size of the previously sintered ceramic did not change or to limit creep of the components being joined. Non-limiting exemplary joining temperatures were about 1100°C. It was also possible to limit creep of the sintered bodies being joined by using spacers or packed powder beds to support the components susceptible to creep.

Joining time was less critical than joining temperature since diffusion was thermally activated and increased exponentially with temperature and only parabolically with time. Joining times were dictated by the densification of the joint and were monitored by dilatometry (shrinkage of the joint), post-sintering leak checking, or microscopy of the polished or fractured cross-sectioned joint. Preferred joining times ranged from 1 minute to 10 hours and were more preferably from 1 hour to 5 hours.

Joining in accordance with this method was conducted in multiple steps or in a single step. Multiple steps were more efficient due to use of furnaces or reaction with setters. A slower, first, joining cycle was used in a first furnace in order to remove the binder and neck the particles together under an applied pressure and a second joining cycle and furnace was used for final sintering with reduced or no external pressure. In order to avoid setter interaction, it was advantageous to use reduced pressure or no applied pressure at sintering temperatures. Setters were materials in the furnace with which the sintered bodies to be joined were in contact. The specific joining conditions were tailored to the ceramic to be joined.

It was possible to grade the composition of the joint when joining dissimilar materials or using joining tapes with different green properties to control the degree of flow in the tapes. Furthermore, it was possible to put the joint in compression or tension by controlling the thermal expansion of the joint. Assuming a biaxial stress state and looking at a sandwich structure in which two plates of thickness t_1 are joined together with a ceramic of thickness t_2 after joining, the residual stress in the joint after firing, σ_2 , was given by:

$$\sigma_2 = 2\Delta T \Delta \alpha E_1 E_2 t_1 / (2E_1 t_1 (1-\nu_1) + E_2 t_2 (1-\nu_2))$$

where ΔT was the temperature range over which stresses were set up, $\Delta\alpha$ was the mismatch in thermal expansion between the joint material and the previously sintered ceramic to be joined, E was Young's modulus, t was thickness, ν was Poisson's ratio, and the subscripts 1 and 2 referred to the sintered bodies to be joined and sintered joint material, respectively. The residual stress in the previously sintered ceramic after joining, σ_1 , was given by:

$$\sigma_1 = -t_2 \sigma_d \frac{2}{2t_1}$$

When a thin joined region was adjacent to a thicker unjoined region it was advantageous to put the joint in compression with a slight residual tensile stress in the thicker previously sintered regions. This was easily accomplished by making $\Delta\alpha$ negative (the joined region having a lower coefficient of thermal expansion than the previously sintered region). The degree of compression was controlled by the thickness of the joint and tailoring the composition of the joint material.

An example of using this method to join stoichiometric $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-d}$ sintered bodies follows:

Two hundred and fifty (250.0) grams of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ powder with a surface area of $2.0 \text{ m}^2/\text{g}$ were added to a one liter high-density polyethylene (HDPE) jar with 250 grams yttria partially-stabilized tetragonal polycrystalline zirconia (Y-TZP) spherical media, 72.8 grams reagent-grade toluene, 18.2 grams denatured ethanol (Synasol PM-509 from Ashland Chemical), and 1.25 grams polyvinyl butryal (PVB) dispersant (grade B-79 from Solutia). The slurry was put on a paint shaker for 30 minutes to disperse the ceramic powder. Plasticizer (9.64 grams grade S-160 butyl benzyl phthalate (BBP) from Ferro) and binder (18.04 grams B-98 PVB from Solutia) were added and the slip put back on the paint shaker for one hour to dissolve the binder. The slip was then mixed for 16 hours on a ball mill before filtering, de-airing, and casting with a doctor blade on a polyester sheet to make a green ceramic joining tape with a thickness of $250 \pm 25 \text{ }\mu\text{m}$ after drying. The dried tape had a solids content of 60 vol. % with a ratio of binder to plasticizer of 2.0 on a mass basis.

Ring shaped gaskets (9.5 mm i.d. by 15.8 mm o.d.) were sheared from the green joining tape. A gasket was used to join a ground $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-d}$ disk to a ground $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-d}$ ring. The disk had an outer diameter of 21 mm and was 2 to 3 mm thick. The ring had an outer diameter of 21 mm and was 2 to 3 mm thick with a 5 mm center hole. The >95% of theoretical density rings and disks were made by sintering tape cast parts at 1450°C for 2 hours. The joining surfaces of the disk and ring were ground flat. Three disk-to-ring joining couples were made. The gaskets were solvent-bonded by roll-coating with a thin layer (1-3 milligrams terpeneol/ cm^2 green tape surface area) of α -terpineol (JT Baker Practical Grade of mixed isomers) to the joining surfaces of the $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-d}$ disks and rings. The three couples were heated with 290 kPa pressure applied to the couple in a direction normal to the joining surface and with air flow (1 to 2 liters/minute) in a furnace at 5°C/hr from 20 to 150°C , 1°C/hr from 250 to 350°C , and 50°C/hr from 350 to 1250°C (with a 4-hour hold at 1250°C), and then cooled at 50°C/hr from 1250°C to 20°C . The joined parts were leak checked before cross-sectioning and polishing.

The leak rate for each couple was measured at room temperature by connecting the 5 mm hole on the ring of each couple to a vacuum source, keeping the exterior of each couple at

atmospheric pressure, establishing a pressure of <7000 kPa at that hole, and measuring the flow rate of gas exiting the couple through the 5 mm hole. The average leak rate for the three couples was 0.11 ± 0.07 standard cubic centimeters/minute (sccm) at room temperature, demonstrating that this joining method produces joints with very low leak rates. Figure 2.3.3.2-5 is a SEM image showing a polished cross-section of a joined region. The slot on the left shows the width of the joined region.

Figure 2.3.3.2-5 A SEM Image of the Further Improved Ceramic-to-Ceramic Joint

This joining method was also qualified and implemented for membrane module fabrication. An example of a commercial-size wafer SEP module that was fabricated using this joining method is shown in Figure 2.3.3.2-6.

Figure 2.3.3.2-6 Single Commercial-size Wafer SEP Module

Subtask 2.3.3.3 Sub-scale Module Fabrication for the PDU

Ceramatec began fabrication of sub-scale modules (PDU modules) as sufficient confidence in the developmental ceramic processing steps, described in Subtask 2.3.3.2, was attained. Even though the ceramic processing steps were not fully developed or optimized, sufficient quality membrane wafers, flow transition wafers, and seal blocks became available. At times, extra steps, such as wafer creep flattening or machining, were required to obtain the desired components needed for module assembly. As the ceramic processing steps were further developed, the quality and quantity of PDU modules improved.

The first PDU modules fabricated generally met the leak rate criteria. However, the air-side pressure drop was excessive. Design modifications and ceramic processing modifications were necessary to resolve the issue (see Subtask 2.3.3.1).

A key milestone in the PDU module fabrication capabilities was the development of the improved ceramic-to-ceramic joining techniques (see Subtask 2.3.3.2). The technique enabled improved fabrication yields and improved quality of the completed modules. The first multi-wafer PDU module (Figure 2.3.3.3-1) was assembled successfully using this technique.

Figure 2.3.3.3-1 Three-wafer PDU Module

During Phase 2, approximately 100 single-wafer PDU modules and 1 three-wafer PDU module were assembled.

Subtask 2.3.4 Installation of Production Development Facility

Portions of the Production Development Facility were completed during the course of this program and are described under Subtask 2.3.3.2. The major processing step not fully commissioned by September 2008 was the automated wafer assembly machine. This piece of equipment was installed and still in the commissioning phase as the DOE-funded program ended. There were also plans to install additional module-joining kilns to increase capacity and accommodate production requirements for the planned SEP project.

Subtask 2.3.5

SEP Membrane and Module Fabrication

Membrane wafers and modules were scaled-up from the PDU size to the SEP commercial wafer size as the provisional SEP wafer design was completed (see Subtask 2.3.1). The ceramic processing steps were modified as required to accommodate the new design. Examples of these modifications included:

The laser cutter was programmed for the slotted layers. The cutting conditions were optimized to get the desired quality of the featured green parts.

Isostatic lamination of the SEP wafer was optimized. Lower pressures were required during the pressing operation.

A new setter was developed to meet the SEP wafer size requirements.

The initial attempts at fabricating these SEP wafers were generally successful, which was a significant achievement given the level of scale-up in size and complexity. However, some cracking, curling and slot distortion were observed. These issues were investigated and resolved.

Improved processing methods, particularly in the development of ceramic-ceramic seals, resulted in successful fabrication of fully intact SEP membrane wafers. Analysis of the membrane wafers confirmed the feasibility of achieving the targeted leak rates.

Prototype SEP module manifold components were fabricated. Inventories of parts were maintained to allow further processing and assembly into subunits. A refined ceramic-ceramic joining process, described in Subtask 2.3.3.2, was successfully demonstrated by joining a full-size wafer to full-size interconnecting spacers and, ultimately, to the manifold components, resulting in the first SEP modules (Figure 2.3.5-1). The all-ceramic joints were formed with no increase in the leak rate of the module. The all-ceramic joining process was a key enabling technology, since it allowed the module to be made of the same ceramic composition throughout. By matching the expansion behavior of module components, stresses in the module are reduced during operation.

Additional SEP modules with commercial-size membranes were manufactured using the proprietary all-ceramic joining method. A fully intact sub-module of five full-size membrane wafers (Figure 2.3.5-2) was successfully assembled. Multi-wafer SEP modules were successfully fabricated by joining sub-modules to the manifold components. An example of a fully intact SEP module of four full-size membrane wafers is shown in Figure 2.3.5-3.

Figure 2.3.5-1 Single-wafer SEP Module

Figure 2.3.5-2 Five-wafer Sub-Module

Figure 2.3.5-3 Four-wafer SEP Module

As noted in Subtask 2.3.1, the membrane wafer design evolved to accommodate improved pressure drop and flow distribution characteristics of the wafer design. These modifications were incorporated into the ceramic processing steps. Improvements to the assembly process also continued and part dimensions and tolerances were reviewed and tightened as experience grew.

Production rates were increased in anticipation of testing requirements. Refinements to fabrication processes continued. Process variability decreased as additional automated processes were brought on-line, and several SEP modules were successfully fabricated within-specified leak rates. More than 25 single-wafer SEP modules were fabricated during the program.

TASK 2.4 NOMINAL 24 MSCFD PDU MODULE TESTING

Subtask 2.4.1 PDU Reactor Vessel Engineering and Fabrication

The ITM Syngas Process Development Unit (PDU) was designed to test wafer modules, reforming catalysts, and seals under ITM syngas commercial conditions. The PDU was used to achieve two primary objectives. The first was to provide data to validate several models used in the design and scale-up of the ITM commercial reactor. These included oxygen flux models, reforming and oxidation catalyst models, and reactor temperature profile models. The second objective was to verify the performance stability of membrane modules, seals, module assemblies, and manifolds, and to assess the effect of short-term aging on performance. A secondary objective was to evaluate operating procedures to be used in the next scale-up stage (the SEP) and in the envisioned commercial reactor.

The PDU was sized to allow testing of sub-scale modules under commercial operating conditions, including temperature, pressure and residence time. The PDU had a nominal capacity of 1000 SCFH of syngas and was capable of operating at pressures up to 420 psig and temperatures up to 950°C. The system was physically capable of testing four sub-scale PDU modules or three commercial-size, single-wafer SEP modules. The modules were arranged in series so that syngas exiting one module entered the next module. Syngas feed flow rate, temperature, and composition are varied to mimic different commercial reactor conditions.

McDermott Technology designed the reactor vessel shown in Figure 2.4.1-1. Fabrication began in May 2000, and the unit was commissioned in late 2001. The reactor was an internally-insulated and heated vessel with a design pressure of 550 psig at 343°C. The reactor had an internal diameter of 30 ¾" and was 110" long from flange to flange. The internal heaters were arranged in six separate control zones. A 13" diameter metal lining provided a barrier between the wet process gases and the internal electric heaters and insulation. The space containing the heaters and insulation was purged with a dry, inert gas. Membrane modules were installed on a beam attached to the inlet flange. There was one beam for testing up to four sub-scale PDU modules, and another for testing up to three commercial-size, single-wafer SEP modules. The flange and beam could be removed for module replacement by using a rail system. Fully assembled, the reactor weighed approximately seven tons. The vessel was heavily instrumented to gather important data for assessing the technology. Figure 2.4.1-2 is a photo of the reactor inlet and the beam supporting four PDU modules.

Figure 2.4.1-1 Reactor Vessel Design – Side View

Figure 2.4.1-2 Photo of the Reactor Vessel and Module Housing Beam

The reactor was in an enclosure (Figure 2.4.1-3) which was purged with nitrogen during operation. The effluent from this enclosure was monitored for carbon monoxide. If any carbon monoxide was detected, the system would initiate a controlled shutdown.

Figure 2.4.1-3 Photo of the Reactor Enclosure Showing Reactor and Inlet Piping

Subtask 2.4.2 Construct and Commission PDU

Balance of Plant

The commercial ITM process may have 100 or more rows of membrane modules arranged in series, with heat generation and methane conversion per module being very low. This is done to limit the heat generated in each module. The scope of the PDU was to simulate the stream conditions of various commercial reactor sections, each consisting of only a few modules. Tube trailers supplied the syngas feed, which can be blended to mimic any gas composition within a commercial reactor. Exhaust gases were directed to a thermal oxidizer. The 1000 SCFH PDU flow capacity was set by the desire for similar syngas and air flow per unit wafer as would be experienced in the envisioned commercial reactor.

Figure 2.4.2-1 shows a block diagram of the PDU process, with each block representing a unit operation. Combustion-heated air was simulated by using the air feed blending system. This mixture was normally heated to the desired temperature and directed to the ITM reactor. In a similar way, the syngas feed was mixed with steam, heated to the desired temperature, and directed to the reactor. The two streams flowed across their respective sides of the ITM membrane in the reactor. The oxygen that passes through the membrane reacted with the gas components on the syngas side to form combusted or partially oxidized products. These products reformed as they passed over the catalyst impregnated in the porous layer of the membrane wafer and/or through the reforming catalyst bed. After passing through four module-catalyst sets, the product gases exited the reactor and were cooled. The streams were converted to full combustion products in a thermal oxidizer and vented to atmosphere.

Figure 2.4.2-1 Process Diagram for the PDU

Air Supply

Air feed was supplied from a rotary screw compressor system that included a pressure swing drier. Air from the system was essentially free of carbon dioxide and had a water dewpoint of <40°C. Nitrogen, carbon dioxide and water could be added to the air system to simulate the composition resulting from direct-fired heating of the air in a commercial facility.

To ensure that PDU operation continued in the event of a single membrane or seal failure, each wafer module had an independent air supply. Once the air feed was blended, it was split into four separate streams and sent to the reactor. A mass flow controller and a set of shutoff valves were used to control each of these process air streams. When the safety shutdown system identified a module failure, the individual air feed and exit lines for that module were closed, isolating the module.

All flow and pressure controls were located inside a ventilated panel. The carbon monoxide content of the panel atmosphere was measured to monitor for leaks. The panel was located close to area monitors so that any release of carbon monoxide or flammables could be rapidly detected.

An electric furnace was used to bring the four process air streams to the reactor operating temperature. The exit temperature of the process air from this heater typically ranged between 750°C and 950°C and varied depending on the test to be performed. The 48" long, single-zone furnace supplied 28 KW heating and was rated for a maximum operating temperature of 1100°C. A Haynes 230 coil (½" ID, 0.083" thick) was used for heating the process air.

Water Supply

Water could be fed to both the air and syngas feed systems. The water quality requirements were very stringent, based on the high reactor operating temperatures and membrane compatibility. The packaged water treatment system included a carbon filter, water softener, reverse osmosis unit, and ion-exchange beds.

Purified water was pumped to 500 psig and supplied to either the air heater or process gas steam heater. Water for the air heater was passed through a tube in the air heater to generate steam, which was injected into the air stream. The mixture was then further heated to operating temperature. The steam heater boiled high-pressure water to be blended with the dry syngas feed. The steam heater supplied 25 KW of heating and was rated for 1100°C.

Syngas Supply

Achieving a syngas velocity similar to that planned for a commercial reactor required a significant amount of feed gas. For this reason, tube trailers were needed to supply feedgas to the PDU. The composition of the gas in the trailers varied depending on the section of the commercial reactor to be simulated. In early PDU trials, only one tube trailer was available to supply a mixed syngas feed. These mixtures contained varying amounts of hydrogen, methane, carbon monoxide, and carbon dioxide. Separate methane and hydrogen supply trailers were added in later trials for greater flexibility in setting reactor feed gas compositions. The maximum dry flow the PDU was designed to handle was 1000 SCFH.

All syngas feed controls were located in a purged enclosure. The control panel was continuously purged with nitrogen and the vent gas was monitored for carbon monoxide. If carbon monoxide was detected in the enclosure, the system would start a controlled shutdown.

Dry syngas feed and steam from the steam heater were mixed together, heated to 850 to 900°C in the syngas heater, and then fed to the reactor. If the process gas required further heating, it was heated inside the reactor. The syngas heater tubing was placed inside a nitrogen-purged metal can. In the event that a coil failure occurred, the feedgas would be contained in the can. The effluent from this enclosure was monitored for carbon monoxide. The system would enter a controlled shutdown if carbon monoxide was detected.

Water Quench

The water quench tank was divided into three sections. One section cooled the syngas stream from the reactor and the exit temperature of the syngas was controlled by adjusting the water level in this section. This same method was used in a second chamber, which cooled the non-permeate air streams. The third section was included solely for safety reasons. Blockage in the feed gas stream or a membrane break could cause a backflow of hot gases. The temperature of

these hot gases exceeded the temperature rating of the instrumentation in the feed system. In order to avoid damaging this instrumentation, the streams coming from the panels passed through the quench tank before going to the heaters. In case of backflow, these streams would be cooled before reaching any section of the panel. The quench tank was continuously purged with nitrogen in case of any undetected leak in the syngas coil.

Thermal Oxidizer Section

All the streams exiting the ITM syngas reactor were sent to a thermal oxidizer. The syngas stream was directed to the combustion chamber. Because the syngas stream had a low heating value, a supplemental fuel was used to stabilize the flame in the thermal oxidizer. Originally, as shown in Figure 2.4.2-1, fuel oil was to be used. However, the final design used natural gas to simplify the system. All other non-flammable streams were fed into the stack at elevated locations. These included steam from the quench tank, vent purges, enclosure purges and non-permeate air streams.

Analytical Equipment

The PDU used mass spectrometry to analyze the process gas samples. Analysis was rotated amongst sample points: air feed, non-permeate air, dry syngas feed, syngas inlet and outlet of each module, syngas exiting the reactor. The samples were analyzed for carbon monoxide, carbon dioxide, methane, hydrogen, oxygen, nitrogen, and argon.

The reactor, all purged enclosures, and lab space were monitored with carbon monoxide, oxygen, and flammable gas analyzers to ensure that there were no undetected leaks during operation.

Construction and Commissioning

The PDU was installed in the Air Products high-bay labs. Construction was completed in mid-2001, and initial commissioning was completed by late 2001. This initial commissioning entailed checking instrumentation, ensuring all process lines were in accordance with the process and instrumentation diagrams, completing all hazard review action items, and ensuring proper functioning of all equipment. Shakedown dry-runs were conducted to verify that all the equipment and controls performed as intended. Additional system shakedown was completed during the initial runs that are described in detail under Subtask 2.4.3.

Subtask 2.4.3 Test Sub-Scale Modules

Subtask 2.4.3.1 PDU Run 1

Objectives

The objectives of this run were to demonstrate the following: (a) successful installation of PDU modules into the housing assemblies; (b) successful startup of a PDU module; and (c) ceramic-to-metal seals.

The objectives did not include oxygen flux measurements because the modules tested had large air-side pressure drops. This made it impossible to flow a significant amount of air given the available pressure from the air compressor. These were some of the first modules produced at Ceramatec and, at the time, these internal restrictions were not well understood.

Results and Discussion

Equipment and Modules

This run was the first attempt to test PDU modules. This was also the first attempt to assemble the module housings, beam piping, and ceramic-to-metal seals. Two modules were assembled and installed on the beam. Both modules were installed with a ceramic-to-metal seal design consisting of a double U-ring with a spacer, a gold wire ring and double gold gasket. There was no catalyst on the modules.

Two approaches were taken on assembling the modules in the housings. With Module 1, larger gaps were left between the metal housing and the module to prevent interference issues. This was at the expense of increased syngas bypass. Module 2 was installed with tighter clearances to the metal housing in order to decrease flow bypass at the expense of increasing the risk of membrane breakage due to ceramic-metal interference. Both modules survived the housing assembly process and were successfully installed in the reactor.

Module and Seal Performance

Less than 5 percent of the design air flow rate was achieved because of high air-side pressure drop through the modules. These modules were known to have significant resistances in the air-side channels. It would have required more than 700 psi to flow at the designed rates. A program (Subtask 2.3.1) was established to identify and correct this issue by redesigning the module internals.

Because of the limited air flow through the modules, it was decided to use nitrogen on the syngas-side of the membrane. This prevents over-reduction of the membranes from lack of air-side oxygen. For this reason, oxygen flux was not measured during this run.

The modules survived startup to approximately 300°C and 80 psig syngas pressure. At this point, the run was interrupted by a lighting strike that shut down and depressurized the reactor. Both modules survived the shutdown, but the leak rate of Module 2 was so significant that it had to be isolated. The run was restarted and Module 1 was successfully heated to 850°C.

During operation at 850°C, it was observed that the process gas cooled down significantly between the syngas heater and the reactor. The temperature drop was approximately 300°C in only 12 feet of piping. All flows to the reactor were stopped in order to investigate the heat losses in the system. The system lost pressure overnight, causing Module 1 to lose its seal and fail. Repeated attempts to seal the module were unsuccessful.

The run was operated at different nitrogen flow rates to evaluate the pressure drop across the syngas-side of the modules. As expected, the pressure drop across Module 1 was negligible due to the large gaps between the module and the metal housing, while a larger pressure drop was observed across Module 2.

Many challenges were overcome to minimize the stresses created by the differential thermal expansion of ceramic and metal parts. The design proved to be successful, and the ceramic modules were sealed at temperature. This was indicated by the initial seal of Modules 1 and 2. Heat management around the PDU needed to be addressed. Excessive heat losses were observed and corrective actions were planned for subsequent runs.

Subtask 2.4.3.2 PDU Run 2

Objectives

The Run 2 objectives were to (a) demonstrate modifications to improve system heating and heat loss; (b) demonstrate successful startup of a PDU module; (c) demonstrate ceramic-to-metal seals; and (d) measure oxygen flux through a PDU module.

Results and Discussion

Equipment and Modules

In PDU Run 1, significant heat loss was observed on the lines leading from both the air and syngas heaters to the reactor. For Run 2, line heaters were added near the reactor inlet to increase the temperature to the as-designed level. Additionally, a 20-foot coil of tubing was added to the syngas feed line within the reactor. The reactor heaters could then provide additional heating of the syngas stream prior to being fed to the first module.

Four modules were installed in the reactor, all of which had air-side pressure drops that exceeded the design. Roughly 5 to 10 percent of the design air flow could be passed through the module.

Module and Seal Performance

After the system was heated to 850°C, Modules 1, 3, and 4 showed good ceramic-to-metal seals. Module 2 initially had a large leak that decreased with increasing temperature and pressure. Figure 2.4.3.2-1 shows the leak rate as a function of system temperature and pressure.

Figure 2.4.3.2-1 Module Seal Leaks Versus Time

Post-test inspection of the ceramic-to-metal seals indicated that the leak on Module 2 may have been caused by interference between the U-ring and the ceramic seal block. The gold wire on one of the seal legs had come loose and overlapped the U-ring (Figure 2.4.3.2-2).

Figure 2.4.3.2-2 Air Piping and Seals Post-Operation

System heat-up went well, and the new syngas and air line heaters provided sufficient energy to reheat the gases prior to entering the reactor. A leak check of the reactor was performed after the system had reached operating temperature. A number of leaks were found, so the reactor was depressurized for repair. When the system was repressurized, it was found that Modules 1, 2, and 3 maintained their seals but Module 4 had lost its seal. After several failed attempts to seal Module 4, this module was isolated.

With the system at 850°C and 100 psig nitrogen on the syngas-side, air was introduced to the modules. The air supply was maintained at 40 psig so that the pressure differential across the U-ring seals would always load the gold washer seal. Soon after the air was introduced, the membranes exhibited a continuous increase in the leak rate and Modules 1, 2, and 3 eventually failed. An attempt to increase the pressure and force the U-ring to seal was unsuccessful. Figure 2.4.3.2-3 shows the leak history of the modules.

January 28-29. Seal loss

Figure 2.4.3.2-3 Seal Leaks Versus Time

Analysis suggested that the failures of Modules 1, 2, and 3 were likely caused by thermal and/or chemical shock after the air feed was introduced. It appeared less likely that failure of the ceramic-to-metal seals caused the module failures. Prior to air introduction, the air side of the modules likely contained primarily nitrogen at reactor temperature. When air was introduced, the cooler air feed and sudden increase in oxygen content may have shocked the module. The procedures were updated to initiate the air feed prior to heating the modules.

Subtask 2.4.3.3 PDU Run 3

Objectives

The objectives of Run 3 were to (a) demonstrate successful installation of PDU modules into the housing assemblies; (b) demonstrate successful startup of a PDU module; (c) demonstrate ceramic-to-metal seals; and, (d) measure oxygen flux through a PDU module.

Excessive heat loss in the system limited operation to approximately 830°C at 200 psig. Run objectives were to be evaluated at these conditions.

Results and Discussion

Equipment and Modules

Three PDU modules and a PDU seal block without an active wafer were installed in the reactor. The air-side pressure drop on all modules was low enough that air could be fed to the modules at the design flow rate. The seal block was installed only to demonstrate performance of the ceramic-to-metal seals.

Two different housing assemblies were also tested. Housing 1 was assembled with the PDU module clearances of 0.004" on the bottom and 0.095" on the top. For Housings 2 and 3, the PDU modules were assembled with bottom and top clearances of 0.004". Table 2.4.3.3-1 lists the arrangement of the modules and seal block in the housings.

Table 2.4.3.3-1 Module Arrangement and General Information for Run 3

Module	Location	Comments
PDUM-23	Housing 1	0.004" clearance between bottom of wafer and housing 0.095" clearance between top of wafer and housing
PDUM-18	Housing 2	0.004" clearance between bottom of wafer and housing 0.004" clearance between top of wafer and housing
PDUM-19	Housing 3	0.004" clearance between bottom of wafer and housing 0.004" clearance between top of wafer and housing
SB-79	Housing 4	Seal block only (no wafer)

Module and Seal Performance

The modules in reactor Housings 2 and 3 failed during heat-up at approximately 410 to 460°C and 65 psig. The failures were attributed to the tighter clearances in Housings 2 and 3. Warping of metal parts during heating or differential thermal expansion between the module and surrounding housing could more easily have led to interference problems in those housings. Figure 2.4.3.3-1 shows an example of the warping that occurred during this run. This machined part is from above the PDUM-18 module in Housing 2. This amount of warping far exceeds the 0.004" clearance above the module.

Figure 2.4.3.3-1 Photo of Machined Housing Part Showing Warping After Operation

Modules PDUM-23 (Housing 1) and SB-79 (Housing 4) both survived heat-up to 830°C, pressurization to 200 psig, and introduction of steam on the syngas side. At these conditions, an oxygen flux of 0.3 to 0.4 sccm/cm² was measured on PDUM-23. As syngas was introduced to the system, the oxygen flux began to increase. Within 30 minutes of adding the syngas, the oxygen flux had increased to 0.9 sccm/cm², but a 580 sccm leak had developed. Less than an hour after syngas introduction, the oxygen flux was 1.4 sccm/cm² and the leak was 1950 sccm. The module failed soon thereafter. Figure 2.4.3.3-2 shows the concentrations of air exit oxygen and carbon dioxide during this period. The oxygen concentration decrease was used to calculate the oxygen flux. The carbon dioxide values were used to calculate the leak from the carbon-containing syngas stream into the carbon-free air feed.

Figure 2.4.3.3-2 Air Exit Oxygen and Carbon Dioxide Concentrations Versus Time

During heat-up, pressurization, and steam introduction, the ceramic-to-metal seals on all modules and the seal block performed well. The failure of the modules is unlikely due to the performance of these seals. The ceramic-to-metal seal for the seal block in Housing 4 maintained its leak-free operation during the entire run.

The overall heat loss of the system remained unacceptably high, limiting the operation to 830°C at 200 psig. Also, one half of the first heater zone failed during the run. Operation was then limited to approximately 780°C at 200 psig.

Post-Test Inspection

PDUM-23 was the last of three modules to fail during this PDU run. The failure occurred shortly after syngas was introduced. The module's P-core porosity was approximately 36.5%, and the module had a total leak rate of 0.388 sccm. Following the run, PDUM-23 was analyzed with SEM/EDS. Traces of chromium were found near the air inlet and within the air manifold of the active wafer near the air inlet. Molybdenum was also occasionally observed. However, chromium and molybdenum were not found farther downstream into the module. Significant levels of Fe-, Ca- and Si-rich phases were also observed within the air inlet and air manifold of the active wafer.

A loosely-adhered dark powder was observed on the outer surfaces of the module. This powder was found to contain a Ca-Fe-Si-rich phase as well as tungsten and molybdenum impurities.

Due to the way in which the powder was bonded to the surface, the phases were probably from an upstream source rather than the membrane. The chromium, molybdenum and tungsten impurities were likely from the alloy-containing components of the PDU.

Optical microscopy was also used for analysis. Several cracks were observed on the rim and air manifold of the active wafer. Some of these cracks extended into the porous body. Most of the cracks appeared to have initiated from the outside edge of the active wafer.

Subtask 2.4.3.4 PDU Run 4

Objectives

The Run 4 objectives were to (a) demonstrate successful startup of a PDU module; (b) demonstrate ceramic-to-metal seals; and (c) measure oxygen flux through a PDU module.

Results and Discussion

Equipment and Modules

Four PDU modules were installed in the reactor. The air-side pressure drop on all modules was low enough that the design air flow could be attained. The clearances between the modules and the housings were increased to minimize the possibility of interference. Table 2.4.3.4-1 lists the arrangement of the modules in the housings.

Table 2.4.3.4-1 Module Arrangement and General Information for Run 4

Module	Location	Comments
PDUM-28	Housing 1	0.008" clearance between bottom of wafer and housing 0.050" clearance between top of wafer and housing Removed side shims to increase clearances
PDUM-26	Housing 2	0.031" clearance between bottom of wafer and housing 0.150" clearance between top of wafer and housing Removed side and top shims to increase clearances S-Seal installed on leading and trailing edges
BK-2	Housing 3	0.008" clearance between bottom of wafer and housing 0.090" clearance between top of wafer and housing Removed side and top shims to increase clearances
PDUM-24	Housing 4	0.008" clearance between bottom of wafer and housing 0.090" clearance between top of wafer and housing Removed side and top shims to increase clearances

Module and Seal Performance

All four modules survived heat-up to 900°C and pressurization to 70 psig. During introduction of steam into the syngas-side flow, the modules in Housings 1, 2, and 3 failed. Steam had condensed in the piping exiting the steam heater. The water then vaporized in the syngas heater and caused a surge of flow to the reactor. This increased flow thermally shocked the modules.

PDUM-24 in Housing 4 survived steam introduction, and for the first time operated for an extended period of time under syngas. This success was due in part to significantly slower syngas introduction compared to previous runs. Additionally, multiple-day holds were used following heat-up and initial syngas introduction to allow for creep relaxation of the modules.

Data collected on PDUM-24 in Housing 4 was limited to an operating temperature of approximately 800°C because of reactor heater failures during the run. PDUM-24 operated under full syngas/steam conditions for 24 days. Decay in oxygen flux was observed during the test period. Despite a significant leak developing during the final cooldown, PDUM-24 was successfully shut down. Figure 2.4.3.4-1 shows the history of the module performance.

Figure 2.4.3.4-1 Operating Performance Data for Run 4

The apparent activation energy for oxygen flux was calculated using data under constant composition and varying temperature (Figure 2.4.3.4-2). The activation energy of 83.4 kJ/gmole is approximately two times greater than measured on earlier ITM test parts (~44 kJ/gmole). Surface contamination, kinetic demixing, and surface oxidation kinetics are potential reasons for the discrepancies.

Figure 2.4.3.4-2 Run 4 Oxygen Flux Versus Temperature Data Used to Calculate the Oxygen Transport Activation Energy

The ceramic-to-metal seals performed well on all modules during the heat-up and pressurization steps. The seal leaks on PDUM-24 were low throughout the testing period, but showed a modest increase during the syngas removal portion of the shutdown (Figure 2.4.3.4-3). A significant leak developed on PDUM-24 during the final cooldown temperature ramp at 435°C.

Figure 2.4.3.4-3 PDUM-24 Leak Rate Versus Time

Post-Test Inspection

PDUM-24 was the sole surviving module from PDU Run 4. The module's P-core porosity was 34.2%, the gap height was 0.061", and the module was hermetic before testing. Following the PDU run, the syngas- and air-side surfaces of the active and FT wafers were analyzed with SEM/EDS.

Silicon contamination was observed on the syngas-side surfaces. The source of silicon was likely the silicon contained in the metal components, which reacted with steam to form $\text{Si(OH)}_4(\text{g})$. This gas then reacted with the membrane to produce a variety of Si-rich phases.

A potential solution to mitigate silicon contamination was to use either magnesium oxide or calcium carbonate as silicon getters. Ideally, magnesium oxide or calcium carbonate will quickly react with the silicon vapors to form a stable silicate. These "sacrificial beds" will be strategically located in the flowing syngas stream.

Chromium contamination was observed on the air-side surfaces. The source of chromium was most likely the hot metal tubing leading to the seal block, which has a high vapor pressure of CrO_3 over it. This volatile chromium species then reacted with the membrane to produce Cr-enriched I4 and calcium chromate, among other products.

A potential solution to mitigate chromium contamination was to use magnesium oxide as a chromium getter. Ideally, magnesium oxide will quickly react with the chromium vapors to form a stable chromite. These "sacrificial beds" will be located in the air-feed tubing, with some as close to the seal block as possible.

The air-feed Haynes 230 tubing will be replaced with Haynes 214, an alumina former, before PDU Run 6. The vapor pressure of CrO_3 over Haynes 214 should be significantly less than that over Haynes 230, thus reducing the amount of chromium contamination. Alloy coating technologies were also investigated.

Iron oxide was observed on air-side surfaces of the permeating dense layers. Most of the observed iron oxide is a likely product of demixing, since the membrane operated above 900°C. Calcium chromate was likely produced from the reaction between $\text{CrO}_3(\text{g})$ and a Ca-rich phase resulting from I4 Ca-excess and/or demixing. These conclusions were based on a microstructure comparison between permeating and non-permeating layers within the S1 slots, where the mass transfer properties over each layer were the same. The non-permeating layer had significantly less iron oxide and no chromium impurities. It should be recognized, however, that these were different layers within the module that may vary slightly in composition and may, therefore, react differently.

Equipment Performance

Heat leak and heater failures continued to be problem. The system needed to be operated at low pressures just to achieve 800°C. At 200 psig, the system operated at less than 800°C. The

heaters will be replaced prior to the next PDU run and the insulation system will also be re-designed to minimize heat leak.

The nickel content of the high-temperature metals used in the PDU resulted in reforming of methane in the syngas feed. This will need to be addressed in future runs.

Subtask 2.4.3.5 PDU Run 5

Objectives

The objectives of Run 5 were to (a) demonstrate modifications to improve reactor heating and heat loss; (b) demonstrate the high pressure nitrogen feed system; (c) demonstrate a reduction in silicon contamination with the new water purification system; (d) demonstrate the successful startup of a PDU module; (e) demonstrate ceramic-to-metal seals; and (f) measure oxygen flux through a PDU module.

Results and Discussion

Equipment and Modules

The failure of the reactor heaters in previous runs required complete rebuilding of the reactor heater and insulation system. There was no definitive cause of the heater failures, so several changes were made in hopes of preventing future failures. With higher-than-design heat leak, the original heaters were operating at nearly full output. Therefore, the reactor heater capacity was increased from 11 kw to 30 kw. In addition, the insulation system was modified to reduce the heat leak. Per the manufacturer's recommendation, the heater elements were pre-oxidized to develop a protective aluminum oxide layer. Finally, argon replaced nitrogen as the reactor heater zone purge gas to prevent the possibility of aluminum nitride formation.

High temperature heat tracing was installed on the line from the steam heater to the syngas heater. In PDU Run 4, steam condensed in this line and then flashed in the syngas heater, resulting in a thermal shock that caused the modules to fail. A high-pressure nitrogen system was installed to allow startup under nitrogen at pressures greater than 80 psig.

The water purification skid was upgraded to a system that was more reliable and produced higher-quality water. Ion-exchange beds were included in the new system to minimize the amount of silicon contaminant in the feed to the process.

Of the four PDU modules installed in the reactor, two had the porous layers impregnated with a bimetallic precious metal catalyst. Table 2.4.3.5-1 lists the arrangement of the modules in the housings.

Table 2.4.3.5-1 Module Arrangement and General Information for Run 5

Module	Location	Housing Style	Comments
PDUM-29	Housing 1	Standard	2 gasket ceramic-ceramic seals
PDUM-31	Housing 2	S-Seal	2 gasket ceramic-ceramic seals
PDUM-33	Housing 3	Standard	Single piece ceramic-ceramic seals Bimetallic precious metal catalyst
PDUM-34	Housing 4	S-Seal	Single piece ceramic-ceramic seals Bimetallic precious metal catalyst

Module and Seal Performance

The two catalyzed modules failed during heat-up with 70 psig nitrogen on the syngas side. Both modules failed within six minutes of each other at a temperature of approximately 345°C. The two non-catalyzed modules were successfully heated to 900°C, pressurized to 215 psig, and transitioned to a steam/syngas feed. The new steam heat tracing system worked well, preventing the condensation that caused the failure of three modules in PDU Run 4. The startup took 27 days.

The maximum flux for this run was observed at 905°C during the initial introduction of steam and syngas. During this period and for several days thereafter, the oxygen flux rapidly decayed by 25 to 30 percent. Although this decay continued, it was significantly less after the first few days. The modules were operated for 20 days at 215 psig and temperatures ranging from 825 to 905°C. As the system was being pressurized, module PDUM-31 failed at 343 psig. Module PDUM-29 was successfully operated at full design conditions of 425 psig, 900°C, and 1000 SCFH dry syngas feed. Despite a modest increase in the leak rate at 400°C during the cooldown, PDUM-29 was successfully shut down. The shutdown process took 22 days. Figure 2.4.3.5-1 shows the module performance over the operating period.

Figure 2.4.3.5-1 Module Performance Data for Run 5

The apparent activation energy for oxygen flux was calculated using data under constant composition and varying temperature (Figure 2.4.3.5-2). Data gathered during the initial period of rapid oxygen flux decay was ignored. Apparent activation energies of 90.9 kJ/gmol and 113.6 kJ/gmol were calculated for PDUM-29 and PDUM-31, respectively. These results were somewhat consistent with the activation energy measured of 83.4 kJ/gmol measured on PDUM-24 in Run 4. However, it was two to three times greater than the activation energy measured on earlier ITM test parts (~44 kJ/gmol). Surface contamination, membrane demixing, and surface oxidation kinetics were potential reasons for the discrepancies.

Figure 2.4.3.5-2 Run 5 Oxygen Flux Versus Temperature Data Used to Calculate the Oxygen Transport Activation Energy

The ceramic-to-metal seals again performed well, as shown in Figure 2.4.3.5-3. Modest leaks were observed during transition periods of heating/cooling and composition changes, but the leak rates were very low. Maximum leak rates of 7 to 10 sccm were significantly lower than the peaks of 200 to 400 sccm observed in Run 4.

Figure 2.4.3.5-3 Module Leak Rates Versus Time

Post-Test Inspection

PDUM-29, located in Housing 1, operated and survived the entire run, including the shutdown cycle. It had measurable flux, low leak rates, and was exposed to a significant P_{O_2} gradient at 900°C for 30 days. Following the PDU run, the syngas- and air-side surfaces of the active and FT wafers were analyzed with SEM/EDS. A variety of secondary phases were found, including tungsten- and silicon-rich phases on the syngas-side surfaces and chromium- and iron-rich phases on the air-side surfaces.

Tungsten and silicon contamination were observed on the syngas-side surfaces. The source of tungsten was the Haynes 230 metal components, which contained approximately 14 wt% tungsten. The tungsten reacted with steam to form $(OH)_2WO_2(g)$. The source of silicon was also the hot metal components. The silicon reacted with steam to form $Si(OH)_4(g)$. These vapor species then reacted with the membrane to produce a variety of W-rich and Si-rich phases.

The outer surfaces of the P-layers were so heavily contaminated with tungsten that the pores were hardly visible. This tungsten layer was several microns thick, and the tungsten penetrated ~25 μm below the outer surface. Little or no contamination was observed below the ~25 μm penetration zone.

A potential solution to mitigate tungsten and silicon contamination during future PDU runs will be to use Cu-plated or Cu-lined metal components. Magnesium oxide guard beds also continue to be investigated. Ideally, the magnesium oxide beds would react quickly with the tungsten and silicon vapors to form a stable magnesium tungstate and silicate, thus reducing the $(\text{OH})_2\text{WO}_2$ and $\text{Si}(\text{OH})_4$ partial pressures by several orders of magnitude. In addition, tungsten-free alloys and/or coating technologies may be used.

Chromium contamination was observed on the air-side surfaces. The source of chromium was the hot metal tubing leading to the module, which had a high P_{CrO_3} over it. This vapor species then reacted with the membrane to produce Cr-enriched I4 and calcium chromate, among other products. The air outlet channels of the module showed no detectable chromium, suggesting that the module successfully scrubbed the chromium vapors during the entire operating period.

A potential solution to mitigate chromium contamination in future PDU runs will be to use both magnesium oxide guard beds and Diffusion Alloys aluminizing coating on all air-side tubing. The guard beds will be located in the air feed for two of the four modules. Ideally, the magnesium oxide beds will react quickly with the chromium vapors to form a stable chromite, thus reducing the CrO_3 partial pressure by an order of magnitude. Our initial studies show that magnesium oxide can successfully scrub chromium vapors from flowing air at 900°C.

Some of the iron oxide observed on the air-side surfaces probably resulted from kinetic demixing. The membrane operated at 900°C, a temperature at which kinetic demixing is likely to occur. This conclusion was also based on a microstructure comparison between the permeating D-layers and non-permeating slotted layers, where the latter had significantly less iron oxide. Some of the iron oxide was a likely byproduct of cation exchange between I4 and chromium species.

Enhanced kinetic demixing may have also occurred based on the observed contamination: W-Ca and Si-Ca on the syngas-side, and Fe/Cr cation exchange on the air-side. These contamination reactions may increase the iron chemical potential gradient through the membrane, thus enhancing the kinetic demixing process.

Equipment Performance

With the original reactor insulation package and the 11 kw heater, the reactor was unable to reach 900°C at the design pressure of 425 psig. The heat loss increased dramatically with pressure, resulting in both reactor shell temperature and heater output reaching their maximum limit at approximately 200 psig. In an effort to reach design pressure and temperature, the reactor heater capacity was increased from 11 kw to 30 kw, and the insulation system was modified to reduce the heat leak.

Figure 2.4.3.5-4 shows the performance of the original and new reactor systems. The data for the original system was at an internal temperature of 800°C; for the new system, the internal temperature was 900°C. A pressure effect on the heat leak still existed, but was significantly reduced. The reactor was now capable of reaching the design temperature and pressure without exceeding the allowable shell temperature or heater output.

Figure 2.4.3.5-4 Reactor Insulation System Performance – Original Versus Modified

Despite changes to improve the reliability of the reactor heaters, the heater below Housing 1 failed early in the run. The loss of this heater hindered, but did not limit, subsequent operation.

The nickel content of the high-temperature metal components in the PDU resulted in methane reforming in the syngas feed. Figure 2.4.3.5-5 shows how a syngas feed of 46% CH₄ reacted to 6% CH₄, nearly at equilibrium, by the time the feed reached the membrane modules. This limited the ability of the system to test a wide range of compositions. Future PDU runs will need to investigate the use of linings and coatings to minimize this reaction.

Figure 2.4.3.5-5 Composition Profile Across the Syngas Heater and the Membrane Modules

Subtask 2.4.3.6 PDU Run 6

Objectives

The objectives of Run 6 were to (a) demonstrate reduced membrane contamination through the use of coatings, linings, and guard beds; (b) demonstrate reduced reaction with hot metals through the use of coatings and linings; (c) demonstrate successful startup of a PDU module; (d) demonstrate ceramic-to-metal seals; and (e) measure oxygen flux through a PDU module.

Results and Discussion

Equipment and Modules

In previous runs, a variety of secondary-phase contaminants were found including tungsten- and silicon-rich phases on the syngas-side surfaces, and chromium- and iron-rich phases on the air-side surfaces. To address contamination on the syngas-side, all syngas-side tubing upstream of the membranes was lined with high-purity copper using a hydro-forming technique. The module housing parts were either plated or lined with copper. Figure 2.4.3.6-1 shows a module housing assembled with copper parts.

Figure 2.4.3.6-1 Photo of Housing Parts Made of High-Purity Copper

To address contamination on the air-side, an aluminizing coating was applied to the upstream Incoloy 800H tubing. Additionally, magnesium oxide guards were installed for two of the four modules (Figure 2.4.3.6-2). The magnesium oxide reacts quickly with the chromium vapors to form a stable chromite, thus reducing the CrO_3 partial pressure by an order of magnitude.

Figure 2.4.3.6-2 Photo of Air-side Guard Bed (Two Cylindrical Vessels in Series)

The nickel content of the high-temperature metal components in the PDU resulted in reforming of methane in the syngas feed. The copper lining and plating used to minimize syngas-side contamination was also expected to reduce the extent of the reforming reaction.

Four non-catalyzed PDU modules were installed in the reactor. Table 2.4.3.6-1 lists the arrangement of the modules in the housings.

Table 2.4.3.6-1 – Module Arrangement and General Information for Run 6

Module	Location	Comments
PDUM-44	Housing 1	Not catalyzed Air-side guard bed
PDUM-45	Housing 2	Not catalyzed
PDUM-47	Housing 3	Not catalyzed Air-side guard bed
PDUM-48	Housing 4	Not catalyzed

Module and Seal Performance

All four membrane modules were successfully heated to 900°C, pressurized to 215 psig, and transitioned to steam/syngas feed. Significant leaks developed on all the modules during heating at approximately 595°C, but most had sealed by the end of heating and pressurization. During steam/syngas introduction, leaks again developed and led to isolation of the modules in

Housings 2 and 3. Module leaks in Housings 1 and 4 led to excessive water in the air lines, limiting the amount of steam/syngas to approximately 30 percent of the total flow. The modules in Housings 1 and 4 operated for more than 30 days.

The maximum oxygen flux was measured for the module in Housing 1 at 910°C, 105 psig, and 30% syngas flow. This was the first time that the measured PDU oxygen flux was consistent with commercial targets. Under similar operating conditions, the oxygen flux for the module in Housing 4 was significantly lower but was consistent with this module's thicker, lower porosity porous layer. The PDU was successfully ramped from 900°C to 825°C and back up to 900°C without any significant oxygen flux degradation. Little or no oxygen flux degradation was observed in the initial phases of this run. This improvement over past runs was attributed to contamination reduction through the use of coatings, linings, and guard beds. Figure 2.4.3.6-3 shows the reduction in oxygen flux degradation versus the PDU Run 5. Figure 2.4.3.6-4 shows the history of module performance in PDU Run 6.

Figure 2.4.3.6-3 Comparison of Oxygen Flux Degradation Between Runs 5 and 6

ITM Syngas PDU Run 6 History

Figure 2.4.3.6-4 Module Performance Data for Run 6

The apparent oxygen transport activation energy was calculated using data gathered under conditions of constant composition and varying temperature (Figure 2.4.3.6-5). An apparent activation energy of 161.3 kJ/gmol was calculated for PDUM-44. This value was higher than the activation energies measured in previous PDU runs (83 to 114 kJ/gmol) and more than three times greater than the activation energy measured on earlier ITM test parts (~44 kJ/gmole). Surface contamination, membrane kinetic demixing, and surface oxidation kinetics may account for the discrepancies.

Figure 2.4.3.6-5 Run 6 Oxygen Flux Versus Temperature Data Used to Calculate the Oxygen Transport Activation Energy

During this run, the ceramic-to-metal seals did not perform as well as in previous runs. During heat-up in nitrogen at 70 psig, leaks of ~1300 sccm developed in modules in Housings 1 and 2. These leaks were twice as large as the leaks experienced in previous runs. The module in Housing 4 had a smaller leak that was more typical of the previous runs. Good seals were established on all the modules by the end of heat-up.

Module leaks developed again when steam and syngas were introduced, as shown in Figure 2.4.3.6-6. Leaks in the modules in Housings 2 and 3 lead to excessive water in the air lines and the isolation of the modules. To avert problems with the remaining modules in Housings 1 and 4, the syngas-side pressure was reduced and some of the steam/syngas flow was replaced with nitrogen.

Figure 2.4.3.6-6 Module Leak Rates Versus Time

Post-test inspection of the seals revealed that the unusual behavior and size of the leaks in this PDU run were caused by an interaction of the air-side gold washers (used in the ceramic-to-metal seals) with the new aluminizing coating on the air tubing. Further investigation showed that alumina and gold formed a low-melting-point mixture that led to the loss of washer material in the seal region and caused the leaks. In future runs, the coating will be removed from areas that contact the gold washers.

Post-Test Inspection

PDUM-44, in Housing 1, operated for most of Run 6 and was exposed to a significant P_{O_2} gradient at $\sim 900^\circ\text{C}$ for 30 days. At 910°C , this module achieved a record oxygen flux, consistent with commercial targets, and had significantly improved flux stability compared to modules from previous runs. The module was equipped with an air-side magnesium oxide guard bed, and the air-side and syngas-side piping had an aluminizing coating and a high-purity copper lining, respectively.

Following PDU Run 6, the syngas-side and air-side surfaces of PDUM-44 were analyzed with SEM/EDS. Silicon-rich and iron-rich secondary phases were found on the syngas-side and air-side surfaces, respectively. The level of contamination on the syngas-side surfaces, however, was significantly less compared to Run 5, and there was no evidence of chromium contamination on the air-side surfaces. The improved oxygen flux stability of PDUM-44, compared to PDUM-29 and PDUM-31 from Run 5, could probably be attributed to the reduced contamination levels. The unprecedented flux performance of PDUM-44 was also likely due to the reduced contamination levels and its thinner, more porous P-layers.

The source of syngas-side silicon was any exposed metal components and/or the water feed. The outer surfaces of the P-layers were contaminated with silicates, but unlike modules in Run 5, the pores were not completely plugged. Little or no contamination was observed below the outer surface of the P-layers. Magnesium oxide guard beds will be implemented for one of four modules in PDU Run 7. Ideally, the magnesium oxide beds will react with the silicon vapors to form a stable silicate, thus reducing the $\text{Si}(\text{OH})_4$ partial pressure by several orders of magnitude.

Some of the observed iron-rich secondary phases on the air-side surfaces were likely products of demixing since the membrane was operated $\geq 900^\circ\text{C}$ (kinetic demixing is known to occur at high temperatures such as this). Enhanced demixing was also possible due to contamination. For example, contamination could alter the metal chemical potential gradients through the membrane, thus enhancing the demixing process. B-site non-stoichiometric excess was also a potential cause for the iron-rich secondary phases.

Significant creeping of the porous and dense layers occurred at the trailing-edge side of the wafer, where the membrane temperature was the highest. Figure 2.4.3.6-7 shows SEM images of the wafer cross-section at the leading, center and trailing edges. The dense layer strains were measured to be 0.07%, 0.39% and 5.36%, respectively.

Figure 2.4.3.6-7 SEM Images of PDUM-44 Wafer Cross Sections at the Leading, Center, and Trailing Edges (From Left to Right)

Equipment Performance

The nickel content of the high-temperature metal components used in the PDU can result in methane reforming in the syngas feed. This reforming reaction limits the system's ability to operate over a wide range of methane compositions. The copper linings and coatings used in PDU Run 6 appear to have significantly reduced the extent of methane reforming. However, the amount of syngas feed was limited in this run due to the large seal leaks. PDU Run 7 will operate at higher methane concentrations to further evaluate the reduction in methane reforming.

One of the twelve reactor heaters failed during the run. This failure will somewhat limit the maximum reactor temperature. Because it is still possible to achieve 900°C gas temperatures, the heater will not be replaced.

Subtask 2.4.3.7 PDU Run 7

Objectives of Run

The Run 7 objectives were to (a) demonstrate reduced membrane contamination through the use of coatings, linings, and guard beds; (b) demonstrate reduced reaction with hot metals through the use of coatings and linings; (c) demonstrate successful startup of a PDU module; (d) demonstrate ceramic-to-metal seals; and (e) measure oxygen flux through a PDU module.

Results and Discussion

Equipment and Modules

Membrane contamination was significantly reduced in PDU Run 6 through the use of coatings, linings, and guard beds. However, there was still some silicon contamination on the syngas-side that likely came from exposed metal components and the water feed, which contains traces of SiO₂. Additionally, some tungsten was found in the syngas feed line. The tungsten was believed to have come from the uncoated Haynes 230 steam line that connects to the dry syngas feed line.

To address further reduction of silicon contamination on the syngas side, a magnesium oxide guard bed was installed upstream of Housing 4. The magnesium oxide particles were placed in a copper-lined box and supported with copper-plated nickel screen at the inlet and outlet of the bed of particles. Figure 2.4.3.7-1 shows photo of the guard bed assembly.

Copper-plated nickel screen

Figure 2.4.3.7-1 Photo of the Syngas-side Guard Bed Between Housings 3 and 4

The steam line was also changed from Haynes 230 to Incoloy 800H to mitigate tungsten evolution.

Four non-catalyzed PDU modules were installed in the reactor. Table 2.4.3.7-1 lists the arrangement of the modules in the housings.

Table 2.4.3.7-1 Module Arrangement and General Information for Run 7

Module	Location	Comments
PDUM-51	Housing 1	Not catalyzed Air-side guard bed
PDUM-52	Housing 2	Not catalyzed Thinner dense layer
PDUM-50	Housing 3	Not catalyzed Air-side guard bed
PDUM-53	Housing 4	Not catalyzed Syngas-side guard bed

Module and Seal Performance

All four membrane modules were successfully heated to 900°C, pressurized to 215 psig, and transitioned to steam/syngas feed. Unlike PDU Run 6, there were no measurable module leaks during startup. Within hours of introducing steam/syngas, the module in Housing 2 developed a leak that slowly increased over several days. It eventually was isolated prior to increasing the steam/syngas feed further. Three of the modules achieved full syngas conditions. Another reactor heater failed during the run, so most of the run was conducted with 10 of the 12 heaters operating. This limited the maximum temperature at which the membranes could be operated.

The modules in Housings 1, 3, and 4 operated under syngas conditions for 33 days, 37 days and 51 days, respectively. All operated with significantly improved oxygen flux stability compared to the modules in previous runs. Wide ranges of operating conditions were tested: 800 to 875°C gas feed temperature, 215 to 425 psig syngas-side pressure, various syngas-side compositions including 0.1 to 55% H₂, and various air-side flows and pressures. The module in Housing 3 set a new record for oxygen flux that exceeded the commercial target. The lower oxygen fluxes for the module in Housing 4 were consistent with its thicker dense layer and thicker, lower-porosity porous layer. Figure 2.4.3.7-2 shows the history of the module performance.

Figure 2.4.3.7-2 Module Performance Data for Run 7

All the module failures occurred soon after various operating conditions were changed. The first module to fail, the module in Housing 2, failed soon after initial syngas introduction. It developed a small leak approximately five hours after adding the syngas, and the leak slowly increased over four days. The leak became so large that the module had to be isolated. The module in Housing 1 failed eight hours after completion of the first temperature study. The Housing 3 module failed 23 hours after changing the syngas feed composition from 24% H₂ to 28 % H₂. The module in Housing 4 failed 35 hours after completing pressurization to 425 psig. Exact causes for the failures were not known. Seal leakage, slow crack growth, and delamination of membrane layers were investigated as possible causes.

The apparent oxygen transport activation energy was calculated using data gathered under conditions of constant gas composition and varying temperature (Figure 2.4.3.7-3). The apparent activation energies ranged from 99 to 122 kJ/gmol. These were consistent with the range of activation energies measured in previous PDU runs, and two to four times greater than the activation energy measured on earlier ITM test parts (~44 kJ/gmole). Surface contamination, membrane demixing, and surface oxidation kinetics were potential reasons for the discrepancies.

Figure 2.4.3.7-3 Run 7 Oxygen Flux Versus Temperature Data Used to Calculate the Oxygen Transport Activation Energy

PDUM-53 in Housing 4 operated at various temperatures at two different hydrogen compositions. The apparent oxygen transport activation energy was calculated at both these compositions. The calculated values, as shown in Figure 2.4.3.7-4, were relatively consistent.

Figure 2.4.3.7-4 Run 7 Oxygen Flux Versus Temperature Data for PDUM-53 at Different Hydrogen Compositions and the Associated Oxygen Transport Activation Energy

In PDU Run 6, the gold in the ceramic-to-metal seals interacted with the aluminizing coating of the air tubing to cause large seal leaks. In this run, the coating was removed from areas that contacted gold, and the ceramic-to-metal seals again performed well (Figure 2.4.3.7-5). Modest leaks were observed during transition periods of heating/cooling and composition changes, but the leaks were manageable. Maximum leak rates of <40 sccm were much lower than the peaks observed in Run 6 (1500 to 2000 sccm).

Figure 2.4.3.7-5 Module Leak Rates Versus Time

Post-Test Inspection

The syngas-side and air-side surfaces of each module were analyzed with SEM/EDS after Run 7. Silicon-rich and iron-rich secondary phases were found on the syngas-side and air-side surfaces, respectively. The level of contamination on the syngas-side surfaces, however, was significantly less compared to Run 5 and similar to Run 6. There was no evidence of chromium contamination on the air-side surfaces of modules containing magnesium oxide guard beds. This further confirmed that (a) the copper internal components and cladding, which were not used before Run 6, reduced contamination levels, and (b) magnesium oxide successfully removed chromium vapor species from the air at PDU operating conditions. The improved oxygen flux stability was likely due to the reduced contamination levels. The unprecedented flux performance of PDUM-50 was also due to the reduced contamination levels, its more favorable porous layer properties, and/or its thinner dense layers.

The source of silicon on the syngas-side was any exposed metal surface and/or the water feed, which contained traces of SiO_2 . The level of syngas-side contamination was similar for all modules. The outer surfaces of the P-layers were contaminated with silicates, but little or no contamination was observed below the outer surface of the P-layers. This observation suggested that the upstream modules were not fully effective at scrubbing silicon vapors from the syngas stream under these conditions. For PDU Run 8, ion-exchange beds will be added on the water feed to further reduce its silicon content. The effectiveness of the syngas-side magnesium oxide guard bed before Housing 4 could not be assessed because the support screens failed and the bed collapsed. The magnesium oxide pellets settled to the bottom of bed, and the syngas bypassed the pellets.

Most of the iron-rich, secondary-phase contaminants on the air-side were probably the result of kinetic decomposition since the membrane operated at, a temperature range where decomposition occurs (≥ 900 °C). Trace levels of chromium were found within PDUM-53. The iron rich secondary phases that were observed may have resulted from enhanced kinetic demixing caused by B-site cation exchange between the membrane and the chromium impurity. B-site non-stoichiometric excess was also a potential reason for the iron-rich secondary phases.

The chromium contamination on PDUM-53 (*no* guard bed) and the absence of chromium on PDUM-50 (guard bed) confirmed that magnesium oxide successfully scrubbed chromium vapor species from the air. The observed chromium contamination on PDUM-53 also suggested that the Diffusion Alloys coating on Incoloy 800H has a limited lifetime under the ITM Syngas PDU operating conditions. The Diffusion Alloys-coated 800H air-side tubing was not replaced between Runs 6 and 7, so an air-side guard bed from PDU Run 6 was analyzed and compared with a bed from Run 7. The chromium content of the Run 6 bed was much less than that of the bed from Run 7, which operated three fewer weeks. These results further demonstrated that chromium evolution from coated Incoloy 800H increased with time, and that the Diffusion Alloys coating was not a long-term solution to inhibit chromium evolution from metal. A decision was made to replace the air feed tubing after each run. Due to the success of magnesium oxide air-side guard beds, beds will be installed for all housings in Run 8.

Significant creeping of the porous and dense layers occurred at the trailing-edge sides of PDUM-50 and PDUM-53, where the membrane temperatures may have exceeded 1000°C. An example is shown in Figure 2.4.3.7-6.

Figure 2.4.3.7-6 SEM Image of a Wafer Cross Section Showing Significant Creeping of the Porous and Dense Layers

Equipment Performance

The magnesium oxide syngas-side guard bed before Housings 4 collapsed due to failure of the support screens. The syngas did not contact the magnesium oxide pellets because the pellets had

settled to the bottom of bed. Perforated plates made from magnesium oxide will be used as bed supports in PDU Run 8.

The nickel content of the high-temperature metal components in the PDU can result in reforming of methane in the syngas feed. This would limit the ability of the system to operate over a wide range of compositions. The copper linings and coatings used in PDU Run 7 significantly reduced the extent of methane reforming. Figure 2.4.3.7-7 shows how the syngas feed composition of 43% CH₄ (dry basis) did not significantly change through the heater and reactor. Under similar conditions without the linings and coatings (PDU Run 5), the methane reacted to 6% CH₄ (dry basis). It was also observed that the reverse water-gas shift reaction of CO₂ to CO was not inhibited by the linings and coatings. Future PDU runs will continue to use linings and coatings for mitigation of contamination and reactions with the metal components.

Figure 2.4.3.7-7 Composition Profile Across the Syngas Heater and the Membrane Modules

Subtask 2.4.3.8 PDU Run 8

Objectives of Run

The Run 8 objectives were to (a) demonstrate reduced membrane contamination through the use of coatings, linings, and guard beds; (b) demonstrate successful startup of a catalyzed PDU module; (c) demonstrate ceramic-to-metal seals; and (d) measure oxygen flux through a catalyzed PDU module.

Results and Discussion

Equipment and Modules

Membrane contamination was significantly reduced in the last two PDU runs through the use of coatings, linings, and guard beds. However, there was still some silicon contamination on the

syngas-side that likely came from exposed metal components and the water feed, which contained traces of SiO_2 .

Ion-exchange beds were added on the water feed to further reduce its silicon content. Installing these beds resulted in a reduction of silica in the water from 200 ppbw to less than 23 ppbw.

To address further reduction of silicon contamination on the syngas-side, a magnesium oxide guard bed was installed upstream of Housing 4. The magnesium oxide particles were placed in a copper-lined box and supported with perforated magnesium oxide plates on the inlet and outlet. Figure 2.4.3.8-1 shows a photo of the guard bed assembly. Additionally, the housing parts around the membrane modules were change from copper to magnesium oxide to provide additional "gettering" capability.

Figure 2.4.3.8-1. Photo of the Syngas-side Guard Bed Between Housings 3 and 4

In PDU Run 7, it was determined that the aluminizing coating on the air-side tubing was effective only over a short operating period. It was also demonstrated that the air-side magnesium oxide guard beds on Housings 1 and 3 were very effective at reducing chromium contamination. Therefore, air-side guard beds were added to the air feed for Housings 2 and 4. Air-feed tubing downstream of the guard beds will be replaced with freshly-coated tubing after each run.

Four catalyzed PDU modules were installed in the reactor. Table 2.4.3.8-1 lists the arrangement of the modules in the housings.

Table 2.4.3.8-1 Module Arrangement and General Information for Run 8

Module	Location	Comments
PDUM-40	Housing 1	Catalyzed membrane Air-side guard bed
PDUM-62	Housing 2	Catalyzed membrane Air-side guard bed
PDUM-63	Housing 3	Catalyzed membrane Air-side guard bed
PDUM-64	Housing 4	Catalyzed membrane Air-side guard bed Syngas-side guard bed

Module and Seal Performance

All four membrane modules failed during initial heating with nitrogen on the syngas-side and air on the air side. The modules in Housings 1, 2, 3, and 4 failed at temperatures of 349°C, 336°C, 327°C, and 293°C, respectively. It was approximately 3½ hours from the first module failure in Housing 4 to the last module failure in Housing 1.

Post-Test Inspection

A post-test assessment was conducted to determine the possible cause for the early failure of the catalyzed modules. Information on module fabrication, catalyst application, module installation, and membrane test data was collected. Fracture analysis of the modules was also performed. Review of the data resulted in the leading hypothesis for failure being a catalyzed reduction of the syngas-side of the module. A small amount of hydrocarbon in the nitrogen feed may have catalytically reacted with the membrane, causing chemical expansion. This hypothesis was supported by TGA, dilatometry and annealing experiments with catalyzed and uncatalyzed parts.

To assess the presence of hydrogen in the system, the PDU was restarted without the membrane modules installed. The following analyzers were installed on the syngas-side system: a ppm oxygen analyzer (± 1 ppm), a ppb oxygen analyzer (± 30 ppb), a hydrogen GC-FID (± 5 ppm), and a total hydrocarbon FID (± 0.3 ppm as CH₄). The PDU reactor was then heated to 400°C. The oxygen concentration in the flowing nitrogen dropped from ~1000 ppb to 200 to 300 ppb across the system. The decrease in oxygen may have resulted from oxidation of copper or other metal parts. Hydrogen was non-detectable through the membrane housings, but was 10 to 60 ppm in the reactor exit. The hydrogen may have come from the moldable insulation used in the reactor insulation pack. Total hydrocarbons were non-detectable through the membrane housings, 10 to 40 ppm exiting Housing 4, and 800 to 1300 ppm in the reactor exit. The hydrocarbons probably originated from the moldable insulation. While this test did not definitively detect hydrocarbons

in the membrane housings, it is possible that a low level of hydrocarbons could have entered the system during the original startup.

The syngas-side surfaces of each module were analyzed with SEM/EDS, which revealed no impurities on the modules. This suggested that the formation of secondary phases due to contamination did not cause the failures.

The recommended solution for startup of the catalyzed modules was to pre-reduce these modules so that chemical expansion of the catalyzed porous layer (relative to other layers in each module) could not occur. PDU start-up procedures were modified for pre-reduced modules so that a reducing atmosphere was present on both the syngas and airsides of the membrane during heat-up.

Subtask 2.4.3.9 PDU Run 9

Objectives of Run

The objectives of Run 9 were to (a) demonstrate reduced membrane contamination through the use of coatings, linings, and guard beds; (b) demonstrate successful startup of a catalyzed PDU module; (c) demonstrate ceramic-to-metal seals; and (d) measure oxygen flux through a catalyzed PDU module.

Results and Discussion

Equipment and Modules

Run 9 was a repeat of Run 8, and the included equipment features were nearly identical. The only difference was modification of the air-side guard beds.

The previous air-side guard beds used magnesium oxide pellets. However, initial designs for commercial-size reactors indicated that this type of guard bed would cause an unacceptably high pressure drop. The preferred commercial guard bed design would use a low-pressure-drop monolith structure. To assess the effectiveness of the monolith guard bed design, tubular guard beds were incorporated into the PDU reactor for each membrane module. The guard bed design (Figure 2.4.3.6-2) had two cylindrical vessels in series. It had previously been determined that all the contaminants were removed by the pellets in the first vessel, thus suggesting that the mass transfer zone was less than half of the installed total bed length. This allowed the first vessel to be converted to a tubular design simulating a monolith structure and still have the second vessel of pellets as the guard bed if the tubular design did not fully remove the air feed contaminants.

The recommended solution for startup of catalyzed modules was to pre-reduce catalyzed modules so that chemical expansion of the catalyzed porous layer relative to the rest of the modules could not occur. PDU start-up procedures were modified for pre-reduced modules so

that a reducing atmosphere was present on both the syngas and air sides of the membrane during heat-up. The PDU was modified to enable startup of pre-reduced modules.

Because two of the twelve reactor heaters had failed and were limiting the temperature capabilities of the reactor, a new heater/insulation pack was design and installed. The new clam-shell heater design allowed for easier and quicker installation and replacement of heaters without moving the reactor shell (Figure 2.4.3.9-1).

Figure 2.4.3.9-1 New Heater and Insulation Pack Installation System

Four PDU modules were installed in the reactor. All were pre-reduced, and three were catalyzed. Table 2.4.3.9-1 lists the arrangement of the modules in the housings.

Table 2.4.3.9-1 Module Arrangement and General Information for Run 9

Module	Location	Comments
PDUM-70	Housing 1	Catalyzed membrane Air-side guard bed
PDUM-74	Housing 2	Uncatalyzed membrane Air-side guard bed
PDUM-67	Housing 3	Catalyzed membrane Air-side guard bed
PDUM-75	Housing 4	Catalyzed membrane Air-side guard bed Syngas-side guard bed

Module and Seal Performance

All four membrane modules were successfully heated to 900°C in a reducing atmosphere (dilute H₂) on both the syngas and air sides of the membrane. This marked the first time that catalyzed PDU modules were heated beyond 350°C without failure. Module leaks of 45 to 525 sccm developed at 600 to 650°C, but decreased over several days of operation at 900°C. The leaks were significant, but manageable and therefore did not require any module to be isolated.

The new start-up procedure required that the air-side feed be transitioned from the reducing atmosphere to dilute O₂ and then to air. The air-side gas composition was successfully ramped from humidified 5000 ppm H₂ in N₂, to humidified N₂, and then to 0.6% O₂ in N₂. Despite the presence of dilute oxygen in the air-side feed and only 1000 ppm hydrogen in the process-side feed, concentrations of 500-2000 ppm H₂ were observed in the air-side exit of the modules. Because of a driving force for proton diffusion to the air-side, the hydrogen on the air-side was thought to come from hydrogen transport through the membrane (perovskites are known to be proton conductors). Procedures for transitioning from dilute O₂ to air were modified to consider the presence of hydrogen on the air side.

Using these modified procedures, the air-side flow was increased to reduce the concentration of hydrogen on the air side. Next, an air stream was slowly blended with the 0.6% O₂ in N₂, with an initial introduction that increased the oxygen concentration in the feed from 0.6 to ~0.9%. However, oscillations in the air feed mass flow controller resulted in several spikes in oxygen concentration as high as 2%. This rapid change in oxygen concentration led to the air-side outlet conditions suddenly becoming oxidizing, resulting in a large chemical expansion in the membrane material. The catalyzed module in Housing 1 failed within a minute of the first concentration spike. This failure stopped the hydrogen transport to the air side of that module and resulted in a sudden increase in process-side hydrogen concentration in the feed to the downstream modules in Housings 2, 3, and 4. This created chemical expansion transients that caused the catalyzed membrane modules in Housings 3 and 4 to fail within minutes of the Housing 1 failure. The non-catalyzed module in Housing 2 survived these transients. The start-up procedure was continued, and this module also survived the transition to air and the introduction of 50% syngas/steam. This module failed when the process-side tubing became obstructed.

With the start-up of pre-reduced modules, the membrane modules are most vulnerable to cascading failures during the transition from reducing to oxidizing conditions. Small process upsets can push the modules from oxidizing to reducing conditions and vice versa. Under full process conditions, the cascading failures were less likely since the oxygen or fuel concentrations were much higher. The failure of an upstream module did not change the process-side concentrations sufficiently to produce a significant change in chemical expansion. Start-up procedures required additional scrutiny to ensure the reliability of the modules.

Several procedural and equipment modifications were planned to improve the reliability of pre-reduced, catalyzed module startup. A parallel, smaller air flow controller and air feed buffer tank will be added to smooth the transition from 0.6% O₂ to air feed. Higher air-side flow rates will

be used when ramping in oxygen on the air side. The syngas-side hydrogen concentration will be minimized during oxygen introduction to minimize permeation of hydrogen to the air side. In general, the transition from reducing to oxidizing conditions on the air side will be done more rapidly to minimize time spent at this sensitive stage.

Equipment Performance

The most likely cause of the syngas-side feed obstruction that led to the failure of the module in Housing 2 was copper particulates from the copper lined tubing. More than 8 grams of copper dust were found in the housing train. A small amount of metal oxides was also found. Inspection of the syngas heater revealed random blistering of the copper in areas that probably run the hottest. For future runs, the syngas heater will be operated at a lower temperature to minimizing blistering of the copper.

Subtask 2.4.3.10 PDU Run 10

Objectives of Run

The Run 10 objectives were to (a) demonstrate reduced membrane contamination through the use of coatings, linings, and guard beds; (b) demonstrate successful startup of a catalyzed PDU module; (c) demonstrate ceramic-to-metal seals; and (d) measure oxygen flux through a catalyzed PDU module.

Results and Discussion

Equipment and Modules

To further reduce silicon contamination on the syngas side, a magnesium oxide guard bed was installed upstream of Housing 4. The magnesium oxide particles were placed in a copper-lined box and supported with perforated magnesium oxide plates on the inlet and outlet. Additionally, the housing parts around the membrane modules were changed from copper to magnesium oxide to provide additional "gettering" capability.

The PDU water system upgrade to ion-exchange beds continued to be used to reduce the silicon content of the water feed to the steam system. The modified air-side guard beds installed in Run 9 were also used in Run 10.

Several procedural and equipment modifications were made to further improve the reliability of pre-reduced, catalyzed module startups. A parallel, smaller air flow controller and a 120-gallon air-feed buffer tank were installed to smooth the transition from 0.6% O₂ to air feed. Higher air-side flow rates were also used when ramping oxygen on the air side. The syngas-side hydrogen concentration was minimized during oxygen introduction to minimize permeation of hydrogen to

the air side. In general, the transition from reducing to oxidizing conditions on the air-side was done more rapidly to minimize time spent at this sensitive stage.

Four pre-reduced PDU modules were installed in the reactor, two of which were catalyzed. Table 2.4.3.10-1 lists the arrangement of the modules in the housings.

Table 2.4.3.10-1 Module Arrangement and General Information for Run 10

Module	Location	Comments
PDUM-65	Housing 1	Uncatalyzed membrane Air-side guard bed
PDUM-69	Housing 2	Catalyzed membrane Air-side guard bed
PDUM-76	Housing 3	Catalyzed membrane Air-side guard bed
PDUM-66	Housing 4	Uncatalyzed membrane Air-side guard bed Syngas-side guard bed

Module and Seal Performance

All four membrane modules were successfully heated to 900°C, pressurized to 115 psig, and transitioned to syngas and air feed. This marked the first successful startup of catalyzed modules. Module leaks of varying magnitude developed at 560 to 575°C. The leaks (130 to 1225 sccm) were generally higher than leaks observed in PDU Run 9. Similar to Run 9, the leaks decreased as oxygen was introduced into the air-side.

Once at operating conditions, Housing 2 module leaks resulted in water accumulation in the air exit tubing. The water created large oscillations in the exit air flow which eventually caused automatic isolation of this module. The modules in Housings 1, 3, and 4 operated for an additional three days at full operating conditions until a high CO alarm on the exhaust system triggered a safety interlock that turned off the syngas feed to the reactor. This resulted in the failure of the remaining three modules. The high CO alarm occurred when syngas from an adjacent lab was vented into the exhaust system during a building exhaust system shutdown. The syngas traveled through the PDU exhaust header and triggered the alarm. Figure 2.4.3.10-1 shows the history of module performance.

ITM Syngas PDU Run 10 History

Figure 2.4.3.10-1 Module Performance Data for Run 10

This run demonstrated the success of the improved start-up procedures for pre-reduced modules. Also, operating performance data was collected on catalyzed and uncatalyzed pre-reduced modules for the first time.

The ceramic-to-metal seal leaks on the pre-reduced modules continued to be higher than in runs with non-reduced modules (Figure 2.4.3.10-2). Leaks greater than 1000 sccm at lower pressures have been observed in the past few runs. Although the leaks are manageable, they have contributed to failures.

The progression of the leaks on pre-reduced modules has shown a pattern: leaks develop at ~600°C, decrease with introduction of steam, and open and close with changes in test conditions. These leak rate changes may be related to variations in the oxidation state of the seal block as the air-side transitions from reducing to oxidizing conditions and the syngas-side transitions between several reducing conditions. Differential expansion between the seal block and the metal seals may be creating these leaks. Reasons for these higher leak rates need to be understood and corrected for future runs.

Figure 2.4.3.10-2 Module Leak Rates Versus Time

Data from this run indicated that very little methane reforming was occurring. Dry-basis syngas compositions are shown in Figure 2.4.3.10-3. Any reaction that occurred was less than the error in the analytical measurements. Methane conversions less than 2% were difficult to accurately measure.

Figure 2.4.3.10-3 Composition Profile Across the Syngas Heater and the Membrane Modules

Post-Test Inspection

The syngas-side and air-side surfaces of PDUM-69, -76 and -66 were analyzed with SEM/EDS. The secondary phases found on the syngas side surfaces were rich in silicon; on the air side surfaces they were calcium- and iron-rich. The level of contamination on the syngas-side surfaces, however, was significantly less than what was observed at the end of Run 5 and similar to the levels measured after Runs 6 and 7. Tungsten and chromium contaminants were also observed on the air-side surfaces, primarily at the leading edge of the active wafers. These findings confirmed that (a) the copper internals and cladding, which were not used before Run 6, reduced contamination levels on the syngas-side; (b) the aluminizing coating on older and/or non-pre-oxidized sections, downstream of the guard beds, was unable to mitigate chromium contamination on the air side, and (c) the humidified air-side gas caused tungsten volatilization during start-up. While the tungsten contamination was measurable, it was not a long-term problem since the humidified gases were present only during the relatively short startup and shutdown periods. The improved oxygen flux stability was at least partly due to the reduced contamination levels.

The porous layers on the syngas-side were not plugged with the contaminant phases, and little or no contamination was found below the outer surface of the porous layers. The level of syngas-side contamination was similar for all three modules, suggesting that the syngas-side guard bed prior to Housing 4 had limited benefit. Testing of syngas-side guard beds was discontinued for future runs since the syngas-side contamination had been minimal in recent runs, and the beds showed little evidence of having reduced contamination levels.

The calcium- and iron-rich secondary phases on the air side were byproducts of contamination. The aluminizing coating on older and/or non-pre-oxidized sections, downstream of the guard beds, was unable to mitigate contamination. In addition, the humidified air-side gas caused tungsten volatilization during start-up. Some of the observed contamination may have occurred post-failure due to cracks in the modules.

Decomposition was also observed in the porous magnesium oxide materials used for some of the reactor internal components. This was due to the formation of Mg(OH)_2 , a product of magnesium oxide reacting with steam at temperatures below 500°C . Steam was not purged from the reactor before cooling during the shutdown in order to preserve any potential blockages in the reactor piping. This experience demonstrated that wet gases need to be purged during shutdowns.

Equipment Performance

During the last few days of the run, an increase in the syngas pressure drop was observed predominantly in the syngas feed line to the reactor. This had been observed in other runs (e.g., Run 9) but in this case it occurred over a much shorter time period. The prime hypothesis was that a partial blockage had developed in the feed line. In order to preserve the partial

blockage, the process gas flow and heaters were shut off without following the normal shutdown procedures.

Upon inspection, significant amounts of carbon were found in the knockout traps and within the syngas heater. Carbon formation was not expected at the steam-to-methane ratios being run at the time of the pressure drop increase. This issue will be considered in setting the operating conditions of future runs.

Subtask 2.4.3.11 PDU Run 11

Objectives of Run

The objectives for Run 11 were to (a) demonstrate reduced membrane contamination through the use of coatings, linings, and guard beds; (b) demonstrate successful startup of a catalyzed PDU module; (c) demonstrate ceramic-to-metal seals; and (d) measure oxygen flux through a catalyzed PDU module.

Results and Discussion

Equipment and Modules

To address contamination on the syngas side, all syngas-side tubing upstream of the membranes and the module housings have been lined with copper starting with PDU Run 6. This significantly reduced contamination of the modules. However, copper particulates have been generated in every run, and some contaminates the module. In PDU Run 9, copper particulates were suspected of plugging the syngas feed line. In an effort to minimize the use of copper and improve contaminant removal, all the copper housing parts were replaced with magnesium oxide parts for this run. Additionally, the copper-lined syngas heater coil was replaced to ensure the syngas heater coil was free of particulates.

Magnesium oxide guard beds were not installed on the syngas side because recent runs have shown minimal contamination, and the guard bed in PDU Run 10 appeared to offer limited protection. Additionally, a syngas-side guard bed can act as filter in the presence of carbon and result in a rapid pressure drop.

Several modifications were made to address seal leaks with pre-reduced modules. The module reduction process time was extended to ensure the module seal blocks were sufficiently reduced, thus minimizing the amount of expansion change that may occur during heating in reducing atmospheres. A spacer was installed on the U-ring seal to apply a mild load on the gold washer face seals. The tool used to press in the metal seals was replaced in case it had become deformed over time.

All four PDU modules installed in the reactor were pre-reduced; three were catalyzed. Table 2.4.3.11-1 lists the arrangement of the modules in the housings.

Table 2.4.3.11-1 Module Arrangement and General Information for Run 11

Module	Location	Comments
PDUM-87	Housing 1	Uncatalyzed membrane Air-side guard bed
PDUM-83	Housing 2	Catalyzed membrane Air-side guard bed
PDUM-85	Housing 3	Catalyzed membrane Air-side guard bed
PDUM-88	Housing 4	Catalyzed membrane Air-side guard bed

Module and Seal Performance

All four membrane modules were successfully heated to 900°C in a reducing atmosphere on both the syngas side and air side. Heating of pre-reduced modules continued to be successful, having a total of eight catalyzed PDU modules successfully heated to operating temperature. However, once again, significant module leaks developed during the heating at 560 to 580°C, with leak rates ranging from 175 to 1700 sccm. The size of the leaks and the temperature at which they leaks developing were very similar to PDU Runs 9 and 10. Also consistent with these runs,, the leaks decreased over several days as oxygen was introduced to the air side. Interestingly, the leak on the Housing 4 module increased to 5500 sccm during the initial phase of air introduction (at ~2600 ppm O₂), but decreased to non-detectable levels after placing the ramp on hold. The leak re-opened when the ramp was resumed and, after several days, the module was intentionally isolated as the leak continued to increase. The remaining modules successfully reached final air feed and initial steam/syngas conditions.

While increasing the syngas feed, the catalyzed module in Housing 2 developed a sudden and large leak (~2500 sccm). Within 1½ hours, the module was isolated when it failed catastrophically. The uncatalyzed module in Housing 1 and the catalyzed module in Housing 3 both survived the transition to full syngas conditions. After one day at full syngas conditions, the module in Housing 1 also suddenly developed a large leak (~2500 sccm). Within 25 minutes, the module failed catastrophically and was isolated. After 9½ days at full syngas conditions, the catalyzed module in Housing 3 also failed suddenly.

Despite the failures, several key milestones were demonstrated. First, the revised startup procedures for pre-reduced and catalyzed membranes were successful. Second, performance data was collected on catalyzed and uncatalyzed, pre-reduced modules for the first time. Third, PDUM-83, -87 and -85 operated under syngas conditions for an extended period (3 to 15 days). Figure 2.4.3.11-1 shows the history of the module performance, and Figure 2.4.3.11-2 shows the leak history. Ceramic-to-metal seal problems continued to be a major issue with operating the pre-reduced modules successfully.

ITM Syngas PDU Run 11 History

Figure 2.4.3.11-1 Module Performance Data for Run 11

Figure 2.4.3.11-2 Module Leak Rates Versus Time

Post-Test Inspection

The syngas- and air-side surfaces of PDUM-87 and -85 were analyzed with SEM/EDS. Secondary-phase contaminants found on the syngas side surfaces were silicon-rich; those on the air side surfaces were rich in calcium and iron. However, the level of contamination on the syngas-side surface was significantly less than what was observed at the end of Run 5 but similar to the levels observed after subsequent runs. These findings continued to confirm that (a) the copper internal components and cladding, which were not used before Run 6, reduced contamination levels on syngas-side surfaces, and (b) the aluminizing coating and magnesium oxide guard beds reduced/eliminated chromium contamination on air-side surfaces. The improved oxygen flux stability was at least partly due to the reduced contamination levels. No creep deformation of the porous or dense layers was observed for either module.

The syngas-side surfaces were contaminated with silicates. However, the pores were not plugged with the contaminant phases, and little or no contamination was found below the outer surface of the porous layers. The level of syngas-side contamination was similar for both modules.

The air-side surfaces were partially covered with Ca- and Fe-rich secondary phases, products of kinetic decomposition. Little or no chromium contamination was detected.

The fracture surfaces, seal block and tube stubs for PDUM-87 and 85 were also examined to assess possible mechanisms for the observed leak rates and failures. The fracture surfaces were unremarkable, and the analysis did not reveal a fracture timeline. However, analysis of the seal blocks revealed high levels of silicon contamination near the face seals, likely caused by the observed leaks and poor sealing of the U-rings. Analysis of the tube stubs also revealed non-uniform loading of the gold washers against the seal block. This poor loading of the tube stubs against the seal block was a possible cause for the observed leak rates.

The inlet and outlet ports of the seal blocks for PDUM-87 and -85 were found to have significant silicon contamination near the outer perimeter of the face seals. This was likely caused by the observed leaks and poor sealing of the U-rings. Tungsten contamination, probably from the Haynes 230 tube stubs, was also observed in some areas of the face seal.

Equipment Performance

Significantly less carbon was found within the reactor after this run, presumably as a result of operating at a higher steam-to-methane ratio. However, small amounts of carbon were still found. One theory for this carbon formation was that carbon formed within a small region of the syngas heater where the dry gas and steam were not well mixed, then traveled and was deposited downstream. The carbon did not gasify due to poor kinetics. Carbon formation may also be attributable to localized hot spots in the syngas heater.

Despite the small amounts of carbon found, the system pressure drop did increase approximately 2 percent per day while under full syngas conditions. This was a much slower rate than in previous runs, but still a concern.

Subtask 2.4.3.12 PDU Run 12

Objectives of Run

The Run 12 objectives were to (a) demonstrate successful startup of a non-catalyzed PDU module with a protective web layer; (b) demonstrate ceramic-to-metal seals; and (c) measure oxygen flux through a non-catalyzed PDU module.

Results and Discussion

Equipment and Modules

Pitting and inclusions on the membrane surface can be reduced by manufacturing the exterior membrane surface with a protective web layer. One of the main objectives of this run was to determine the effects of this web layer on start-up and operating reliability.

Seal leaks were a major problem with pre-reduced modules in PDU Runs 9 through 11. This run used non-reduced modules to more definitely demonstrate that the seal problem was associated with pre-reduced modules only. A new composite washer design was also used in the ceramic-to-metal seal. This design was being considered for the commercial-size modules, and if successful, might improve the seal performance of pre-reduced modules. Cross-sections of the baseline and composite seals are shown in Figure 2.4.3.12-1.

Figure 2.4.3.12-1 Comparison of Baseline and New Composite Seal Gaskets

An independent supply of hydrogen was added to the PDU system to provide greater flexibility with syngas feed composition and smoother transitions when changing syngas trailers. Previous runs had experienced large changes in oxygen flux and module temperature when trailers with different compositions were exchanged.

Three PDU modules and a PDU seal block were installed in the reactor. Table 2.4.3.12-1 lists the arrangement of the modules in the housings.

Table 2.4.3.12-1 Module Arrangement and General Information for Run 12

Module	Location	Comments
PDUM-89	Housing 1	Not catalyzed Protective web layer Composite ceramic-metal seal Air-side guard bed
PDUM-90	Housing 2	Not catalyzed Protective web layer Baseline ceramic-metal seal Air-side guard bed
PDUM-71	Housing 3	Not catalyzed Baseline ceramic-metal seal Air-side guard bed
DPS-107-3	Housing 4	Seal block only Composite ceramic-metal seal Air-side guard bed

Module and Seal Performance

All three membrane modules and the seal block were successfully heated to 900°C, pressurized to 215 psig, and transitioned to steam/syngas feed. Leaks on all modules and the seal block were below detectable limits for the entire startup. This performance confirmed that the leaks observed in Runs 9 through 11 were related to pre-reduced modules. Modules with the protective web design survived maximum startup stresses and appeared to be as reliable as the non-web design. Modules in Housings 1 and 2 failed when the syngas feed line plugged for a period of time after 23 days of operation under syngas conditions. The module in Housing 3 and the seal block survived the entire test period: a total of 92 days (2200 hrs) with 48 different operating conditions. Figure 2.4.3.12-2 shows the history of the module performance.

ITM Syngas PDU Run 12 History

Figure 2.4.3.12-2 Module Performance Data for Run 12

Data from PDUM-71 suggested that carbon dioxide had a negative impact on oxygen flux. Data taken at similar hydrogen concentrations and temperatures showed that the oxygen flux decreased 24 percent when the carbon dioxide content of the feed gas increased from 0.1 to 3.1 percent (Table 2.4.3.12-2). This change in oxygen flux was too great to be explained solely by contamination-related degradation or slight differences in hydrogen concentration.

Unfortunately, methane and carbon monoxide concentrations also increased as a result of the feed gas being used and, hence, the actual carbon dioxide effect was not definitive. The ability to independently control the methane and carbon dioxide concentrations will be implemented for future runs.

**Table 2.4.3.12-2 Operating Data Showing the Impact of
Carbon Dioxide Concentration on Oxygen Flux**

Temp (°C)	855	856	856	856
% N₂	77.3	77.3	73.3	68.6
% H₂	14.9	14.5	14.2	14.0
% CH₄	0.6	0.2	0.8	1.5
% CO₂	0.1	0.3	1.6	3.1
% CO	0.3	0.6	2.7	5.2
% H₂O	6.8	7.1	7.4	7.6
Relative O₂ Flux	Base	90%	79%	76%

Tests were also conducted to investigate the effect of air mass flow on oxygen flux. The air velocity was kept roughly constant by varying both the air flow rate and air pressure. The results are shown in Table 2.4.3.12-3. The oxygen flux did not change when the air flow was decreased 58 percent; however, the oxygen flux decreased by 19 percent when the air flow was increased 49 percent. One hypothesis was that this was a heat transfer phenomenon: at a higher flow rate, the air was not heated as high prior to entering the module or the higher air flow removed more heat from the module. In either case, the module was cooled, reducing the oxygen flux.

**Table 2.4.3.12-3 Operating Data Showing the Impact of
Air Mass Flow on Oxygen Flux**

Temp (°C)	906	905	906
% N₂	76.6	76.6	76.7
% H₂	14.5	14.5	14.6
% CH₄	0.3	0.3	0.3
% CO₂	0.5	0.5	0.5
% CO	1.0	1.0	0.9
% H₂O	7.1	7.1	7.0
Air Feed Pressure (psig)	26.4	10.3	47.3
Air Inlet Flow (SCFH)	32.0	13.5	47.7
Relative O₂ Flux	Base	100%	81%

The apparent oxygen transport activation energy was calculated using data gathered during conditions of constant composition and varying temperature (Figure 2.4.3.12-3). The apparent activation energies ranged from 109 -120 kJ/gmol. This was consistent with the range of activation energies measured in previous PDU runs, and approximately three times greater than the activation energy measured on earlier ITM test parts (~44 kJ/gmole). Surface contamination, membrane kinetic demixing, and surface oxidation kinetics were potential reasons for the discrepancies.

Figure 2.4.3.12-3 Run 12 Oxygen Flux Versus Temperature Data Used to Calculate the Oxygen Transport Activation Energy

The module in Housing 3 and the seal block underwent testing of a new shutdown protocol that would drastically reduce the time for shutdown. The protocol attempted to keep the ceramic parts in a constant strain condition during cooldown. The shutdown successfully cooled the parts to 600°C in 2.5 days, compared to 20 days if normal shutdown procedures were used. However, at 600°C the module in Housing 3 failed. The seal block survived the entire shutdown.

Both the baseline and composite seals performed extremely well. Module and seal block leaks never exceeded 20 sccm during operation (Figure 2.4.3.12-4). However, during the shutdown, leaks did develop and reached unacceptably high rates (Figure 2.4.3.12-5). The leaks that developed during shutdown were probably caused by U-ring creep from extended operation at high temperature. The composite seals may have contributed to the survival of the seal block during shutdown.

Figure 2.4.3.12-4 Module Leak Rates Versus Time

Figure 2.4.3.12-5 Module Leak Rates Versus Time During the Last Two Weeks of Run 12

Post-Test Inspection

The syngas-side and air-side surfaces of PDUM-71 and Seal Block DP5-107-3 were analyzed with SEM/EDS. Silicon-rich and calcium-iron-rich secondary phases were found on the syngas-side and air-side surfaces, respectively. The level of silicon contamination was similar to that observed at the end of Run 11 despite the fact that Run 12 lasted approximately six times longer. These findings suggested that (a) silicon was depleted from older, exposed metal components over time, and (b) the aluminizing coating and magnesium oxide guard beds reduced/eliminated chromium contamination on the air side. Relatively low creep strains were observed for PDUM-71 despite its long operation, which suggested improved temperature control in the PDU.

Creep deformation of the porous and dense layers was not observed for PDUM-90 or for PDUM-71 at the leading edge, while creep strains of 2950 ppm and 4380 ppm were observed for PDUM-71 at the center and trailing edges, respectively. The increase in creep strain across PDUM-71, which operated six times longer than PDUM-90, was due to the temperature increase across the active wafer.

The modules were in relatively good condition after Run 12, with one notable exception—the bottom web layer on PDUM-89 and -90 delaminated with the separation occurring a few microns into the porous layer. The leading theory for the delamination was marginal adhesion of the web, which was later compromised by creep/gravity during operation.

Analysis of the tube stubs for PDUM-71 and DP5-107-3 revealed uniform interdiffusion of the gold washers and tube stubs with no detectable voids, unlike pre-reduced modules from Run 11. This improved, uniform bonding suggested that pre-reducing of the modules caused poor, non-uniform loading of tube stubs against the seal block during operation.

Equipment Performance

The reactor heaters were operated successfully at 400 psig for the first time since they were installed prior to Run 9. Unlike the earlier heater design, this system continued to operate reliably through four consecutive runs.

No carbon was found within the reactor, which was attributed to operating at higher steam-to-methane ratios toward the latter half of the run. However, after operating for the first half of the run (~13 days) at a lower steam-to-methane ratio, the syngas feed line briefly plugged. The obstruction increased the system pressure drop from ~53 psi to more than 167 psi, but cleared within a few minutes. Based on post-test inspection of previous PDU runs, the most likely cause of the blockage was copper particles, carbon, or steam-system impurities. Forty-five grams (1.3% of upstream copper lining) of sintered copper particles were found in the system.

Subtask 2.4.4 Test Full-Size Membrane Modules

Subtask 2.4.4.1 PDU Run 13

Objectives of Run

The objectives of Run 13 were to (a) demonstrate operation using the new SEP beam and housing design; (b) demonstrate successful transport and installation of a SEP air manifold assembly; (c) demonstrate the SEP module seals; (d) successfully start up the system with a SEP air manifold assembly intact; and (e) demonstrate iso-strain shutdown procedures on a SEP air manifold assembly.

Results and Discussion

Equipment and Modules

A new PDU beam was designed to accommodate three single-wafer commercial modules. This module was similar to those that were planned for the next phase of scale-up, the Sub-Scale Engineering Prototype (SEP). For this reason, the beam and modules were referred to as the SEP beam and SEP modules. The ceramic-to-metal seal design and the housing internal components also closely represented what were planned for the SEP program. Figure 2.4.4.1-1 is a photo of the new beam. Figure 2.4.4.1-2 is a photo of a SEP air manifold assembly installed in the metal seal block.

Figure 2.4.4.1-1 Photo of a SEP Beam and Housings

Figure 2.4.4.1-2 Photo of a SEP Air Manifold Assembly Installed in Metal Seal Block

The syngas pre-heater was lined with copper, while most of the syngas-side metal components within the housings were unlined. Each of the housings was equipped with a magnesium oxide air-side guard bed, and most of the metal components downstream of the guard beds were either coated or lined with refractory.

Three SEP air manifold assemblies (modules without wafers) were installed in the reactor. The air manifold in Housing 3 was installed without a gasket to assess its impact on seal performance. The gasket provides compliance between the metal loading ring and the ceramic. Two different loading forces were also used to assess the impact on seal performance. A lower torque is preferred since it is less likely to damage the ceramic.

Table 2.4.4.1-1 Module Arrangement and General Information for Run 13

Module	Location	Comments
Air Manifold Assembly 1	Housing 1	Bolts 25 in-lb torque
Air Manifold Assembly 17	Housing 2	Bolts 45 in-lb torque
Air Manifold Assembly ##	Housing 3	Bolts 45 in-lb torque No gasket

Module and Seal Performance

The air manifold in Housing 3 was isolated during heat-up due to a very large leak, possibly from the absence of a gasket. The leak was 600 sccm at the beginning of the run and increased

to ~50,000 sccm during pressurization and heating. Without the compliance of the mica gasket, the ceramic may have cracked during installation. The remaining two manifolds were successfully heated to 900°C, pressurized to 215 psig, and transitioned to steam/syngas conditions. The leaks during the entire start-up remained less than 100 sccm. These leak rates were as low as PDU module seal leaks despite a significantly greater sealing area. The two manifolds operated under syngas conditions for 18 days. They were successfully pressure cycled between 215 and 400 psig and thermally cycled between 900°C and 750°C. The ISO-strain procedures used during the shutdown took only three days. However, the air manifold assembly in Housing 2 failed at 585°C during the shutdown. The air manifold assembly in Housing 1 survived the shutdown, but developed a leak of 880 sccm. A leak rate history is shown in Figure 2.4.4.1-3.

Figure 2.4.4.1-3 Air Manifold Assembly Leak Rates Versus Time

The leading hypotheses for the failure of the Housing 2 manifold during iso-strain shutdown were: (a) the intended iso-strain profile wasn't achieved; (b) contamination poisoned the permeate-side and/or air-side surface reactions; (c) contamination degraded the creep and strength properties of the ceramic; (d) contamination caused an unexpected cation stoichiometry gradient through the ceramic, resulting in an unexpected and unfavorable oxygen non-stoichiometry gradient; (e) the module may have developed a large leak at the ceramic-to-metal seal due to the CTE mismatch between the ceramic and metal.

Post-Test Inspection

The syngas-side and air-side surfaces of the tested SEP air manifold assemblies were analyzed upon completion of PDU Run 13. Significant silicon contamination was observed on the syngas-side surfaces; molybdenum and chromium were found on the air-side surfaces. These contaminants could have poisoned the surface reactions and/or degraded the creep and strength properties of the ceramic. The level of contamination was not unexpected due to the lack of liners on some of the syngas- and air-side metal components. Appropriate lining and insulation materials were planned for Run 14.

Equipment Performance

Carbon formation was observed during this run. Experiments were conducted under identical operating conditions in a separate unit, but no carbon was formed. Further assessment of carbon formation in the PDU was planned.

Appropriate lining and insulation materials were planned for Run 14 to reduce contamination levels. This included the design and purchase of a dense magnesium oxide tube to be inserted through the ID of the air-side bellows, a magnesium oxide housing liner, and magnesium oxide insulation material.

Subtask 2.4.4.2 PDU Run 14

Objectives of Run

The Run 14 objectives were to (a) demonstrate successful transport and installation of a SEP module; (b) demonstrate the SEP ceramic-to-metal seal; (c) demonstrate successful startup and shutdown of a SEP module; (d) measure oxygen flux through a SEP module; and (e) test new coatings and linings for remediation of contamination and reaction on hot metal.

Results and Discussion

Equipment and Modules

The syngas pre-heater was lined with copper, and the housings were lined with magnesium oxide brick and dense magnesium oxide plates. The housings were also equipped with magnesium oxide air-side guard beds, and the metal components upstream and downstream of the guard beds were coated or refractory lined.

The first installation of SEP module housings onto the beam resulted in broken modules. The beam lid contacted thermocouples protruding above the module housings (Figure 2.4.4.2-1), pushing the thermocouples into the membrane surface. Two of three SEP modules broke. Metal interference pins were attached to the top of the module housings to prevent the beam lid from contacting the thermocouples in future assemblies.

Figure 2.4.4.2-1 Photos of Housings with Protruding Thermocouples (Left) and the Lack of Clearance After the Beam Lid Was Installed (Right)

Three SEP modules were successfully installed in the reactor for testing. This was the first test of full-size wafers in the PDU. The table below lists the arrangement of the modules in the housings.

Table 2.4.4.2-1 Module Arrangement and General Information for Run 14

Module	Location	Comments
SEPM-0008	Housing 1	Uncatalyzed membrane Protective web layer Air-side guard bed 25 in-lb seal bolt torque
SEPM-0009	Housing 2	Uncatalyzed membrane Protective web layer Air-side guard bed 25 in-lb seal bolt torque
SEPM-0006	Housing 3	Uncatalyzed membrane Protective web layer Air-side guard bed 25 in-lb seal bolt torque

Module and Seal Performance

PDU Run 14 was very successful, especially considering that it was the first test of single-wafer SEP modules. All three SEP modules survived the high-stress startup conditions, being successfully heated to 900°C, pressurized to 215 psig, and transitioned to steam/syngas feed conditions. Oxygen flux data was obtained for all three modules, and the ceramic-to-metal SEP seals for each module performed well, with leak rates comparable to PDU seals despite the

significantly larger sealing perimeter. SEPM-0008 operated for 60 days under various syngas conditions, while SEPM-0009 and SEPM-0006 operated for 28 days before failing.

The syngas-side process gas was diluted with nitrogen to manage the large temperature gradients across the SEP modules. The leading-to-trailing edge gas temperature difference was as high as 100°C. These gradients were the result of two primary factors. The first was the larger membrane area of a SEP module relative to a PDU module without a proportional increase in syngas-side flow. Modification of the PDU for larger flow rates was deferred due to projected cost and downtime. Startup using the existing flow capacity created a more severe thermal stress condition that should be improved with increased flow rate. The second factor influencing the temperature profile was the bypass of a portion of the syngas flow around the modules. It was estimated that 65 percent of the syngas feed to each module was leaking out of the housing. This meant only 35 percent of the total feed reached Housing 2, and only 12 percent of the total feed reached Housing 3.

All three SEP modules survived a two-week hold under syngas/steam/nitrogen conditions. The oxygen flux was stable for the module in Housing 1, but declined for the other two modules during this hold period. Potential causes for the flux decline were contamination from system components and increasing syngas bypass around wafers resulting in reduced reactant feed to the modules. Following the two-week hold, the syngas composition was ramped to a new condition. The module in Housing 2 failed just prior to end of the ramp, when a mass flow controller dropped offline. The module in Housing 3 failed within two minutes after the failure of the module in Housing 2, likely due to thermal and chemical shock created by failure of the Housing 2 module. There were no unusually high stress conditions preceding the failure of the module in Housing 2.

The Housing 1 module was tested at different temperatures and hydrogen concentrations to better understand performance under limited porous layer diffusion conditions. The module was also tested over a range of carbon dioxide concentration. The oxygen flux decreased 32% when the CO₂ in the syngas feed was increased from 0 to 0.7% (Table 2.4.4.2-2). This was very similar to the effect observed with PDU modules in Run 12.

Table 2.4.4.2-2 Operating Data Showing the Impact of Carbon Dioxide Concentration on Oxygen Flux

Inlet Temp	787	787	787	787	787
Outlet Temp	859	852	845	841	836
% N₂	46.05	46.01	45.86	45.81	45.86
% H₂	9.26	9.20	9.15	9.09	9.06
% CH₄	0.00	0.00	0.00	0.00	0.00
% CO₂	0.01	0.17	0.34	0.52	0.69
% CO	0.00	0.02	0.05	0.07	0.10
% H₂O	44.67	44.60	44.60	44.50	44.29
O₂ Flux	Base	89%	81%	74%	68%

The module in Housing 1 eventually failed due to an interruption of the syngas-side feed. The sudden loss of feed caused large chemical and thermal shock to the module, leading to its failure. The module would have been predicted to fail under changes of these magnitudes. It had operated under syngas for 60 days. Figure 2.4.4.2-2 shows the history of the module performance.

ITM Syngas PDU Run 14 History

Figure 2.4.4.2-2 Module Performance Data for Run 14

In its first PDU test, the SEP ceramic-to-metal seal design performed extremely well (Figure 2.4.4.2-3). SEP module leaks during operation were well below 50 sccm. These leaks were similar to those observed with PDU module seals despite the significantly larger perimeter of the SEP seal.

Figure 2.4.4.2-3 Module Leak Rates Versus Time

Post-Test Inspection

After the run, the modules were removed from their housings and analyzed to evaluate reactor and module performance. The modules were in relatively good condition, including SEPM-0009 and SEPM-0006, which both failed 32 days before the end of the run. Copper dust was found on the upper surfaces of SEPM-0008, mostly trapped within the channels of the web layer. Little or no copper was found on SEPM-0009 or SEPM-0006. SEPM-0008 likely scrubbed/trapped the majority of the copper dust entering the reactor.

The syngas-side surfaces of SEPM-0008 were partially contaminated with silicon in the form of calcium silicate. The porous layers were not plugged with the contaminant phases, and little or no contamination was found below the outer surface of the porous layers. The deposited silicon and copper dust were bound to the ITM material. The copper dust was porous and over 200 μm thick in heavily-contaminated areas. The contaminants had no apparent effect on the flux performance of SEPM-0008, but the oxygen flux was likely limited by porous layer diffusion due to the low H_2 fraction. Therefore, any effect of contamination on flux may have been difficult to detect. The level of silicon contamination was much less compared to Run 13 due to the addition of appropriate liners and insulating materials on the hot syngas-side metal components. Overall, more silicon was observed on the active wafer of SEPM-0008 than on the active wafer of SEPM-0009 and the highest levels of contamination were found on the air manifolds due to their close proximity to bare metal. The varying contamination levels on the active wafers were likely the result of the volatile contaminants being scrubbed from the gas

stream by upstream modules or the magnesium oxide internals. Flow bypass and the resulting varying mass transfer of the volatile contaminants could have also been an issue.

Creep deformation of the porous and dense layers over the slots was observed for SEPM-0008 at the center and trailing edge of the active wafer, while no creep deformation was detected for SEPM-0009 at any location. The observed creep strains for SEPM-0008 increased from leading edge to trailing edge and were a result of the temperature increase across the active wafer. The greater creep deformation of SEPM-0008 was also not unexpected. SEPM-0008 operated twice as long as SEPM-0009 and also had trailing-edge gas-phase temperatures of 880 to 920°C for 25 percent of the operating time, 840 to 880°C for 50 percent of the time, and less than 840°C for the remaining time, all at a pressure differential of 200 psi.

Little or no chromium contamination was detected on the active membrane on the air side, but molybdenum and chromium contaminants were found within the non-permeating air channels upstream of the active membranes. The likely source of the contamination was the molybdenum- and chromium-containing Hastelloy 276 parts in the ceramic-to-metal seal. The parts were lined with dense magnesium oxide, but these liners proved unsuccessful at completely mitigating contamination. Haynes 214 (a molybdenum-free alloy) will be used for these parts in Run 15. The air-side magnesium oxide guard bed for Housing 1 was also analyzed and showed no trend in chromium concentration and minimal chromium uptake. Guard bed analysis also suggested that the newly-applied aluminizing coating on the air-side metal surfaces, both upstream and downstream of the guard beds, was working well to mitigate chromium evolution from the base alloy after a few months of operation. The guard beds will be examined after Run 15 to further evaluate coating and bed performance.

The center and trailing edges of the air-side active membranes for both modules were mostly covered with Ca- and Fe-rich secondary phases, products of kinetic decomposition. These secondary phases had no apparent effect on the flux performance of SEPM-0008, but oxygen flux was likely limited by gas-phase mass transfer through the porous layer (rather than solid-state bulk diffusion) due to the operating conditions. The leading edges of each module had low, immeasurable rates of kinetic decomposition. Typically less than 50 percent of the dense-layer surfaces were covered with thin kinetic decomposition products. The low rates of kinetic decomposition at the leading edge were not unexpected due to the relatively low, leading-edge gas-phase temperatures for SEPM-0008 and the short run time for SEPM-0009.

The system was operated with a high steam-to-carbon ratio during Run 14 and little or no carbon was found in the housings.

Equipment Performance

Leaks of syngas feed from the module housings led to larger temperature rises across the modules and diminished the quality of the data collected in this run. Post-test inspection showed that the housing leaks were primarily through the four thermocouple holes in the housing lids (Figure 2.4.4.2-4). Additionally, there was some leakage at the seams between housings.

Figure 2.4.4.2-4 Module Housing Cross Section Showing Syngas-side Gas Flow Bypass Paths

Leaks from these locations were made worse by a blockage in the housing exit line (Figure 2.4.4.2-5) which was caused by the copper liner melting. As the exit line became restricted, more gas was forced through the leak paths. This may explain the change in oxygen flux performance under steady-state conditions. As the leak rates increased, less hydrogen was probably available for combustion.

Figure 2.4.4.2-5 Photos of the Housing Exit Line Blockage

Several modifications were made to minimize housing leaks in future runs. Gaps between the housings and around the thermocouples were sealed with metal gaskets or ceramic pastes. The housing exit flow area was significantly enlarged to reduce backpressure on the housings. After the modifications were in place, a flow test confirmed that housing leaks had been reduced to nearly zero.

Subtask 2.4.4.3 PDU Run 15

Objectives

The Run 15 objectives were to (a) demonstrate successful transport and installation of a SEP module; (b) demonstrate the SEP ceramic-to-metal seal; (c) demonstrate successful startup and shutdown of a SEP module; (d) measure oxygen flux through a SEP module; and (e) evaluate performance of Chevron coating to minimize contamination and an undesired gas-phase reaction catalyzed by the hot metal.

Results and Discussion

Equipment and Modules

In prior runs, the syngas heater was lined with copper. The copper creates particulates during operation that lead to contamination of the modules and possible plugging of the syngas feed line. For Run 15, a metal coating technology provided by Chevron was applied to the syngas heater and reactor feed lines. The Chevron coating was expected to remediate module contamination and undesired gas phase reaction catalyzed by the hot metal.

As in Run 14, the housings were lined with magnesium oxide brick and dense magnesium oxide plates. Magnesium oxide air-side guard beds were also installed on all the housings, and the metal components upstream and downstream of the guard beds were either coated or refractory lined.

Three SEP modules were installed in the reactor for testing. Table 2.4.4.3-1 lists the arrangement of the modules in the housings.

Table 2.4.4.3-1 Module Arrangement and General Information for Run 15

Module	Location	Comments
SEPM-0010	Housing 1	Uncatalyzed membrane Protective web layer Air-side guard bed 25 in-lb seal bolt torque
SEPM-0011	Housing 2	Uncatalyzed membrane Air-side guard bed 25 in-lb seal bolt torque
SEPM-0013	Housing 3	Uncatalyzed membrane Protective web layer Air-side guard bed 25 in-lb seal bolt torque

Module and Seal Performance

The run was very successful, especially considering that it was only the second test of single-wafer SEP modules. The three modules were installed without incident and survived the high-stress startup conditions. Oxygen flux data was obtained for all three modules. The ceramic-to-metal SEP seals for each module performed well, with leak rates comparable to PDU seals despite the significantly larger sealing perimeter. SEPM-0010 and SEPM-0011 operated for 79 days and 142 days, respectively, under syngas conditions. SEPM-0013 operated for 155 days under varying syngas conditions (95 different operating conditions were tested). This was the longest run of ITM Syngas modules.

The syngas-side process gas was diluted with nitrogen to manage the large temperature gradients across the modules. The leading-to-trailing edge gas temperature differences were as high as 60°C. This temperature increase was nearly half of that observed in Run 14 and was the result of eliminating the leaks from the housings. Syngas flow over the modules was much greater, thereby providing more cooling. The temperature increase was still large compared with PDU modules because of the increased membrane area of a SEP module without a proportional increase in syngas-side flow. Modification of the PDU for larger flow rates was deferred due to projected cost and downtime. Startup using the existing flow capacity creates a more severe thermal stress condition that should be improved with increased flow rate.

All three SEP modules survived a two-week hold under syngas/steam/nitrogen. The oxygen flux was stable for all three modules. A decline in oxygen flux was observed in Run 14 that was attributed to the increasing leak rate of syngas from the housings. With the housing leaks eliminated, the oxygen flux was stable for Run 15.

The ceramic-to-metal seals performed well during this period, but leaks suddenly developed on two modules after about two months of operation. The location and cause of the leaks were not determined. After 79 days of operation, the module in Housing 1 developed a leak that needed to be isolated to prevent possible failures of the other modules. The Housing 1 module was successfully isolated without causing failure of the modules in Housings 2 and 3. This was a major accomplishment given past experiences of failures. After 142 days, the module in Housing 2 also developed a sizable leak that continued to increase. This module was also successfully isolated without causing the failure of the Housing 3 module. The module in Housing 3 operated during the entire run (155 days) without any measureable leaks. A history of the module leaks is shown in Figure 2.4.4.3-1.

Figure 2.4.4.3-1 Module Leak Rates Versus Time

Operating flux data was collected for model validation. In total, 95 run conditions were tested covering various combinations of pressure, temperature, and composition. The tests were limited to hydrogen concentrations less than 9 percent in order to limit the temperature gradients on the modules. On the syngas-side, carbon dioxide, hydrogen, and methane concentrations were varied. Oxygen, carbon dioxide, and water concentrations, along with air pressure and flow, were varied on the air-side. Figure 2.4.4.3-2 shows the history of the module performance.

ITM Syngas PDU Run 15 History

Figure 2.4.4.3-2 Module Performance Data for Run 15

Variations in the syngas-side carbon dioxide concentration (0 to 8 percent) appeared to have a large negative effect on oxygen flux (Figure 2.4.4.3-3) was observed. The effect was reversible when the carbon dioxide was removed. Carbon dioxide has consistently resulted in a significant reduction in oxygen flux with both PDU modules (Run 12) and SEP modules (Runs 14 and 15). Thermodynamic models indicated that the ITM material was stable under these conditions. However, these models also suggested that calcium, a component of the ITM material, would react with carbon dioxide to form calcium carbonate under the tested conditions. The negative oxygen flux effect observed with carbon dioxide could be some form of chemi-sorption of the carbon dioxide on "CaO-like" surface sites. The reaction of carbon dioxide with lanthanum-rich demixing products, although not as well understood, was another possibility.

Figure 2.4.4.3-3 Operating Data Showing the Impact of Carbon Dioxide Concentration on Oxygen Flux

Figure 2.4.4.3-4 shows that the oxygen flux was linearly proportional to the hydrogen concentration, which varied from 0.7 to 9 percent. The linear regression suggested that, for this range of hydrogen concentration, the oxygen flux was limited by hydrogen diffusion through the porous layer. This hypothesis was further supported by the limited impact of the steam-to-hydrogen ratio on the oxygen flux. The steam-to-hydrogen ratio determines the equilibrium partial pressure of oxygen, which would have a stronger impact on oxygen flux if the dense layer membrane was the limiting resistance. This data will be used to validate the porous-layer parameters in the model.

Figure 4.2.2.3-4 Operating Data Showing the Impact of Hydrogen Concentration on Oxygen Flux

The methane concentration on the syngas-side was varied from 0 to 10 percent, and the oxygen flux was slightly dependent on the methane concentration (Figure 2.4.4.3-5). The small improvement in oxygen flux may also, in part, be caused by small changes in hydrogen concentration resulting from some methane reforming. This small methane effect on oxygen flux suggested minimal methane oxidation was occurring under these operating conditions.

Figure 2.4.4.3-5 Operating Data Showing the Impact of Methane Concentration on Oxygen Flux

Air pressure and air flow had only a small effect on oxygen flux (Figure 2.4.4.3-6). The oxygen flux decreased only a few percent when the air flow or absolute operating pressure was doubled. The changes in oxygen flux with air flow rate were smaller than the changes observed with PDU modules in Run 12. However, testing with PDU modules was done at a higher oxygen flux and with greater air flow per unit membrane area.

Figure 2.4.4.3-6 Operating Data Showing the Impact of Air Flow and Air Pressure on Oxygen Flux

Changes in water and oxygen concentration on the air side resulted in no change in oxygen flux. The carbon dioxide concentration in the air was varied from 0 to 5 percent and had varying degrees of impact on the oxygen flux. At 500 ppm CO₂ (a level similar to ambient air), there was no short-term impact on oxygen flux. At 785°C, 5% CO₂ (a level similar to feed from a direct-fired heater) had an irreversible, negative impact on oxygen flux. The arrows in Figure 2.4.4.3-7 show the progression of testing at 785°C. The oxygen flux decreased when 5% CO₂ was initially added to the air feed (5% CO₂ and 20% air-side oxygen). The oxygen flux did not recover when the CO₂ was replaced by nitrogen, and remained constant when the oxygen concentration was further diluted with nitrogen (0% CO₂ and ~18% air-side oxygen). When 5% CO₂ was added in place of nitrogen (5% CO₂ and ~18% air-side oxygen), the oxygen flux remained nearly constant. Finally, when the CO₂ and nitrogen were removed, returning the air-side composition back to air, the oxygen flux remained 20 percent lower than originally measured. Thermally cycling the module to 840°C and back to 785°C did not recover the 20% loss in oxygen flux. The Housing 3 module data in Figure 2.4.4.3-7 represent a module held at 835°C during the same CO₂ composition cycle. At this temperature, the 5 percent CO₂ had no measurable effect on the oxygen flux.

Figure 2.4.4.3-7 The Impact of Carbon Dioxide in the Air Feed on the Oxygen Flux at Two Different Temperatures

The effect on oxygen flux of 5 percent CO₂ at low temperatures was surprising. Thermodynamic models indicated that the ITM material was stable under these conditions. Unlike the syngas-side, calcium carbonate formation was not favored under the operating conditions. One theory was that CaO, an observed kinetic decomposition product, reacted with CO₂ during the air-side CO₂ experiments to form CaCO₃, causing as high as a 120-percent volumetric expansion of the kinetic decomposition layer. If the decomposition layer detached as a result of the CO₂ reaction, this could explain the permanent flux loss for SEPM-0011 after the CO₂ studies due to a reduction of active membrane area and an increase in gas-phase mass transfer resistance.

Post-Test Inspection

After the run, the modules were removed from their housings and analyzed to evaluate reactor and module performance. The modules were in relatively good condition, including SEPM-0010 which failed 76 days before the end of the run. Some silicon contamination was observed on the syngas-side surface, but only on the outer surface of the porous layers and dense rims. Little or no contamination was observed on the air side of the active dense layers.

The syngas-side surfaces were partially contaminated with silicon in the form of calcium silicate. The porous layers were not plugged with the contaminant phases, and no contamination was

found below the outer surface of the porous layers. The contaminants had no apparent effect on the flux performance during the first 60 days of the run, when conditions were repeated to assess flux stability. However, oxygen flux may have been limited by porous layer diffusion due to the low hydrogen fraction, so any effect of contamination on flux may have been difficult to assess. The level of silicon contamination was much less than that observed after Run 13 due to the addition of magnesium oxide liners and insulating materials on the hot syngas-side metal. In addition, the Chevron coating in the syngas heater appeared to reduce contamination levels compared to shorter runs with copper liners that had similar levels of contamination. The highest levels of contamination were found on the outer surface of the air manifolds due to their proximity to bare metals. The varying contamination levels on the active wafers were likely due to scrubbing of volatile contaminants by upstream modules or magnesium oxide internal components, and/or issues of flow bypass and varying mass transfer of the volatile contaminants.

Creep deformation of the porous and dense layers over the S1 slots was observed for SEPM-0011 at the center and trailing edges of the active wafer (Figure 2.4.4.3-8), and for SEPM-0013 at all locations. The observed increase in creep strain from the leading to the trailing edge was due to a temperature rise across the active wafer. SEPM-0013 had peak trailing-edge gas-phase temperatures of 900 to 935°C for 50 percent of the run. SEPM-0011 had peak trailing-edge gas-phase temperatures of 860 to 900°C.

Figure 2.4.4.3-8 SEM Images of Wafer Cross Sections from SEPM-0011 Showing Varying Degrees of Creep Deformation of the Porous and Dense Layers at the Center and Edges of the Wafer

Little or no chromium contamination was detected on the air-side active membranes. There was also no molybdenum contamination. In Run 14, molybdenum and chromium contaminants evolved from the Hastelloy 276 parts in the ceramic-to-metal seal assembly. However, in Run 15 the parts were made of Haynes 214, a molybdenum-free alloy that is more inert with respect to chromium evolution.

The air side of the active membranes for SEPM-0011 and SEPM-0013 at the center and trailing edges were partially- to fully-covered with Ca- and Fe-rich secondary phases, products of kinetic decomposition. The amount of products generally increased from the leading to the trailing edge of the membrane due to the expected temperature increase along the membrane. The kinetic decomposition rates for the top and bottom D-layers and left and right sides of the wafer were similar at each location, suggesting that issues of flow bypass and temperature variation were not

a major factor. The products of kinetic decomposition, though in lower levels, also had no apparent effect on flux performance during the first 60 days of the run, when operating conditions were repeated to assess flux stability.

Relatively thick kinetic decomposition layers in SEPM-0011 were detached from the membrane surface (Figure 2.4.4.3-9). One theory was that CaO, an observed kinetic decomposition product, reacted with CO₂ during the air-side CO₂ experiments to form CaCO₃, causing as high as a 120% volumetric expansion of the kinetic decomposition layer. The permanent flux loss for SEPM-0011 after the CO₂ experiments might be explained if the decomposition layer detached as a result of this large expansion. This theory was further supported by the discovery of more detached kinetic decomposition layers in SEPM-0011 than SEPM-0013, potentially due to the lower membrane temperatures of SEPM-0011 and, consequently, the more thermodynamically-favored reaction of CaO with CO₂.

Figure 2.4.4.3-9 SEM Image of a Wafer Cross Section Showing a Detached Kinetic Decomposition Layer on the Air Side of the Dense Membrane

Equipment Performance

Little or no carbon was found in the housings as a result of operating at high steam-to-carbon ratios, which were intentionally selected to reduce the potential for carbon formation. The absence of carbon in the housings was also the result of operating without methane in the feed during the latter half of the run.

Early in the startup, a significant restriction occurred in the syngas feed line. The restriction was short-lived and an exact cause was not determined. The cause was probably due to the accumulation of debris from the Chevron-coated tubing or possibly materials left over from early attempts to clean the coated syngas heater coil. No additional restrictions were encountered for the remainder of the run.

The Chevron-coated tubing appeared to prevent undesirable gas-phase reactions catalyzed by the hot metal. Figure 2.4.4.3-10 shows how the composition of a syngas feed of 10.6% CH₄ did not

significantly change through the syngas heater and tubing leading to the reactor, both of which were treated with the Chevron coating. Under similar conditions in Run 5, the methane reacted to equilibrium in unlined and uncoated tubing. Consistent with results of tests using copper-lined tubing, the reverse water-gas shift reaction of CO₂ to CO was not inhibited by the Chevron-coated tubing.

Figure 2.4.4.3-10 Composition Profile Across the Syngas Heater and the Membrane Modules

Subtask 2.5.1

SEP Project Definition

According to the development plan, the Small-scale Engineering Prototype (SEP) would be the next technology scale-up upon successful operation of the PDU. The SEP was intended to test and demonstrate critical components of the technology that were to be included in the proposed commercial design. Figure 2.5.1-1 shows the envisioned process design for GTL market applications. This process design, developed under Subtask 2.1.1, was based on the intermediate injection of the F-T recycle gas. The overall SEP goal was to demonstrate technical risk resolution concepts that would significantly reduce risks for subsequent technology scale-ups.

Figure 2.5.1-1 Commercial Process Design Flowsheet for the GTL Market Application

The SEP project definition was initiated in the first quarter of fiscal year 2002. The goals were to develop a conceptual scope for the project, choose a potential site, develop a preliminary cost estimate, and identify the major technology risks associated with proceeding with the project. The nominal SEP syngas capacity was targeted to be 500 MSCFD, equivalent to about 15 bbl/day of F-T liquids. This capacity was considered to be a sizable, but acceptable, scale-up from the PDU capacity of 24 MSCFD.

The critical objectives of the project were as follows:

- Operate in a safe manner
- Demonstrate key features of the commercial reactor design (Figure 2.5.1.2)
- Demonstrate startup/shutdown procedures
- Design the facility for flexibility (ability to add bulk catalyst, operate a single section of a full-conversion reactor, etc.)
- Provide appropriate performance data for the next level of technology scale-up

Figure 2.5.1-2 Commercial ITM Reactor Concept

The SEP project was expected to utilize full-size, commercial membrane wafers in "short" modules. The wafer count in these "short" modules was to be much less than in the full-scale commercial modules. The most current membrane, wafer, and module designs were to be incorporated into the reactor design, which would be flexible enough to accommodate future membrane, wafer, and module design modifications needing to be tested in the SEP facility during its period of operation.

The Air Products LaPorte, TX facility was considered the primary site for this project, having been the site of a previous DOE R&D demonstration. The site also included commercial hydrogen and carbon monoxide facilities and air separation facilities. Thus, costs for the SEP project could be reduced by taking advantage of the existing infrastructure. This infrastructure potentially included feedstocks, utilities, used process and analytical equipment, control rooms and other buildings. In addition, Air Products' on-site operations personnel could be used to support the SEP facility.

A conceptual process flow diagram for the SEP was developed and is shown in Figure 2.5.1.3. A key feature of this process flow diagram was the reheating of intermediate reactor streams in a convection section. This feature was intended to provide flexibility to ensure operation at the desired temperatures, since the expected heat leak for equipment of this size would exceed the heat generated by the partial oxidation reactions. In the PDU, this flexibility was attained by including electric heaters in the reactor, but this solution was considered too expensive for the SEP. Another key feature of the design was having five separate reactor vessels operating in series, such that each reactor vessel would complete a portion of the overall conversion of the feed. These separate vessels would facilitate the intermediate reheating of the syngas and make fabrication, transportation, and maintenance easier. Finally, the F-T recycle gas would be simulated by blending appropriate gases obtained from the host facility.

Figure 2.5.1-3 Process Flow Diagram for the SEP

Air Products developed the heat and material balances, a P&ID, and equipment specifications for this SEP design. McDermott Technologies completed a preliminary reactor design, which included an internal flow duct that allowed telescoping the shell to gain access to the reactor internal components. Figure 2.5.1.4 shows the basic concept of the preliminary reactor design. Air Products developed a plot plan and an equipment layout. Equipment cost summaries were prepared based on Air Products in-house estimates and select vendor quotes. The installed cost for the SEP was estimated based on standard Air Products practices.

Figure 2.5.1-4 Conceptual Design of the SEP Reactor

Air Products conducted a value engineering exercise to reduce the cost of the project. The following ideas were considered:

- Reduce capacity from 500 MSCFD to 330 MSCFD.
- Install only one of the five reactor shells and design the other areas of the plant to provide the appropriate gases to this reactor to simulate any of the five original reactors (partial conversion rather than full conversion).

The new process flow diagram resulting from this exercise is shown in Figure 2.5.1.5.

Figure 2.5.1-5 Revised Process Flow Diagram for the SEP

A factored estimate was generated based on the original estimate and the proposed modifications.

The following major SEP technical risks were identified:

- The PDU was still undergoing upgrades to ensure reliable operation (see Subtask 2.4.3).
- There was very limited performance data for PDU modules and no performance data for SEP modules.
- Catalyzed membrane development was just being initiated.
- Reactor design details needed further development.

The technical risks of scaling up to the SEP plant, financial risk, and budget prioritization led to a revised program strategy. The major focus of this strategy was to resolve technical risk at the smallest scale possible to minimize cost and time. This concept translated to an expanded focus

on PDU testing, including tests of full-size membrane wafers in the PDU. This strategy postponed the SEP project to some future time.

In the ensuing years, significant progress was made toward resolving the technical risks. Catalyzed PDU modules were successfully tested after a challenging development period. Modifications were made to the PDU in order to test single-wafer SEP modules, albeit at lower-than-commercial flow rates. These PDU modifications let to successful testing of SEP modules.

As time progressed, revised SEP strategies emerged. In particular, the successful technical risk resolution led the team to consider a larger SEP size. Capacities of 1.1 MMSCFD to 2.2 MMSCFD of syngas (equivalent to 40 to 80 bbl/day of F-T liquids, respectively) were considered. As the DOE-funded project was ending, another SEP project definition was being planned in which the SEP nominal syngas capacity would be a 1.1 MMSCFD.

INTELLECTUAL PROPERTY

ITM Syngas US Patents and Published Patent Applications

During the course of the research program, key inventive concepts were developed to solve various technical challenges that were encountered. These enabling concepts were critical to the development and the practice of the technology. The patent estate has a number of issued patents and published patent applications. These are listed in the attached table and pdf files of each patent and published patent application are included in Appendix A-1.

INTELLECTUAL PROPERTY (CONTINUED)

ITM Syngas US Patents and Published Patent Applications *

Patent Number	Title	Inventors	Date of Filing	Date of Patent
6,114,400	Synthesis gas production by mixed conducting membranes with integrated conversion to liquid products	Nataraj et al	9/21/1998	9/5/2000
6,492,290	Mixed conducting membranes for syngas production	Dyer et al	8/22/2000	12/10/2002
7,094,301	Method of forming a joint	Butt et al	3/21/2003	8/22/2006
7,279,027	Planar ceramic membrane assembly and oxidation reactor system	Carolan et al	3/21/2003	10/9/2007
7,335,247	Ion Transport membrane module and vessel system	Stein et al	1/29/2007	2/26/2008
7,425,231	Feed gas contaminant removal in ion transport membrane systems	Carolan et al	1/3/2005	9/16/2008
Published Application Number	Title	Inventors	Date of Filing	Date of Publication
20060180022	Ion Transport membrane module and vessel system with internal directed gas flow	Holmes et al	11/22/2005	8/17/2006
20070079703	Feed gas contaminant control in ion transport membrane systems	Carolan et al	10/11/2005	4/12/2007
20080085236	Planar ceramic membrane assembly and oxidation reactor	Carolan et al	8/22/2007	4/10/2008
20080136179	Seal assembly for materials with different coefficients of thermal expansion	Minford	11/17/2005	6/12/2008
20080168901	Liners for ion transport membrane systems	Carolan et al	8/14/2007	7/17/2008
20080302013	Staged membrane oxidation reaction system	Repasky	6/5/2007	12/11/2008

* As of 31 December 2008

CONCLUSION

The Air Products-led team successfully developed ITM Syngas technology, a new disruptive technology, from the concept stage to a stage where a small-scale engineering prototype was about to be built. This effort solved many significant technical challenges and successfully scaled-up key aspects of the technology to prototype or near-commercial scale. Throughout the project, the technology showed significant economic benefits over conventional technologies. While there are still on-going technical challenges to overcome, the progress made under the DOE-funded development project proved that the technology was viable and that continued development post the DOE agreement is warranted.

The discussion that follows provides insights into the major accomplishments made during the DOE-funded development project and the current status of key aspects of the technology.

Materials

The DOE-funded effort began with identified oxygen ion conducting materials that showed promise for separating oxygen from air and reacting the oxygen with methane in a single unit operation. However, early testing showed that these materials were not as stable as would be required under full commercial operating conditions. This finding caused the program to begin an unplanned materials development effort to improve the materials. Targets were set by process and economic studies and an understanding of the commercial applications.

The I(4) family of materials was successfully developed to meet commercial targets for oxygen flux, stability, and lifetime. This effort was a major part of the Phase 1 scope and continued to be a significant portion of Phase 2. Testing and material composition adjustments continued throughout the program as new insight was attained on material properties, ceramic processing, membrane performance, and process cycles. Today, the chosen material composition has been broadly tested and its properties are well understood. This material meets the requirements necessary for the next stage of technology development, a small-scale engineering prototype.

Future enhancements that may be beneficial include higher operating temperature capability and additional contaminant resistance. Materials with these characteristics may be good candidates for second generation membranes.

Ceramic Processing

Ceramic processing development has demonstrated that membranes can be made from the chosen material using conventional ceramic processing technologies. In addition, complex membrane structures and membrane modules were fabricated and tested successfully.

Early in the program, studies showed that using tubular membranes was not as cost effective or as practical as planar membranes. This finding caused a major shift in the direction of the

CONCLUSION (CONTINUED)

development program --the original tubular membrane concepts were abandoned in favor of planar membranes. New membrane structures were designed and the associated ceramic processing steps were developed. Initially, in Phase 2, a subscale membrane wafer and module were developed for testing. Later in Phase 2, the membrane wafer was scaled-up to commercial size and an SEP membrane module was designed and built for testing.

The necessary ceramic processing equipment was successfully demonstrated at a small scale. As the equipment was tested and used, improvements were made as necessary. Scale-up of this equipment was successfully completed as increasing numbers of test articles were required by the program. Automated wafer assembly equipment, required for large-scale commercial manufacturing, was developed and installed to support the production requirements for the SEP project, but was still in commissioning as the DOE-funded program ended. Sintering and joining kiln capacity will need to be improved during scale-up to commercial production levels rather than merely putting more kilns in parallel.

Although the current ceramic processing yields were improved during the latter stages of Phase 2, they are still below commercial targets. To attain commercial economics, yield improvements will need to continue and may require further ceramic processing development.

New ceramic-to-ceramic joining techniques were successfully developed that enabled excellent module fabrication yields in accordance with stringent leak-tightness criteria. Multi-wafer modules using commercial-size wafers were successfully fabricated using these techniques. These modules included up to five wafers. Scale-up to commercial modules with as many as 100 wafers appears feasible but has not yet been demonstrated.

Oxygen Flux

The strategy was to measure oxygen flux over a wide range of conditions, validate the model with actual data, and use the model to predict the oxygen flux at every stage in the commercial reactor. This strategy provided a fundamental understanding of oxygen flux, minimized the amount of testing required, and streamlined the development process as changes were made to membrane design, process operating conditions, and reactor configurations.

Oxygen flux was measured on a large number of test articles, PDU modules, and SEP modules over a very wide range of operating conditions (temperature, pressure, and composition). Oxygen fluxes were measured that met or exceeded the commercial target value. The effect of contaminants was also assessed and, in some cases, was found to be substantial. Where necessary, strategies to eliminate contaminants were developed and successfully demonstrated.

Models were also developed to fundamentally predict membrane performance. The initial simplified models were useful in the early stages of the program but were insufficient for actual reactor design. Therefore, more comprehensive models were developed. The current model did not predict the experimental results in all circumstances. In these cases, there appeared to be additional surface resistances that the model does not fully take into account. The fact that an on-membrane catalyst enhances oxygen flux supports this hypothesis. These additional surface

CONCLUSION (CONTINUED)

resistances must be further understood and incorporated into the model to enhance its predictive capability.

Using the current membrane model, membrane design, and reactor operating conditions, the predicted oxygen flux profile across the reactor resulted in a membrane area that exceeded the commercial target. Oxygen flux can be increased by implementing various changes to membrane design parameters and features and/or reactor operating conditions. This optimization capability should make the commercial target attainable.

Membrane Mechanical Integrity

The mechanical integrity of the membrane under proposed operating conditions has been successfully demonstrated for both PDU modules and single-wafer SEP modules. These types of modules were successfully subjected to:

- Pressure differentials consistent with commercial reactor conditions.
- Temperature gradients greater than commercial reactor conditions.
- Controlled startup and shutdown cycles acceptable for commercial applications (although faster startup and shutdown times are desirable).

The fundamental material properties at high temperature were measured and are understood.

Scale-up to full-size commercial modules has not been demonstrated but is considered to be feasible.

Membrane Lifetime

Membrane lifetime is determined by many factors, with the most important being creep and kinetic decomposition. Both were studied extensively and are understood for the I4(D) material.

Observed and predicted creep rates suggest that, under proposed reactor operating conditions, the predicted membrane life is consistent with commercial targets. The highest membrane operating temperatures near the outlet of the reactor result in the highest creep rates. If higher operating temperatures are desired, further optimization of the membrane material or wafer, reactor, or process designs may be required.

Observed and predicted kinetic decomposition rates suggest that, under proposed reactor operating conditions, the predicted membrane life is consistent with commercial targets. The highest membrane operating temperatures near the outlet of the reactor result in the highest kinetic decomposition rates. There is little data on the effect of kinetic decomposition on the oxygen flux. A secondary phase, resulting from kinetic decomposition, has been shown to have

CONCLUSION (CONTINUED)

the potential for spalling, which can impact membrane mechanical integrity and oxygen flux. If higher operating temperatures or thinner membranes are desired, further optimization of the membrane material or wafer design may be required.

Testing has demonstrated that slow crack growth is not an issue with the I4(D) material and hence does not affect membrane lifetime.

Process Design and Controls

Significant process cycle work was completed and has provided continuing evidence that ITM technology can offer significant benefits for the production of syngas and hydrogen, including scenarios that require carbon dioxide capture. While the balance of plant generally uses existing technology, there are equipment challenges that remain to be demonstrated. These primarily include preheating steam, air, and pre-reformed mixed feed to the desired temperatures, which are beyond conventional practice.

The overall process control of the membrane system has been recognized as a challenge by the various organizations attempting to develop the technology, as evidenced by the number of patent applications and patents. The Air Products approach was a fundamental use of thermodynamic equilibrium to avoid the potential for run-away reactions and to ensure robust operation over the wide range of conditions typically used by commercial plants over the lifetime of the production unit. These patent-pending concepts still must be demonstrated in practice, which is the main role of the SEP.

Reactor Design

The membrane reactor design has been challenging, but significant progress was made on its development during the course of the DOE-funded program. The key objectives for reactor design were to ensure an appropriate environment for the membranes, make the system easy to assemble and maintain, and provide an acceptable lifetime for the mechanical system. Conceptual designs were completed for commercial reactors and for the PDU reactor. The PDU conceptual design evolved into an actual design that was built and has been operating successfully for several years. Designing, building, and operating the PDU enabled a better understanding of many mechanical features and resulting modifications led to excellent robustness and reliability. These learnings were carried into the early design of the SEP reactor and into the updates of the commercial reactor design. As the future SEP project begins another phase of reactor design, further details and improvements are expected to be realized.

One of the major mechanical challenges was providing robust ceramic-to-metal seals where it was necessary to connect the membranes to conventional high-temperature piping. Such seals were developed for all levels of testing (tubes, PDU modules, and SEP modules). These seals had various degrees of success, and these experiences generated significant understanding. The testing ultimately culminated with excellent performance of the ceramic-to-metal seals used for the SEP modules, a significant improvement over the ceramic-to-metal seals used for the PDU

CONCLUSION (CONTINUED)

modules. These SEP module seals are a smaller version of the design contemplated for use with commercial modules.

Lessons Learned on Managing Complex, Multi-Disciplined, High-Risk R&D Programs

Complex, multi-disciplined, high-risk R&D programs for step-out technologies require special management consideration. The ITM Syngas program is an excellent example of such a program that has successfully developed an innovative technology from the concept stage to a stage that is poised to kick-off a small scale engineering prototype project. Looking back on how this project was executed and managed and summarizing its accomplishments and challenges will assist other programs of a similar nature.

Partnering and Teams

No single organization can contain all of the skills required to successfully develop and commercialize large, high-risk, long-term R&D programs such as ITM Syngas. Partnerships are required, and we found that it is critical to assemble a diverse team. The diversity comes from different skill bases, different experiences, different perspectives, and different drivers. Along with these differences, it is also critical to have similarities. Similarities are important for several critical factors, including: the level of technical competency, strong organizational commitment to the success of the program, openness to a common approach, and willingness to communicate openly and rationally with other partnering organizations.

Air Products assembled such a partnership and managed it over the duration of the project. While there was a desire to keep the membership stable, there was also a realization that the dynamics of the program and the partners would result in some changes to the team over the course of the long-term program. These changes were driven by changing priorities within partner organizations and changing skill needs within the team. Successfully managing team member additions and departures was critical to maintaining progress.

Understanding the strategic drivers of our partners was important and critical for maintaining their organizational commitment. The program has been based on the following strategic drivers:

- The DOE's broad national interests were important drivers for their participation. In particular, the program supported their interests in the utilization of remote gas for the United States energy supply and hydrogen and fuels for clean power (stationary and vehicular). The United States has considerable natural gas reserves, much of which is located in remote locations (e.g., the Gulf of Mexico and Alaska). Converting these reserves into transportable liquid fuels using GTL technology could extend the life of the Trans-Alaskan Pipeline System and provide valuable products to our country's energy supply. Also, ITM Syngas had the potential to be a part of the hydrogen supply infrastructure required for the future implementation of fuel cells for high-efficiency

CONCLUSION (CONTINUED)

power generation and clean transportation. Thus, these strategic drivers were key reasons for DOE's significant, long-term support of the program and provided specific targets for development. Ultimately, as the DOE's interests shifted from natural gas to clean coal, their interest in the program declined and led to the termination of the cooperative agreement at the end of FY2008.

- Air Products' long-term strategic interests were and continue to be focused on serving the energy industry with hydrogen/syngas, industrial gases and equipment. These interests also include supplying equipment and technology for producing liquefied natural gas (LNG), the widely-used current approach to monetizing remote natural gas.
- Our industrial partners, Chevron, Norsk Hydro, and Sasol have had long-term strategic interest in GTL technology and/or large-scale hydrogen production. These interests were key reasons for their participation in the ITM Syngas development program. Having these end-users of the technology participate in its development was critical to setting important performance targets and development timeframes for the program. Chevron has maintained their participation through the entire program. Norsk Hydro dropped out, as their corporate focus shifted. Sasol was the most recent addition to the partnership.
- Ceramatec's strategic interest was and continues to be development and commercialization of advanced ceramic technologies. Their experience in ceramic processing development and manufacture was and continues to be a critical skill set within the team.
- Eltron Research brought key skills to the partnership, especially their initial ground-breaking work in ion transport membrane materials. They also had significant membrane testing capabilities that were invaluable to the partnership. Their materials work decreased over time as Air Products developed improved materials and testing capability.
- McDermott Technology was a key global supplier to the energy industry through their contract engineering business, special equipment design expertise, and manufacturing capability. They brought key mechanical engineering skills to the partnership. As their corporate ownership and strategies changed, their role in the program diminished and eventually ended.
- Battelle, through its relationship with PNNL, and our three academic contributors, Penn State University, the University of Pennsylvania and the University of Alaska, all had strong scientific interests in participating in leading-edge ceramic membrane development focused on early commercialization.

There were many different strategic drivers within the team. While it was advantageous that our drivers were not the same, they needed to be complementary. It was essential that each team member be driven and committed to the common goal (i.e., more economical syngas and hydrogen production for future energy needs), while recognizing each participant's different

CONCLUSION (CONTINUED)

interests. The partnership needed to be flexible and respond appropriately to changes in membership and skill needs.

These partners did not supply all the skills that were needed during the development program. Therefore, when necessary, subcontractors were used to supplement or add skills to the partnership.

Development Strategies

R&D is often carried out in a sequential manner. The classic sequential development strategy is one where each subsequent stage builds on the knowledge learned from the previous stage and a well-informed decision is made prior to advancing to the next and typically more expensive stage of development. Success relies on the existence of a relatively well-understood technology, reasonably accurate predictive capability, quantifiable risk, and modest feedback of experimental results to fine-tune predictions of the future value of the technology. A hypothetical example would be the development of a new separation process using packed-column distillation to separate two different liquid components. A development strategy that would likely be successful would be to (1) develop a flow sheet for the separation, (2) estimate the thermodynamics, (3) develop a heat and material balance around the flow sheet to understand the necessary theoretical stages, (4) use design methods to estimate the distillation column height and diameter of the packing, (5) estimate the costs relative to other separation processes, and, if still attractive, (6) test the design methods and equilibrium data with a small test column. Next, the performance data would be fed back into the process simulation and finally, if the development still looked promising, a large-scale plant would be designed and built using appropriate design safety factors to assure success. Applying this approach to the development of functional ceramic-based processes might result in the approach shown in Figure 1, where the key steps might include (1) cycle development and economic comparisons, (2) process modeling, (3) materials and seal development, (4) ceramic processing development, and (5) reactor design.

Figure 1-A A Sequential Development Strategy

CONCLUSION (CONTINUED)

However, the successful development of novel, complex technologies such as ITM Syngas must be different. A unique approach is required because ITM Syngas is truly a pioneering technology in which the underlying phenomena are not well understood. Therefore, predictive capability is limited and a high level of integration is required between process, materials and ceramic functionality and processing. If a sequential strategy were used for the development of a complex and pioneering ceramic-based process, the rework would be enormous and a progress would be very slow at best.

The alternative strategy uses the principal skill areas in a fully-integrated, parallel-path manner as shown in Figure 2. The multi-disciplined approach has all areas of development progressing at the same time and learning from each other as new information is gathered. The tasks are highly integrated. This methodology is much more complex to manage, requiring particular attention to broad communications among the various disciplines and significant detailed planning. The outcome, however, is an earlier identification of problems and a more global search for solutions. Meaningful progress and good efficiency (i.e., minimum re-work) are achievable from this type of approach as long as the program is well-managed. Since most of the major disciplines are active simultaneously, such approaches generally lead to higher spend rate programs, but with significantly faster and robust progress. The success of the ITM Syngas development program demonstrates that this approach should be considered on other similar development programs.

Figure 2-A An Integrated Parallel Path Development

CONCLUSION (CONTINUED)

Resolving Risk

The high-risk nature of this development program required a specific approach to understanding and resolving risks associated with unknown factors. To manage development costs, it became critical to develop an understanding of an issue and test solutions at the smallest scale possible. Once understood on this scale, the solution could be carried forward to the next appropriate scale. There were many examples of this philosophy in action, such as:

- Expanding the use of the PDU to test single-wafer SEP modules and delaying the initial SEP project.
- Testing catalyzed membranes under proposed start-up conditions in the MTU before being used in the PDU.
- Identifying guard bed materials that might be effective for contaminant removal through the use of thermodynamic models, and testing the effectiveness of the identified guard bed materials in small test rigs before being used in the PDU.

Intellectual Property Strategy

As with any new technology development, there were key aspects of this technology that were novel and critical to its successful development. Patent applications for these concepts were aggressively pursued and obtained. The list of patents and published applications, provided in the Results section of this report, includes all fundamental, enabling patents that are a significant patent estate for the ITM Syngas technology.

Other concepts have been kept as know-how. For example, ceramic processing techniques that were critical to the success of the development effort were, by intent, chosen from techniques that were often widely used by the ceramic industry. While these techniques were widely used, they needed to be uniquely tailored for the materials and structures that were critical to this program. Keeping these types of concepts as know-how, however, does not diminish their importance in the success of the development effort.

Finally, other concepts have been published when patenting was not an option, for example when there was similar prior art or that the concept was merely an enhancement to other patented or known concepts. These defensive publications in technical papers, presentations, and searchable databases, such as IP.com, ensured that the Air Products-led team would be able to practice these concepts.

Another important factor in our strategy was to leverage other ITM programs being developed in parallel with ITM Syngas. For example, the ITM Oxygen program often focused on solving problems similar to those also faced in the ITM Syngas development effort. Patents and know-how developed in these programs provided useful information for the ITM Syngas program. These patents also added significant protection for the ITM Syngas technology.

CONCLUSION (CONTINUED)

Cost Estimating

For many development programs, the primary incentive is to reduce operating or capital costs associated with providing a specific product or service. The cost estimating challenges can be significant. First, it is desirable to establish a baseline cost for conventional technology that can be used for comparison. The best conventional technology, however, is often not the same for different applications, is not fully specified, and may change with time. For example, for ITM Syngas, the best conventional technology for GTL applications has been Autothermal Reforming (ATR), a technology that requires a cryogenic Air Separation Unit (ASU). For hydrogen applications, the best conventional technology is either SMR or ATR, depending on plant capacity. Second, the costs of the new technology need to be estimated, which can be particularly difficult due to a lack of a detailed scope and uncertainties about the cost structure and scope associated with the pioneering technology. There are four methods of costing that might be useful for long-term R&D efforts, such as ITM Syngas. These include: (1) cost judgments; (2) absolute comparisons of costs with appropriate comparable scopes, including off-sites; (3) cost scaling; and (4) relative cost comparisons. All four have their application and usefulness during the course of such a development program.

Good cost judgments can be made on pioneering technology by analyzing differences in the flow sheet (compared to conventional technology), the anticipated size of the new equipment, and the relative efficiency of the new technology. Flow sheet simplification is typically indicative of capital cost savings, and ITM Syngas has significant potential through the elimination of the cryogenic ASU. In addition to flow sheet simplification, consideration of equipment size also showed that if design targets were reached, ITM Syngas reactors would be substantially smaller in both footprint and volume compared to conventional equipment. These are first-order judgments that suggest significant potential for cost savings. However, more detailed costing was required to substantiate these judgments.

Detailed estimates can be made in an absolute manner -- for example the differences in the total cost of new technology scope compared to the total cost of conventional technology scope. These cost estimates are significant undertakings if a true "apples to apples" comparison is desired. The new and conventional technologies must be separately optimized and then each must have preliminary equipment specifications developed. Finally, capital cost and utility costs can be estimated, with results for both subject to uncertainty in scope and costing errors. Due to the inherent technical risks and costing errors associated with the development of pioneering technology, the cost incentive at an early stage needs to be larger for these developments than for shorter-term, lower-risk programs. In latter stages of pioneering technology development, when risks might be lower, the cost incentive may not need to be so high. Absolute cost comparisons are important to understand the target costs for critical components of the new technology development effort, as well as the sensitivity of the overall benefits to target uncertainties. The relative cost between comparable cases is more useful than the specific cost level.

Detailed costing results can be used along with experienced-based scaling rules to estimate the sensitivity of cost savings to certain design or size changes. This approach can also be used to establish targets for these scaling rules, and to help prioritize future engineering efforts on the

CONCLUSION (CONTINUED)

most critical aspects. This technique can also be used to judge the initial results from new absolute costs comparisons to assure that both the pioneering technology option and the conventional technology option have been fully optimized. Deviations from what would be expected using scaling rules often indicates that an "apples to oranges" comparison is being made rather than an "apples to apples" comparison.

In addition to absolute comparisons or total scope costs, more detailed relative cost comparisons can be particularly advantageous to focus R&D effort on the better solution paths. In the ITM Syngas case, we used this technique to determine whether shell and tube reactor configurations were more or less costly than planar reactor configurations. Both designs were developed in detail giving full consideration to factors such as the changing driving force within the reactor, the pressure differential loads, and the vessel size. When reasonable design targets were used for both cases, it became clear that the costs of shell and tube configurations exceeded those expected from planar design concepts. These results were compared to the total benefits of ITM Syngas technology anticipated over conventional technology. This comparison showed that a significant fraction of the technology-related cost advantage would be lost if the shell and tube configuration was selected instead of the planar design. This cost analysis made it easy to decide our forward work direction.

GLOSSARY OF TERMS

AGR: acid gas removal

ASU: air separation unit

ATR: autothermal reformer

BBL: barrels

BPD: barrels per day

CTE: coefficient of thermal expansion

EDAX: energy dispersive X-ray

EDS: Energy Dispersive Spectroscopy

FCV: fuel cell vehicle

FPSO: floating production storage and off-loading

FT: flow transition (not F-T: Fischer-Tropsch)

F-T: Fischer-Tropsch

GHR: gas-heated reformer

GPa: Giga Pascals

GTCC: gas turbine combined-cycle

GTL: gas-to-liquid

HHV: high heating value

HPTGA: high-pressure thermal gravimetric analyzer

Ion Transport Membrane Module: An assembly of a plurality of membrane wafers which have a reactant inflow region and a reactant outflow region disposed such that gas flows across the external surfaces of the membrane wafers. The wafers also have internal gas flows of an oxygen-containing stream.

Ion Transport Membrane System: An array of multiple ion transport membrane modules used for oxidation reactions.

GLOSSARY OF TERMS (CONTINUED)

ITM: Ion Transport Membrane, an active layer of ceramic membrane material comprising mixed metal oxides capable of transporting or permeating oxygen ions at elevated temperatures.

KW: kilowatts

KWH: kilowatt hours

LHV: lower heating value

Mixed Conductor Membrane: An ion transport membrane that transports electrons as well as oxygen ions.

MPa: mega Pascals

MMBTU: millions of BTUs

MMSCFD: millions of standard cubic feet per day

mS/cm: milli-Siemens per centimeter

MT/D: metric tons per day

MW: megawatts

NG: natural gas

NIST: National Institute of Science and Technology

OD/ID: outside diameter/inside diameter

P&IDs: process and instrumentation diagrams

PDS: porous-dense-slotted

PDU: process development unit

PDUM: process development unit modules

PNNL: Pacific Northwest National Laboratory

PSA: pressure swing adsorption

GLOSSARY OF TERMS (CONTINUED)

psi: pounds per square inch

psia: pounds per square inch absolute

psig: pounds per square inch gauge

reactant gas or reactant feed gas: A gas comprising at least one component which reacts with oxygen to form an oxidation product.

SAM: scanning acoustic microscopy

S/C: steam to carbon

sccm: standard cubic centimeters per minute

SEM: scanning electron microscope

SOFC: solid oxide fuel cells

SEP: subscale engineering prototype

SMR: steam methane reformer

syngas: synthesis gas, a gas mixture containing at least hydrogen and carbon oxides

S/cm: Siemens per centimeter

syncrude: synthetic crude oil

TGA: thermal gravimetric analyzer

TLP: transient liquid phase

TOS: time on stream

wafer: A membrane structure having a center or interior region and an exterior region wherein the wafer is formed by two parallel planar members sealed about at least a portion of the peripheral edges thereof.

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

APPENDICES

A-1 U.S. PATENTS AND PUBLISHED APPLICATIONS

A-1.1 Patents (See Attached)

US6114400A1	Synthesis Gas Production by Mixed Conducting Membranes with Integrated Conversion into Liquid Products
US6492290B1	Mixed Conducting Membranes for Syngas Production
US7094301B2	Method of Forming a Joint
US7279027B2	Planar Ceramic Membrane Assembly and Oxidation Reactor System
US7335247B2	Ion Transport Membrane Module and Vessel System
US7425231B2	Feed Gas Contaminant Removal in Ion Transport Membrane Systems

A-1.2 Published Patent Applications (See Attached)

US20060180022A1	Ion Transport Membrane Module and Vessel System with Directed Internal Gas Flow
US20070079703A1	Feed Gas Contaminant Control in Ion Transport Membrane Systems
US20080085236A1	Planar Ceramic Membrane Assembly and Oxidation Reactor System
US20080136179A1	Seal Assembly for Materials with Different Coefficients of Thermal Expansion
US20080168901A1	Liners for Ion Transport Membrane Systems
US20080302013A1	Staged Membrane Oxidation Reactor System

The below Patent Application was submitted to the United States Patent and Trademark Office on May 25, 2010 (See Attached)

06783 USA	Fabrication of Catalyzed Ion Transport Membrane Systems
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APPENDICES (CONTINUED)

A-2 PUBLICATIONS AND PRESENTATIONS

A-2.1 SYNGAS Publications/Presentations

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
Advanced Gas-to-Liquid Processes for Syngas and Liquid-Phase Conversion	E. P. (Ted) Foster P. J. A. Tijm D.L. Bennett	E. P. (Ted) Foster	5 th Natural Gas Conversion Symposium; ITALY	20-25 Sep 1999
Engineering Development of Ceramic Membrane Reactor Systems For Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels	Paul N. Dyer Christopher M. Chen	Christopher M. Chen	Conference on Energy Products for the 21 st Century - U.S. Department of Energy - Federal Energy Technology Center; Cincinnati, OH	21-22 Sep 1999
Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels. Air Product and Chemicals, Inc. (DE-FC26-97FT96052)	Paul N. Dyer	N/A	Annual Operating Plan, U.S. DOE Hydrogen Program, Energy Efficiency and Renewable Energy	Feb 2000
Development of the High Pressure ITM Syngas Process	Air Products: Michael F. Carolan Paul N. Dyer Eric Minford Ceramatec: Darryl P. Butt Raymond I. Cutler Dale M. Taylor Eltron: Thomas F. Barton David Peterson Anthony F. Sammells	Paul N. Dyer	6 th Natural Gas Conversion Symposium; Gerwood, Alaska	17-22 Jun 2001

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
An Integrated ITM Syngas/Fischer Tropsch Process for GTL Conversion	Air Products: Christopher M. Chen Paul N. Dyer Chevron: Karl F. Gerdes Cliff M. Lowe McDermott: Shree R. Akhave Dan R. Rowley Norsk Hydro: K. I. Åsen E. H. Eriksen	Christopher M. Chen	6 th Natural Gas Conversion Symposium; Gerwood, Alaska	17-22 Jun 2001
Development of the ITM Syngas Process for GTL Conversion	Christopher M. Chen Paul N. Dyer	Christopher M. Chen	American Chemical Society National Meeting; Chicago, IL	Aug 2001
Economics of Syngas Generation from Natural Gas and Liquid Phase Methanol Synthesis	Christopher M. Chen	Bob Tsao	Presented at the Sino-American Technology and Engineering Conference	Oct 2001
ITM H ₂ /Syngas: Scaleup of Ceramic Membrane Fabrication (part of larger presentation)	Christopher M. Chen	Bill Parks (DOE)	National Academy of Science Conference on "Materials & Society from Research to Manufacture"	11 Mar 2002
ITM Syngas Process for Offshore GTL Conversion	McDermott: Shree R. Akhave George J. Montgomery Michael J. Holms Daniel R. Rowley Air Products: Christopher M. Chen	D. R. Rowley	2002 Offshore Technology Conference; Houston, TX	May 2002

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
Reactions in Catalytic Membrane Reactors Containing Ion-Electron Conducting Phases	DOE: Arun C. Bose Daniel C. Cicero Air Products: Christopher M. Chen Eltron: Anthony F. Sammells	Arun Bose	5 th International Conference on Catalytic Membrane Reactors; Dalian, China	Jun 2002
Engineering Development of Ceramic and Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels	Michael F. Carolan Christopher M. Chen Steven W. Rynders	C. M. Chen	2002 U.S. Dept. of Energy Hydrogen Program Annual Review	7 May 2002
Development of Ceramic to Metal Seals for Ceramic Membrane Applications	Eric Minford	Eric Minford	57th Annual Forum of the Pennsylvania Ceramics Association; Penn State University, PA	19-20 Sep 2002
Testing to Ensure Reliability of Ceramic Membranes	Richard E. Tressler David L. Shelleman Kent N. Hutchings	R. E. Tressler	57th Annual Forum of the Pennsylvania Ceramics Association; Penn State University, PA	19-21 Sep 2002
Ion Transport Membranes for Gas Separation	Joseph M. Abrardo Phil A. Armstrong Michael F. Carolan Christopher M. Chen	M. F. Carolan	57th Annual Forum of the Pennsylvania Ceramics Association; Penn State University, PA	19-21 Sep 2002
Development of the Ceramic Membrane ITM Syngas/ITM Hydrogen Process	Michael F. Carolan Christopher M. Chen Steven W. Rynders William E. Waldron	Steve Rynders	ACS National Meeting; New Orleans, LA	25 Mar 2003
Development of the Ceramic Membrane ITM Syngas/ITM Hydrogen Process	Michael F. Carolan Christopher M. Chen Steven W. Rynders William E. Waldron	Christopher Chen	AIChE Spring National Meeting; New Orleans, LA	30 Mar 2003

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for liquid Transportation Fuels (DE-FC26-97FT96052)	Christopher M. Chen	Christopher M. Chen	U.S. Dept. of Energy Hydrogen Program Annual Review; Berkeley, CA	19 May 2003
ITM SYNGAS: Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and synthesis Gas for Liquid Transportation Fuels.	Christopher M. Chen	Christopher M. Chen	U.S. DOE Clean Fuels Program Merit Review; Houston, TX.	4 Jun 2003
ITM SYNGAS: Engineering Development of Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas for Liquid Transportation Fuels	Christopher M. Chen	- -	DOE Hydrogen, Fuel Cells, & Infrastructure FY2003 Annual Report	Jun 2003
Development of the ITM Syngas Ceramic Membrane Technology	Air Products: Joseph M. Abrardo Douglas L. Bennett Michael F. Carolan Christopher M. Chen William E. Waldron ChevronTexaco: William L Schinski	Douglas L. Bennett	Spring 2004 AIChE National Meeting; New Orleans, LA	25-29 Apr 2004
Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen (ITM Syngas)	Christopher M. Chen	Christopher M. Chen	DOE-EE Program Review	24 May 2004

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
ITM Syngas Ceramic Membrane Technology for Synthesis Gas Production	Air Products: Christopher M Chen Douglas L. Bennett Michael F. Carolan Edward P. Foster ChevronTexaco: William L Schinski Ceramatec, Inc: Dale M. Taylor	E. P. Foster	7th Natural Gas Conversion Symposium; Dalian, China	6-10 Jun 2004
Hydrogen and Syngas Production Using Ion Transport Membranes	Michael F. Carolan	Michael F. Carolan	8th International Conference on Inorganic Membranes	18-21 Jul 2004
ITM Syngas for GTL Economic Improvement	Douglas L. Bennett Christopher M. Chen Edward P. Foster	E. P. Foster	EFI Gas-to-Market Conference; Washington, DC	29 Sep-1 Oct 2004
ITM Ceramic Membrane Technology to Produce Synthesis Gas	Air Products: Christopher F. Miller Michael F. Carolan Christopher M. Chen Eric Minford William E. Waldron Ceramatec: James J. Steppan	Christopher F. Miller	230th American Chemical Society National Meeting; Washington, DC	28 Aug-1 Sep 2005

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas	Air Products: Douglas L. Bennett Michael F. Carolan Christopher M. Chen Ceramatec: Dale M. Taylor Merrill A. Wilson McDermott: Theodore R. Ohrn	Christopher M. Chen	2005 AIChE National Meeting; Atlanta, GA	12 Apr 2005
ITM Ceramic Membrane Technology to Produce Synthesis Gas	Air Products: Michael F. Carolan Christopher M. Chen Christopher F. Miller Eric Minford William E. Waldron Ceramatec: James J. Steppan	Christopher F. Miller	208th Electrochemical Society Meeting; Los Angeles, CA	19 Oct 2005
ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas	Michael F. Carolan	Michael. F. Carolan	CatCon 2005 Conference; Philadelphia, PA	25-26 Oct 2005
ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas	Michael F. Carolan	Michael F. Carolan	Catalyst Club of Chicago; Chicago, IL	13 Mar 2006

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas	Air Products: Christopher M. Chen Douglas L. Bennett Michael F. Carolan Christopher F Miller William E. Waldron Ceramatec: James J. Steppan	Christopher M. Chen	AIChE Spring National Meeting; Orlando, FL	23-27 Apr2006
ITM Ceramic Membrane Technology to Produce Synthesis Gas	Air Products: Christopher F. Miller Michael F. Carolan Christopher M. Chen Eric Minford William E. Waldron Ceramatec: James J. Steppan	Christopher F. Miller	2006 Fall Materials Research Society Meeting; Boston, MA	27 Nov 2006
No Longer a Dream	Paul Waldoch	Paul Waldoch	World GTL 7 Summit Conference; London, England	Apr 2007
ITM Technology for Synthesis Gas Production	Air Products: Christopher M. Chen Douglas L. Bennett Michael F. Carolan Edward P. Foster Ceramatec: Dale M. Taylor	E. P. Foster	NGCS-8 Natural Gas Conversion Symposium, Natal, Brazil	24-31 May 2007

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
ITM Syngas: Next Generation Syngas Production from Natural Gas	Chevron: Karl F. Gerdes Clifford M. Lowe Sandra L. Anderson Air Products: Douglas L. Bennett Michael F. Carolan Christopher M. Chen John M. Repasky	Karl F. Gerdes	The Synfuel Alternative GTL/CTL International Advanced Technology Symposium; Canberra, Australia.	17-19 Jul 2007
ITM Ceramic Membrane Technology to Produce Synthesis Gas	Air Products: Christopher F. Miller Michael F. Carolan Christopher M. Chen Eric Minford William E. Waldron Ceramatec: James J. Steppan	Christopher F. Miller	ACS 234 th National Meeting & Exposition; Boston, MA	19-23 Aug. 2007
Industrial Gas Technologies that Enable Remote Gas Monetization: LNG, ASU, ITM	E. P. Ted Foster Jim Solomon B. Todd Newman	Ted Foster	EFI Gas-to-Market Conference; Washington, DC	24-26 Sep 2007
ITM Syngas: Ceramic Membrane Technology for Lower Cost Conversion of Natural Gas	Air Products: John M. Repasky Christopher M. Chen Michael F. Carolan Douglas L. Bennett Chevron: Clifford M. Lowe Sandra L. Anderson Karl F. Gerdes	John M. Repasky	AIChE Fall National Meeting; Salt Lake City, UT	4-9 Nov 2007

APPENDICES (CONTINUED)

A-2.1 SYNGAS Publications/Presentations (Continued)

TITLE	AUTHORS	PRESENTER	PRESENTED AT OR PUBLISHED IN	DATE
ITM Syngas Technology for Lower Cost Syngas Production from Natural Gas	Chevron: Christopher M. Chen Karl F. Gerdes Air Products: E. P Ted Foster	Christopher F. Chen	Gastech 2008 Conference; Bangkok, Thailand	10-13 Mar 2008
ITM Ceramic Membrane Technology to Produce Synthesis Gas	Air Products: Christopher F. Miller Michael F. Carolan Eric Minford William E. Waldron Chevron: Christopher M. Chen Ceramatec, Inc.: Jack Chen	Christopher F. Miller	213 th ECS Meeting; Phoenix, AZ	18-23 May 2008

ION TRANSPORT MEMBRANE MODULE AND VESSEL SYSTEM WITH DIRECTED INTERNAL GAS FLOW

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation-in-Part of Ser. No. 11/028,124 filed on Jan. 3, 2005, which is a Continuation-in-Part of Ser. No. 10/635,695 filed on Aug. 6, 2003, the specification and claims which are incorporated by reference and made a part of this patent application.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under Contract Number DE-FC26-97FT96052 between Air Products and Chemicals, Inc. and the U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0003] The permeation of oxygen ions through ceramic ion transport membranes is the basis for a variety of gas separation devices and oxidation reactor systems operating at high temperatures in which permeated oxygen is recovered on the permeate side as a high purity oxygen product or is reacted on the permeate side with oxidizable compounds to form oxidized or partially oxidized products. The practical application of these gas separation devices and oxidation reactor systems requires membrane assemblies having large surface areas, means to contact feed gas with the feed sides of the membranes, and means to withdraw product gas from the permeate sides of the membranes. These membrane assemblies may comprise a large number of individual membranes arranged and assembled into modules having appropriate gas flow piping to introduce feed gas into the modules and withdraw product gas from the modules.

[0004] Ion transport membranes may be fabricated in either planar or tubular configurations. In the planar configuration, multiple flat ceramic plates are fabricated and assembled into stacks or modules having piping means to pass feed gas over the planar membranes and to withdraw product gas from the permeate side of the planar membranes. In tubular configurations, multiple ceramic tubes may be arranged in bayonet or shell-and-tube configurations with appropriate tube sheet assemblies to isolate the feed and permeate sides of the multiple tubes.

[0005] The individual membranes used in planar or tubular module configurations typically comprise very thin layers of active membrane material supported on material having large pores or channels that allow gas flow to and from the surfaces of the active membrane layers. The ceramic membrane material and the components of the membrane modules can be subjected to significant mechanical stresses during normal steady-state operation and especially during unsteady-state startup, shutdown, and upset conditions. These stresses may be caused by thermal expansion and contraction of the ceramic material and by dimensional variance caused by chemical composition or crystal structure changes due to changes in the oxygen stoichiometry of the membrane material. These modules may operate with significant pressure differentials across the membrane and membrane seals, and stresses caused by these pressure

differentials must be taken into account in membrane module design. In addition, the relative importance of these phenomena may differ depending on whether the modules are operated in gas separation or oxidation service. The potential operating problems caused by these phenomena may have a significant negative impact on the purity of recovered products and on membrane operating life.

[0006] Membrane modules may be installed in pressure vessels adapted to introduce feed gas to the modules and withdraw product gas from the modules and to operate at least one side of the membranes at super-atmospheric pressures. The design of these modules and the module orientation within the pressure vessels should allow the use of compact and cost-effective pressure vessels.

[0007] There is a need in the field of high temperature ceramic membrane reactor systems for new membrane module and vessel designs that address and overcome these potential operating problems. Such designs should include features to allow efficient operation, long membrane life, minimum capital cost, the ability to specify membrane systems over a wide range of production rates, and compact pressure vessels. Embodiments of the invention disclosed herein address these design problems and include improved module and vessel designs for both oxygen production and oxidation systems.

BRIEF SUMMARY OF THE INVENTION

[0008] An embodiment of the invention relates to an ion transport membrane system comprising (a) a pressure vessel having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis; (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and (c) one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to change a direction of gas flow within the vessel.

[0009] Each planar membrane module may comprise a plurality of wafers having planar parallel surfaces, the pressure vessel may be cylindrical, and the axis may be parallel to some or all of the planar parallel surfaces of the wafers.

[0010] The system may further comprise a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct has an interior region, surrounds the plurality of planar ion transport membrane modules, and is in flow communication with the inlet and outlet of the pressure vessel, and wherein the one or more gas flow control partitions are disposed in the interior region of the flow containment duct. The flow containment duct and the one or more gas flow control partitions may comprise an oxidation-resistant metal alloy containing iron and one or more elements selected from the group consisting of nickel and chromium.

[0011] At least two of the planar ion transport membrane modules may define a module axis, the pressure vessel may be cylindrical, and may have an axis that is parallel to or coaxial with the module axis; alternatively, the axis may be perpendicular to the module axis.

[0012] The one or more flow control partitions may be oriented such that an initial direction of gas flow is diverted to a final direction of gas flow, wherein the angle formed between the initial direction of gas flow and the final direction of gas flow forms an angle of greater than zero degrees and less than or equal to 180 degrees or alternatively forms an angle of greater than 90 degrees and less than or equal to 180 degrees. In another alternative, the one or more flow control partitions may be oriented such that the initial direction of gas flow is diverted to a final direction of gas flow wherein the angle formed between the initial direction of gas flow and the final direction of gas flow forms an angle of 180 degrees.

[0013] The system of this embodiment may further comprises (d) one or more additional pressure vessels, each having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis; (e) a plurality of planar ion transport membrane modules disposed in the interior of each of the pressure vessels and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and (f) one or more gas flow control partitions disposed in the interior of each of the pressure vessels and adapted to change a direction of gas flow within any of the one or more pressure vessels; wherein at least two of the pressure vessels may be arranged in series such that the outlet of one pressure vessel is in flow communication with the inlet of another pressure vessel.

[0014] The system of this embodiment alternatively may further comprise (d) one or more additional pressure vessels, each having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis; (e) a plurality of planar ion transport membrane modules disposed in the interior of each of the pressure vessels and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and (f) one or more gas flow control partitions disposed in the interior of each of the pressure vessels and adapted to change a direction of gas flow within any of the one or more pressure vessels; wherein at least two of the pressure vessels may be arranged in parallel such that any inlet of one pressure vessel and any inlet of another pressure vessel are in flow communication with a common feed conduit.

[0015] The system may further comprise catalyst disposed between any two of the planar ion transport membrane modules arranged in series. The catalyst may comprise one or more metals or compounds containing metals selected from the group consisting of nickel, cobalt, platinum, gold, palladium, rhodium, ruthenium, and iron. The reactor catalyst may be placed between a plurality of the modules in series and the activity of the catalyst varies at different locations between the modules in series.

[0016] Another embodiment of the invention relates to a method for the recovery of oxygen from an oxygen-containing gas comprising

[0017] (a) providing an ion transport membrane separator system comprising

[0018] (1) a pressure vessel having an interior, an inlet adapted to introduce gas into the interior of the

vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;

[0019] (2) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and

[0020] (3) one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to change a direction of gas flow within the vessel;

[0021] (b) providing a heated, pressurized oxygen-containing feed gas stream, introducing the feed gas stream via the pressure vessel inlet to the exterior regions of the membrane modules, and contacting the feed gas stream with the mixed metal oxide ceramic material;

[0022] (c) permeating oxygen ions through the mixed metal oxide ceramic material, recovering high purity oxygen gas product in the interior regions of the membrane modules, and withdrawing the high purity oxygen gas product from the interior regions of the membrane modules through the gas manifolds to the exterior of the pressure vessel; and

[0023] (d) withdrawing an oxygen-depleted oxygen-containing gas from the pressure vessel outlet.

[0024] The pressure of the oxygen-containing feed gas may be greater than the pressure of the high purity oxygen gas product. The method may further comprise a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct has an interior region and an exterior region, surrounds the plurality of planar ion transport membrane modules, and is in flow communication with the inlet and outlet of the pressure vessel, and wherein the one or more gas flow control partitions are disposed in the interior region of the flow containment duct. The pressure differential between the interior region and the exterior region of the flow containment duct at any point between the inlet and outlet of the pressure vessel may be maintained at a value equal to or greater than zero, and wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct.

[0025] An alternative embodiment of the invention includes an oxidation process comprising

[0026] (a) providing an ion transport membrane reactor system comprising

[0027] (1) a pressure vessel having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;

[0028] (2) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and

[0029] (3) one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to change a direction of gas flow within the vessel;

[0030] (b) providing a heated, pressurized reactant feed gas stream, introducing the reactant feed gas stream via the pressure vessel inlet to the exterior regions of the membrane modules;

[0031] (c) providing an oxygen-containing oxidant gas to the interior regions of the membrane modules, permeating oxygen ions through the mixed metal oxide ceramic material, reacting oxygen with components in the reactant feed gas stream in the exterior regions of the membrane modules to form oxidation products therein, and withdrawing the oxidation products from the exterior regions of the membrane modules through the outlet to the exterior of the pressure vessel to provide an oxidation product stream; and

[0032] (d) withdrawing oxygen-depleted oxygen-containing gas from the interior regions of the membrane modules via the one or more manifolds to the exterior of the pressure vessel.

[0033] The pressure of the pressurized reactant feed gas stream may be greater than the pressure of the oxygen-containing oxidant gas. The process may further comprise a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct has an interior region and an exterior region, surrounds the plurality of planar ion transport membrane modules, and is in flow communication with the inlet and outlet of the pressure vessel, and wherein the one or more gas flow control partitions are disposed in the interior region of the flow containment duct. The pressure differential between the interior region and the exterior region of the flow containment duct at any point between the inlet and outlet of the pressure vessel may be maintained at a value equal to or greater than zero, wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct.

[0034] The pressurized reactant feed gas stream may comprise one or more hydrocarbons having one or more carbon atoms and specifically may comprise methane. The oxidation product stream may comprise hydrogen and carbon oxides.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0035] FIG. 1 is a schematic front view of a membrane wafer stack or module for use in oxygen recovery or in oxidation processes according to embodiments of the present invention.

[0036] FIG. 2A is a side view of the membrane wafer stack or module of FIG. 1 for use in oxidation processes.

[0037] FIG. 2B is a side view of the membrane wafer stack or module of FIG. 1 for use in oxygen recovery.

[0038] FIG. 3A is a sectional view of a membrane wafer of FIGS. 1, 2A, and 2B.

[0039] FIG. 3B is another sectional view of the membrane wafer of FIGS. 1, 2A, and 2B.

[0040] FIG. 3C is a sectional view of an alternative membrane wafer of FIGS. 1, 2A, and 2B.

[0041] FIG. 3D is another sectional view of the alternative membrane wafer of FIGS. 1, 2A, and 2B.

[0042] FIG. 4A is a schematic side view of the interior of a membrane separator vessel for use in oxygen recovery.

[0043] FIG. 4B is a cross sectional view of FIG. 4A.

[0044] FIG. 5 is a schematic side view of the interior of a membrane reactor vessel for use in oxidation processes.

[0045] FIG. 6 is a cross sectional view of FIG. 5.

[0046] FIG. 7 is an embodiment of FIG. 4B showing the placement of insulation material.

[0047] FIG. 8 is a second embodiment of FIG. 4B showing an alternative placement of thermal insulation material.

[0048] FIG. 9 is a third embodiment of FIG. 4B showing an alternative placement of thermal insulation material.

[0049] FIG. 10 is a fourth embodiment of FIG. 4B showing an alternative placement of thermal insulation material.

[0050] FIG. 11 is a fifth embodiment of FIG. 4B showing an alternative placement of thermal insulation material.

[0051] FIG. 12 is a sixth embodiment of FIG. 4B showing an alternative placement of thermal insulation material.

[0052] FIG. 13 is a seventh embodiment of FIG. 4B showing the placement of insulation thermal material.

[0053] FIG. 14 is a schematic side view of the interior of an alternative membrane vessel and module arrangement for use in oxygen recovery or in oxidation processes.

[0054] FIG. 15 is a sectional plan view of a flow containment duct in FIG. 4A having coaxial parallel membrane modules.

[0055] FIG. 16 is a sectional plan view of a flow containment duct with offset banks of parallel membrane modules.

[0056] FIG. 17A is an embodiment of the membrane reactor vessel and membrane modules with internal partitions for direction of gas flow.

[0057] FIG. 17B is view of section 10-10 of FIG. 17A.

[0058] FIG. 18A is an alternative embodiment of the membrane reactor vessel and membrane modules with internal partitions for direction of gas flow.

[0059] FIG. 18B is view of section 12-12 of FIG. 18A.

[0060] FIG. 19 is a modified version of the system of FIG. 18B.

[0061] FIG. 20 is another alternative embodiment of the membrane reactor vessel and membrane modules with internal partitions for direction of gas flow.

[0062] The drawings of FIGS. 1-20 are not necessarily to scale.

DETAILED DESCRIPTION OF THE INVENTION

[0063] Embodiments of the present invention are directed toward the design and operation of ion transport membrane systems that utilize multiple membrane modules operating in series for use in either oxygen recovery or oxidation processes. It has been found that when oxygen transport across a membrane results in an exothermic reaction, for example in the production of synthesis gas from methane,

the degree of reactant conversion across an individual membrane must be limited to prevent an excessive temperature gradient across the membrane. It also has been found that when a membrane is transporting oxygen into a lower-pressure permeate stream, the amount of oxygen extraction across an individual membrane must be limited to prevent an excessive oxygen vacancy gradient in the membrane material between the leading edge and trailing edge of the membrane. Excessive temperature or oxygen vacancy gradients may cause excessive stresses in the membranes that could limit the membrane life quite drastically.

[0064] The present invention addresses these problems by orienting multiple membrane modules or banks of modules in series so that the amount of oxygen extracted across membranes in each module is sufficiently low to prevent an excessive oxygen vacancy gradient in the membrane material. The amount of oxygen extracted across each individual module may be limited by appropriate module sizing, and the total desired degree of oxygen extraction may be achieved by operating a selected plurality of modules in series. When oxygen transport across a membrane results in an exothermic reaction, the degree of reactant conversion across individual membranes in each module should be sufficiently low to prevent an excessive temperature gradient across the membrane in the flow direction. The degree of conversion across each individual module may be limited by appropriate module sizing, and the total desired conversion may be achieved by operating a plurality of selected modules in series.

[0065] The gas flowing over the outside of the membranes in each membrane module preferably is at a higher pressure than the gas on the inside of the membranes in the interior of the module as described below. In order to minimize gas-phase mass transport resistance, the higher pressure gas should be directed across the outer surface of the membranes at high velocity and as uniformly as possible.

[0066] Because of the unique operating conditions of an ion transport membrane system, the system design may include a pressure vessel, an optional gas flow containment device or duct disposed within the vessel and surrounding the series membrane modules, and thermal insulation within the vessel to allow the vessel wall to operate at a lower temperature than the membrane modules. The proper physical positioning of each of these components as described below improves the prospects for fabrication, installation, and long-term operability of the system. In addition, other internal design features are disclosed that may contribute to the long-term reliability of the overall ion transport membrane system.

[0067] The following definitions apply to terms used in the description of the embodiments of the invention presented herein.

[0068] An ion transport membrane module is an assembly of a plurality of membrane structures which has a gas inflow region and a gas outflow region disposed such that gas flows across the external surfaces of the membrane structures. Gas flowing from the inflow region to the outflow region of a membrane module changes in composition as it passes across the surfaces of the membrane structures in the module. Each membrane structure has an oxygen-containing gas feed side and a permeate side separated by an active membrane layer or region that allows oxygen ions to permeate

therethrough. Each membrane structure also has an interior region and an exterior region. In one embodiment, in which the membrane module is operated as an oxygen separation device, the oxygen-containing gas feed side may be adjacent to the exterior region of the membrane structure and the permeate side may be adjacent to the interior region of the membrane structure.

[0069] In an alternative embodiment, in which the membrane module is operated as an oxidation reaction device, the oxygen-containing gas feed side may be adjacent to the interior region of the membrane structure and the permeate side may be adjacent to the exterior region of the membrane structure. In this alternative embodiment, a reactant feed gas flows through the exterior region of the membrane structure and reacts with the permeated oxygen. Thus in this embodiment the permeate side is also the reactant gas side of the membrane structure.

[0070] A membrane structure may have a tubular configuration in which an oxygen-containing gas flows in contact with one side of the tube (i.e., in either the interior region or the exterior region of the tube) and oxygen ions permeate through active membrane material in or on the tube walls to the other side of the tube. The oxygen-containing gas may flow inside or outside of the tube in a direction generally parallel to the tube axis, or conversely may flow over the outer side of the tube in a direction which is not parallel to the tube axis. A module comprises multiple tubes arranged in bayonet or shell-and-tube configurations with appropriate tube sheet assemblies to isolate the feed and permeate sides of the multiple tubes.

[0071] Alternatively, the membrane structure may have a planar configuration in which a wafer having a center or interior region and an exterior region is formed by two parallel planar members sealed about at least a portion of the peripheral edges thereof. Oxygen ions permeate through active membrane material that may be placed on either or both surfaces of a planar member. Gas can flow through the center or interior region of the wafer, and the wafer has one or more gas flow openings to allow gas to enter and/or exit the interior region of the wafer. Thus oxygen ions may permeate from the exterior region into the interior region, or conversely may permeate from the interior region to the exterior region.

[0072] Components of a membrane module include an active membrane layer that transports or permeates oxygen ions and may also transport electrons, structural components that support the active membrane layer, and structural components to direct gas flow to and from the membrane surfaces. The active membrane layer typically comprises mixed metal oxide ceramic material and also may comprise one or more elemental metals. The structural components of the membrane module may be made of any appropriate material such as, for example, mixed metal oxide ceramic materials, and also may comprise one or more elemental metals. Any of the active membrane layer and structural components may be made of the same material.

[0073] Single modules may be arranged in series, which means that a number of modules are disposed along a single axis. Typically, gas which has passed across the surfaces of the membrane structures in a first module flows from the outflow region of that module, after which some or all of this gas enters the inflow region of a second module and there-

after flows across the surfaces of the membrane structures in the second module. The axis of a series of single modules may be parallel or nearly parallel to the overall flow direction or axis of the gas passing over the modules in series.

[0074] Modules may be arranged in banks of two or more parallel modules wherein a bank of parallel modules lies on an axis that is not parallel to, and may be generally orthogonal to, the overall flow direction or axis of the gas passing over the modules. Multiple banks of modules may be arranged in series, which means by definition that banks of modules are disposed such that at least a portion of gas which has passed across the surfaces of the membrane structures in a first bank of modules flows across the surfaces of the membrane structures in a second bank of modules.

[0075] Any number of single modules or banks of modules may be arranged in series. In one embodiment, the modules in a series of single modules or in a series of banks of modules may lie on a common axis or common axes in which the number of axes equals one or equals the number of modules in each bank. In another embodiment described below, successive modules or banks of modules in a series of modules or banks of modules may be offset in an alternating fashion such that the modules lie on at least two axes or on a number of axes greater than the number of modules in a bank, respectively. Both of these embodiments are included in the definition of modules in series as used herein.

[0076] Preferably, the gas in contact with the outer surfaces in the exterior regions of the membrane modules is at a higher pressure than the gas within the interior regions of the membrane modules.

[0077] A flow containment duct is defined as a conduit or closed channel surrounding a plurality of series membrane modules which directs flowing gas over modules in series.

[0078] A manifold is an assembly of pipes or conduits which directs gas to enter and/or exit the interior regions of the membrane modules. Two manifolds may be combined by installing a first or inner conduit within a second or outer conduit wherein the first conduit provides a first manifold and the annulus between the conduits provides a second manifold. The conduits may be concentric or coaxial, wherein these two terms have the same meaning. Alternatively, the conduits may not be concentric or coaxial but may have separate parallel or nonparallel axes. This configuration of inner and outer conduits to provide a combined manifold function is defined herein as a nested manifold.

[0079] Flow communication means that components of membrane modules and vessel systems are oriented relative to one another such that gas can flow readily from one component to another component.

[0080] A wafer is a membrane structure having a center or interior region and an exterior region wherein the wafer is formed by two parallel planar members sealed about at least a portion of the peripheral edges thereof. Active membrane material may be placed on either or both surfaces of a planar member. Gas can flow through the center or interior region of the wafer, i.e., all parts of the interior region are in flow communication, and the wafer has one or more gas flow openings to allow gas to enter and/or exit the interior region of the wafer. The interior region of the wafer may include porous and/or channeled material that allows gas flow

through the interior region and mechanically supports the parallel planar members. The active membrane material transports or permeates oxygen ions but is impervious to the flow of any gas.

[0081] Oxygen is the generic term for forms of oxygen comprising the element having an atomic number of 8. The generic term oxygen includes oxygen ions as well as gaseous oxygen (O_2 or dioxygen). An oxygen-containing gas may include, but is not limited to, air or gas mixtures comprising one or more components selected from the group consisting of oxygen, nitrogen, water, carbon monoxide, and carbon dioxide.

[0082] A reactant gas or reactant feed gas is a gas comprising at least one component which reacts with oxygen to form an oxidation product. A reactant gas may contain one or more hydrocarbons, wherein a hydrocarbon is a compound comprising primarily or exclusively hydrogen and carbon atoms. A hydrocarbon also may contain other atoms, such as, for example, oxygen.

[0083] Synthesis gas is a gas mixture containing at least hydrogen and carbon oxides.

[0084] An ion transport membrane is an active layer of ceramic membrane material comprising mixed metal oxides capable of transporting or permeating oxygen ions at elevated temperatures. The ion transport membrane also may transport electrons as well as oxygen ions, and this type of ion transport membrane typically is described as a mixed conductor membrane. The ion transport membrane also may include one or more elemental metals thereby forming a composite membrane.

[0085] An ion transport membrane system is a generic term for an array of multiple ion transport membrane modules used for oxygen recovery or for oxidation reactions. An ion transport membrane separation system is an ion transport membrane system used for separating and recovering oxygen from an oxygen-containing gas. An ion transport membrane reactor system is an ion transport membrane system used for oxidation reactions.

[0086] The series membrane modules in the embodiments of the present invention may be fabricated in either tubular or planar configurations as described above. Planar configurations are preferred for many applications, and various configurations of planar membrane modules are possible. Planar membrane module configurations are described, for example, in copending United States patent application having Ser. No. 10/394,620 filed on Mar. 21, 2003, which application is incorporated herein by reference.

[0087] The indefinite articles "a" and "an" as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of "a" and "an" does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article "the" preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective "any" means one, some, or all indiscriminately of whatever quantity.

[0088] An exemplary planar membrane module is illustrated in FIG. 1, which is a schematic front view of a

membrane wafer stack or module for use in oxygen recovery or in oxidation processes according to embodiments of the present invention. The stack or module in this example comprises a plurality of planar wafers **1** separated by hollow spacers **3** and having an optional cap **5**. The wafers and spacers are placed and joined in alternating fashion as shown and form stack or module axis **7**. The wafers may be any shape in plan view, but square or rectangular shapes are generally preferred. The dimension of any side of a square or rectangular wafer may be between 2 and 45 cm. The number of wafers in a stack may range up to 1000.

[0089] The exterior region of the stack or module is that region surrounding the outer surfaces of the wafers and spacers. As described in detail below, wafers **1** have interior regions which are placed in flow communication with the interiors of spacers **3** wherein gas-tight seals are formed between the wafers and spacers. Opening **9** in bottom hollow spacer **11** allows gas to enter and/or exit the interior region of the stack or module wherein the interior region of the module is formed by the interior regions of the wafers and the openings in the hollow spacers. Thus opening **9** is in flow communication with the interior region of the module.

[0090] A side view of the module of **FIG. 1** is shown in **FIG. 2A**, which illustrates an exemplary configuration for use in oxidation processes. In this example, spacers **201** between wafers **200** each have two separate sets of openings **203** and **205**. Openings **203** in spacers **201**, and additional openings in spacers disposed above and below spacers **201**, form an internal manifold that is in flow communication with the interior regions of the wafers by way of appropriately placed openings (not shown) through the layers of the wafers at the left ends of the wafers. These openings through the layers of the wafers also place the internal openings **203** of spacers **201** and the internal openings in spacers above and below spacers **201** in flow communication with each other. Likewise, openings **205** in spacers **201**, and additional openings in spacers disposed above and below spacers **201**, form an internal manifold that is in flow communication with the interior regions of the wafers by way of appropriately placed openings (not shown) through the layers of the wafers at the right ends of the wafers. These openings through the layers of the wafers also place the internal openings **205** of spacers **201** and the internal openings in spacers above and below spacers **201** in flow communication with each other.

[0091] In this example configuration, gas stream **207** flows upward through the internal manifold formed by openings **203** and openings above them, and then flows horizontally through the interior regions of the wafers. Gas from the interior regions of the wafers then flows downward through the interior manifold formed by openings **205** and openings above them, and exits the module as gas stream **209**. A second gas **211** at the gas inflow region of the module flows through the exterior region of the module on either side of spacers **201** and in contact with the outer surfaces of wafers **200**. Gas **213**, after contacting the outer surfaces of wafers **200**, flows through the gas outflow region of the module. The module may operate in a typical temperature range of 600 to 1100° C.

[0092] The module of **FIG. 2A** may be used as part of an oxidation reactor system wherein representative gas **211** is a reactant gas and representative gas **207** is an oxidant or

oxygen-containing gas. The oxygen-containing gas **207** flows through the internal manifold via openings **203** and through the interior regions of the wafers, oxygen permeates the active membrane material in the planar members of the wafers, and oxygen-depleted gas **209** flows from the module via openings **205**. Permeated oxygen reacts with reactant components in reactant gas or reactant feed gas **211** as the gas flows over the outer surfaces of the wafers and forms oxidation products. Exit gas **213** from the module contains the oxidation products and unreacted components. In one example embodiment, reactant gas **211** comprises methane or a methane-containing feed gas and exit gas **213** is a mixture of unreacted methane, hydrogen, carbon oxides, and water, oxygen-containing gas **207** is air, and oxygen-depleted gas **209** is enriched in nitrogen and depleted in oxygen relative to gas **207**. Typically, the pressure of gases **211** and **213** is higher than the pressure of the gas in the interior region of the module.

[0093] An alternative side view of the module of **FIG. 1** is shown in **FIG. 2B**, which illustrates an exemplary configuration for use in processes for the recovery of high purity oxygen from an oxygen-containing gas. In this example, spacers **215** between wafers **217** have openings **219** wherein openings **219** and additional openings in spacers disposed below spacers **215** form an internal manifold that is in flow communication with the interior regions of the wafers. Opening **221** thus places the interior region of the module in flow communication with a product gas conduit (not shown). Oxygen-containing gas **223**, for example air, at the gas inflow region of the module flows through the exterior region of the module on either side of spacers **215** and in contact with the outer surfaces of wafers **217**. After contacting the outer surfaces of wafers **217**, oxygen-depleted gas **225** flows through the gas outflow region of the module. The module may operate in a typical temperature range of 600° C. to 1100° C.

[0094] As the oxygen-containing gas flows through the exterior region of the module and the gas contacts the outer surfaces of the wafers, oxygen permeates the active membrane material in the planar members of the wafers and high purity oxygen gas collects in the interior region of the module. High purity oxygen product gas **227** flows from opening **221**. Typically, the pressure of oxygen-containing gases **223** and **225** is higher than the pressure of the high purity oxygen in the interior region of the module.

[0095] One possible exemplary configuration of the interior regions of the wafers in **FIGS. 1, 2A, and 2B** is illustrated in the sectional views of **FIGS. 3A and 3B**. Referring to **FIG. 3A**, which represents section 2-2 of **FIG. 1**, the wafer has outer support layers **301** and **303** of porous ceramic material that allows gas flow through the pores. Dense active membrane layers of **305** and **307** are in contact with outer support layers **301** and **303** and are supported by supporting ribs **321** and **329** which are part of flow channel layers **315** and **317**. These ribs are in turn supported by slotted support layer **309** that has openings or slots **313** for gas flow. Open channels **319** and **325** are in flow communication via openings or slots **313**. Optionally, support layers **301** and **303** may not be required when the module of **FIG. 2B** is used for recovering oxygen from an oxygen-containing gas.

[0096] The term “dense” refers to a ceramic material through which, when sintered or fired, a gas cannot flow.

Gas cannot flow through dense ceramic membranes made of mixed-conducting multi-component metal oxide material as long as the membranes are intact and have no cracks, holes, or imperfections which allow gas leaks. Oxygen ions can permeate dense ceramic membranes made of mixed-conducting multi-component metal oxide material at elevated temperatures, typically greater than 600° C.

[0097] FIG. 3B, which represents section 4-4 of FIGS. 2A and 2B, illustrates a wafer section rotated 90 degrees from the section of FIG. 3A. This section shows identical views of outer support layers 301 and 303 and of dense active membrane material layers 305 and 307. This section also shows alternate views of slotted support layer 309 and flow channel layers 315 and 317. Open channels 331 are formed between alternating supporting ribs 333 and allow gas flow through the interior region of the wafer. The interior region of the wafer is therefore defined as the combined open volume within flow channel layer 315, flow channel layer 317, and slotted support layer 309.

[0098] The dense active membrane layers 305 and 307 preferably comprise a mixed metal oxide ceramic material containing at least one mixed-conducting multi-component metal oxide compound having the general formula $(La_xCa_{1-x})_yFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and δ is a number which renders the composition of matter charge neutral. Any appropriate material can be used for porous support layers 301 and 303, and this material may be, for example, a ceramic material having the same composition as that of active membrane layers 305 and 307. Preferably, porous support layers 301 and 303 are mixed-conducting multi-component metal oxide material. Any appropriate material can be used for the structural members of slotted support layer 309 and flow channel layers 315 and 317, and this material may be, for example, a ceramic material having the same composition as that of active membrane layers 305 and 307. The material of channeled support layer preferably is a dense ceramic material. In one embodiment, active membrane layers 305 and 307, porous support layers 301 and 303, slotted support layer 309, and flow channel layers 315 and 317 all may be fabricated of material having the same composition.

[0099] Dense active membrane layers 305 and 307 optionally may include one or more oxygen reduction catalysts on the oxidant side. The catalyst or catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0100] Porous support layers 301 and 303 optionally may include one or more catalysts to promote hydrocarbon oxidation, reforming, and/or other reactions that occur in the porous layer. The catalyst or catalysts may be disposed on either or both surfaces of porous support layers 301 and 303, or alternatively may be dispersed throughout the layer. The one or more catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof. If desired for structural and/or process reasons, an additional porous layer may be disposed between active membrane layers 305 and 307 and the adjacent flow channel layers 315 and 317 respectively.

[0101] Another possible configuration of the interior regions of the wafers for the oxygen recovery application in FIGS. 1, 2A, and 2B are illustrated in the sectional views of FIGS. 3C and 3D. Referring to FIG. 3C, which represents section 2-2 of FIG. 1, the wafer has outer dense layers 351 and 353. Porous ceramic layers of 355 and 357 are in contact with outer dense layers 351 and 353. Porous ceramic layer 355 is supported by supporting ribs 371, which are part of flow channel layer 365. Porous ceramic layer 355 is in contact with flow channels 366, which are part of flow channel layer 365. Porous ceramic layer 357 is in contact with flow channels 368, which are part of flow channel layer 367.

[0102] Ribs 371 are supported in turn by flow channel layer 358 that has openings or slots 363 for gas flow. Flow channel layer 367 is supported by ribs 373 of flow channel layer 359, and bridges 379 form the ends of flow channels 368. Bridges 372 form the ends of the flow channels 363 and flow channels 368 are in flow communication with flow channels 374 of flow channel layer 359. Open channels 374 and 363 are in flow communication.

[0103] FIG. 3D, which represents section 4-4 of FIGS. 2A and 2B, illustrates a section of the wafers rotated 90 degrees from the section of FIG. 3C. This section shows identical views of outer dense layers 351 and 353 and of porous ceramic layers 355 and 357. Porous ceramic layer 355 is supported by flow channel layer 365. Porous ceramic layer 355 is in contact with flow channels 366, which are part of flow channel layer 365. Porous ceramic layer 357 is supported by ribs 378 of flow channel layer 367. Porous layer 357 is in flow communication with flow channels 368, which are part of flow channel layer 367.

[0104] Ribs 378 are supported in turn by flow channel layer 359 that has openings or slots 374 for gas flow. Flow channel layer 365 is supported by ribs 375 of flow channel layer 358. Bridges 371 form the ends of flow channels 366. Bridges 376 form the ends of the flow channels 374 and flow channels 366 are in flow communication with flow channels 363 of flow channel layer 358. Open channels 374 and 363 are in flow communication.

[0105] The interior region of the wafer therefore is defined as the combined open volume within flow channel layer 365, flow channel layer 367, flow channel layer 358 and flow channel layer 359. The flow channels in layers 365 and 358 may be orthogonal to each other, as may be the flow channels in layers 367 and 359. Alternatively, flow channels 358 and 359 may be replaced by a single flow channel layer that comprises flow channels that radiate from the center of the wafer and are in flow communication with a central port in the center of the wafer.

[0106] Exemplary compositions for the dense active membrane are described in U.S. Pat. No. 6,056,807, which is incorporated herein by reference. Dense active membrane layers 351 and 353 preferably comprise a mixed metal oxide ceramic material containing at least one mixed-conducting multi-component metal oxide compound having the general formula $(La_xSr_{1-x})Co_yO_{3-\delta}$ wherein $1.0 < x < 0.4$, $1.02 \geq 2y > 1.0$, and δ is a number which renders the composition of matter charge neutral. Any appropriate ceramic material can be used for porous support layers 355 and 357, and may be, for example, material of the same composition as that of active membrane layers 351 and 353. Preferably,

porous support layers **355** and **357** are mixed-conducting multi-component metal oxide material. Any appropriate material can be used for the structural members of flow channel layers **365**, **367**, **358** and **359**, and this material may be, for example, a ceramic material having the same composition as that of active membrane layers **351** and **353**. The material of channeled flow layers preferably is a dense ceramic material. In one embodiment, active membrane layers **351** and **353**, porous support layer **355** and **357**, and channeled flow layers **358**, **359**, **365** and **367** all may be fabricated of material having the same composition.

[0107] Optionally, a porous layer may be applied on the outside surface of dense layers **351** and **353**. Other exemplary configurations for the interior regions of the wafers for the oxygen generation application are given in U.S. Pat. No. 5,681,373, which is incorporated herein by reference.

[0108] Embodiments of the present invention utilize multiple membrane modules arranged in series as defined above. The series modules in turn may be installed in one or more vessels with appropriate gas flow containment ducts, conduits, and/or manifolds to direct gas streams to and from the modules. One of these embodiments is illustrated in **FIG. 4A**, which is a schematic side view of the interior of an exemplary membrane separator vessel for use in recovering high purity oxygen from an oxygen-containing gas. Membrane modules **401**, **403**, **405**, **407**, and **409** are installed in series in optional flow containment duct **411** within pressure vessel **413**. These membrane modules may be, for example, similar to the module described above with reference to **FIGS. 1 and 2B**. Optional flow containment duct **411** has inlet **415** to direct inlet gas stream **417** through the duct to contact the outer surfaces of the wafers in modules **401** to **409**. The inlet gas stream is a pressurized oxygen-containing oxidant gas, for example air, that has been heated by any appropriate method (not shown) to a temperature of 600° C. to 1100° C. The pressure of the gas within duct **411** may be in the range of 0.2 to 8 MPa. The flow containment duct preferably comprises an oxidation-resistant metal alloy containing iron and one or more elements selected from the group consisting of nickel and chromium. Commercially-available alloys that may be used for flow containment ducts include Haynes® 230, Incolloy 800H, Haynes® 214, and Inconel® 693 alloys.

[0109] The gas pressure in the interior of flow containment duct **411** preferably is greater than the gas pressure in the interior of pressure vessel **413** between the inner wall of the vessel and the outer wall of flow containment duct **411**. The pressure differential between the interior and the exterior of duct **411** at any point between the inlet and outlet of pressure vessel **413** preferably is maintained at a value equal to or greater than zero, wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct. This may be accomplished, for example, by purging the space outside the duct with a gas at lower pressure than the process gas inside the duct; allowing flow communication between the space outside the duct and the process gas in the duct at process gas outlet **421**; introducing a purge gas into the space outside the duct, or withdrawing the purge gas through a purge gas outlet while using pressure controllers on a purge gas outlet to maintain a lower pressure in the space outside the duct than inside the duct.

[0110] As the oxygen-containing gas passes in series over the surfaces of the wafers in membrane modules **401** to **409**, oxygen permeates the dense active membrane layers and collects in the interior regions of the modules. Oxygen-depleted gas stream **419** exits the duct and pressure vessel via outlet **421**. High purity oxygen permeate product from the interior regions of the modules flows via primary manifolds **423**, **425**, **427**, **429**, and **431**, secondary manifolds **433**, **435**, **437**, **439**, and **441**, and main manifold **445**, and exits the system as high purity gas product stream **447**. At least two of membrane modules **401** to **409** define a module axis which may be parallel to or coincident with the axis of pressure vessel **413** or with the axis of flow containment duct **411**.

[0111] While the exemplary membrane separator vessel described above has a single inlet for feed gas to the membrane modules, a single flow containment duct, and a single outlet from the membrane modules, other embodiments are possible in which multiple inlets, multiple flow containment ducts, and/or multiple outlets may be used. For example, a pressure vessel may have two (or more) flow containment ducts, each having one or more inlets and one or more outlets. Generically, when a separator vessel is described as having an inlet and an outlet, this means that it has one or more inlets and one or more outlets. Generically, when a separator vessel is described as having a flow containment duct, this means that it has one or more flow containment ducts.

[0112] Another view of the exemplary membrane separator vessel of **FIG. 4A** is given by section 6-6 as shown in **FIG. 4B**. In this embodiment, a bank of three membrane modules **401a**, **401b**, and **401c** is installed in parallel in duct **411** and has three primary manifolds **423a**, **423b**, and **423c** that are connected to secondary manifold **433**. Secondary manifold **433** is connected in turn to main manifold **445**. Alternatively, one membrane module, two parallel membrane modules, or more than three parallel membrane modules may be used in each bank.

[0113] While secondary manifolds **433**, **435**, **437**, **439**, and **441**, and main manifold **445** are located in the interior of pressure vessel **413** in the embodiments of **FIGS. 4A and 4B**, these manifolds may be located outside of the pressure vessel in an alternative embodiment. Primary manifolds **423**, **425**, **427**, **429**, and **431** would pass through the wall of pressure vessel **413** in this alternative embodiment.

[0114] In an alternative embodiment, planar membrane modules **401** through **409** may be replaced by tubular membrane modules placed in series relationship relative to the longitudinal flow of gas through optional duct **411**. These modules may utilize multiple single tubes or may utilize bayonet-type tubes, and the modules may be oriented such that gas flows across the tubes in crossflow or contacts the tubes in parallel flow. In this alternative embodiment, all manifolds are located inside the pressure vessel as shown in **FIGS. 4A and 4B**.

[0115] Another embodiment of the invention is illustrated in **FIG. 5**, which is a schematic side view of the interior of an exemplary membrane reactor vessel for use in oxidation processes. Membrane modules **501**, **503**, **505**, **507**, and **509** are installed in series in flow containment duct **511** within pressure vessel **513**. These membrane modules may be, for example, similar to the module described above with refer-

ence to **FIGS. 1 and 2A**. Optional flow containment duct **511** has inlet **515** to direct inlet gas stream **517** through the duct to contact the outer surfaces of the wafers in modules **501** to **509**. The inlet gas stream is a reactant feed gas containing one or more components which react with oxygen at elevated temperatures wherein the inlet reactant feed gas is heated by any appropriate method (not shown) to a temperature of 600° C. to 1100° C. The pressure of the gas within duct **511** may be in the range of 0.2 to 8 MPa. An example of a reactant feed gas is a mixture of steam and natural gas wherein the natural gas comprises mostly methane with smaller amounts of light hydrocarbons. The mixture may be prereformed at a temperature below about 800° C. to yield a reactant feed gas containing steam, methane, and carbon oxides. Other oxidizable reactant feed gases may include, for example, various mixtures of hydrogen, carbon monoxide, steam, methanol, ethanol, and light hydrocarbons.

[0116] The gas pressure in the interior of flow containment duct **511** preferably is greater than the gas pressure in the interior of pressure vessel **513** between the inner wall of the vessel and the outer wall of flow containment duct **511**. The pressure differential between the interior and the exterior of duct **511** at any point between the inlet and outlet of pressure vessel **513** preferably is maintained at a value equal to or greater than zero, wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct. This may be accomplished, for example, by purging the space outside the duct with a gas at lower pressure than the process gas inside the duct; allowing flow communication between the space outside the duct and the process gas in the duct at the process gas outlet, **559**; introducing a purge gas into the space outside the duct, and withdrawing the purge gas through a purge gas outlet while using pressure controllers on a purge gas outlet to maintain a lower pressure in the space outside the duct than inside the duct.

[0117] The interior regions of membrane modules **501** to **509** are in flow communication with two manifold systems, one to introduce an oxygen-containing oxidant gas into the modules and the other to withdraw oxygen-depleted oxidant gas from the modules. The first of these manifold systems comprises main inlet manifold **519**, primary inlet manifolds **521**, **523**, **525**, **527**, and **529**, and secondary inlet manifolds **531**, **533**, **535**, **537**, and **539**. The second of these manifold systems comprises main outlet manifold **541** and primary outlet manifolds **543**, **545**, **547**, **549**, and **551**.

[0118] In an alternative configuration (not shown) to the configuration of **FIG. 5**, secondary inlet manifolds **531**, **533**, **535**, **537**, and **539** may be combined with primary outlet manifolds **543**, **545**, **547**, **549**, and **551**, respectively, when located within flow containment duct **511**. Two manifolds may be combined by installing a first or inner conduit within a second or outer conduit wherein the first conduit provides a first manifold and the annulus between the conduits provides a second manifold. The conduits may be concentric or coaxial; alternatively, the conduits may not be concentric or coaxial and may have separate parallel or nonparallel axes. This configuration of inner and outer conduits to provide a combined manifold function is defined herein as a nested manifold.

[0119] In this alternative configuration, gas **553** would flow through the central conduit and gas **555** would flow

through the annulus of each set of these nested manifolds. The nested manifolds would transition to separate manifolds exterior to flow containment duct **511**, i.e., would transition to secondary inlet manifolds **531**, **533**, **535**, and **539** and primary outlet manifolds **543**, **545**, **547**, **549**, and **551** as shown in **FIG. 5**. Optionally, primary outlet manifolds **543**, **545**, **547**, **549**, and **551** may be nested within secondary inlet manifolds **531**, **533**, **535**, **537**, and **539**, respectively, within flow containment duct **511**. In this option, gas **555** would flow through the central conduit and gas **553** would flow through the annulus of each set of these nested manifolds. In generic terms, therefore, the secondary inlet manifolds and the primary outlet manifolds may be nested when located within flow containment duct **511**, and either a secondary inlet manifold or a primary outlet manifold may be provided by the annulus

[0120] Heated, pressurized oxygen-containing oxidant gas **553**, for example, air that has been heated by any appropriate method (not shown) to a temperature of 600 to 1100° C., enters main inlet manifold **519** and flows via primary inlet manifolds **521**, **523**, **525**, **527**, and **529** and secondary inlet manifolds **531**, **533**, **535**, **537**, and **539** to the inlets of membrane modules **501**, **503**, **505**, **507**, and **509**. Oxygen from the oxidant gas in the interior regions of the membrane modules permeates the dense active membrane layers in the wafers of modules **501** to **509** and the permeated oxygen reacts with the reactive components in the exterior regions of the membrane modules. Oxygen-depleted oxidant gas exits the outlets of the interior regions of the membrane modules via primary outlet manifolds **543**, **545**, **547**, **549**, and **551** and main outlet manifold **541**, and the final oxygen-depleted oxidant gas is withdrawn as gas stream **555**. Outlet gas stream **557**, which contains reaction products and unreacted feed components, is withdrawn from the reactor system via outlet **559**.

[0121] While the exemplary reactor vessel described above has a single inlet for reactant feed gas to the membrane modules, a single flow containment duct, and a single outlet from the membrane modules, other embodiments are possible in which multiple inlets, multiple flow containment ducts, and/or multiple outlets may be used. For example, a pressure vessel may have two or more flow containment ducts, each having one or more inlets and one or more outlets. Generically, when a reactor vessel is described as having an inlet and an outlet, this means that it has one or more inlets and one or more outlets. Generically, when a reactor vessel is described as having a flow containment duct, this means that it has one or more flow containment ducts.

[0122] Another view of the exemplary membrane reactor vessel of **FIG. 5** is given in section 8-8 as shown in **FIG. 6**. In this embodiment, a bank of three membrane modules **503a**, **503b**, and **503c** are installed in parallel in duct **511**. Oxidant gas flows through main inlet manifold **519**, primary inlet manifold **523**, and secondary inlet manifolds **533a**, **533b**, and **533c** to the inlets of membrane modules **503a**, **503b**, and **503c**. Oxygen-depleted oxidant gas exits membrane modules **503a**, **503b**, and **503c** via primary outlet manifolds **545a**, **545b**, and **545c** (located behind secondary inlet manifolds **533a**, **533b**, and **533c**), secondary outlet manifold **561**, and main outlet manifolds **541a** and **541b**. While three parallel membrane modules are shown in the embodiment of **FIG. 6**, one membrane module, two parallel

membrane modules, or more than three parallel membrane modules may be used as desired.

[0123] A guard bed (not shown) may be installed in inlet 415 of pressure vessel 413 and/or in inlet 515 to pressure vessel 513 to remove trace contaminants from inlet stream 417 and/or 517. Alternatively, the guard bed may be installed in the interior of the pressure vessel between the inlet and the first membrane module. The contaminants may include, for example, sulfur-, chromium- and/or silicon-containing gaseous species. The guard bed may contain one or more materials selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, strontium oxide, zinc oxide, and alkaline-earth-containing perovskites. These materials react with and remove the contaminants from the inlet stream of reactant gas or oxygen-containing gas.

[0124] Additional pressure vessels may be installed in series with pressure vessel 413 such that the outlet gas from one vessel feeds the other vessel. Additional pressure vessels may be placed in parallel wherein a plurality of pressure vessels operate in parallel and in series. Likewise, additional pressure vessels may be installed in series with pressure vessel 513 such that the outlet gas from one vessel feeds the other vessel. Additional pressure vessels may be placed in parallel wherein a plurality of pressure vessels operate in parallel and in series. Guard beds may be placed between any series pressure vessels as desired.

[0125] In the embodiments described above, it is desirable to use internal insulation to maintain the walls of pressure vessel 413 and 513 at temperatures lower than the temperatures of the respective membrane modules 401 to 409 and 501 to 509. This may be accomplished by various insulation alternatives in FIGS. 7 through 13, which illustrate insulation configurations for the embodiment of FIGS. 4A and 4B used for the recovery of oxygen from an oxygen-containing gas. Similar insulation configurations (not shown) may be used for the oxidation reactor embodiment of FIGS. 5 and 6.

[0126] The first of these alternatives is shown in FIG. 7 wherein insulation 701 is disposed within and may be in contact with the interior walls of pressure vessel 703. In this embodiment, a flow containment duct is not used; instead, cavity 705 is formed by the insulation itself and this cavity serves to direct gas flow over the exterior regions of the membrane modules. The insulation may be in contact with primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445.

[0127] A second insulation configuration is shown in FIG. 8 wherein insulation 801 is disposed adjacent to and may be in contact with the inner wall of pressure vessel 413. In this embodiment, flow containment duct 411 is used and preferably is not in contact with insulation 801. The insulation preferably is not in contact with primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445.

[0128] A third insulation configuration is shown in FIG. 9 wherein insulation 901 completely fills the interior region of the pressure vessel between the inner walls of the vessel and the exterior surfaces of flow containment duct 411, primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445. The insulation may be in contact

with the inner vessel walls and the exterior surfaces of flow containment duct 411, primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445.

[0129] Another alternative insulation configuration is shown in FIG. 10 wherein insulation 1001 forms a cavity 1003 around the membrane modules and this cavity serves to direct gas flow over the exterior regions of the modules. Insulation 1001 may be in contact with primary manifolds 423a, 423b, and 423c, and typically is not in contact with the inner walls of pressure vessel 413.

[0130] FIG. 11 shows another alternative insulation configuration in which insulation 1101 surrounds flow containment duct 411, which in turn surrounds the membrane modules as described above. Insulation 1101 may be in contact with primary manifolds 423a, 423b, and 423c, and typically is not in contact with the inner walls of pressure vessel 413 and the outer surface of flow containment duct 411.

[0131] Another insulation configuration is shown in FIG. 12 wherein insulation 1201 surrounds flow containment duct 411, which in turn surrounds the membrane modules as described above. Insulation 1201 may be in contact with primary manifolds 423a, 423b, and 423c, typically is in contact with the outer surface of flow containment duct 411, and typically is not in contact with the inner walls of pressure vessel 413.

[0132] A final insulation configuration is shown in FIG. 13 wherein insulation 1303 is placed within and typically is in contact with the inner walls of flow containment duct 411, wherein the insulation forms a cavity 1305 around the membrane modules and this cavity serves to direct gas flow over the exterior regions of the modules. Insulation 1303 may be in contact with primary manifolds 423a, 423b, and 423c.

[0133] In any of the embodiments described above of FIGS. 7-13, a metal-to-ceramic seal typically is used in primary manifolds 423a, 423b, and 423c to transition from metal manifolds to the ceramic modules. Likewise, in the oxidation reactor embodiment of FIG. 6 and corresponding insulation embodiments similar to those of FIGS. 7-13, a metal-to-ceramic seal typically is used in primary manifolds 533a, 533b, and 533c to transition from metal manifolds to the ceramic modules. In the embodiments of FIGS. 10-13 (and similar embodiments for the oxidation reactor), these seals preferably are located within insulation 1001, 1101, 1201, and 1303 (in contact with manifolds 423a, 423b, and 423c but not with manifold 433) to obtain desired seal operating temperatures.

[0134] In any of the embodiments of FIGS. 7-13, additional insulation (not shown) may be placed around the external surface of the pressure vessel, for example to protect operating personnel from a potentially hot vessel surface. This additional insulation also may serve to ensure that the vessel interior is above the dew point of any gas within the vessel. In any of the embodiments of FIGS. 10-13, additional insulation (not shown) may be placed adjacent to the inner surface of the pressure vessel. In any of the embodiments of FIGS. 4A, 4B, and 5-13, any of the manifolds may be insulated internally and/or externally (not shown). This insulation would serve to improve the thermal expansion uniformity of flow containment duct 411 and the manifolds.

[0135] The insulation used in the embodiments of FIGS. 7-13 may contain alumina, alumino-silicate, silica, calcium silicate, or other conventional insulation materials suitable for use at elevated temperatures. The insulation may comprise, for example, one or more materials selected from the group consisting of fibrous alumina, fibrous alumino-silicate, porous alumina, and porous alumino-silicate. In the embodiments of FIGS. 7, 10, and 13, wherein the insulation itself forms a cavity around the membrane modules, the interior walls of the cavity may be coated or covered with a material which prevents volatile components from the insulation from contacting the membrane modules. For example, the cavity may be lined with a foil made of a metal such as Haynes 214 to prevent Si-containing vapor species, which may be generated from insulation materials, and/or Cr-containing vapor species, which may be generated from metal piping materials, from contacting the membrane modules.

[0136] The insulation may include one or more additional materials selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, strontium carbonate, sodium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites wherein these materials may be applied to the surface of the insulation and/or dispersed throughout the insulation. These additional materials may be used in place of or in addition to the guard bed or beds described above. These materials react with and remove contaminants that may be present in the inlet stream of reactant gas; these contaminants may include, for example, sulfur-, chromium-, silicon-, or oxygen-containing containing gaseous species.

[0137] An alternative embodiment for placing groups of wafers in a series flow configuration is shown in FIG. 14. In this embodiment, a tall stack is formed of wafers and spacers as described above and the stack is installed in pressure vessel 1401. Inlet line 1403 and outlet line 1405 are connected to gas manifold shroud assembly 1407 which directs the flow of inlet gas 1408 to flow in alternating directions across groups of wafers and through outlet line 1405 as outlet stream 1409. In this embodiment, the stack is divided by the shroud assembly into first wafer zone 1411, second wafer zone 1413, and third wafer zone 1415. Inlet gas 1408 thus flows in series across wafer zones 1411, 1413, and 1415 and exits via outlet line 1405. While three wafer zones are shown here for illustration purposes, any number of wafer zones can be used as required.

[0138] The embodiment of FIG. 14 may be used as an oxygen recovery device or as an oxidation reactor device. When used as an oxygen recovery device, the stack is formed of wafers and spacers as earlier described with reference to FIGS. 1 and 2B. In an oxygen recovery process, inlet gas 1408 is a heated, pressurized oxygen-containing gas (for example, air), outlet stream 1409 is an oxygen-depleted oxygen-containing gas, and stream 1417 flowing through outlet line 1419 is a high purity oxygen product stream typically at a lower pressure than the pressurized oxygen-containing gas. When used as an oxidation reactor system, the stack is formed of wafers and spacers as earlier described with reference to FIGS. 1 and 2A. In an oxidation process, inlet gas 1408 is a heated, pressurized reactant gas and outlet gas 1409 is a mixture of oxidation reaction products and unreacted reactant gas components. Stream 1417 is an oxygen-depleted oxygen-containing gas

stream typically at a lower pressure than the pressurized reactant gas. Fresh oxygen-containing oxidant gas (for example, air) flows into the stack through an internal stack manifold as described with reference to FIG. 2A; the inlet to this manifold is not seen in FIG. 14 because it lies behind outlet line 1419.

[0139] The embodiment of FIG. 14 can be operated with multiple pressure vessels in series and/or in parallel as desired. Multiple modules may be installed in a single pressure vessel if desired.

[0140] The series membrane modules may be arranged in banks of parallel modules as earlier described with reference to FIGS. 4A, 4B, 5, and 6. This is illustrated in FIG. 15, which is a sectional plan view (not to scale) of flow containment duct 511 and the membrane modules within the duct. In this exemplary embodiment, five banks of three parallel modules are arranged such that each individual set of series modules lies on a common module axis, i.e., modules 501a, 503a, 505a, 507a, and 509a lie on the same axis, modules 501b, 503b, 505b, 507b, and 509b lie on the same axis, and modules 501c, 503c, 505c, 507c, and 509c lie on the same axis. Thus in this example there are three axes, equal to the number of modules in each bank. Each bank comprises a plurality of modules in parallel; for example, modules 501a, 501b, and 501c constitute one bank of modules in parallel. A plurality of modules also may be arranged in series; for example, modules 501c, 503c, 505c, 507c, and 509c constitute modules in series. The definition of series modules also can include banks of modules; for example, the bank of modules 501a, 501b, and 501c is in series with the bank of modules 503a, 503b, and 503c. The module configuration in FIG. 15 thus includes modules in series and modules in parallel.

[0141] As a practical matter, it may be desirable to promote substantial radial mixing (i.e., gas flow in directions deviating from the axis of a series of modules) of gas between successive banks of modules to minimize the deleterious effect of gas bypassing around the membrane modules. The module configuration in FIG. 15 thus may be best described as including modules in parallel and banks of parallel modules operating in series. As in the design of many gas flow distribution systems, the degree of radial mixing can be maximized by proper selection of the axial and radial spacing between internal elements (i.e. membrane modules) and/or the use of flow baffles to promote gas mixing.

[0142] Inlet gas stream 1501 in inlet 1503 flows in series over each bank of radially-oriented (i.e., parallel) modules. With proper selection of the axial and radial spacing between modules, a small amount of gas may bypass modules 501a, 501b, and 501c, but eventually will contact downstream modules as it mixes or diffuses in a radial direction. Exit gas stream 1505 flows through outlet 1507. The gas flow over each successive bank of modules defines the series arrangement of this embodiment wherein all or nearly all of the gas from one bank of parallel modules contacts the next bank of parallel modules in the series of modules. Any desired number of modules may be used in parallel radially and any desired number of banks of parallel modules may be used in series axially.

[0143] In an alternative embodiment of the invention related to FIGS. 4A and 4B or to FIGS. 5 and 6, banks of

parallel membrane modules may be oriented in a staggered or offset series arrangement such that a first bank of three modules is followed in series by an offset second bank of three modules which in turn is followed in series by an offset third bank of three modules, and so forth. This is illustrated in **FIG. 16** wherein a first bank of three modules **502a**, **502b**, and **502c** is followed in series by a second bank of three modules **504a**, **504b**, and **504c** offset in a direction perpendicular to the axis of flow containment duct **511**. A third bank of three modules **506a**, **506b**, and **506c** is offset with respect to the second bank but the modules are coaxial with the modules in the first bank. This offset relationship may continue in similar fashion through the fourth bank of modules **508a**, **508b**, and **508c** and the fifth bank of modules **510a**, **510b**, and **510c**. Each bank may comprise a plurality of modules in parallel; for example, modules **502a**, **502b**, and **502c** constitute one bank of modules in parallel. A plurality of modules also may be arranged in series; for example, modules **502c**, **504c**, **506c**, **508c**, and **510c** may constitute modules in series. The definition of series modules also can include banks of modules; for example, the bank of modules **502a**, **502b**, and **502c** is in series with the bank of modules **504a**, **504b**, and **504c**. The module configuration in **FIG. 16** thus includes modules in series and modules in parallel.

[0144] The modules in **FIG. 16** lie on six axes, i.e., modules **502c**, **506c**, and **510c** lie on one axis, modules **504c** and **508c** lie on another axis, and so forth. These axes may be parallel to the overall flow direction of gas over the modules. In this embodiment, the number of axes is greater than the number of modules in each bank of modules.

[0145] In the embodiment of **FIG. 16**, inlet gas stream **1601** enters through inlet **1603** and flows over modules **502a**, **502b**, and **502c** in the first bank. A portion of this gas may bypass module **502a** but, in the absence of significant radial mixing, will at least contact offset module **504a**. Gas that flows between modules **502a**, **502b**, and **502c**, will at least contact the next series of offset modules **504b** and **504c**. Portions of the gas that flows from module **502a** in the first bank will contact at least two modules (**504a** and **504b**) in the second bank. In this way, such an offset arrangement prevents gas from bypassing straight through a gap between rows of modules on a common axis. Instead, gas bypassing any module in a bank of modules will impinge directly on a module in the next bank of modules. In the absence of significant radial mixing, at least a portion of the gas from one or more of the modules in a bank will contact one or more of the modules in the next bank, and this defines the series arrangement of modules in this embodiment.

[0146] The definition of modules arranged in series according to the present invention thus includes both embodiments described above with reference to **FIGS. 15** and **16**. In these embodiments, the axes of banks of modules and the axes of series modules may be generally orthogonal to each other, and the axes of series modules may be generally parallel to the overall direction of gas flow through the vessel. Alternative embodiments are possible wherein the axes of banks of modules are not generally orthogonal to the axes of the series modules and/or wherein the axes of series modules are not generally parallel to the overall direction of gas flow through the vessel. In these alternative embodiments, the banks of modules lie at acute angles to the overall direction of gas flow through the vessel. These

alternative embodiments are included in the definition of modules arranged in series according to the present invention.

[0147] The series reactor system described above may be used in oxidation service to produce synthesis gas from a hydrocarbon-containing feed gas such as natural gas. In this application, reforming catalyst may be disposed between any series modules, any parallel modules, any series and parallel modules, and/or following the final modules in a vessel. The reforming catalyst promotes the endothermic reactions of water and/or carbon dioxide with hydrocarbons, especially methane, to generate hydrogen and carbon monoxide. The catalyst may be used to complement or balance the exothermic oxidation reactions that occur between permeated oxygen and reactants adjacent to the surfaces of the active membrane material in the modules. By appropriate use of reforming catalyst at strategic locations between the modules in a multiple-module series reactor system, the temperature profiles across the reactor and the product gas composition may be controlled to achieve optimum reactor operation.

[0148] An embodiment of the present invention is illustrated by the exemplary placement of appropriate catalyst between the modules of a multiple-module series oxidation reactor system. For example, referring to **FIG. 15**, catalyst **501d**, **501e**, and **501f** may be placed in series fashion in the space between any modules in the first bank of modules **501a**, **501b**, and **501c** and the second bank of modules **503a**, **503b**, and **503c**. Alternatively, catalyst **501d**, **501e**, and **501f** may extend continuously between the inner walls of flow containment duct **511**. Likewise, catalyst may be placed between any or all of the second and third banks of modules, the third and fourth bank of modules, the fourth and fifth banks of modules, or following the fifth bank (not shown). Similarly, catalyst may be placed in series fashion between any or all of the offset banks of modules in the embodiment of **FIG. 16**. For example, referring to **FIG. 16**, catalyst **502d**, **502e**, and **502f** may be placed in series fashion in the space between the first and second banks of modules. Alternatively, catalyst **502d**, **502e**, and **502f** may extend continuously between the inner walls of flow containment duct **511**. In general, catalyst may be placed in series fashion between or downstream of any or all of the series banks of modules in **FIGS. 15** and **16**.

[0149] Additionally or alternatively, catalyst may be placed between the modules in a bank of parallel modules to promote reforming reactions in the gas passing between the modules. For example, in **FIG. 15** catalyst **505d** and **505e** may be placed between modules **505a** and **505b** and between **505b** and **505c**. Alternatively, catalyst **505d**, and **505e** may extend continuously in the axial direction between the first through fifth banks of modules. For example, in **FIG. 16** catalyst **506d** and **506e** may be placed between modules **406a** and **506b** and between **506b** and **506c**. In general, catalyst may be placed in parallel fashion between any or all of the parallel modules in **FIGS. 15** and **16**.

[0150] In the broadest application of this concept, therefore, catalyst may be placed in the space between any two adjacent modules in the embodiments of **FIGS. 15** and **16**, or in any other embodiments with both of series and parallel module placement. In addition, when pressure vessel **513** is operated in series with another similar pressure vessel,

catalyst may be placed between the vessels such that the effluent gas from one pressure vessel passes through the catalyst before passing into the second pressure vessel.

[0151] The catalyst may be varied in type and/or amount depending on the axial or radial location among the modules in the pressure vessel. In one alternative, for example, the catalyst activity may be varied in the axial direction for optimal control of the module temperatures through the reactor. For example, catalyst sections near the inlet of the reactor may comprise catalyst which is active at lower temperature (i.e. a high Ni loading), whereas in higher temperature regions of the reactor the optimal catalyst composition may involve lesser activity and greater thermal stability (i.e. a low Ni loading). In this way, optimal catalyst activity can be achieved at every axial location in the reactor, while maintaining thermal stability of the catalyst. Other catalyst arrangements are possible and fall within the scope of embodiments of the claimed invention.

[0152] The catalyst for use in this embodiment may include one or more metals or compounds containing metals selected from the group consisting of nickel, cobalt, platinum, gold, palladium, rhodium, ruthenium, and iron. The catalyst may be supported on alumina or other oxide supports and may include additions such as lanthanum or potassium. The catalyst may be placed between modules by any known means including, for example, using monoliths or using granular catalysts in appropriate catalyst holders that fit in the spaces between the modules.

[0153] The ion transport membrane systems described above utilize multiple membrane modules operating in series for use in either oxygen recovery or oxidation processes, and the modules are arranged in a series flow configuration to control the amount of oxygen extracted across an individual module or the degree of conversion across an individual module. When the single modules or banks of multiple modules are arranged in series along an axis that is generally parallel with the vessel axis, the vessel length is determined by the number of modules or banks in series. A large number of modules may require an excessively long vessel, and shorter vessel lengths may be needed in many design situations. The transportation of very long vessels, for example, can be difficult and expensive. Also, the plot plan area or 'footprint' required for very long vessels can present problems in space-limited applications such as, for example, urban environments, offshore platforms, and ships. Also, in certain applications, a significantly shorter vessel with a slightly larger diameter may be more cost-effective.

[0154] These problems are addressed in the following embodiments of the present invention by a vessel design that incorporates multiple passes of the gas flowing over the exterior surfaces of the membrane modules. In one application, an even number of passes allows placement of the gas inlet nozzle and the gas outlet nozzle at the same end of the vessel, thereby reducing the length or complexity of piping runs to other process equipment such as heat exchangers. This may lead to a more compact plant layout with lower capital and operating costs achieved through reduced heat loss from piping.

[0155] In the single pass or multiple parallel pass systems earlier described, gas flowing over the outside of the membranes flows through the membrane module vessel in a

generally axial direction, i.e., flow is generally parallel with the axis of the vessel from inlet to outlet. Localized non-axial flow may be caused by gas flow impinging on the membrane modules, but the bulk flow is in the axial direction. The axis of a vessel having a first end and a second end is defined by a straight line passing through the vessel from the first end to the second end and parallel to the sides. Most vessels for pressurized operation are cylindrical, and in cylindrical vessels the axis is common to the cylinder axis and is parallel to the vessel walls.

[0156] Multiple gas flow passes are achieved in the various embodiments of the present invention by the use of one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to direct the flow of gas in any direction and/or divert the flow of gas in a non-axial direction within the vessel. For example, the gas flow control partitions may be installed to change the gas flow in a direction of between about 90 degrees and about 180 degrees from the vessel axis as described below. Gas flow control in any direction relative to the vessel axis is possible.

[0157] A gas flow control partition is defined as a member of any shape disposed or installed within a vessel and adapted to direct the flow of gas within the vessel and/or to change the flow direction of gas within the vessel. A gas flow control partition is separate from the vessel walls, but the partition may be attached to a vessel wall and may work in concert with the wall to control and/or direct the flow of gas within the vessel. A gas flow control partition is different and distinct from the membrane modules or catalyst installed within the vessel. The terms "direction of gas flow" or "gas flow direction" are equivalent and mean the direction of gas flowing over the outside of the membranes between a first location and a second location in the vessel. While localized gas flow may contain eddies, turbulence, or crosscurrents, the bulk flow of the gas defines the direction of gas flow between the first location and the second location.

[0158] An embodiment of multiple gas flow passes is illustrated in FIG. 17A. Flow containment duct 1701 is externally similar to those of FIGS. 15 and 16 and has outer walls 1703, inlet 1705, and outlet 1707. The duct may be installed coaxially in a pressure vessel as shown, for example, in FIGS. 4A and 5. The duct is fitted with gas flow control partition 1709 connected to gas flow control partition 1711. The duct also is fitted with gas flow control partition 1713 connected to gas flow control partition 1715. The channel formed by lower wall 1703, gas flow control partition 1709, and gas flow control partition 1711 contains membrane modules 1717, 1719, 1721, 1723, and 1725. The channel formed by gas flow control partitions 1709, 1711, 1713, and 1715 contains membrane modules 1727, 1729, 1731, 1733, and 1735. The channel formed by gas flow control partition 1715, gas flow control partition 1713, and upper wall 1703 contains membrane modules 1737, 1739, 1741, 1743, and 1745. These membrane modules may be any of the modules earlier described for oxygen recovery or oxidation processes.

[0159] Inlet gas flow stream 1747 is diverted by gas flow control partition 1709 and flows successively over membrane modules 1717, 1719, 1721, 1723, and 1725 in the channel between wall 1703 and gas flow control partition 1711. Gas flow stream 1749 is reversed 180° relative to the duct axis and the pressure vessel axis by gas flow control

partition **1713** and the adjacent portion of wall **1703**, and the reversed gas flows successively over membrane modules **1727**, **1729**, **1731**, **1733**, and **1735** in the channel between gas flow control partitions **1711** and **1715**. Gas flow stream **1751** is reversed 180° by gas flow control partition **1709** and the adjacent portion of vessel wall **1703**, and the reversed gas flows parallel to the duct axis and the pressure vessel axis successively over membrane modules **1737**, **1739**, **1741**, **1743**, and **1745** in the channel between gas flow control partition **1715** and wall **1703**. Outlet gas flow stream **1753** exits the duct via outlet **1707**. The use of these gas flow control partitions directs gas flow in series over membrane modules **1717** through **1745** in a duct and vessel length that is approximately one third the length of a duct and vessel without these partitions.

[0160] Gas streams **1747**, **1749**, **1751**, and **1753** thus pass through non-axial directions while the gas flowing over the outside of the membranes changes direction as shown in FIG. **17A**.

[0161] FIG. **17B** is view of section 10-10 (rotated 90°) of FIG. **17A** and illustrates the flow of gas through the channels formed by the gas flow control partitions and duct walls. Gas flow stream **1747a** (which has contacted module **1717**) is shown flowing into the plane of FIG. **17B** into channel **1755** formed by wall **1703**, gas flow control partition **1711**, upper duct wall **1712**, and lower duct wall **1714** wherein the gas flows over membrane module **1719** and the successive modules **1721-1725** (not shown). The gas flow stream **1749** is reversed and passes over modules **1727-31** (not shown) and **1733** via channel **1757** formed by gas flow control partitions **1711** and **1715**, upper duct wall **1712**, and lower duct wall **1714**, and gas stream **1749a** is shown flowing out of the plane of FIG. **17b**. This gas stream passes over module **1735** (not shown), is reversed 180° by flow control partition **1709** and the adjacent wall section (FIG. **17A**), and passes over module **1737** (not shown). The gas stream, now shown as stream **1751a**, flows into the plane of FIG. **17B** and into channel **1759** formed by gas flow control partition **1715**, upper duct wall **1712**, lower duct wall **1714**, and wall **1703**, over module **1739**, and modules **1741-1745** (not shown).

[0162] The modules of FIGS. **17A** and **17B** may be either oxygen separation modules (as in FIGS. **4A** and **4B**) or oxidation reaction modules (as in FIGS. **5** and **6**).

[0163] An alternative embodiment is illustrated in FIG. **18A** wherein the flow containment duct is designed to surround two sets of parallel membrane modules such that the inlet gas and outlet gas flows are at the same end of the duct and the pressure vessel (not shown) which contains the duct. Duct **1801** comprises inlet **1803**, outlet **1805**, first wall **1807**, second wall **1809**, end wall **1811**, and internal gas flow control partition **1813**. Inlet gas **1815** flows over two parallel sets of five membrane modules **1817** through **1825** and **1827** through **1835**. Intermediate gas stream **1836** then is diverted 180° by end wall **1811** and flows over two parallel sets of five membrane modules **1837** through **1845** and **1847** through **1855**. Outlet gas stream **1857** exits via outlet **1805**.

[0164] FIG. **18B** is view of section 12-12 (rotated 90°) of FIG. **18A** and illustrates the flow of gas through the channels formed by the gas flow control partition and duct walls. Inlet gas stream **1815** is shown flowing into the plane of FIG. **18B** and channel **1859** formed between wall **1809**,

internal partition **1813**, upper wall **1861**, and lower wall **1863**. Gas flows over parallel modules **1817** and **1827** and further over parallel modules **1819** through **1825** and **1829** through **1835** (not shown). Gas flow is reversed as described above, and the gas flows through channel **1865** formed by wall **1807**, gas flow control partition **1813**, upper wall **1861**, and lower wall **1863**, wherein the gas passes over parallel modules **1837** through **1843** and **1847** through **1853** (not shown). The gas finally passes over modules **1845** and **1855**, and outlet gas stream **1857** exits via outlet **1805**.

[0165] The modules of FIGS. **18A** and **18B** may be either oxygen separation modules (as in FIGS. **4A** and **4B**) or oxidation reaction modules (as in FIGS. **5** and **6**).

[0166] A modification of the system of FIGS. **18A** and **18B** is shown in FIG. **19**. In this alternative arrangement, the gas makes four passes in the flow containment duct, and the passages are in more than one horizontal plane. In FIG. **19**, passages **1901** and **1903** are in the lower horizontal plane, while passages **1905** and **1907** are in the upper horizontal plane. Passage **1901** is formed by side wall **1909**, lower wall **1914**, gas flow control partition **1921**, and gas flow control partition **1923**. Passage **1903** is formed by side wall **1911**, lower wall **1914**, gas flow control partition **1921**, and gas flow control partition **1923**. Passage **1905** is formed by side wall **1911**, upper wall **1913**, gas flow control partition **1921**, and gas flow control partition **1923**. Passage **1907** is formed by side wall **1909**, upper wall **1913**, gas flow control partition **1921**, and gas flow control partition **1923**.

[0167] In this modification, the two parallel sets of modules in passages **1905** and **1907** are inverted, and the module manifolds are above the membrane modules. This allows the cooler manifold and seal region to be placed toward the cooler region near the outside of the flow duct, providing for a longer component life. Another embodiment (not shown) is for all the modules to be upright (i.e. not inverted) with all the module manifolds oriented in generally the same direction. In order to keep the seal region at a cooler temperature, the manifold could protrude from the flow duct at the sides or the bottom.

[0168] Another embodiment is illustrated in FIG. **20** wherein the gas flow control partitions are oriented such that the gas flow directions change in a combination of 90° and 180° turns. In this embodiment, flow containment duct **2001** is defined by outer walls **2003**, **2005**, **2007**, and **2009**, inlet **2011**, and outlet **2013**. Inlet gas stream **2015** flows through the internal region of duct **2001** with successive flow direction changes of 90° , 180° , 90° , 180° , and 180° , and the final gas stream **2017** exits via outlet **2013**. These changes in the gas flow directions are effected, respectively, by wall **2003** with gas flow control partition **2019**, wall **2005**, gas flow control partition **2109** with gas flow control partition **2021**, gas flow control partition **2023** with wall **2009**, wall **2007**, gas flow control partition **2023** with gas flow control partition **2025**, gas flow control partition **2021**, and gas flow control partition **2025** with wall **2005**. This combination of walls and gas flow control partitions provides successive flow channels **2027**, **2029**, **2031**, **2033**, **2035**, **2037**, **2039**, and **2041**. Gas flow through these channels passes in series as shown over 13 membrane modules **2043** through **2067**.

[0169] The flow of gas through the passages formed by the gas flow control partitions need not be generally parallel with the axis of the vessel, and may be in any desired

advantageous direction. Also, multiple passages may be arranged along different axes within the same flow duct or vessel, and other angles also are possible. Passages which are orthogonal to the vessel axis may have an advantage in facilitating maintenance or removal of sections of the membrane modules or vessel, especially if the vessel and flow duct have body flanges at one or more points along the length of the vessel. In addition, having passages which are orthogonal to the vessel axis may help to maintain a temperature, pressure, and/or gas composition profile that changes monotonically with axial distance down the length of the vessel. This may result in lower thermal-chemical-mechanical stresses in the membranes and vessel, which may increase the operating life of the membrane module and vessel system. Vessels may be connected in series, and each vessel may have a different arrangement of partitions and gas passages that are tailored to the specific process operating conditions of the system.

[0170] The internal gas flow control partitions may be made of any desired materials such as, for example, carbon steel, steel alloys, high-temperature alloys, and ceramic. The gas flow control partition and joints between partitions or between partitions and the flow duct do not necessarily need to be leak tight, and a small amount of leakage between passages is acceptable. The gas flow control partition may be mounted or attached using any desired methods such as, for example, welded, bolted, press-fit, spring-mounted, or clamped connections.

[0171] The multiple-pass vessel designs described above may be applied to any ion transport membrane systems that utilize multiple membrane modules operating in series for use in either oxygen recovery or oxidation processes. For example, any of the embodiments may be applied to membrane modules for oxygen recovery as described with reference to **FIGS. 4A and 4B**. Alternatively, any of the embodiments may be applied to membrane modules for effecting oxidation processes as discussed earlier with reference to **FIGS. 5 and 6**. The series membrane modules may have reforming catalyst disposed between any of the series modules as described earlier with reference to **FIGS. 15 and 16**.

1. An ion transport membrane system comprising

- (a) a pressure vessel having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;
- (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and
- (c) one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to change a direction of gas flow within the vessel.

2. The system of claim 1 wherein each planar membrane module comprises a plurality of wafers having planar parallel surfaces, and wherein the pressure vessel is cylindrical and the axis is parallel to some or all of the planar parallel surfaces of the wafers.

3. The system of claim 1 which further comprises a flow containment duct disposed in the interior of the pressure

vessel, wherein the flow containment duct has an interior region, surrounds the plurality of planar ion transport membrane modules, and is in flow communication with the inlet and outlet of the pressure vessel, and wherein the one or more gas flow control partitions are disposed in the interior region of the flow containment duct.

4. The system of claim 3 wherein the flow containment duct and the one or more gas flow control partitions comprise an oxidation-resistant metal alloy containing iron and one or more elements selected from the group consisting of nickel and chromium.

5. The system of claim 1 wherein at least two of the planar ion transport membrane modules define a module axis, and wherein the pressure vessel is cylindrical and has an axis that is parallel to or coaxial with the module axis.

6. The system of claim 1 wherein at least two of the planar ion transport membrane modules define a module axis, and wherein the pressure vessel is cylindrical and has an axis that is perpendicular to the module axis.

7. The system of claim 1 wherein each of the one or more flow control partitions is oriented such that an initial direction of gas flow is diverted to a final direction of gas flow wherein the angle formed between the initial direction of gas flow and the final direction of gas flow forms an angle of greater than zero degrees and less than or equal to 180 degrees.

8. The system of claim 7 wherein each of the one or more flow control partitions is oriented such that the initial direction of gas flow is diverted to a final direction of gas flow wherein the angle formed between the initial direction of gas flow and the final direction of gas flow forms an angle of greater than 90 degrees and less than or equal to 180 degrees.

9. The system of claim 7 wherein each of the one or more flow control partitions is oriented such that the initial direction of gas flow is diverted to a final direction of gas flow wherein the angle formed between the initial direction of gas flow and the final direction of gas flow forms an angle of 180 degrees.

10. The system of claim 1 which further comprises

- (d) one or more additional pressure vessels, each having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;
- (e) a plurality of planar ion transport membrane modules disposed in the interior of each of the pressure vessels and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and
- (f) one or more gas flow control partitions disposed in the interior of each of the pressure vessels and adapted to change a direction of gas flow within any of the one or more pressure vessels;

wherein at least two of the pressure vessels are arranged in series such that the outlet of one pressure vessel is in flow communication with the inlet of another pressure vessel.

11. The system of claim 1 which further comprises

- (d) one or more additional pressure vessels, each having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;

- (e) a plurality of planar ion transport membrane modules disposed in the interior of each of the pressure vessels and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and
- (f) one or more gas flow control partitions disposed in the interior of each of the pressure vessels and adapted to change a direction of gas flow within any of the one or more pressure vessels;

wherein at least two of the pressure vessels are arranged in parallel such that any inlet of one pressure vessel and any inlet of another pressure vessel are in flow communication with a common feed conduit.

12. The system of claim 1 which further comprises catalyst disposed between any two of the planar ion transport membrane modules arranged in series.

13. The reactor system of claim 12 wherein the catalyst comprises one or more metals or compounds containing metals selected from the group consisting of nickel, cobalt, platinum, gold, palladium, rhodium, ruthenium, and iron.

14. The reactor system of claim 12 wherein the catalyst is placed between a plurality of the modules in series and the activity of the catalyst varies at different locations between the modules in series.

15. A method for the recovery of oxygen from an oxygen-containing gas comprising

- (a) providing an ion transport membrane separator system comprising
 - (1) a pressure vessel having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;
 - (2) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and
 - (3) one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to change a direction of gas flow within the vessel;
- (b) providing a heated, pressurized oxygen-containing feed gas stream, introducing the feed gas stream via the pressure vessel inlet to the exterior regions of the membrane modules, and contacting the feed gas stream with the mixed metal oxide ceramic material;
- (c) permeating oxygen ions through the mixed metal oxide ceramic material, recovering high purity oxygen gas product in the interior regions of the membrane modules, and withdrawing the high purity oxygen gas product from the interior regions of the membrane modules through the gas manifolds to the exterior of the pressure vessel; and
- (d) withdrawing an oxygen-depleted oxygen-containing gas from the pressure vessel outlet.

16. The method of claim 15 wherein the pressure of the oxygen-containing feed gas is greater than the pressure of the high purity oxygen gas product.

17. The method of claim 15 which further comprises a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct has an

interior region and an exterior region, surrounds the plurality of planar ion transport membrane modules, and is in flow communication with the inlet and outlet of the pressure vessel, and wherein the one or more gas flow control partitions are disposed in the interior region of the flow containment duct.

18. The method of claim 17 wherein the pressure differential between the interior region and the exterior region of the flow containment duct at any point between the inlet and outlet of the pressure vessel is maintained at a value equal to or greater than zero, and wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct.

19. An oxidation process comprising

- (a) providing an ion transport membrane reactor system comprising
 - (1) a pressure vessel having an interior, an inlet adapted to introduce gas into the interior of the vessel, an outlet adapted to withdraw gas from the interior of the vessel, and an axis;
 - (2) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region; and
 - (3) one or more gas flow control partitions disposed in the interior of the pressure vessel and adapted to change a direction of gas flow within the vessel;
- (b) providing a heated, pressurized reactant feed gas stream, introducing the reactant feed gas stream via the pressure vessel inlet to the exterior regions of the membrane modules;
- (c) providing an oxygen-containing oxidant gas to the interior regions of the membrane modules, permeating oxygen ions through the mixed metal oxide ceramic material, reacting oxygen with components in the reactant feed gas stream in the exterior regions of the membrane modules to form oxidation products therein, and withdrawing the oxidation products from the exterior regions of the membrane modules through the outlet to the exterior of the pressure vessel to provide an oxidation product stream; and
- (d) withdrawing oxygen-depleted oxygen-containing gas from the interior regions of the membrane modules via the one or more manifolds to the exterior of the pressure vessel.

20. The process of claim 19 wherein the pressure of the pressurized reactant feed gas stream is greater than the pressure of the oxygen-containing oxidant gas.

21. The process of claim 19 which further comprises a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct has an interior region and an exterior region, surrounds the plurality of planar ion transport membrane modules, and is in flow communication with the inlet and outlet of the pressure vessel, and wherein the one or more gas flow control partitions are disposed in the interior region of the flow containment duct.

22. The process of claim 21 wherein the pressure differential between the interior region and the exterior region of the flow containment duct at any point between the inlet and outlet of the pressure vessel is maintained at a value equal

to or greater than zero, and wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct.

23. The process of claim 19 wherein the pressurized reactant feed gas stream comprises one or more hydrocarbons having one or more carbon atoms.

24. The process of claim 23 wherein the pressurized reactant feed gas stream comprises methane.

25. The process of claim 23 wherein the oxidation product stream comprises hydrogen and carbon oxides.

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(57) **ABSTRACT**

Ion transport membrane oxidation system comprising an enclosure having an interior and an interior surface, inlet piping having an internal surface and adapted to introduce a heated feed gas into the interior of the enclosure, and outlet piping adapted to withdraw a product gas from the interior of the enclosure; one or more planar ion transport membrane modules disposed in the interior of the enclosure, each membrane module comprising mixed metal oxide material; and a preheater adapted to heat a feed gas to provide the heated feed gas to the inlet piping, wherein the preheater comprises an interior surface. Any of the interior surfaces of the enclosure, the inlet piping, and the preheater may be lined with a copper-containing metal lining. Alternatively, any of the interior surfaces of the inlet piping and the preheater may be lined with a copper-containing metal lining and the enclosure may comprise copper.

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FIG. 1

FEED GAS CONTAMINANT CONTROL IN ION TRANSPORT MEMBRANE SYSTEMS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] This invention was made with government support under Contract Number DE-FC26-97FT96052 between Air Products and Chemicals, Inc. and the U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0002] The permeation of oxygen ions through ceramic ion transport membranes is the basis for a variety of gas separation devices and oxidation reactor systems operating at high temperatures in which permeated oxygen is recovered on the permeate side as a high purity oxygen product or is reacted on the permeate side with oxidizable compounds to form oxidized or partially oxidized products. The practical application of these gas separation devices and oxidation reactor systems requires membrane assemblies having large surface areas, gas distribution systems to contact feed gas with the feed sides of the membranes, and product collection systems to withdraw product gas from the permeate sides of the membranes. These membrane assemblies may comprise a large number of individual membranes arranged and assembled into modules having appropriate gas flow piping to introduce feed gas into the modules and withdraw product gas from the modules.

[0003] Ion transport membranes may be fabricated in either planar or tubular configurations. In the planar configuration, multiple flat ceramic plates are fabricated and assembled into stacks or modules having piping systems to pass feed gas over the planar membranes and to withdraw product gas from the permeate side of the planar membranes. In tubular configurations, multiple ceramic tubes may be arranged in bayonet or shell-and-tube configurations with appropriate tube sheet assemblies to isolate the feed and permeate sides of the multiple tubes.

[0004] The individual membranes used in planar or tubular module configurations typically comprise very thin layers of active membrane material supported on material having large pores or channels that allow gas flow to and from the surfaces of the active membrane layers. Each active ceramic membrane operates in a highly-reactive chemical and electrochemical environment, and the presence of certain contaminants in the hot feed gas in this environment may adversely affect the membrane stoichiometry and operating efficiency. The adverse results may differ depending on whether the membrane is operated in gas separation or oxidation service. The potential operating problems caused by these phenomena can have a significant negative impact on the purity of recovered products and on membrane operating life.

[0005] The solid ion-conducting metallic oxide materials used in these membrane modules may degrade in the presence of volatile gas-phase contaminants at the high operating temperatures required to effect ion conduction, thereby reducing the ability of the membranes to conduct or permeate oxygen ions. Because of this potential problem, there is a need in the art for methods to control certain contaminants in the feed gas to the membrane modules and in reactive gases within the membrane modules to ensure the successful

operation of ion-conducting metallic oxide membrane systems. These needs are addressed by embodiments of the present invention as disclosed below and defined by the claims that follow.

BRIEF SUMMARY OF THE INVENTION

[0006] An embodiment of the invention is an ion transport membrane oxidation system comprising

[0007] (a) an enclosure having an interior and an interior surface, inlet piping having an internal surface and adapted to introduce a heated feed gas into the interior of the enclosure, and outlet piping adapted to withdraw a product gas from the interior of the enclosure;

[0008] (b) one or more planar ion transport membrane modules disposed in the interior of the enclosure, each membrane module comprising mixed metal oxide material; and

[0009] (c) a preheater adapted to heat a feed gas to provide the heated feed gas to the inlet piping of the enclosure, wherein the preheater comprises an interior surface;

wherein either

[0010] (1) any of the interior surfaces of the enclosure, the inlet piping, and the preheater are lined with a copper-containing metal lining, or

[0011] (2) any of the interior surfaces of the inlet piping and the preheater are lined with a copper-containing metal lining, and the enclosure comprises copper.

[0012] In this embodiment, each membrane module may have an interior region and an exterior region, and wherein the inlet and the outlet of the vessel may be in flow communication with the exterior region of each membrane module.

[0013] The copper-containing metal lining may comprise greater than about 99 weight % copper. Alternatively or additionally, the copper-containing metal lining may comprise less than about 0.0005 weight % oxygen. The type of copper-containing metal lining may be selected from the group consisting of electroplating, foil, cladding, tubing, and pipe. The system may further comprise refractory material disposed between the copper-containing metal lining and any of the interior surfaces of the enclosure and the inlet piping. Any of the enclosure, the inlet piping, and the preheater comprise one or more elements may be selected from the group consisting of nickel, silicon, and tungsten.

[0014] In this embodiment, the enclosure may be a flow containment duct that surrounds the one or more planar ion transport membrane modules and wherein the flow containment duct is disposed in the interior of a pressure vessel. Alternatively, the enclosure may be a pressure vessel that surrounds the one or more planar ion transport membrane.

[0015] The mixed conducting metal oxide material may have the general stoichiometric composition $(Ln_{1-x}A_x)_w(B_{1-y}B'_y)O_{3-\delta}$, wherein Ln represents one or more elements selected from La, the D block lanthanides of the IUPAC periodic table, and Y; wherein A represents one or more elements selected from Mg, Ca, Sr and Ba; wherein B and B' each represent one or more elements selected from Sc, Ti, V, Mn, Fe, Co, Ni, Copper, Cr, Al, Zr, Mg, and Ga; wherein

$0 \leq x \leq 1$, $0 \leq y \leq 1$, and $0.95 < w < 1.05$; and wherein δ is a number that renders the compound charge neutral. More specifically, the mixed conducting metal oxide material may have the general stoichiometric composition $(La_xCa_{1-x})_wFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \geq w > 1.0$, and δ is a number which renders the composition charge neutral.

[0016] Another embodiment of the invention relates to a process for generating synthesis gas comprising

[0017] (a) providing an ion transport membrane oxidation system including

[0018] (1) an enclosure having an interior and an interior surface, inlet piping having an internal surface and adapted to introduce a heated feed gas into the interior of the enclosure, outlet piping adapted to withdraw a product gas from the interior of the enclosure, and a preheater adapted to heat a feed gas to provide the heated feed gas to the inlet piping of the enclosure, wherein the preheater has an interior surface; and

[0019] (2) one or more planar ion transport membrane modules disposed in the interior of the enclosure, each membrane module comprising mixed metal oxide material;

[0020] wherein either

[0021] (3) any of the interior surfaces of the enclosure, the inlet piping, and the preheater are lined with a copper-containing metal lining, or

[0022] (4) any of the interior surfaces of the inlet piping and the preheater are lined with a copper-containing metal lining, and the enclosure comprises copper.

[0023] (b) introducing a heated oxygen-containing gas into the interior region of each membrane module, introducing a hydrocarbon-containing feed gas into the preheater, withdrawing a preheated hydrocarbon-containing feed gas from the preheater, and introducing the preheated hydrocarbon-containing feed gas into the exterior region of each membrane module; and

[0024] (c) withdrawing a synthesis gas product from the interior of the enclosure via the outlet piping.

[0025] The hydrocarbon-containing feed gas may comprise at least methane and water and optionally may comprise any of hydrogen, carbon monoxide, and carbon dioxide. The hydrocarbon-containing feed gas may be pre-reformed natural gas. The synthesis gas may comprise at least hydrogen, carbon monoxide, and carbon dioxide. The feed gas may be heated in the feed gas preheater to a temperature in the range of 600 to 1100° C.

[0026] In this embodiment, the copper-containing metal lining may comprise greater than about 99 weight % copper. Additionally or alternatively, the copper-containing metal lining may comprise less than about 0.0005 weight % oxygen. The type of copper-containing metal lining may be selected from the group consisting of electroplating, foil, cladding, tubing, and pipe. Refractory material may be disposed between the copper-containing metal lining and any of the interior surfaces of the enclosure and the inlet piping. Any of the vessel, the inlet piping, and the preheater

may comprise one or more elements selected from the group consisting of nickel, silicon, and tungsten.

[0027] The enclosure may be a flow containment duct that surrounds the one or more planar ion transport membrane modules in which the flow containment duct is disposed in the interior of a pressure vessel. Alternatively, the enclosure may be a pressure vessel that surrounds the one or more planar ion transport membrane modules.

[0028] The mixed conducting metal oxide material may have the general stoichiometric composition $(Ln_{1-x}A_x)_w(B_{1-y}B'_y)O_{3-\delta}$, wherein Ln represents one or more elements selected from La, the D block lanthanides of the IUPAC periodic table, and Y; wherein A represents one or more elements selected from Mg, Ca, Sr and Ba; wherein B and B' each represent one or more elements selected from Sc, Ti, V, Mn, Fe, Co, Ni, Copper, Cr, Al, Zr, Mg, and Ga; wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, and $0.95 < w < 1.05$; and wherein δ is a number that renders the compound charge neutral. More specifically, the mixed conducting metal oxide material may have the general stoichiometric composition $(La_xCa_{1-x})_wFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \geq w \geq 1.0$, and δ is a number which renders the composition charge neutral.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0029] FIG. 1 illustrates an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0030] In the generation of synthesis gas by ion transport membrane oxidation systems, the exposure of the system metallurgy to high temperature synthesis gas or to mixtures of steam and methane can lead to two problems. First, conventional superalloys that have the necessary mechanical properties for use at high temperatures contain silicon and in some cases contain tungsten. Under high temperature conditions at high steam partial pressures, $Si(OH)_4$ and/or $(OH)_2WO_2$ vapors form, and these vapors can react with the ion transport membrane materials. This can poison the membranes, cause reduced oxygen flux performance, and degrade the mechanical properties of the membrane. There is a need for methods to construct the reactor systems such that the metal components in contact with hot synthesis gas will not generate these contaminants while having sufficient mechanical strength at high operating temperatures to withstand high mechanical loads.

[0031] Refractory-lined pipe may be used to prevent contact of the hot synthesis gas with hot metal surfaces. However, this is not a solution to the contamination problem, because most refractories contain silicon compounds that can generate volatile $Si(OH)_4$ by contact with synthesis gas.

[0032] The second problem is that high-temperature superalloys, particularly alloys containing nickel, will catalyze the steam reforming of methane. This is an endothermic reaction that can decrease the temperature of the synthesis gas in the reactor, thereby requiring additional preheating of the feed gas to the membrane reactor system. Thus there is a need for reactor designs using metal components that do not promote the steam-methane reforming reaction prior to the membrane system.

[0033] A solution to these two problems should be economical, easily implemented, and use readily-available components. It has been found that these problems can be reduced or eliminated by lining the flow path of the feed gas and synthesis gas with a copper-containing metal. Copper does not catalyze the steam-methane reforming reaction nearly as much as the nickel present in most high-temperature superalloys. Copper also blocks the transport of volatile silicon and tungsten species from the superalloy into the synthesis gas stream, is relatively inexpensive, and is easy to form into the required shapes.

[0034] Lining of the piping and reactor internal surfaces with a copper-containing metal may be achieved by any method known in the vessel and piping metallurgical art. For low-pressure gas flow, alloy piping and vessels subject to low mechanical loads may be lined by electroplating with copper, applying copper foil, or by copper cladding. For high-pressure gas flow, the high-temperature superalloy pipe may be lined by any of these methods or may be lined with copper by hydro-forming copper tubing or pipe to the inside surface of the superalloy pipe and vessels. When the piping, vessels, and/or other parts are subject to low mechanical loads, they may be fabricated directly of copper or copper alloys.

[0035] It is not necessary to achieve an entirely seamless lining of copper-containing metal in the gas flow path, and some gaps in the lining can exist. It is only necessary to reduce the amount of exposed non-copper metal or refractory sufficiently to reduce the amount of contaminants emitted by non-copper metal or refractory into the synthesis gas stream to acceptable levels and/or to reduce the amount of reforming that occurs on the exposed non-copper metal to acceptable levels.

[0036] In the present disclosure, the noun “lining” means a layer of metal comprising copper that is in contact with, and/or adheres to, and/or is adjacent a surface of a part made of another metal. The part may be an item of process equipment such as, for example, piping, heat exchange surfaces, a vessel, an enclosure, and the like. The verbs “lined” and “lining” mean the process of applying a lining comprising copper to the surface of another metal. The generic terms “copper”, “copper-containing metal”, and “copper lining” include elemental copper metal as well as any copper-containing alloy that is effective in reducing to acceptable levels the amount of contaminants emitted by non-copper metal or refractory into the synthesis gas stream and/or the amount of reforming that occurs on the exposed non-copper metal.

[0037] The indefinite articles “a” and “an” as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of “a” and “an” does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article “the” preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective “any” means one, some, or all indiscriminately of whatever quantity. The term “and/or” placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity.

[0038] The copper-containing metal may be elemental copper metal, which is available in many different grades. It has been found that grades with a low oxygen content (i.e., less than about 0.0005 weight % oxygen) are particularly advantageous for surfaces in contact with hot synthesis gas at temperatures above about 374° C. Copper that contains oxygen may blister during high temperature service in synthesis gas, possibly due to diffusion of hydrogen into the copper and reaction with the oxygen to form steam. In some applications, it may be desirable to use a copper-containing alloy instead of elemental copper metal, while in other applications, elemental copper metal may be preferred. Typically, the copper content of the lining material is greater than about 99 wt %. Exemplary copper-containing alloys that may be used in embodiments of the invention include, for example, Cu-Ag and Cu-Ni alloys.

[0039] When the piping, vessels, and/or other parts are subject to low mechanical loads, any of them may be fabricated directly of elemental copper metal or copper-containing alloys having the properties described above for lining applications.

[0040] The method described above may be applied to any type of ion transport membrane synthesis gas production system. One exemplary design of an ion transport membrane synthesis gas production system is illustrated in the FIG. 1, which is a schematic side view of the interior of an exemplary membrane reactor vessel for use in oxidation processes. Membrane modules 501, 503, 505, 507, and 509 are installed in series in optional enclosure or flow containment duct 511 within pressure vessel 513. Each of these membrane modules has a plurality of stacked hollow wafers with an interior region and an exterior region. Optional flow containment duct 511 has inlet 515 to direct inlet gas stream 517 through the duct to contact the outer surfaces of the wafers in modules 501 to 509. The inlet gas stream is a reactant feed gas containing one or more components which react with oxygen at elevated temperatures wherein the inlet reactant feed gas is heated by any appropriate method (not shown) to a temperature of 600° C. to 1100° C. The pressure of the gas within duct 511 may be in the range of 0.2 to 8 MPa. An example of a reactant feed gas is a mixture of steam and natural gas wherein the natural gas comprises mostly methane with smaller amounts of light hydrocarbons. The mixture may be pre-reformed at a temperature below about 800° C. to yield a pre-reformed natural gas feed containing steam, methane, and carbon oxides. Other oxidizable reactant feed gases may include, for example, various mixtures of hydrogen, carbon monoxide, steam, methanol, ethanol, and light hydrocarbons.

[0041] The waters of the membrane modules may comprise mixed conducting metal oxide material having the general stoichiometric composition $(Ln_{1-x}A_x)_w(B_{1-y}B'_y)O_{3-\delta}$, wherein Ln represents one or more elements selected from La, the D block lanthanides of the IUPAC periodic table, and Y; wherein A represents one or more elements selected from Mg, Ca, Sr and Ba; wherein B and B' each represent one or more elements selected from Sc, Ti, V, Mn, Fe, Co, Ni, Copper, Cr, Al, Zr, Mg, and Ga; wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, and $0.95 < w < 1.05$; and wherein δ is a number that renders the compound charge neutral. More specifically, the mixed conducting metal oxide material may have the general

stoichiometric composition $(La_xCa_{1-x})_wFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \geq w > 1.0$, and δ is a number which renders the composition charge neutral.

[0042] The gas pressure in the interior of flow containment duct 511 preferably is greater than the gas pressure in the interior of pressure vessel 513 between the inner wall of the vessel and the outer wall of flow containment duct 511. The pressure differential between the interior and the exterior of duct 511 at any point between the inlet and outlet of pressure vessel 513 preferably is maintained at a value equal to or greater than zero, wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct. This may be accomplished, for example, by purging the space outside the duct with a gas at lower pressure than the process gas inside the duct; allowing flow communication between the space outside the duct and the process gas in the duct at the process gas outlet, 559; introducing a purge gas into the space outside the duct, and withdrawing the purge gas through a purge gas outlet while using pressure controllers on a purge gas outlet to maintain a lower pressure in the space outside the duct than inside the duct.

[0043] The interior regions of membrane modules 501 to 509 are in flow communication with two manifold systems, one to introduce an oxygen-containing oxidant gas into the modules and the other to withdraw oxygen-depleted oxidant gas from the modules. The first of these manifold systems comprises main inlet manifold 519, primary inlet manifolds 521, 523, 525, 527, and 529, and secondary inlet manifolds 531, 533, 535, 537, and 539. The second of these manifold systems comprises main outlet manifold 541 and primary outlet manifolds 543, 545, 547, 549, and 551.

[0044] In an alternative configuration (not shown) to the configuration shown in FIG. 1, secondary inlet manifolds 531, 533, 535, 537, and 539 may be combined with primary outlet manifolds 543, 545, 547, 549, and 551, respectively, when located within flow containment duct 511. Two manifolds may be combined by installing a first or inner conduit within a second or outer conduit wherein the first conduit provides a first manifold and the annulus between the conduits provides a second manifold. The conduits may be concentric or coaxial; alternatively, the conduits may not be concentric or coaxial and may have separate parallel or nonparallel axes. This configuration of inner and outer conduits to provide a combined manifold function is defined herein as a nested manifold.

[0045] In this alternative configuration, gas 553 would flow through the central conduit and gas 555 would flow through the annulus of each set of these nested manifolds. The nested manifolds would transition to separate manifolds exterior to flow containment duct 511, i.e., would transition to secondary inlet manifolds 531, 533, 535, and 539 and primary outlet manifolds 543, 545, 547, 549, and 551 as shown in FIG. 1. Optionally, primary outlet manifolds 543, 545, 547, 549, and 551 may be nested within secondary inlet manifolds 531, 533, 535, 537, and 539, respectively, within flow containment duct 511. In this option, gas 555 would flow through the central conduit and gas 553 would flow through the annulus of each set of these nested manifolds. In generic terms, therefore, the secondary inlet manifolds and the primary outlet manifolds may be nested when located

within flow containment duct 511, and either a secondary inlet manifold or a primary outlet manifold may be provided by the annulus.

[0046] Heated, pressurized, oxygen-containing oxidant gas 553, for example, air that has been heated by any appropriate method (not shown) to a temperature of 600 to 1100° C., enters main inlet manifold 519 and flows via primary inlet manifolds 521, 523, 525, 527, and 529 and secondary inlet manifolds 531, 533, 535, 537, and 539 to the inlets of membrane modules 501, 503, 505, 507, and 509. Oxygen from the oxidant gas in the interior regions of the membrane modules permeates the dense active membrane layers in the wafers of modules 501 to 509 and the permeated oxygen reacts with the reactive components in the exterior regions of the membrane modules. Oxygen-depleted oxidant gas exits the outlets of the interior regions of the membrane modules via primary outlet manifolds 543, 545, 547, 549, and 551 and main outlet manifold 541, and the final oxygen-depleted oxidant gas is withdrawn as gas stream 555. Outlet gas stream 557, which contains reaction products and unreacted feed components, is withdrawn from the reactor system via outlet 559.

[0047] In this exemplary embodiment, the copper lining described above is installed adjacent the interior surfaces of either or both of flow containment duct 511 and inlet 515. Advantageously, the interior surfaces of flow containment duct 511 and inlet 515 are both lined with the copper lining. Alternatively, flow containment duct 511 may be fabricated completely from copper or a copper-containing alloy when structural requirements permit. In this alternative, inlet 515 would be lined with copper or a copper alloy.

[0048] While the exemplary reactor vessel described above has a single inlet for reactant feed gas to the membrane modules, a single flow containment duct, and a single outlet from the membrane modules, other embodiments are possible in which multiple inlets, multiple flow containment ducts, and/or multiple outlets may be used. For example, a pressure vessel may have two or more flow containment ducts, each having one or more inlets and one or more outlets. Generically, when a reactor vessel is described as having an inlet and an outlet, this means that it has one or more inlets and one or more outlets. Generically, when a reactor vessel is described as having a flow containment duct, this means that it has one or more flow containment ducts. In these embodiments, the copper lining may be installed advantageously adjacent the interior surfaces of all flow containment ducts and inlets that are in contact with hot synthesis gas or hot steam-methane mixtures. Alternatively, the multiple flow containment ducts may be fabricated completely from copper or a copper-containing alloy when structural requirements permit. In this alternative, the inlets are lined with copper or a copper-containing alloy.

[0049] In an alternative embodiment, optional enclosure or flow containment duct 511 is not used, and membrane modules 501 to 509 are installed directly in the interior of pressure vessel 513. In this alternative embodiment, main inlet manifold 519, primary inlet manifolds 521, 523, 525, 527, and 529, secondary inlet manifolds 531, 533, 535, 537, and 539, main outlet manifold 541, and primary outlet manifolds 543, 545, 547, 549, and 551 may be located in the interior of the pressure vessel as shown in the Figure.

[0050] Some or all of these manifolds may be installed outside of the pressure vessel with appropriate piping pass-

ing through the vessel wall. In this alternative embodiment, the interior surfaces of the pressure vessel advantageously are lined with copper and the exterior surfaces of any manifolds within the pressure vessel also may be lined with copper.

[0051] In any of the embodiments described above, a feed gas preheater may be installed upstream of the reactor vessel to preheat the feed gas to a temperature in the range of 400° C. to 1100° C. The feed gas preheater has an interior surface that may be lined with a lining comprising copper, wherein the type of lining may be selected from the group consisting of electroplating, foil, cladding, tubing, and pipe.

[0052] In any of the embodiments described above, refractory material may be disposed between the lining and any of the interior surfaces of the flow containment duct and the inlet piping. Either or both of the flow containment duct and the inlet piping may be fabricated from alloys that comprise one or more elements selected from the group consisting of nickel, silicon, and tungsten.

EXAMPLE 1

Contamination of an Ion Transport Membrane by Nickel Superalloy Piping

[0053] A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. The piping was heated to 900° C., and 1129 scfh of a feed gas mixture consisting of (in vol %) 21.5% H₂, 24.5% CH₄, 5.1% CO₂, 2.0% CO, and 46.8% H₂O at a pressure of 215 psig (15.8 bara) was fed to the preheater. An ion transport membrane was placed downstream of the preheater. The membrane was housed in a flow duct also made from Haynes 230. The flow duct fit around the outside of the membrane such that a space approximately 2.5 mm high was left between the duct and the membrane for synthesis gas flow. The membrane was initially maintained at 900° C. and a pressure of 215 psig (15.8 bara). The membrane was a two-sided flat plate membrane as described in U.S. Patent Publication 20040186018 and was 3.5 inches wide and 5 inches long. The flat plate membrane had an overall composition of La_{1-x}Ca_xFeO_{3-d} where 0.95 > x > 0.5 and d is a number to make the compound charge neutral. Air was manifolded to flow inside the membrane through internal channels. The hot feed gas mixture flowed over the exterior of the membrane while the membrane was held at temperatures between 800 and 900° C. and pressure for 20 days. Over the course of the 20 day experiment, the flux through the membrane decreased by 25% from the initial value when measured at the same temperature and gas composition values.

[0054] At the end of the experiment, the membrane was cooled to room temperature, removed from the reactor, and examined using scanning electron microscopy and energy dispersive spectroscopy. The examination revealed that the surface of the membrane was covered with a 10 μm thick layer of a Ca—W—O phase. The W contamination likely resulted from the reaction of the steam in the synthesis gas with the W in the Haynes 230 to form the volatile species WO₂(OH)₂ via the reaction

The WO₂(OH)₂ then reacted with the Ca in the membrane to form the contaminant phase. The build-up of this contami-

nant phase on the surface of the membrane resulted in decreasing oxygen flux with time.

EXAMPLE 2

Reduction in Contamination of an Ion Transport Membrane by Using Copper-Lined Nickel Superalloy Piping Upstream of the Membrane

[0055] A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. A fully-annealed C10100 copper tube with an outer diameter of 0.3125 inch and a wall thickness of 0.017 inch was inserted inside the Haynes tube and hydroformed to the inner surface of the Haynes tube. The copper thickness after hydroforming was 0.015 inch. The piping was heated to 900° C., and 1060 scfh of a feed gas mixture consisting of (in vol %) 25.1% H₂, 25% CH₄, 5.8% CO₂, 0.9% CO, 1% N₂ and 42.2% H₂O at a pressure of 223 psig (16.3 bara) was fed to the preheater. An ion transport membrane was placed downstream of the preheater, and the membrane was housed in a flow duct also lined with copper metal. The flow duct fit around the outside of the membrane, leaving a space of approximately 2.5 mm high between the duct and the membrane for the feed gas mixture to flow. The membrane was initially maintained at 900° C. and a pressure of 215 psig (15.8 bara). The membrane was a two-sided flat plate membrane as described in U.S. Patent Publication 20040186018 and was 3.5 inches wide and 5 inches long. The composition of the membrane was La_{1-x}Ca_xFeO_{3-d} where 0.95 > x > 0.5 and d is a number to make the compound charge neutral. Air was manifolded to flow inside the membrane through internal channels and the hot feed gas flowed over the exterior of the membrane. The membrane was held at temperature between 800 and 900° C. and 215 psia pressure for 50 days. Over the course of the 50-day experiment, the flux through the membrane did not change measurably from the initial value when measured at the same temperature and gas composition values.

[0056] At the end of the experiment, the membrane was cooled to room temperature, removed from the reactor, and examined using scanning electron microscopy and energy dispersive spectroscopy. No evidence of any W was found on the surface of the membrane. The copper lining of the hot synthesis gas flow path had completely prevented significant quantities of volatile tungsten species from entering the synthesis gas stream and reacting with the membrane.

EXAMPLE 3

Reforming of Synthesis Gas on Nickel Superalloy Piping

[0057] A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. The piping was heated to 900° C. and 1129 scfh of a feed gas mixture consisting of (in vol %) 21.5% H₂, 24.5% CH₄, 5.1% CO₂, 2.0% CO and 46.8% H₂O at a pressure of 215 psig (15.8 bara) was fed to the preheater. On a dry basis the gas composition was (in vol %) 40.5% H₂, 46.2% CH₄, 9.6% CO₂ and 3.8% CO. The composition of the gas exiting the preheater was measured using a gas chromatograph and the exit gas composition on a dry basis was (in vol %) 70% H₂, 6% CH₄, 8.1% CO₂ and 14.9% CO. Most of the methane in the feed had been converted to CO

and CO₂ via the steam methane reforming reaction, and the gas had nearly reached reforming equilibrium at the given conditions.

EXAMPLE 4

Reduction of Reforming of Synthesis Gas by Using Copper-Lined Nickel Superalloy Piping

[0058] A synthesis gas preheater was constructed from 118 feet of Haynes 230 tubing with an inside diameter of 0.33 inch. A fully annealed C10100 copper tube with an outer diameter of 0.3125 inch and a wall thickness of 0.017 inch was inserted inside the Haynes tube and hydroformed to the inner surface of the Haynes tube. The copper thickness after hydroforming was 0.015 inch. The piping was heated to 900° C., and 1060 scfh of a gas mixture consisting of (in vol %) 25.1% H₂, 25% CH₄, 5.8% CO₂, 0.9% CO, 1% N₂ and 42.2% H₂O at a pressure of 223 psig (16.3 bara) was fed to the preheater. On a dry basis, the gas composition was (in vol %) 43.4% H₂, 43.2% CH₄, 10.1% CO₂, 1.7% N₂ and 1.6% CO. The composition of the gas exiting the preheater was measured using a gas chromatograph, and the exit gas composition on a dry basis was (in vol %) 43.0% H₂, 43.0% CH₄, 9.1% CO₂, 1.1% N₂ and 3.3% CO. A negligible amount of the methane was consumed by the steam methane reforming reaction. The copper lining effectively stopped the reforming reaction from occurring.

EXAMPLE 5

Measurement of Reforming on Haynes 230 Tubing

[0059] A group of Haynes 230 tubes with dimensions of 8 ½ inch OD×0.083 inch wall thickness×6 inches long was bundled and used to measure the amount of reforming that occurred on the tubing. The bundle was placed in a high pressure reactor, and a gas mixture consisting of (in vol %) 23.6% H₂, 23.8% CH₄, 5.0% CO₂, 1.9% CO, 1.1% N₂, and 44.6% H₂O at a temperature of 850° C. and a pressure of 29.5 bara was fed to the bundle of tubes by manifolding such that the flow went through the inside of the tubes in parallel. The composition of the gas exiting the bundle was measured using gas chromatography, and it was observed that 19.3% of the methane in the feed gas was converted under these conditions. By comparison, the expected conversion at equilibrium was 51.4%.

EXAMPLE 6

Measurement of Reforming on Copper-Plated Haynes 230 Tubes

[0060] A group of Haynes 230 tubes with dimensions of 8 ½ inch OD×0.083 inch wall thickness×6 inches long was bundled and coated with copper using electroplating to achieve a copper coating with a thickness of approximately 0.015-0.020 inch. These copper-plated tubes were used to measure the amount of reforming that occurred on the tubing. The bundle was placed in a high pressure reactor and a feed gas mixture consisting of (in vol %) 23.6% H₂, 23.8% CH₄, 5.0% CO₂, 1.9% CO, 1.1% N₂, and 44.6% H₂O at a temperature of 850° C. and a pressure of 29.5 bara was fed to the bundle of tubes. The feed gas mixture was manifolded such that the flow went through the inside of the tubes in parallel. The composition of the gas exiting the bundle was

measured using gas chromatography, and it was observed that only 9.5% of the methane was converted under these conditions. Therefore, the copper plating significantly reduced the amount of reforming that occurred on the tubes compared with the uncoated tubes of Example 5.

1. An ion transport membrane oxidation system comprising

- (a) an enclosure having an interior and an interior surface, inlet piping having an internal surface and adapted to introduce a heated feed gas into the interior of the enclosure, and outlet piping adapted to withdraw a product gas from the interior of the enclosure;
- (b) one or more planar ion transport membrane modules disposed in the interior of the enclosure, each membrane module comprising mixed metal oxide material; and
- (c) a preheater adapted to heat a feed gas to provide the heated feed gas to the inlet piping of the enclosure, wherein the preheater comprises an interior surface;

wherein either

- (1) any of the interior surfaces of the enclosure, the inlet piping, and the preheater are lined with a copper-containing metal lining, or

- (2) any of the interior surfaces of the inlet piping and the preheater are lined with a copper-containing metal lining, and the enclosure comprises copper.

2. The system of claim 1 wherein each membrane module has an interior region and an exterior region, and wherein the inlet and the outlet of the vessel are in flow communication with the exterior region of each membrane module.

3. The system of claim 1 wherein the copper-containing metal lining comprises greater than about 99 weight % copper.

4. The system of claim 1 wherein the copper-containing metal lining comprises less than about 0.0005 weight % oxygen.

5. The system of claim 1 wherein the type of copper-containing metal lining is selected from the group consisting of electroplating, foil, cladding, tubing, and pipe.

6. The system of claim 1 further comprising refractory material disposed between the copper-containing metal lining and any of the interior surfaces of the enclosure and the inlet piping.

7. The system of claim 1 wherein any of the enclosure, the inlet piping, and the preheater comprise one or more elements selected from the group consisting of nickel, silicon, and tungsten.

8. The system of claim 1 wherein the enclosure is a flow containment duct that surrounds the one or more planar ion transport membrane modules and wherein the flow containment duct is disposed in the interior of a pressure vessel.

9. The system of claim 1 wherein the enclosure is a pressure vessel that surrounds the one or more planar ion transport membrane.

10. The system of claim 1 wherein the mixed conducting metal oxide material has the general stoichiometric composition (Ln_{1-x}A_x)_w(B_{1-y}B'_y)O_{3-δ}, wherein Ln represents one or more elements selected from La, the D block lanthanides of the IUPAC periodic table, and Y; wherein A represents one or more elements selected from Mg, Ca, Sr and Ba; wherein B and B' each represent one or more elements

selected from Sc, Ti, V, Mn, Fe, Co, Ni, Copper, Cr, Al, Zr, Mg, and Ga; wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, and $0.95 < w < 1.05$; and wherein δ is a number that renders the compound charge neutral.

11. The method of claim 10 wherein the mixed conducting metal oxide material has the general stoichiometric composition $(La_xCa_{1-x})_wFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 > w > 1.0$, and δ is a number which renders the composition charge neutral.

12. A process for generating synthesis gas comprising

(a) providing an ion transport membrane oxidation system including

- (1) an enclosure having an interior and an interior surface, inlet piping having an internal surface and adapted to introduce a heated feed gas into the interior of the enclosure, outlet piping adapted to withdraw a product gas from the interior of the enclosure, and a preheater adapted to heat a feed gas to provide the heated feed gas to the inlet piping of the enclosure, wherein the preheater has an interior surface; and
- (2) one or more planar ion transport membrane modules disposed in the interior of the enclosure, each membrane module comprising mixed metal oxide material;

wherein either

- (3) any of the interior surfaces of the enclosure, the inlet piping, and the preheater are lined with a copper-containing metal lining, or
 - (4) any of the interior surfaces of the inlet piping and the preheater are lined with a copper-containing metal lining, and the enclosure comprises copper.
- (b) introducing a heated oxygen-containing gas into the interior region of each membrane module, introducing a hydrocarbon-containing feed gas into the preheater, withdrawing a preheated hydrocarbon-containing feed gas from the preheater, and introducing the preheated hydrocarbon-containing feed gas into the exterior region of each membrane module; and
- (c) withdrawing a synthesis gas product from the interior of the enclosure via the outlet piping.

13. The process of claim 12 wherein the hydrocarbon-containing feed gas comprises at least methane and water and optionally comprises any of hydrogen, carbon monoxide, and carbon dioxide.

14. The process of claim 12 wherein the hydrocarbon-containing feed gas is pre-reformed natural gas.

15. The process of claim 12 wherein the feed gas is heated in the feed gas preheater to a temperature in the range of 600 to 1100° C.

16. The process of claim 12 wherein the synthesis gas comprises at least hydrogen, carbon monoxide, and carbon dioxide.

17. The process of claim 12 wherein the copper-containing metal lining comprises greater than about 99 weight % copper.

18. The process of claim 12 wherein the copper-containing metal lining comprises less than about 0.0005 weight % oxygen.

19. The process of claim 12 wherein the type of copper-containing metal lining is selected from the group consisting of electroplating, foil, cladding, tubing, and pipe.

20. The process of claim 12 further comprising refractory material disposed between the copper-containing metal lining and any of the interior surfaces of the enclosure and the inlet piping.

21. The process of claim 12 wherein any of the vessel, the inlet piping, and the preheater comprise one or more elements selected from the group consisting of nickel, silicon, and tungsten.

22. The process of claim 12 wherein the enclosure is a flow containment duct that surrounds the one or more planar ion transport membrane modules and wherein the flow containment duct is disposed in the interior of a pressure vessel.

23. The process of claim 12 wherein the enclosure is a pressure vessel that surrounds the one or more planar ion transport membrane modules.

24. The process of claim 12 wherein the mixed conducting metal oxide material has the general stoichiometric composition $(Ln_{1-x}A_x)_w(B_{1-y}B'_y)O_{3-\delta}$, wherein Ln represents one or more elements selected from La, the D block lanthanides of the IUPAC periodic table, and Y; wherein A represents one or more elements selected from Mg, Ca, Sr and Ba; wherein B and B' each represent one or more elements selected from Sc, Ti, V, Mn, Fe, Co, Ni, Copper, Cr, Al, Zr, Mg, and Ga; wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$, and $0.95 < w < 1.05$; and wherein δ is a number that renders the compound charge neutral.

25. The process of claim 24 wherein the mixed conducting metal oxide material has the general stoichiometric composition $(La_xCa_{1-x})_wFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 > w > 1.0$, and δ is a number which renders the composition charge neutral.

* * * * *

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(19) **United States**(12) **Patent Application Publication**
Carolan et al.(10) **Pub. No.: US 2008/0085236 A1**(43) **Pub. Date: Apr. 10, 2008**(54) **PLANAR CERAMIC MEMBRANE
ASSEMBLY AND OXIDATION REACTOR
SYSTEM****Publication Classification**(51) **Int. Cl.****C01B 3/26** (2006.01)**C01B 3/24** (2006.01)(52) **U.S. Cl.** **423/650**

(57)

ABSTRACT

Planar ceramic membrane assembly comprising a dense layer of mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a porous layer of mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled support layer in contact with the second side of the dense layer. The planar ceramic membrane assembly can be used in a ceramic wafer assembly comprising a planar ceramic channeled support layer having a first side and a second side; a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the first side of the ceramic channeled support layer; a first outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the first dense layer; a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the second side of the ceramic channeled layer; and a second outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the second dense layer.

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(62) Division of application No. 10/394,620, filed on Mar. 21, 2003, now Pat. No. 7,279,027.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6A

FIG. 6B

FIG. 7A

FIG. 7B

FIG. 8A

FIG. 8B

FIG. 9A

FIG. 9B

FIG. 10

PLANAR CERAMIC MEMBRANE ASSEMBLY AND OXIDATION REACTOR SYSTEM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This is a divisional of application Ser. No. 10/394,620, filed on Mar. 21, 2003, the specification and claims which are incorporated by reference and made a part of this application.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with Government support under Contract No. DE-FC26-97FT96052 between Air Products and Chemicals, Inc. and the U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0003] Oxygen can be separated from oxygen-containing gases by mixed-conducting ceramic membranes operating at high temperatures wherein the membranes conduct both oxygen ions and electrons. Oxygen gas is produced on the permeate side of the membrane and can be recovered as a high-purity product. Alternatively, the permeated oxygen can be reacted directly with a hydrocarbon-containing gas, either catalytically or non-catalytically, to yield a hydrocarbon oxidation product. Various oxygen-containing gases, such as air, can be used and numerous alternative hydrocarbon oxidation products are possible depending on the operating conditions and catalyst if used.

[0004] There is a significant and growing commercial interest in the production of synthesis gas from natural gas and air using mixed-conducting ceramic membrane reactor systems. This technology is presently in the development stage and commercial applications are envisioned in future years as the technology matures. Mixed-conducting ceramic membrane reactor systems produce synthesis gas by the partial oxidation of methane to form the synthesis gas components CO, H₂, CO₂, and H₂O. The process is carried out by introducing a methane-containing feed gas and an air feed gas into the membrane reactor system, contacting one surface of the membrane with methane, and contacting the other surface with air. Oxygen permeates through the membrane, methane reacts with permeated oxygen to form a methane/synthesis gas mixture, and methane is further converted into synthesis gas as the mixture travels through the reactor while reacting with additional permeated oxygen.

[0005] This process can be integrated favorably with upstream and downstream processes if the methane/synthesis gas stream is at a high pressure, typically 250-450 psig. In addition, process economics are most favorable if the air is at a low pressure, typically less than 50 psig. Therefore, the membranes in the membrane reactor system must be designed to withstand a significant pressure differential between the air side and the methane/synthesis gas side. To achieve high oxygen fluxes through the membrane, the active separating layer of the membrane should be thin, typically less than 200 microns. However, a freestanding membrane of this thickness could not withstand a typical pressure differential of 200-400 psid, and the thin separating layer therefore must be structurally supported in some fashion.

[0006] Various designs for ceramic oxygen-conducting membrane systems capable of withstanding high pressure differentials have been described in the art. For example, a tubular ceramic membrane can be subjected to high pressure methane on one side and low pressure air on the other side, but such a membrane must have a sufficiently thick wall to withstand the pressure differential; as a consequence, this membrane cannot achieve a high oxygen flux. To address this problem, composite tubular membranes have been developed which incorporate a thin, dense oxygen-permeating layer on a thicker porous support.

[0007] Flat plate membrane configurations have been described in the art wherein the active separating layer is supported by a porous layer or layers on the low pressure side of the membrane, which typically is the permeate side of the membrane. These membrane systems typically are designed to produce a pure oxygen product on the permeate side. If these membranes are used with low pressure air on the low pressure side of the membrane, the porous support layers on the low pressure side of the membrane introduce a gas phase diffusional resistance for transport of oxygen from the oxidant or air to the surface of the dense separating layer. Porous layers that are thick enough to provide support for the thin active separating layer introduce diffusional resistance to the transport of oxygen to the membrane surface, and this resistance will decrease the oxygen flux through the membrane. A need exists, therefore, for composite membrane designs that use a thin active membrane under a high pressure differential without unacceptably high gas phase diffusional resistance on the oxidant side of the membrane.

[0008] Porous materials have lower mechanical strength than dense materials. Membrane designs that use porous supports on the low pressure side of a membrane subject the porous support to a compressive stress. This stress may exceed the crush strength of the porous support layer if the differential pressure is high enough, causing the support layer to fail and the thin active layer to leak or fail. The strength of a porous layer is a function of the porosity of the layer material—a lower porosity material is generally stronger than a higher porosity material. Unfortunately, a stronger material with a lower porosity is less permeable than a weaker material with a higher porosity, and increasing the strength of a porous support layer thus increases the gas phase diffusional resistance of the layer. This tradeoff between strength and permeability in porous support materials makes it difficult to design composite membranes that can withstand high pressure differentials and the resulting high compressive stresses. Thus there is a need for membrane designs that avoid placing porous layers under high compressive stresses.

[0009] Oxygen transport through a dense oxygen-conducting ceramic membrane is thermally activated. This means that the oxygen flux through the membrane increases exponentially with temperature in the absence of any other mass transfer resistances. When a dense oxygen-conducting membrane is used in a membrane reactor system to conduct an exothermic reaction such as hydrocarbon oxidation, the thermally activated oxygen transport can lead to local hot spots on the membrane. A thin spot on the membrane will experience a higher oxygen flux relative to thicker surrounding regions on the membrane, and the membrane will heat up at this thin spot relative to its surroundings as the

oxidation rate increases. This will increase the flux further, thereby further increasing the temperature at that spot. These local temperature gradients generate undesirable thermal stresses that are detrimental to the mechanical integrity of the membrane.

[0010] There is a need in the ceramic membrane reactor field for a membrane design capable of withstanding high pressure differentials while also preventing local hot spots from occurring. In particular, there is a need for a hydrocarbon partial oxidation reactor membrane design that will allow the use of a thin oxygen-permeable membrane layer operating under a large pressure differential without developing hot spots caused by localized high oxygen diffusion and high exothermic oxidation rates. This need is addressed by the present invention as described below and defined by the claims that follow.

BRIEF SUMMARY OF THE INVENTION

[0011] One embodiment of the invention relates to a planar ceramic membrane assembly comprising a dense layer of mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a porous layer of mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled support layer in contact with the second side of the dense layer. The dense layer and the porous layer may be formed of multi-component metal oxide material with the same composition. The dense layer, the channeled support layer, and the porous layer may be formed of multi-component metal oxide material with the same composition.

[0012] In the planar ceramic membrane assembly, the mixed-conducting multi-component metal oxide material may comprise one or more components having the general composition $(La_xCa_{1-x})_yFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \leq y < 1.0$, and δ is a number which renders the composition of matter charge neutral. The porous layer may have a porosity between about 10% and about 40% and a tortuosity between about 3 and about 10.

[0013] The porous layer may comprise one or more catalysts that include metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof.

[0014] Another embodiment of the invention includes a planar ceramic wafer assembly comprising

[0015] (a) a planar ceramic channeled support layer having a first side and a second side;

[0016] (b) a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein portions of the inner side are in contact with the first side of the ceramic channeled support layer;

[0017] (c) a first outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the first dense layer,

[0018] (d) a second dense layer of mixed-conducting multi-component metal oxide material having an inner

side and an outer side, wherein portions of the inner side are in contact with the second side of the ceramic channeled support layer; and

[0019] (e) a second outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the second dense layer.

[0020] The thickness of the wafer assembly may be between about 2 and about 8 mm as measured from the outer side of the first outer support layer to the outer side of the second outer support layer. The thickness of each of the first and second outer support layers may be between about 50 microns and about 1 mm. The thickness of each of the first and second dense layers may be between about 10 and about 500 microns. The thickness of the planar ceramic channeled support layer may be between about 100 and about 2000 microns.

[0021] An embodiment of the invention includes a planar ceramic wafer assembly comprising

[0022] (a) a planar ceramic channeled support layer having a first side, a second side, a periphery, and a plurality of flow channels extending through the channeled support layer between the first and second sides and extending from a first region within the periphery to a second region within the periphery, wherein the flow channels place the first region and the second region in flow communication;

[0023] (b) a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the first side of the ceramic channeled layer;

[0024] (c) a first outer support layer comprising porous ceramic material, the layer having an inner side, an outer side, and a periphery, wherein the inner side is in contact with the outer side of the first dense layer,

[0025] (d) a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the second side of the ceramic channeled layer;

[0026] (e) a second outer support layer comprising porous ceramic material, the layer having an inner side, an outer side, and a periphery, wherein the inner side is in contact with the outer side of the second dense layer;

[0027] (f) a first opening extending through a layered assembly defined by (a) through (e) from a first side to a second side of the layered assembly, wherein the first side is defined by the outer side of the first outer support layer and the second side is defined by the outer side of the second outer support layer, and wherein the first opening passes through the first region of the channeled support layer and is in flow communication with the plurality of flow channels in the channeled support layer; and

[0028] (g) a second opening extending through the planar ceramic wafer assembly from the first side to the second side thereof, wherein the second opening passes

through the second region of the channeled support layer and is in flow communication with the plurality of flow channels in the channeled support layer.

[0029] The first and second outer support layers may comprise dense ceramic material surrounding the first and second openings. The first and second outer support layers may comprise dense ceramic material adjacent the periphery.

[0030] Another embodiment of the invention relates to a ceramic membrane stack comprising

[0031] (a) a plurality of planar ceramic wafer assemblies, each planar ceramic wafer assembly containing a first multi-component metal oxide and comprising

[0032] (1) a planar ceramic channeled support layer having a first side, a second side, a periphery, and a plurality of flow channels extending through the channeled support layer between the first and second sides and extending from a first region within the periphery to a second region within the periphery, wherein the flow channels place the first region and the second region in flow communication;

[0033] (2) a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the first side of the ceramic channeled layer;

[0034] (3) a first outer support layer comprising porous ceramic material, the layer having an inner side, an outer side, and a periphery, wherein the inner side is in contact with the outer side of the first dense layer;

[0035] (4) a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the second side of the ceramic channeled layer;

[0036] (5) a second outer support layer comprising porous ceramic material, the layer having an inner side, an outer side, and a periphery, wherein the inner side is in contact with the outer side of the second dense layer;

[0037] (6) a first opening extending through a layered assembly defined by (1) through (5) from a first side to a second side of the layered assembly, wherein the first side is defined by the outer side of the first outer support layer and the second side is defined by the outer side of the second outer support layer, and wherein the first opening passes through the first region of the channeled support layer and is in flow communication with the plurality of flow channels in the channeled support layer; and

[0038] (7) a second opening extending through the layered assembly from the first side to the second thereof, wherein the second opening passes through the second region of the channeled support layer and is in flow communication with the plurality of flow channels in the channeled support layer; and

[0039] (b) a plurality of ceramic spacers, each spacer containing a second multi-component metal oxide,

wherein each spacer has a first surface, a second surface generally parallel to the first surface, a first manifold opening extending from the first surface to the second surface and a second manifold opening extending from the first surface to the second surface;

wherein the stack is formed by alternating ceramic spacers and planar ceramic wafer assemblies in an axial direction such that the first manifold openings in the spacers and the first openings in the layered assemblies are aligned to form a first manifold extending through the stack perpendicular to the planar ceramic wafer assemblies, and such that the second manifold openings in the spacers and the second openings in the layered assemblies are aligned to form a second manifold extending through the stack perpendicular to the planar ceramic wafer assemblies.

[0040] The thickness of the wafer assembly may be between about 1.5 mm and about 8 mm as measured in the axial direction from the outer side of the first outer support layer to the outer side of the second outer support layer. The distance between successive wafer assemblies in the axial direction as defined by the thickness of the spacer assembly may be between about 0.5 mm and about 5 mm.

[0041] The ceramic membrane stack may further comprise a joint material at each interface between a planar ceramic wafer assembly and a ceramic spacer, wherein the joint material comprises at least one metal oxide having at least one shared metal contained in at least one of the first multi-component metallic oxide and the second multi-component metallic oxide, and wherein the joint material has a melting point below a sintering temperature of the first multi-component metallic oxide and below a sintering temperature of the second multi-component metallic oxide.

[0042] One aspect of the invention includes a planar ceramic channeled support layer assembly comprising

[0043] (a) a planar ceramic slotted support layer having a first surface, a second surface, and an outer periphery, wherein the slotted support layer includes

[0044] (1) a region defined by a right parallelogram enclosing a first plurality of parallel slots passing through the support layer and oriented parallel to a first side and an opposing second side of the parallelogram,

[0045] (2) a second plurality of parallel slots that extend through the support layer from the first side to the second side, are perpendicular to the first plurality of parallel slots, and are disposed between the periphery and the first side of the parallelogram, and

[0046] (3) a third plurality of parallel slots that pass through the support from the first side to the second side, are perpendicular to the first plurality of parallel slots, and are disposed between the periphery and the second side of the parallelogram;

[0047] (b) a first planar ceramic flow channel layer in contact with the first surface of the planar ceramic slotted support layer, wherein the first planar ceramic flow channel layer includes a plurality of parallel flow channels that extend therethrough, and wherein the plurality of parallel flow channels are adjacent to,

perpendicular to, and in fluid flow communication with the first plurality of parallel slots in the support layer;

[0048] (c) a second planar ceramic flow channel layer in contact with the second surface of the planar ceramic slotted support layer, wherein the second planar flow channel layer includes a plurality of parallel flow channels that extend therethrough, and wherein the plurality of parallel flow channels are adjacent to, perpendicular to, and in fluid flow communication with the first plurality of parallel slots in the support layer; and

[0049] (d) a first and a second series of parallel slots that pass through the ceramic channeled support layer assembly formed by the first planar ceramic flow channel layer, the support layer, and the second planar ceramic flow channel layer, wherein

[0050] (1) the first and second series of parallel slots are perpendicular to the plurality of parallel flow channels in the first and second planar ceramic flow channel layers,

[0051] (2) the first series of parallel slots is disposed between the periphery and the first side of the parallelogram and the slots in the first series of parallel slots pass through and intersect the second plurality of parallel slots extending through the support layer, and

[0052] (3) the second series of parallel slots is disposed between the periphery and the second side of the parallelogram and the slots in the second series of parallel slots pass through and intersect the third plurality of parallel slots extending through the support layer;

wherein the slots in the first and second series of parallel slots are in fluid flow communication with all slots in the first planar ceramic flow channel layer, the support layer, and the second planar ceramic flow channel layer.

[0053] The width of each slot in the first plurality of parallel slots in the planar ceramic slotted support layer may be between about 0.2 and about 2 mm and the distance between adjacent parallel slots in the first plurality of parallel slots may be between about 0.2 and about 4 mm.

[0054] A process-related embodiment of the invention includes a hydrocarbon oxidation process comprising

[0055] (a) providing a planar ceramic membrane reactor assembly comprising a dense layer of mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a support layer comprising porous mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled support layer in contact with the second side of the dense layer;

[0056] (b) passing a heated oxygen-containing oxidant feed gas through the ceramic channeled layer and in contact with the second side of the dense layer;

[0057] (c) permeating oxygen ions through the dense layer and providing oxygen on the first side of the dense layer;

[0058] (d) contacting a heated hydrocarbon-containing feed gas with the support layer wherein the hydrocarbon-containing feed gas diffuses through the support layer; and

[0059] (e) reacting the hydrocarbon-containing feed gas with the oxygen to yield a hydrocarbon oxidation product.

[0060] The hydrocarbon-containing feed gas may comprise one or more hydrocarbon compounds containing between one and six carbon atoms. The oxygen-containing oxidant feed gas may be selected from the group consisting of air, oxygen-depleted air, and combustion products containing oxygen, nitrogen, carbon dioxide, and water. The hydrocarbon oxidation product may comprise oxidized hydrocarbons, partially oxidized hydrocarbons, hydrogen, and water.

[0061] The oxygen-containing oxidant feed gas and the hydrocarbon-containing feed gas may flow cocurrently through the ceramic membrane reactor assembly. The support layer may include one or more catalysts comprising metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof.

[0062] Another embodiment of the invention relates to a method of making a green ceramic planar channeled support layer assembly comprising

[0063] (a) preparing a green ceramic planar slotted support layer having a first surface, a second surface, and an outer periphery, wherein the slotted support layer includes

[0064] (1) regions on the first and second surface, each region defined by a right parallelogram within the outer periphery wherein each parallelogram has a first side and an opposing second side,

[0065] (2) a first plurality of parallel slots that extend through the support layer from the first side to the second side, are perpendicular to the first side of each parallelogram, and are disposed between the periphery and the first side of each parallelogram, and

[0066] (3) a second plurality of parallel slots that pass through the support from the first side to the second side, are perpendicular to the second side of each parallelogram, and are disposed between the periphery and the second side of each parallelogram;

[0067] (b) preparing a first and a second green ceramic planar flow channel layer, each of which includes a plurality of parallel flow channels that extend therethrough;

[0068] (c) placing the first green ceramic planar flow channel layer in contact with the first surface of the green ceramic planar slotted support layer such that the plurality of parallel flow channels are oriented parallel to the first and second plurality of parallel slots in the support layer and are disposed within the region on the first surface defined by the right parallelogram;

[0069] (d) placing the second green ceramic planar flow channel layer in contact with the second surface of the green ceramic planar slotted support layer such that the

plurality of parallel flow channels are oriented parallel to the first and second plurality of parallel slots in the support layer and are disposed within the region on the second surface defined by the right parallelogram; and

[0070] (e) cutting a first and a second series of parallel slots through the green ceramic planar channeled support layer assembly formed by the first green ceramic planar flow channeled layer, the green ceramic planar slotted support layer, and the second green ceramic planar flow channeled layer, wherein

[0071] (1) the first and second series of parallel slots are perpendicular to the plurality of parallel flow channels in the first and second green ceramic planar flow channel layers,

[0072] (2) the first series of parallel slots is disposed between the periphery and the first side of the parallelogram and the slots in the first series of parallel slots pass through and intersect the first plurality of parallel slots extending through the support layer,

[0073] (3) the second series of parallel slots is disposed between the periphery and the second side of the parallelogram and the slots in the second series of parallel slots pass through and intersect the second plurality of parallel slots extending through the support layer; and

[0074] (f) cutting a third series of parallel slots through the green ceramic planar channeled support layer assembly formed by the first green ceramic planar flow channeled layer, the green ceramic planar slotted support layer, and the second green ceramic planar flow channeled layer, wherein slots in the third series of parallel slots are parallel to slots in the first and second series of parallel slots and lie between the first and second series of parallel slots;

wherein the slots in the first and second series of parallel slots are in fluid flow communication with all slots in the first green ceramic planar flow channel layer, the green ceramic planar slotted support layer, and the second green ceramic planar flow channel layer.

[0075] The ceramic multi-component metal oxide material may include one or more components, and the material may have the general composition $(La_xCa_{1-x})_yFeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and δ is a number which renders the composition of matter charge neutral.

[0076] An alternative embodiment of the invention includes a planar ceramic membrane assembly comprising a dense layer of mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a porous layer of mixed-conducting multi-component metal oxide material in contact with portions of the first side of the dense layer, a ceramic channeled support layer in contact with the second side of the dense layer, and a coating of porous mixed-conducting multi-component metal oxide material on the portions of second side of the dense layer that are not in contact with the ceramic channeled support layer.

[0077] The coating may include one or more oxygen reduction catalysts comprising metals selected from, or compounds containing metals selected from, the group

consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0078] Another alternative embodiment of the invention includes a planar ceramic wafer assembly comprising

[0079] (a) a planar ceramic channeled support layer having a first side and a second side;

[0080] (b) a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein portions of the inner side are in contact with the first side of the ceramic channeled support layer;

[0081] (c) a first outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the first dense layer,

[0082] (d) a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein portions of the inner side are in contact with the second side of the ceramic channeled layer;

[0083] (e) a second outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the second dense layer; and

[0084] (f) a coating of porous mixed-conducting multi-component metal oxide material on the portions of the inner sides of the first and second dense layers that are not in contact with the first and second sides of the ceramic channeled support layer.

[0085] The coating may include one or more oxygen reduction catalysts comprising metals selected from, or compounds containing metals selected from, the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0086] In another embodiment, the invention may include a method of making a planar ceramic membrane assembly comprising

[0087] (a) providing a planar ceramic membrane structure comprising a dense layer of mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a porous layer of mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled support layer in contact with portions of the second side of the dense layer; and

[0088] (b) applying a coating of porous mixed-conducting multi-component metal oxide material to portions of the surface of the dense layer that are not in contact with the channeled support layer.

[0089] A related embodiment includes a method of making a planar ceramic wafer assembly comprising

[0090] (a) providing a planar ceramic wafer structure comprising

- [0091] (1) a planar ceramic channeled support layer having a first side and a second side;
- [0092] (2) a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein portions of the inner side are in contact with the first side of the ceramic channeled support layer;
- [0093] (3) a first outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the first dense layer;
- [0094] (4) a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein portions of the inner side are in contact with the second side of the ceramic channeled layer; and
- [0095] (5) a second outer support layer comprising porous mixed-conducting multi-component metal oxide material and having an inner side and an outer side, wherein the inner side is in contact with the outer side of the second dense layer;
- [0096] (b) flowing a slurry of multi-component metal oxide powder suspended in a liquid through the channeled support layer and depositing a layer comprising the metal oxide powder and the liquid on interior surfaces of the channeled support layer, first dense layer, and second dense layer; and
- [0097] (c) evaporating the liquid from the layer to form a coating of the multi-component metal oxide powder on the interior surfaces of the channeled support layer, first dense layer, and second dense layer.
- [0098] The method may further comprise partially sintering the coating by heating the planar ceramic wafer assembly to temperatures between 900° C. and 1600° C. for 0.5 to 12 hours.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

- [0099] FIG. 1 is a schematic cross-sectional view of an exemplary membrane assembly in an embodiment of the present invention.
- [0100] FIG. 2 is a plan view of a flow channel layer for an exemplary membrane assembly that is an embodiment of the present invention.
- [0101] FIG. 3 is an enlarged view of a flow channel region of the flow channel layer of FIG. 2.
- [0102] FIG. 4 is a plan view of a slotted support layer for the exemplary membrane assembly that is an embodiment of the present invention.
- [0103] FIG. 5 is a plan view of a completed channeled support layer using the components of FIGS. 2 and 4.
- [0104] FIG. 6A is a plan view of a completed wafer assembly.
- [0105] FIG. 6B is a plan view of an alternative completed wafer assembly.

[0106] FIG. 7A is a sectional view defined by Section 1-1 of FIGS. 6A and 6B.

[0107] FIG. 7B is a sectional view defined by Section 2-2 of FIGS. 6A and 6B.

[0108] FIG. 8A is a schematic side view of a ceramic spacer for use in embodiments of the present invention.

[0109] FIG. 8B is a schematic top view of the ceramic spacer of FIG. 8A.

[0110] FIG. 9A is a schematic front view of an exemplary membrane stack formed by alternating wafers and spacers.

[0111] FIG. 9B is a schematic side view of the stack of FIG. 9A.

[0112] FIG. 10 illustrates the oxidant and reactant gas flows in the exemplary stack of FIG. 9B.

DETAILED DESCRIPTION OF THE INVENTION

[0113] The embodiments of the present invention provide hydrocarbon partial oxidation reactor membrane designs that allows the use of a thin oxygen-permeable membrane layer operating under a large pressure differential without developing hot spots caused by localized high oxygen diffusion and high exothermic oxidation rates. This can be accomplished in part by providing significant diffusional resistance on either the low pressure or oxidant side of the membrane or on the high pressure or reactant side of the membrane. By limiting the diffusion rate of either oxygen or reactants to the surfaces of the active membrane layer, the development of hot spots on the membrane can be reduced or eliminated. A porous layer in contact with the active membrane layer can provide means to limit this diffusion rate, and the porous layer may be placed on either or both sides of the active membrane.

[0114] In embodiments of the present invention, the porous layer preferably is placed on the side of the active membrane having the highest gas phase diffusivities. In membrane reactors for the oxidation of hydrocarbons using an air feed, for example, the gas on the hydrocarbon or reactant side of the membrane exhibits higher gas phase diffusivities in porous media than the gases on the oxidant or air side of the active membrane. Thus a porous support layer preferably is placed on the reactant side of the membrane to minimize gas phase diffusional resistances.

[0115] In a membrane reactor having a high differential pressure between the reactant and oxidant sides of the active membrane, wherein the pressure is higher on the reactant side, a porous layer on the oxidant side is subjected to higher compressive stresses than would occur if the porous support were placed on the reactant side of the active membrane. This is another reason to preferably place the porous support layer on the reactant side of the active membrane. Placing the porous support on the reactant side of the membrane can control hot spots on the active membrane while also minimizing compressive stresses on the porous material.

[0116] The active dense membrane layer also should be supported on the oxidant side of the membrane. In embodiments of the present invention, this may be accomplished by placing a ceramic channeled layer or channeled support layer on the oxidant side of the membrane wherein an

oxidant, for example air, flows through channels formed in the channeled support layer and directly contacts the surface of the active membrane. Thus an embodiment of the present invention includes a membrane assembly with a dense active layer having a porous support layer on one side and a channeled support layer on the other side. More particularly, one embodiment of the invention includes a planar ceramic membrane assembly comprising a dense layer of dense mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a porous layer of mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled layer or channeled support layer in contact with the second side of the dense layer. The mixed-conducting multi-component metal oxide material conducts both oxygen ions and electrons.

[0117] An embodiment of the invention is illustrated in FIG. 1, which is a schematic cross-sectional view (not necessarily to scale) of an exemplary membrane assembly that may be used in a hydrocarbon oxidation membrane reactor. Active membrane layer 1 is a dense layer of mixed-conducting multi-component metal oxide material and may have a thickness in the range of about 10 μm to about 500 μm . One side of the active membrane layer, which may be defined as the outer side, is in contact with and preferably bonded to porous support layer 3. The other side of the active membrane layer, which may be defined as the inner side, is in contact with and preferably bonded to channeled layer or channeled support layer 5 which comprises ceramic support ribs 7 interspersed with oxidant flow channels 9 that extend through the layer. One side of porous support layer 3, which may be defined as the inner side, is in contact with the outer side of active membrane layer 1. The other side of porous support layer 3 may be defined as the outer side.

[0118] In the present disclosure, the terms “channeled layer” and “channeled support layer” have the same meaning. By definition, a channeled layer has channels or openings extending between the two surfaces of the layer, and gas can flow freely through these channels. Typically, the channeled layer is made of dense ceramic material. The terms “porous layer” and “porous support layer” have the same meaning. The terms “support layer” and “outer support layer” have the same meaning and define a layer comprising porous ceramic material. The terms “porous layer”, “porous support layer”, “support layer”, and “outer support layer” may be used interchangeably. The term “porous” applies to sintered or fired ceramic material or layers having through pores, i.e., pores which are interconnected such that gas can flow through the layer.

[0119] For the membrane to operate, reactants must be supplied to both surfaces of the active membrane layer. An oxygen-containing oxidant feed gas is supplied to the inner surface of the active membrane layer and a hydrocarbon-containing gas is supplied to the outer surface of the active membrane layer. The oxygen-containing oxidant feed gas may be selected from the group consisting of air, oxygen-depleted air, and combustion products containing oxygen, nitrogen, carbon dioxide, and water. The hydrocarbon-containing gas may comprise one or more hydrocarbon compounds containing between one and six carbon atoms.

[0120] The mass transport resistance to the surface of the active membrane layer can be lower when the surface is not

covered with a porous support layer. Gaseous species permeating through a porous layer will encounter diffusional resistance. Gas can flow freely through the channels in a channeled layer. The hydraulic diameter of the channels in a channeled support layer are typically 2 to 3 orders of magnitude larger than the average diameter of the pores in a porous support layer. The hydraulic diameter of a channel with a rectangular cross section is defined as 4 times the cross sectional area divided by the wetted perimeter.

[0121] The term “dense” refers to a ceramic material through which, when sintered or fired, a gas cannot flow. Gas cannot flow through dense ceramic membranes made of mixed-conducting multi-component metal oxide material as long as the membranes are intact and have no cracks, holes, or imperfections which allow gas leaks. Oxygen ions can permeate dense ceramic membranes made of mixed-conducting multi-component metal oxide material. The term “green ceramic” means a material comprising ceramic powder before sintering or firing. Green ceramics additionally may comprise organic binders, organic dispersants, or organic pore formers. The term “ceramic” used alone refers to the material after sintering or firing.

[0122] Channeled support layer 5 may be made of mixed-conducting multi-component metal oxide material and may have a typical thickness in the range of about 100 μm to about 4 mm. Porous support layer 3 may have a thickness in the range of about 50 μm to about 1 mm, a porosity, defined as the volume fraction of pores, between about 10% and about 40%, and a tortuosity, between about 3 and about 10. The tortuosity is defined as the ratio of the gas phase diffusivity multiplied by the porosity divided by the measured effective diffusivity through the porous layer. A more detailed definition of tortuosity can be found in *Chemical Engineering Kinetics and Reactor Design* by Charles Hill, John Wiley and Sons, 1977, page 435.

[0123] When the membrane assembly is used in a hydrocarbon oxidation membrane reactor wherein the reactant or hydrocarbon side is at a higher pressure than the oxidant side, porous support layer 3 preferably is on the reactant side and channeled support layer 5 preferably is on the oxidant side. When the hydrocarbon oxidation membrane reactor is operated to convert a methane feed gas to synthesis gas by reaction with oxygen from an air feed gas, porous support layer 3 preferably is on the methane/synthesis gas side and channeled support layer 5 preferably is on the oxidant or air side of active membrane layer 1.

[0124] The dense material in active membrane layer 1 may comprise a mixed-conducting multi-component metal oxide compound having the general formula $(\text{La}_x\text{Ca}_{1-x})_y\text{FeO}_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and δ is a number which renders the composition of matter charge neutral.

[0125] Any appropriate ceramic material can be used for porous support layer 3, and may be, for example, material of the same composition as that of active membrane layer 1. Preferably, porous support layer 3 is a mixed-conducting multi-component metal oxide material. Any appropriate ceramic material can be used for the structural members of channeled support layer 5, and this ceramic material may have, for example, the same composition as that of active membrane layer 1. The material of channeled support layer preferably is a dense ceramic material. In one embodiment, active membrane layer 1, porous support layer 3, and

channeled support layer 5 all may be fabricated of material having the same composition.

[0126] Active membrane layer 1 optionally may include one or more oxygen reduction catalysts on the oxidant side. The catalyst or catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0127] Porous support layer 3 optionally may include one or more catalysts to promote hydrocarbon oxidation and other reactions that occur in the porous layer. The catalyst or catalysts may be disposed on either or both surfaces of porous support layer 3, or alternatively may be dispersed throughout the layer. The one or more catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof.

[0128] If desired for structural and/or process reasons, an additional porous layer may be disposed between active membrane layer 1 and channeled support layer 5.

[0129] Various tubular or flat plate membrane configurations may be envisioned which use the basic structural characteristics of the membrane illustrated in FIG. 1, and any of these various configurations are considered to be within the scope of embodiments of the present invention. Flat plate or planar membrane module configurations are particularly useful in the application described above for hydrocarbon oxidation reactors.

[0130] One exemplary embodiment of the present invention is a planar ceramic wafer assembly comprising a planar ceramic channeled layer having a first side and a second side, a first dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the first side of the ceramic channeled layer, and a first porous ceramic layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the outer side of the first dense layer. This wafer assembly also includes a second dense layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the second side of the ceramic channeled layer, and a second porous layer of mixed-conducting multi-component metal oxide material having an inner side and an outer side, wherein the inner side is in contact with the outer side of the second dense layer. The wafer assembly in this embodiment thus has a central channeled layer sandwiched between two active membrane layers, and the two active membrane layers are sandwiched between two outer porous support layers.

[0131] In an alternative embodiment, a thin coating of porous mixed-conducting multi-component metal oxide material (not shown) may be applied to portions of the surface of active membrane layer 1 that face oxidant flow channels 9, i.e., those portions of the surface of active membrane layer 1 that are not in contact with support ribs 7. This coating increases the active surface area of active membrane layer 1 and promotes mass transfer at the interface between active membrane layer 1 and the oxidant or

oxygen-containing gas flowing through the oxidant flow channels. This coating additionally may coat the walls of support ribs 7. The coating may comprise one or more oxygen reduction catalysts on the oxidant side. The one or more catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese. Methods of applying this coating are described below.

[0132] The properties and characteristics of the components of the membrane assembly described above are typical of the dense layers, channeled support layers, and porous support layers of the embodiments described below.

[0133] A description of the fabrication of this exemplary embodiment of a planar ceramic wafer assembly begins with the channeled layer or channeled support layer. This exemplary channeled support layer may be fabricated from three planar components—a planar green ceramic slotted support layer and two identical planar green ceramic flow channel layers—wherein the slotted support layer is sandwiched between the flow channel layers. This is illustrated below by describing each of the planar components in turn.

[0134] FIG. 2 is a plan view (not necessarily to scale) of a flow channel layer. This layer is formed from planar dense green ceramic material having a selected composition and may be square, rectangular, round, or any other appropriate shape. Flow channel layer 201 is rectangular and has two rectangular channeled regions 203 and 205 formed therein. Each channeled region has a pattern of through channels passing through the layer with a lattice of solid ribs formed between the channels. This pattern is better illustrated in FIG. 3, which is a magnified plan view (not necessarily to scale) of the channels in regions 203 and 205 of FIG. 2, showing a pattern of alternating open channels 301 formed by representative alternating supporting ribs 303 that are parallel to through channels 301 and intermediate supporting ribs 305 that are perpendicular to through channels 301.

[0135] FIG. 4 is a plan view (not necessarily to scale) of a slotted support layer. This layer is formed from planar dense green ceramic material having a selected composition and may be square, rectangular, round, or any other appropriate shape, and typically has a similar shape and outer perimeter dimensions as the flow channel layer of FIG. 2. Slotted support layer 401 has a first generally rectangular region containing parallel slots 403 passing through the layer between support ribs 405 and a second generally rectangular region containing parallel slots 407 passing through the layer between support ribs 409. Typically, the width of support ribs 405 and 409 (or the distance between slots 403 and 407) is between about 0.2 and about 4 mm and the width of slots 403 and 407 is between about 0.2 and about 2 mm.

[0136] Slotted support layer 401 also has a plurality of parallel slots 411 passing through the layer that are perpendicular to parallel slots 403 and disposed between one side of the first generally rectangular region and outer periphery 413. Slotted support layer 401 also has a plurality of parallel slots 415 passing through the layer that are perpendicular to parallel slots 403 and disposed between an opposite side of the first generally rectangular region and outer periphery 417. Slotted support layer 401 also has a plurality of parallel

slots **419** passing through the layer that are perpendicular to parallel slots **407** and disposed between one side of the second generally rectangular region and outer periphery **419**. Slotted support layer **401** also has a plurality of parallel slots **423** passing through the layer that are perpendicular to parallel slots **407** and disposed between the opposite side of the second generally rectangular region and outer periphery **425**.

[0137] A slotted support layer, such as slotted support layer **401**, is sandwiched between two flow channel layers, such as flow channel layer **201**, to form an intermediate channeled support layer. In this intermediate channeled support layer, alternating supporting ribs **303** (FIG. 3) of flow channel layer **201** are supported by support ribs **405** and **409**. Intermediate supporting ribs **305** are superimposed on slots **403** and **407** and are narrower than the width of parallel slots **403** and **407** such that neighboring channels **301** in the lengthwise direction can be in flow communication, i.e., intermediate supporting ribs **305** do not block or bridge slots **403** and **407**.

[0138] The intermediate green ceramic channeled support layer formed by placing a slotted support layer between two flow channel layers is modified as illustrated in FIG. 5, which is a plan view (not necessarily to scale) of a completed channeled support layer **501**. The modification comprises cutting parallel slots **503** and **505** on either side of rectangular channeled region **507**, wherein these slots are parallel to slots **403** and **407** in the slotted support layer. These slots pass completely through channeled support layer **501** and therefore cut through and intersect slots **411** and **415** (FIG. 4) in the slotted support layer (not seen in FIG. 5). The modification also includes cutting parallel slots **509** and **511** on either side of rectangular channeled region **513**. These slots pass completely through channeled support layer **501** and therefore cut through and intersect slots **419** and **423** (FIG. 4) in the slotted support layer (not seen in FIG. 5).

[0139] Slots **503** and **505** therefore are in flow communication with slots **403** (FIG. 4) and with the slots in rectangular channeled region **507**, and also with the other rectangular channeled region (not seen in this view) on the opposite side of channeled support layer **501**. In addition, slots **509** and **511** therefore are in flow communication with slots **407** (FIG. 4) and with the slots in rectangular channeled region **513**, and also with the other rectangular channeled region (not seen in this view) on the opposite side of channeled support layer **501**.

[0140] In an alternative method of making an intermediate green ceramic channeled support layer, slots **403** and **407** are not cut initially in layer **401** (FIG. 4). Instead, a center layer similar to layer **401** (but without slots **403** and **407**) is laminated between two layers **201** (FIG. 2) and then slots similar to slots **403** and **407** are cut completely through the center layer and the two outer layers **201**.

[0141] The completed green ceramic channeled support layer **501** then is modified by placing a thin layer of a green ceramic material that is a precursor of the active membrane material (described earlier as active membrane layer **1** in FIG. 1) in contact with each side of support layer **501**. In one embodiment, a layer of a green ceramic material that is a precursor of the porous support layer described earlier is placed in contact with each of the thin layers of the green ceramic material that is the precursor of the active mem-

brane material. In an alternative embodiment, a composite support layer of green ceramic material is placed in contact with each of the thin layers of the green ceramic material that is the precursor of the active membrane material.

[0142] Each of these composite support layers is formed by applying green ceramic tape that is a precursor of a dense ceramic material around the periphery of the layer and across the center region of the layer to form a frame defining two windows that may approximately match the dimensions of rectangular channeled regions **507** and **513** of the channeled support layer of FIG. 5. Green ceramic material that is a precursor of the porous support material is applied within these windows in contact with the green ceramic material that is a precursor of the active membrane material in contact with each side of support layer **501**. These two embodiments yield completed assemblies that define green ceramic wafer assemblies having a central channeled layer sandwiched between two active dense membrane layers with two outer ceramic precursor support layers.

[0143] In the first of the above embodiments, the green ceramic wafer assembly is completed as shown in FIG. 6A by cutting holes, for example, four holes **601**, **603**, **605**, and **607**, completely through the center region of the wafer assembly. More than four holes may be used if desired. Hole **601** intersects and is in flow communication with slots **503** and **509** (FIG. 5). Likewise, hole **607** intersects and is in flow communication with slots **505** and **511** (FIG. 5). Holes **601** and **607** thus provide internal manifolds in flow communication with slots **403** and **407** (FIG. 4) and with the slots in rectangular channeled regions **507** and **513** (FIG. 5).

[0144] In the second of the above embodiments, the green ceramic wafer assembly is completed as shown in FIG. 6B by cutting holes, for example, four holes **609**, **611**, **613**, and **615** completely through the center region of the wafer assembly. More than four holes may be used if desired. Hole **609** intersects and is in flow communication with slots **503** and **509** (FIG. 5). Likewise, hole **615** intersects and is in flow communication with slots **505** and **511** (FIG. 5). Holes **609** and **615** thus provide internal manifolds in flow communication with slots **403** and **407** (FIG. 4) and with the slots in rectangular channeled regions **507** and **513** (FIG. 5). In this embodiment, regions **617** and **619** of the support layer contain the green ceramic material that is a precursor of the porous support material. The remaining region of the support layer, i.e., the region surrounding holes **609-615**, region **617**, and region **619**, contains the green ceramic tape described above that is a precursor of a dense ceramic material.

[0145] These green ceramic wafer assemblies are then fired to sinter all ceramic material in the assemblies. After firing, the internal configurations of the completed wafer assemblies in FIGS. 6A and 6B allow gas to flow through hole **601** or **609**, through slots **403** and **407** as well as the slots in regions **507** and **513**, thereby contacting the gas with the surfaces of the two active dense membrane layers on either side of central channeled support layer **501**. After contact with the two active dense membrane layers, the gas flows into hole **607** or **615**. Holes **603** and **611**, and holes **605** and **613**, are not in direct flow communication with the internal slots and channels in channeled support layer **501**, since these holes pass through the middle region of the support layer between slotted regions **507** and **513**. Holes

603 and **605**, or holes **611** and **613**, may serve as part of a stack flow manifold as described below.

[0146] The completed wafer assemblies of FIGS. 6A and 6B may have a width between 5 and 40 cm, a length of between 5 and 40 cm, and a thickness between 1.5 mm and 8 mm.

[0147] The internal structure of the wafer assemblies described above is illustrated in FIG. 7A, which shows (not necessarily to scale) representative internal section 1-1 of FIGS. 6A and 6B. Outer support layers **701** and **703** of porous ceramic material were described earlier as porous support layer **3** of FIG. 1. Active dense membrane layers **705** and **707** were described earlier as active membrane layer **1** in FIG. 1. Slotted support layer **709** corresponds to slotted support layer **401** of FIG. 4 and shows portions **711** of parallel support ribs **405** or **409** of FIG. 4. Also shown are representative open slots **713**, which correspond to parallel slots **403** or **407** of FIG. 4.

[0148] Flow channel layers **715** and **717** correspond to the flow channel layer of FIG. 2 and the enlarged view of FIG. 3. Representative open channels **719** correspond to open channels **301** formed by alternating supporting ribs **303** in FIG. 3. Representative intermediate supporting ribs **721** and **723** correspond to intermediate supporting ribs **305** in FIG. 3. Representative open channels **725** are representative of open channels **301** formed by alternating supporting ribs **303** in FIG. 3. Representative intermediate supporting ribs **727** and **729** correspond to intermediate supporting ribs **305** in FIG. 3. Representative open slots **713** are wider than intermediate supporting ribs **721**, **723**, **727**, and **729**, so that open channels **719** and **725** are in flow communication via open slots **713**.

[0149] The internal structure of the exemplary wafer assembly described above is further illustrated in FIG. 7B, which shows (not necessarily to scale) a representative internal section 2-2 of FIGS. 6A and 6B. Outer support layers **701** and **703** and active dense layers **705** and **707** are identical to those of FIG. 7A. Section 2-2 shows a longitudinal view of slotted support layer **709**, which view corresponds to longitudinal section of a portion of slot **403** or **407** of FIG. 4.

[0150] Flow channel layers **715** and **717** correspond to the flow channel layer of FIG. 2 and the enlarged view of FIG. 3. Section 2-2 shows a section across open channels **301** and alternating supporting ribs **303** in FIG. 3. Porous support layers **701** and **703**, as well as dense layers **705** and **707**, are also shown in FIG. 7B.

[0151] In FIGS. 7A and 7B, a channeled support layer may be defined by slotted support layer **709** and flow channel layers **715** and **717**. The channeled support layer has a first side defined by the interface between the inner side of dense layer **705** and flow channel layer **715**. The channeled support layer has a second side defined by the interface between the inner side of dense layer **707** and flow channel layer **717**. Portions of dense layer **705** are in contact with alternating supporting ribs **303** and other portions are not in contact with these ribs. Also, portions of dense layer **707** are in contact with alternating supporting ribs **303** and other portions are not in contact with these ribs. Thus only portions of a dense layer are in actual contact with a side of a channeled support layer and the remaining portions of the dense layer are not in actual contact with the channeled support layer.

[0152] In an alternative embodiment, a thin coating of porous mixed-conducting multi-component metal oxide material (not shown) may be applied to portions of active dense membrane layers **705** and **707** that face open channels **719** and **725** (FIG. 7A) and open channels **301** (FIG. 7B). These portions are the portions of active dense membrane layers **705** and **707** that are not in contact with intermediate supporting ribs **721**, **723**, **727**, and **729** (FIG. 7A) and alternating support ribs **303** (FIG. 7B). This coating increases the active surface area of active dense membrane layers **705** and **707** and promotes mass transfer at the interface between active dense membrane layers **705** and **707** and the oxidant or oxygen-containing gas flowing through the oxidant flow channels. The coating may comprise one or more oxygen reduction catalysts on the oxidant side. The one or more catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0153] The coating may be applied by flowing a slurry of multi-component metal oxide powder through the channels of the wafer after the wafer has been assembled, either in the green state or after sintering. The slurry may be made by mixing multi-component metal oxide powder with a liquid such as water or an organic solvent. Dispersants optionally may be added to the slurry to stabilize the dispersion of the powder. Pore forming agents such as microcellulose or graphite may be added to the slurry to aid in the production of porosity. The slurry then is forced to flow through the wafer channels, filling the channels with the slurry. The liquid from the slurry then is evaporated from the inside of the wafer by heating the wafer. This leaves a coating of the multi-component metal oxide powder on the inside surface of the dense layer as well as the walls of the channels of the channeled support layer. Alternatively, air or another gas is blown through the channels after the slurry has filled the channels to force out excess slurry, leaving a coating of the slurry on the inside surface of the dense layer as well as the walls of the channels of the channeled support layer. The slurry then is dried by heating the wafer to remove the liquid.

[0154] The multi-component metal oxide powder then is partially sintered to bond the powder to the inside surface of the dense layer. Sintering of the coating is accomplished by first heating to remove any liquid or organics that were present in the slurry. The temperature is then increased to a level sufficient to partially sinter the powder and produce a well adhered porous coating of multi-component metal oxide to the inside surface of the dense layer. Typical conditions are 900-1600° C. for 0.5-12 hours. The porous coating may be 1 to 100 μm thick and preferably may be <50 microns thick. The porous coating may be 10-50% porous and preferably may be 25-50% porous.

[0155] The complete wafer assembly described in FIG. 4, 5, 6A or 6B, 7A, and 7B forms one of the basic repeating elements for a multi-wafer stack. The other repeating element is the ceramic spacer shown in the views of FIGS. 8A and 8B. The ceramic spacer is made of a selected ceramic material, has openings **801** and **803** separated by rib **805**, and has a width similar to the width of the wafer assembly of FIGS. 6A and 6B. The ceramic material should be dense and non-porous so that gas cannot flow through the spacer walls surrounding openings **801** and **803**. Opening **801** is sized to

fit over holes 601 and 603 of FIG. 6A or holes 609 and 611 of FIG. 6B. Opening 803 is sized to fit over holes 605 and 607 of FIG. 6A or holes 613 and 615 of FIG. 6B. The height of the spacer (the vertical dimension in FIG. 8A) may be in the range of 0.5 mm to 5 mm.

[0156] A plurality of wafer assemblies and spacers can be fabricated into a ceramic membrane stack having alternating wafers and spacers as shown in the front and side views of FIGS. 9A and 9B, respectively. This ceramic stack can be fabricated by assembling green ceramic components and firing the resulting green stack assembly, or alternatively by firing individual green ceramic components and joining the fired components with a joining compound as described below.

[0157] The views of FIGS. 9A and 9B illustrate the placement of stack components and are not to scale. FIG. 9A shows a plurality of parallel wafer assemblies 901 and spacers 903 stacked congruently and in alternating fashion along axis 905. The wafer assemblies are supported in the center of the stack by the spacers and are cantilevered out to the edges of the stack. Optionally, spacers 907 can be placed between the wafers on opposite sides of the stack as shown to provide support and reduce the bending moment on the wafers near the central spacers. These spacers may extend across the full width of the stack, i.e., extending perpendicularly into the page in FIG. 9A. Cap 909 is placed on the top wafer of the stack to close holes 601, 603, 605, and 607 (FIG. 6A) or holes 609, 611, 613, and 615 (FIG. 6B).

[0158] FIG. 9B shows a side view of the stack having wafers 901, spacers 907, and cap 909. This view corresponds to a vertical edge view of the wafer in FIGS. 6A and 6B. Openings 911 (each of which corresponds to opening 801 of the spacer in FIGS. 8A and 8B) and holes 601 and 603 (FIG. 6A) or holes 609 and 611 (FIG. 6B) form an internal manifold extending through the length of the stack. Likewise, openings 913 (each of which corresponds to opening 803 of the spacer in FIGS. 8A and 8B) and holes 605 and 607 (FIG. 6A) or holes 613 and 615 (FIG. 6B) form an internal manifold extending through the length of the stack. These two internal manifolds are in flow communication through the wafers via the internal slots and channels in the channel support layer as earlier described. A complete stack, a portion of which is shown schematically in FIGS. 9A and 9B, may contain between 1 and 200 wafers and may have a height of 2.5 mm to 2.6 m. When assembled from green ceramic stack components, the stack described above may be sintered by firing at temperatures in the range of 1000-1600° C. for 0.5 to 12 hours.

[0159] Alternatively, the stack described above may be fabricated by first assembling a plurality of individual green wafers as described above, making a plurality of green spacers as described above, and sintering these individual green ceramic wafer and spacer subcomponents at temperatures from 1000-1600° C. for 0.5 to 12 hours. The wafer subcomponents may comprise a first multi-component metallic oxide having a first crystal structure selected from the group consisting of a perovskitic structure and a fluorite structure and the spacer subcomponent may comprise a second multi-component metallic oxide having a second crystal structure identical to the first crystal structure. The first and second multi-component metallic oxide compositions may be the same. In an exemplary stack assembly, the

wafer and spacer subcomponents both may have a composition defined by the formula $(\text{La}_{0.85}\text{Ca}_{0.15})_{101}\text{FeO}_3$.

[0160] Sintered wafer and spacer subcomponents then may be assembled into a stack as described above with reference to FIGS. 9A and 9B by applying at each interface between a wafer and a spacer a joint material comprising at least one metal oxide. The at least one metal oxide may comprise at least one shared metal contained in at least one of the first multi-component metallic oxide and the second multi-component metallic oxide. The joint material preferably is free of carbon, silicon, germanium, tin, lead, phosphorus and tellurium. The at least one metal oxide in the joint material preferably has a melting point below the sintering temperature of the first multi-component metallic oxide and below the sintering temperature of the second multi-component metallic oxide. The stack formed in this manner is heated to a temperature above the melting point of the at least one metal oxide in the joint material, below the sintering temperature of the first multi-component metallic oxide, and below the sintering temperature of the second multi-component metallic oxide. This yields a completed stack as described above with reference to FIGS. 9A and 9B.

[0161] In an exemplary method of making the gaskets described above, a slip was made by adding 920.2 grams of $(\text{La}_{0.9}\text{Ca}_{0.1})_{1.005}\text{FeO}_3$ powder and 9.2 grams of Fe_2O_3 to a one-liter high density polyethylene container containing one kilogram of spherical zirconia media, 242.1 grams of reagent grade toluene, 60.5 grams of denatured ethanol, and 4.65 grams polyvinyl butyral. The slip was put on a paint shaker for 30 minutes. Plasticizer (53.56 grams butyl benzyl phthalate) and binder (48.9 grams of polyvinyl butyral) were added to the slip and it was put back on the paint shaker for an additional hour. The slip was rolled overnight and a viscosity of 1500 mPa-s was measured using a viscometer at 25° C. The slip was then filtered, degassed, and cast on polyester to make dried tape approximately 250 μm thick. Gaskets with the appropriate shape and dimensions were sheared out of the tape and placed between the wafers and the spacers to be joined, thereby forming a stack. A pressure of 170 kPa was applied to the joints and stack, and the assembly was slowly heated to 1250° C. to remove the organics and sinter the joint compound, thereby forming a leak-tight stack.

[0162] Similar technology is disclosed in two copending applications filed on even date herewith, one entitled "Method of Joining ITM Materials Using a Partially or Fully-Transient Liquid Phase", and having the Attorney Docket No. 06272 USA, and the other entitled "Method of Forming a Joint", and having the Attorney Docket No. 06067 USA.

[0163] In an alternative embodiment, a thin coating of porous mixed-conducting multi-component metal oxide material may be applied to portions of the active dense membrane layers in the completed ceramic stack of FIGS. 9A, 9B, and 10. As described above for the wafer assemblies, this coating is applied to the portions of the active dense membrane layers which face the internal oxidant gas flow channels and which are not in contact with intermediate and alternating supporting ribs. In this embodiment, the coating may be applied to the internal regions of the completed ceramic stack including the active dense membrane layers. This coating increases the active surface area of the

active dense membrane layers and promotes mass transfer at the interface between active dense membrane layers and the oxidant or oxygen-containing gas flowing through the oxidant flow channels. The coating may comprise one or more oxygen reduction catalysts on the oxidant side. The one or more catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0164] The coating may be applied by flowing a slurry of multi-component metal oxide powder through the channels of the stack after the stack has been assembled. The slurry may be made by mixing multi-component metal oxide powder with a liquid such as water or an organic solvent. Dispersants optionally may be added to the slurry to stabilize the dispersion of the powder. Pore forming agents such as microcellulose or graphite may be added to the slurry to aid in the production of porosity. The slurry is then forced to flow through the channels in the stack, filling the channels with the slurry. The liquid from the slurry then is drained and the residual slurry inside the stack is dried by heating the stack. This leaves a coating of the multi-component metal oxide powder on all of the inside surfaces of the stack including the exposed dense layers. Alternatively, air or another gas may be blown through the channels after the slurry has filled the channels to force out excess slurry, leaving a coating of the slurry on the inside surface of the dense layer as well as the walls of the channels of the channeled support layers in the stack. The slurry then may be dried by heating the stack to remove the liquid.

[0165] The multi-component metal oxide powder then is partially sintered to bond the powder to the inside surface of the dense layer. Sintering of the coating is accomplished by first heating the stack to remove any liquid or organics that were present in the slurry. The temperature is then increased to a level sufficient to partially sinter the powder and produce a well-adhered porous coating of multi-component metal oxide on the inside surfaces of the stack including the exposed surface portions of the dense active layers. Typical conditions are 900-1600° C. for 0.5-12 hours.

[0166] A plurality of completed ceramic stacks can be operated at temperatures in the range of 650 to 1100° C. to convert a reactant hydrocarbon-containing feed gas and an oxygen-containing oxidant feed gas into a hydrocarbon oxidation product and unreacted feed gas. The hydrocarbon-containing feed gas may comprise one or more hydrocarbon compounds containing between one and six carbon atoms. The oxygen-containing oxidant feed gas may comprise air, oxygen-depleted air, or combustion products containing oxygen, nitrogen, carbon dioxide, and water. The hydrocarbon oxidation product may comprise oxidized hydrocarbons, partially oxidized hydrocarbons, hydrogen, and/or water. In one exemplary application, the hydrocarbon-containing feed gas is natural gas, the oxidant feed gas is a combustion product containing oxygen, nitrogen, carbon dioxide, and water, and the hydrocarbon oxidation product is synthesis gas containing hydrogen, carbon monoxide, carbon dioxide, and water.

[0167] The gas flows in an operating stack are illustrated in FIG. 10. Reactant gas containing hydrocarbon feed components flows into the stack and flows over the outer porous

support layers of each wafer. Reactant gas and products exit the opposite side of the stack as shown. Oxidant gas enters at the bottom of the stack and flows upward through the first internal manifold, through the channeled support layer in each wafer, and downward through the second internal manifold. Oxygen-depleted oxidant gas leaves the stack as shown. The oxidant and reactant gases thus flow through the stack cocurrently.

[0168] While the planar ceramic membrane components and stack described above have a rectangular configuration and each wafer has four active membrane areas, other features and configurations can be envisioned that would utilize the principles described above and would be included in embodiments of the present invention. Wafers may be square, round, or any other desired shape, and may have more than four or less than four active membrane areas. Other configurations of the channels in the channeled support layer can be envisioned and would be included in embodiments of the present invention. Other internal manifold configurations are possible within the scope of the invention and would depend on the wafer shape and number of active regions in each wafer. For example, the number and orientation of the slots and channels in the channeled support layer as described above also may be varied to change the structural and flow characteristics of the layer, and these variations would be considered within embodiments of the present invention.

1. A hydrocarbon oxidation process comprising

- (a) providing a planar ceramic membrane reactor assembly comprising a dense layer of mixed-conducting multi-component metal oxide material, wherein the dense layer has a first side and a second side, a support layer comprising porous mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled support layer in contact with the second side of the dense layer;
- (b) passing a heated oxygen-containing oxidant feed gas through the ceramic channeled layer and in contact with the second side of the dense layer;
- (c) permeating oxygen ions through the dense layer and providing oxygen on the first side of the dense layer;
- (d) contacting a heated hydrocarbon-containing feed gas with the support layer wherein the hydrocarbon-containing feed gas diffuses through the support layer; and
- (e) reacting the hydrocarbon-containing feed gas with the oxygen to yield a hydrocarbon oxidation product.

2. The hydrocarbon oxidation process of claim 1 wherein the hydrocarbon-containing feed gas comprises one or more hydrocarbon compounds containing between one and six carbon atoms.

3. The hydrocarbon oxidation process of claim 2 wherein the oxygen-containing oxidant feed gas is selected from the group consisting of air, oxygen-depleted air, and combustion products containing oxygen, nitrogen, carbon dioxide, and water.

4. The hydrocarbon oxidation process of claim 2 wherein the hydrocarbon oxidation product comprises oxidized hydrocarbons, partially oxidized hydrocarbons, hydrogen, and water.

5. The hydrocarbon oxidation process of claim 2 wherein the oxygen-containing oxidant feed gas and the hydrocarbon-containing feed gas flow cocurrently through the ceramic membrane reactor assembly.

6. The hydrocarbon oxidation process of claim 2 wherein the support layer comprises one or more catalysts compris-

ing metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof.

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(19) **United States**(12) **Patent Application Publication**
Minford(10) **Pub. No.: US 2008/0136179 A1**(43) **Pub. Date: Jun. 12, 2008**(54) **SEAL ASSEMBLY FOR MATERIALS WITH
DIFFERENT COEFFICIENTS OF THERMAL
EXPANSION****Publication Classification**(51) **Int. Cl.**
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(52) **U.S. Cl.** **285/368**(76) **Inventor:** **Eric Minford**, Laurys Station, PA
(US)(57) **ABSTRACT**

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Seal assembly comprising (a) two or more seal elements, each element having having a coefficient of thermal expansion; and (b) a clamping element having a first segment, a second segment, and a connecting segment between and attached to the first and second segments, wherein the two or more seal elements are disposed between the first and second segments of the clamping element. The connecting segment has a central portion extending between the first segment of the clamping element and the second segment of the clamping element, and the connecting segment is made of a material having a coefficient of thermal expansion. The coefficient of thermal expansion of the material of the connecting segment is intermediate the largest and smallest of the coefficients of thermal expansion of the materials of the two or more seal elements.

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FIG. 1

FIG. 2

FIG. 3

FIG. 4

SEAL ASSEMBLY FOR MATERIALS WITH DIFFERENT COEFFICIENTS OF THERMAL EXPANSION

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] This invention was made with government support under Contract Numbers DE-FC26-97FT96052 and DE-FC26-98FT40343 between Air Products and Chemicals, Inc. and the U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0002] The reliable containment of high-temperature pressurized gases is an important factor in the design and operation of piping and reactor systems in many diverse industries. Temperature cycles occur in these systems during startup, shutdown, and process upset conditions, and such cycles also may occur during normal process operations. The piping and process equipment in these systems often are constructed of various materials, many of which have different coefficients of thermal expansion. Couplings and joints between components with different coefficients of thermal expansion are problematic, especially when subjected to large temperature cycles. In order to minimize gas leakage, careful design of these couplings and joints is required.

[0003] Certain high-temperature systems such as ceramic gas separation membrane systems, ceramic membrane reactor systems, and solid oxide fuel cells utilize ceramic components operating at high temperatures. Gas flow to and from these ceramic components typically is provided by metal alloy piping systems, thereby requiring ceramic-to-metal joints. Because ceramic materials and metals usually have different thermal expansion characteristics, proper sealing at these ceramic-to-metal joints presents significant challenges in the design and operation of these systems. The seals at these joints must be reliable at high operating temperatures and must tolerate thermal cycling in order to achieve stable performance over the anticipated operating life of the system. In addition, the performance of these seals should be verifiable at room temperature during apparatus construction, and the seals should be economical and easy to assemble.

[0004] There is a need in the art of high-temperature gas processing for improved seals in couplings and joints between materials with different coefficients of thermal expansion. This need is addressed by the embodiments of the invention as described below and defined by the claims that follow.

BRIEF SUMMARY OF THE INVENTION

[0005] An embodiment of the invention relates to a seal assembly comprising (a) two or more seal elements, each element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the seal elements are stacked such that adjacent faces are parallel and the axes are parallel or coincident, and wherein each of the seal elements is made of a material having a coefficient of thermal expansion; and (b) a clamping element having a first segment, a second segment, and a connecting segment between and attached to the first and second segments, wherein the two or more seal elements are disposed between the first and second segments of the clamping element and the clamping element is adapted to exert axial

clamping forces on the two or more seal elements, wherein the connecting segment has a central portion extending between a plane formed by the face of a seal element adjacent the first segment of the clamping element and a plane formed by the face of a seal element adjacent the second segment of the clamping element, and wherein the connecting segment is made of a material having a coefficient of thermal expansion. The coefficient of thermal expansion of the material of the connecting segment is intermediate the largest and smallest of the coefficients of thermal expansion of the materials of the two or more seal elements.

[0006] In this embodiment, the seal assembly may further comprise a compliant sealing member disposed at any interfacial zone between adjacent seal elements and between a segment of the clamping element and an adjacent seal element.

[0007] Another embodiment of the invention includes a seal assembly comprising

[0008] (a) a first seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;

[0009] (b) a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the first seal element is made of a first material having a first coefficient of thermal expansion, and wherein the first face of the second seal element is in forcible contact with the second face of the first seal element; and

[0010] (c) a clamping element adapted to urge the first seal element axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the first seal element, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the first face of the first seal element and the second face of the second seal element, is generally parallel to the axes of the first and second seal elements, and is made of a third material having a third coefficient of thermal expansion;

wherein the third coefficient of thermal expansion is intermediate the first and second coefficients of thermal expansion.

[0011] In this embodiment, either of the first segment of the clamping element and the second segment of the clamping element may be permanently attached to the connecting segment of the clamping element. Alternatively, either of the first segment of the clamping element and the second segment of the clamping element may be removably attached to the connecting segment of the clamping element.

[0012] The first material may be selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels. The second material may be selected from the group consisting of aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, mixed metal perovskites, $(La_xSr_{1-x})_yCoO_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral), and $(La_xCa_{1-x})_yFeO_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 > y \geq 1.0$, and z is a number which

renders the composition of matter charge neutral). The third material may be selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

[0013] The second seal element may consist of a first subcomponent and a second subcomponent, each subcomponent having first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the first face of the first subcomponent is the first face of the second seal element, wherein the second face of the second subcomponent is the second face of the second seal element that is in forcible contact with the second segment of the clamping element. Either of the first segment of the clamping element and the second segment of the clamping element may be removably attached to the connecting segment of the clamping element.

[0014] In this embodiment, the seal assembly may further comprise a compliant sealing member disposed between the second segment of the clamping element and the second face of the second seal element. Alternatively or additionally, the seal assembly may further comprise a compliant sealing member disposed between the first segment of the clamping element and the first face of the first seal element.

[0015] In the seal assembly of this embodiment,

[0016] (1) the second seal element may be a flange attached to a first cylindrical pipe having an outer diameter, wherein the flange has an outer diameter;

[0017] (2) the clamping element may comprise a toroidal body having a first ring that forms the first segment of the clamping element and has an inner and an outer diameter, a second ring that forms the connecting segment of the clamping element and has an inner and an outer diameter, and a third ring that forms the second segment of the clamping element and has an inner and an outer diameter;

[0018] (3) the first seal element may be a compensating spacer ring having an inner and an outer diameter;

[0019] (4) the inner diameter of the first ring that forms the first segment of the clamping element may be greater than the outer diameter of the first cylindrical pipe;

[0020] (5) the inner diameter of the compensating spacer ring may be greater than the outer diameter of the first cylindrical pipe and the outer diameter of the compensating spacer ring may be less than the inner diameter of the second ring that forms the connecting segment of the clamping element; and

[0021] (6) the outer diameter of the flange may be less than the inner diameter of the second ring that forms the connecting segment of the clamping element.

[0022] The flange and first cylindrical pipe may be made of ceramic material, the clamping element may be a metallic material, and the compensating spacer ring may be a metallic material. The first material may be selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels. The second material may be selected from the group consisting of aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, mixed metal perovskites, $(\text{La}_x\text{Sr}_{1-x})_y\text{CoO}_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral), and $(\text{La}_x\text{Ca}_{1-x})_y\text{FeO}_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral). The third

material may be selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

[0023] An alternative embodiment of the invention relates to a seal assembly comprising

[0024] (a) a first seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element has a first reference dimension defined by the axial distance between the first and second faces at a reference temperature, and wherein the first seal element is made of a first material having a first coefficient of thermal expansion;

[0025] (b) a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the second seal element has a second reference dimension defined by the axial distance between the first and second faces at the reference temperature, wherein the first seal element is made of a first material having a first coefficient of thermal expansion, and wherein the first face of the second seal element is in contact with the second face of the first seal element; and

[0026] (c) a clamping element adapted to urge the first seal element axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the first seal element, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the first face of the first seal element and the second face of the second seal element and is generally parallel to the axes of the first and second seal elements, and wherein the central portion is made of a third material having a third coefficient of thermal expansion;

wherein the first material, the reference thickness of the first seal element, the second material, the reference thickness of the second seal element, and the third material have values such that, at any selected temperature,

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch}$$

where

$$A_T = A_R(\alpha_A)(T - T_R),$$

$$B_T = B_R(\alpha_B)(T - T_R), \text{ and}$$

$$C_T = C_R(\alpha_C)(T - T_R),$$

and where T is the selected temperature, T_R is the reference temperature, A_R is the first reference dimension, B_R is the second reference dimension, A_R is the sum of B_R and C_R , α_A is the coefficient of thermal expansion of the a first material, α_B is the coefficient of thermal expansion of the second material, and α_C is the coefficient of thermal expansion of the third material.

[0027] Another alternative embodiment includes a ceramic-to-metal seal assembly comprising

[0028] (a) a toroidal compensating spacer ring having a first face, a second face generally parallel to the first face, an inner diameter, an outer diameter, and an axis orthogonal to the first and second faces, wherein torroi-

dal compensating spacer ring is made of a first metal having a first coefficient of thermal expansion;

[0029] (b) a cylindrical ceramic tube having an inner diameter, an outer diameter, and a ceramic flange formed at an end of the cylindrical ceramic tube, the ceramic flange having an outer diameter, wherein

[0030] (1) the inner diameter of the torroidal compensating spacer ring is greater than the outer diameter of the cylindrical ceramic tube and is disposed around the ceramic tube,

[0031] (2) the ceramic flange forms a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the torroidal compensating spacer ring,

[0032] (3) the first face of the second seal element is in forcible contact with the second face of the torroidal compensating spacer ring, and

[0033] (4) the ceramic flange is made of a ceramic material having a second coefficient of thermal expansion; and

[0034] (c) a torroidal clamping element adapted to urge the torroidal compensating spacer ring axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the torroidal compensating spacer ring, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment (1) has a central portion extending between planes formed by the first face of the torroidal compensating spacer ring and the second face of the second seal element, (2) is generally parallel to the axes of the torroidal compensating spacer ring and the second seal element, and (3) is made of a second metal having a third coefficient of thermal expansion;

wherein the third coefficient of thermal expansion is intermediate the first and second coefficients of thermal expansion.

[0035] In this alternative embodiment, the first metal may be selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels. The second metal may be selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels. The ceramic flange may be made of a material selected from the group consisting of aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, mixed metal perovskites, $(\text{La}_x\text{Sr}_{1-x})_y\text{CoO}_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \cong y \geq 1.0$, and z is a number which renders the composition of matter charge neutral), and $(\text{La}_x\text{Ca}_{1-x})_y\text{FeO}_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 \cong y \geq 1.0$, and z is a number which renders the composition of matter charge neutral). The ceramic tube may be made of the same material as the ceramic flange, wherein the ceramic tube and the ceramic flange form an integrated flanged ceramic tube.

[0036] A related embodiment of the invention includes a seal assembly comprising

[0037] (a) a seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;

[0038] (b) a compliant sealing member adjacent the second face of the seal element;

[0039] (c) a clamping element having a first segment with a face in forcible contact with the first face of the seal element, a second segment having a face in forcible contact with the compliant seal member, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the face of the first segment and the face of the second segment, is generally parallel to the axis of the seal element, and is made of a second material having a second coefficient of thermal expansion, and wherein the a clamping element is adapted to urge the seal element axially toward the face of the second segment of the clamping element to compress the compliant seal member;

wherein the first coefficient of thermal expansion is greater than the second coefficient of thermal expansion.

[0040] Another related embodiment of the invention includes a method of making and operating a seal assembly comprising

[0041] (a) providing at a temperature equal to a reference temperature a seal assembly comprising

[0042] (1) a first seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;

[0043] (2) a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the second seal element is made of a second material having a second coefficient of thermal expansion, and wherein the first face of the second seal element is in forcible contact with the second face of the first seal element; and

[0044] (3) a clamping element adapted to urge the first seal element axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the first seal element, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the first face of the first seal element and the second face of the second seal element, is generally parallel to the axes of the first and second seal elements, and is made of a third material having a third coefficient of thermal expansion;

[0045] (b) changing the temperature of the seal assembly to a selected temperature different than the reference temperature; and

[0046] (c) maintaining the seal assembly at the selected temperature such that

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch}$$

where A_T , B_T , and C_T are temperature-compensated dimensions defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R),$$

$$B_T = B_R(\alpha_B)(T - T_R), \text{ and}$$

$$C_T = C_R(\alpha_C)(T - T_R),$$

and where T is the selected temperature; T_R is the reference temperature; B_R is the axial distance between the faces of the first seal element at the reference temperature; C_R is the axial distance between the faces of the second seal element at the reference temperature; α_A is the coefficient of thermal expansion of the first material; α_B is the coefficient of thermal expansion of the second material; α_C is the coefficient of thermal expansion of the third material; and $A_R = B_R + C_R$.

[0047] An alternative related embodiment includes a method of making and operating a seal assembly comprising

[0048] (a) providing at a temperature equal to a reference temperature a seal assembly comprising

[0049] (1) a seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;

[0050] (2) a compliant sealing member adjacent the second face of the seal element;

[0051] (3) a clamping element having a first segment with a face in forcible contact with the first face of the seal element, a second segment having a face in forcible contact with the compliant seal member, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the face of the first segment and the face of the second segment, is generally parallel to the axis of the seal element, and is made of a second material having a second coefficient of thermal expansion, and wherein the a clamping element is adapted to urge the seal element axially toward the face of the second segment of the clamping element to compress the compliant seal member;

[0052] (b) changing the temperature of the seal assembly to a selected temperature different than the reference temperature; and

[0053] (c) maintaining the seal assembly at the selected temperature such that

$$|A_T - C_T| \leq 0.002 \text{ inch}$$

[0054] where A_T and C_T are temperature-compensated dimensions defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R)$$

$$C_T = C_R(\alpha_C)(T - T_R)$$

[0055] where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material; α_C is the coefficient of thermal expansion of the second material; C_R is the axial distance between the first face and the second face of the seal element at the reference temperature;

[0056] C'_R is the axial distance between the second face of the seal element and the face of the second segment of the clamping element at the reference temperature; and $A_R = C_R + C'_R$.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0057] The various embodiments of the invention are illustrated by the following Figures, which are not necessarily to scale.

[0058] FIG. 1 is a schematic diagram illustrating a generic sealing assembly used in various embodiments of the present invention.

[0059] FIG. 2 a schematic diagram illustrating the use of the generic sealing assembly of FIG. 1 in an embodiment of the invention.

[0060] FIG. 3 a schematic diagram illustrating the use of the generic sealing assembly of FIG. 1 in another embodiment of the invention.

[0061] FIG. 4 a schematic diagram illustrating another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0062] The embodiments of the invention are directed to seal assemblies for forming a seal between two pipes or vessels having different coefficients of thermal expansion. The seal assembly includes a clamping element provides axial clamping forces against sealing elements, some of which are parts of the two pipes or vessels being sealed. When the seal is designed, the axial dimensions of the clamping and seal elements at ambient conditions and the coefficients of thermal expansion of the materials of the clamping and seal elements are selected so that as the assembled seal element is heated the absolute difference between the length of the clamping element connecting segment and the sum of the axial dimensions of the seal elements is less than 0.002 inch.

[0063] One of the embodiments utilizes a seal assembly having a rigid clamping element that exerts a clamping force on a first seal element and a second seal element adjacent the first seal element. The first and second segments of the clamping element are in forcible contact with the first and second sealing elements, and the first seal element is in forcible contact with the second seal element. The clamping element has a connecting segment opposite the first and second seal elements, and the coefficient of thermal expansion of the connecting segment is intermediate the coefficients of thermal expansion of the first and second seal elements.

[0064] As illustrated below, the first seal element is a compensating spacer element, the second seal element may be a part of first vessel or piping system, and either of or both of the segments of the clamping element may be part of a second vessel or piping system that is sealably connected to the first vessel or piping system. Depending on the system configuration and the relative differential pressures across the seal element, a compliant seal or gasket may be placed at any of the interfacial zones between the first seal element and the first segment of the clamping element, the first seal element and the compensating spacer element, and the compensating spacer element and the second segment of the clamping element. Some embodiments specifically do not utilize a compliant seal or gasket at the interfacial zone between the compensating spacer element and the second segment of the clamping element, and the compensating spacer element is in direct contact with the second segment of the clamping element.

[0065] Certain design parameters may be selected to compensate for the differences in thermal expansion of the seal components as the seal assembly is heated. These parameters include the material of the first seal element, the material of the compensating spacer element, the material of the connecting segment of the clamping element, the initial dimension of the first seal element or compensating spacer element at ambient temperature, and the second seal element at ambient temperature. By appropriate choice of these parameters, the

net differential expansion between (1) the connecting segment of the clamping element and (2) the combined first seal element and compensating spacer element during heating can be minimized or eliminated, thereby maintaining the initial clamping loads placed on the first seal element and compensating spacer element.

[0066] The seal assembly discussed above is illustrated generically in FIG. 1. Seal assembly 1 comprises a clamping element having first segment 3, connecting segment 5, and second segment 7; first seal element or compensating spacer element 9; and second seal element 11. First segment 3, connecting segment 5, and second segment 7 of the clamping element may be the same materials or may be different materials. First segment 3 may be removably attached to connecting segment 5 by a bolt or other fastening device (not shown) at interfacial zone 13. Alternatively, first segment 3 and connecting segment 5 may be a single piece of a common material. Alternatively or additionally, second segment 7 may be removably attached to connecting segment 5 by a bolt or other fastening device (not shown) at interfacial zone 15. Alternatively, second segment 7 and connecting segment 5 may be a single piece of a common material.

[0067] First seal element or compensating spacer element 9 typically is a separate piece as shown. Second seal element 11 may be a part of and connected to a first vessel or piping system, and either of or both of segments 3 and 7 of the clamping element may be part of a second vessel or piping system that is sealably connected to the first vessel or piping system.

[0068] The clamping element urges first segment 3 into forcible contact with compensating spacer element 9 at interfacial zone 17 and second segment 7 into forcible contact with second seal element 11 at interfacial zone 19. As a result, compensating spacer element 9 and second segment 7 are urged into forcible contact at interfacial zone 21. Compensating spacer element 9 is characterized by dimension B, which is the orthogonal or axial distance between the plane formed by the surface of the compensating spacer element at interfacial zone 17 and the plane formed by the surface of the compensating spacer element at interfacial zone 21. Second seal element 11 is characterized by dimension C, which is the orthogonal or axial distance between the plane formed by the surface of second seal element 11 at interfacial zone 21 and the plane formed by the surface of the second seal element at interfacial zone 19. The dimension A is defined as the sum of dimensions B and C. Dimension A is equivalent to the portion of connecting segment 5 that lies between the plane formed by the surface of compensating spacer element 9 at interfacial zone 17 and the plane formed by the surface of second seal element 11 at interfacial zone 19. Connecting segment 5 is characterized by dimension D, which lies between the plane formed by the surface of first segment 3 at interfacial zone 17 and the plane formed by the surface of second segment 7 at interfacial zone 19, i.e., D is the distance between the faces of the clamping element.

[0069] Interfacial zone 17 may be an interface formed by contact between flat surfaces on first segment 3 and compensating spacer element 9. Alternatively, interfacial zone 17 may include an intermediate member (not shown) such as a compliant sealing member as discussed later. Interfacial zone 19 may be an interface formed by contact between flat surfaces on second segment 7 and second seal element 11. Alternatively, interfacial zone 19 may include an intermediate member (not shown) such as a compliant sealing member as

discussed later. Typically, interfacial zone 21 is an interface formed by direct contact between flat surfaces on compensating spacer element 9 and second seal element 11. Alternatively, interfacial zone 21 may include an intermediate member (not shown) such as a compliant sealing member as discussed later.

[0070] The term “forcible contact” as applied at the interfacial zone of two parts means that both parts on either side of the interfacial zone are urged together by axial compressive forces applied by the clamping element. For example, at interfacial zone 17, the forcible contact may be formed directly by actual contact between flat surfaces on first segment 3 and compensating spacer element 9. Alternatively, if interfacial zone 17 includes an intermediate seal member as discussed above, the forcible contact between first segment 3 and compensating spacer element 9 will occur via the intermediate member, i.e., the axial compressive force will be transmitted from first segment 3 to the intermediate member and from the intermediate member to compensating spacer element 9. In another example, at interfacial zone 19, the forcible contact may be formed directly by actual contact between flat surfaces on second segment 7 and second seal element 11. Alternatively, if interfacial zone 19 includes an intermediate member as discussed above, the forcible contact between second segment 7 and second seal element 11 will occur via the intermediate member. In yet another example, at interfacial zone 21, the forcible contact may be formed directly by actual contact between flat surfaces on compensating spacer element 9 and second seal element 11. Alternatively, if interfacial zone 21 includes an intermediate member as discussed above, the forcible contact between compensating spacer element 9 and second seal element 11 will occur via the intermediate member. Thus the term “forcible contact” at an interfacial zone includes either (1) actual contact between two surfaces or (2) contact of a first surface with a surface of an intermediate member and contact of a second surface with another surface of the intermediate member, wherein all surfaces and, if present, the surfaces of the intermediate member, are urged together by compressive axial forces applied by the clamping element.

[0071] The term “seal element” is defined as a rigid part of a seal assembly disposed within a clamping element. The seal element is not deformed by the application of axial clamping forces. The term “compliant sealing member” is defined as a deformable part of a seal assembly that is deformed by the application of axial clamping forces. Axial clamping forces are the forces exerted on a seal assembly that cause forcible contact between the seal elements and between seal elements and compliant sealing members in the direction of the axes of the seal members. Ceramic material is defined as an inorganic, non-metallic material. A metallic material is a pure metal, metal alloy, or mixture of metals, or a composite material containing a pure metal, metal alloy, or mixture of metals.

[0072] The indefinite articles “a” and “an” as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of “a” and “an” does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article “the” preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used.

The adjective “any” means one, some, or all indiscriminately of whatever quantity. The term “and/or” placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity.

[0073] First segment 3, connecting segment 5, and second segment 7 of the clamping element may be the same materials or may be different materials. Compensating spacer element 9 is made of a first material having a first coefficient of thermal expansion, second seal element 11 is made of a second material having a second coefficient of thermal expansion, and connecting segment 5 is made of a third material having a third coefficient of thermal expansion. The third coefficient of thermal expansion is intermediate the first and second coefficients of thermal expansion.

[0074] First seal element or compensating spacer element 9 has a reference thickness or dimension defined by a reference dimension B_R at a reference temperature, second seal element 11 has a reference thickness or dimension defined by the dimension C_R at the reference temperature, and dimension A_R at the reference temperature is the sum of reference dimensions B_R and C_R at the reference temperature. The geometric definitions of reference dimensions A_R , B_R , and C_R correspond to the geometric definitions of A, B, and C, respectively, as given above. The reference temperature may be any temperature, but advantageously the reference temperature is an ambient temperature between about 15 and 35° C. When the seal assembly is at the reference temperature, the clamping element applies an initial axial compressive force that presses compensating spacer element 9 and second seal element 11 together in forcible contact.

[0075] The reference dimensions of compensating spacer element 9 (B_R) and seal element 11 (C_R), and the materials of compensating spacer element 9, second seal element 11, and connecting segment 5, are initially selected when the seal assembly is designed. The proper selection of these parameters is made so that, at any selected temperature, a temperature-compensated dimension, A_T , differs from the sum of temperature-compensated dimensions B_T and C_T at the selected temperature by an absolute value of less than about 0.002 inch. Typically, this difference is within the compliance tolerance that can be achieved by commercially-available compliant sealing elements such as, for example, C-rings and O-rings.

[0076] The temperature-compensated dimensions A_T , B_T , and C_T at any selected temperature are defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R) \quad (1)$$

$$B_T = B_R(\alpha_B)(T - T_R) \quad (2)$$

$$C_T = C_R(\alpha_C)(T - T_R) \quad (3)$$

where T is the selected temperature, T_R is the reference temperature, α_A is the coefficient of thermal expansion of the material of connecting segment 5 of the clamping element, α_B is the coefficient of thermal expansion of the material of compensating spacer element 9, α_C is the coefficient of thermal expansion of the material of second seal element 11, and $A_R = B_R + C_R$.

[0077] The reference dimensions of compensating spacer element 9 (B_R) and seal element 11 (C_R), and the materials of compensating spacer element 9, second seal element 11, and connecting segment 5, are initially selected when the seal

assembly is designed such that, at any selected temperature, dimensions of the seal assembly are described by the equation

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch} \quad (4)$$

[0078] The seal assembly components are assembled at the reference temperature (typically ambient temperature) and an initial axial loading is placed on compensating spacer element 9, second seal element 11, and compliant sealing member(s) or spring-type member(s), if used, by the clamping element. This initial clamping force may be provided, for example, by set screws or threaded studs and bolts for attaching segment 3 and/or second segment 7 to connecting segment 5. Other known methods of generating axial clamping or compression forces may be used. When the coefficients and initial dimensions of the seal components are properly selected as described above, the initial axial loading of the seal assembly will be sufficient after heating such that sealing is maintained by the components of the sealing assembly at elevated temperatures.

[0079] The working seal or seals of the seal assembly may be provided at any of interfacial zones 17, 19, and 21. A working seal is an element that provides the actual sealing contact between the two adjacent surfaces to minimize or eliminate gas leakage across the seal assembly. A working seal may be formed by an interface between carefully machined mating surfaces or at an interfacial zone by commercially-available compliant sealing elements such as, for example, C-rings and O-rings. The location of the working seal or seals will depend on the actual configuration of the seal assembly and the relative pressure differential across the seal assembly. The seal assembly may be attached to the piping or vessel systems that are sealably connected in any desired configuration as illustrated below. In FIG. 1, any of first segment 3, second segment 7, and second seal element 11 may be attached to the piping or vessel systems being sealably connected by the seal assembly. Typically, compensating spacer element 9 is independent of and not attached to the piping or vessel systems being sealably connected.

[0080] The generic seal assembly may be utilized in the embodiment illustrated in FIG. 2. Seal assembly 201 is a toroidal assembly comprising a clamping element having first clamp segment or ring 203, clamp connecting segment 205, and second clamp segment 207; first seal element or compensating spacer element 209; and intermediate seal element 211. In this embodiment, clamp connecting segment 205 and second clamp segment 207 comprise a single piece of material forming a second ring of the clamping element. Intermediate seal element 211 forms a flange portion of cylindrical pipe or vessel 213 and is made of the same material. Clamp connecting segment 205, first seal element or compensating spacer element 209, and intermediate seal element 211 are made of different materials.

[0081] First clamp segment or ring 203 is removably attached to clamp connecting segment 205 by set screws 215. The set screws typically are made of the same material as clamp connecting segment 205, and ring 203 may be made of the same material as set screws 215 and clamp connecting segment 205. Alternatively, any other known type of fastening devices may be used. For example, threaded studs may be screwed into clamp connecting segment 205 and extend through stud holes in first clamp segment or ring 203, and bolts may be placed on the studs and tightened to connect first clamp segment or ring 203 to clamp connecting segment 205 and generate axial clamping forces on the seal assembly.

[0082] Hole 219 extends through second clamp segment 207 and may be utilized to connect a second pipe or vessel (not shown) via a threaded or welded connection so that seal element 201 provides an operating seal between the second pipe or vessel and pipe or vessel 213. Alternatively, second clamp segment 207 may have no hole and thus would serve as a cap to seal cylindrical pipe or vessel 213.

[0083] The clamping element urges first clamp segment or ring 203 into forcible contact with compliant seal member 221, thereby urging compliant seal member 221 into forcible sealing contact with compensating spacer element 209 at interfacial zone 217 and second clamp segment 207 into forcible sealing contact with intermediate seal element 211 at interfacial zone 223. Compliant seal member 221 may be, for example, a suitable commercially-available compliant gasket, O-ring, C-ring, or other sealing device. For example, Metal C-Rings or Metal O-Rings manufactured by Advanced Products Company, Inc., may be used in this service. Compensating spacer element 209 and intermediate seal element 211 are urged into forcible contact at interfacial zone 223 to place an axial load on compliant seal member 221.

[0084] Clamp connecting segment 205 is characterized by dimension D, which lies between the plane formed by the surface of first clamp segment or ring 203 at interfacial zone 217 and the plane formed by the surface of second clamp segment 207 at interfacial zone 223. Compensating spacer element 209 is characterized by dimension B, which is the orthogonal or axial distance between the plane formed by the surface of the compensating spacer element at interfacial zone 217 and the plane formed by the surface of the compensating spacer element at interfacial zone 225. Second seal element 211 is characterized by dimension C, which is the orthogonal or axial distance between the plane formed by the surface of second seal element 211 at interfacial zone 225 and the plane formed by the surface of the second seal element at interfacial zone 223.

[0085] Interfacial zone 217 includes compliant sealing member 221 to provide sealing force for seal assembly 201. Alternatively, interfacial zone 217 may be an interface formed by contact between flat surfaces on first segment 203 and compensating spacer element 209. Interfacial zone 223 may be an interface formed by contact between flat surfaces on second segment 207 and second seal element 211. Alternatively, interfacial zone 223 may contain an intermediate member (not shown) such as a compliant sealing member. Interfacial zone 225 is an interface formed by contact between flat surfaces on compensating spacer element 209 and second seal element 211.

[0086] As described above, dimension A is the sum of dimensions B and C. Dimension A is equivalent to the portion of connecting segment 205 that lies between the plane formed by the surface of compensating spacer element 209 at interfacial zone 217 and the plane formed by the surface of second seal element 211 at interfacial zone 223. Dimension D is the distance between the faces of the clamping element at interfaces 217 and 223. In this embodiment, dimension D differs from dimension A by the height of compliant sealing member 221.

[0087] Seal assembly 201 is designed by selecting the materials and reference dimensions of the components of the assembly. In particular, the reference dimensions of compensating spacer element 209 (B_R) and seal element 211 (C_R), and the materials of compensating spacer element 209, second seal element 211, and connecting segment 205, are prop-

erly selected. The coefficient of thermal expansion of connecting segment 205 is intermediate the coefficients of thermal expansion of compensating spacer element 209 and second seal element 211. The seal components are assembled at ambient conditions and an initial axial compressive force is applied by the clamping element. The completed seal assembly then is changed, for example by heating, to a selected temperature, T. As a result of the proper selection of the parameters defined above, the temperature-compensated dimension A_T differs from the sum of the temperature-compensated dimensions B_T and C_T at the selected temperature by an absolute value of less than about 0.002 inch as defined in equation (4) above.

[0088] In an alternative embodiment of FIG. 2, a flat compliant seal gasket may be used at interface 223 instead of compliant sealing member 221. In addition, a spring-type compression ring (not shown) may be installed at interface 217 to maintain the axial load on the seal assembly and to compensate for the small differences in the seal element dimensions that may occur when the seal element is heated. A circular groove may be cut in the face of second seal element or flange 211 at interfacial zone 223 to contain this compression ring.

[0089] In another alternative embodiment of FIG. 2, compensating spacer element 209 is eliminated. Clamp connecting segment 205 is made of a first material. First clamp segment or ring 203, clamp connecting segment 205, and second clamp segment 207 all may be made of the same first material. Second seal element or flange 211 is made of a second material. In this alternative, the coefficient of thermal expansion of the first material of clamp connecting segment 205 is less than the coefficient of thermal expansion of the second material of second seal element or flange 211.

[0090] In this alternative embodiment, a dimension C' is defined as the distance at interface 223 between second clamp segment 207 and second seal element or flange 211. At a reference temperature and after the seal assembly is assembled and axial force is applied to compress compliant sealing member 221, the distance at interface 223 between second clamp segment 207 and second seal element or flange 211 is the reference distance C'_R . Another parameter, A' , is defined as the sum of dimensions C and C' . In this alternative, the first material, the second material, the dimension C of second seal element or flange 211 at the reference temperature (i.e., C_R), and the dimension C' at the reference temperature (i.e., C'_R) are selected in the design of the seal element so that at any selected temperature

$$|A_T - C_T| \leq 0.002 \text{ inch} \quad (5)$$

where the temperature-compensated dimensions A_T and C_T at any selected temperature are defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R) \quad (6)$$

$$C_T = C_R(\alpha_C)(T - T_R) \quad (7)$$

where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material; α_C is the coefficient of thermal expansion of the second material; $\alpha_A < \alpha_C$; and $A_R = C_R + C'_R$.

[0091] While this alternative embodiment has fewer design parameters and is more limited in material selection than the previous embodiment of FIG. 2, there may be scenarios in which the design features of this alternative seal assembly are desirable.

[0092] The generic seal assembly of FIG. 1 may be applied to an alternative embodiment illustrated in FIG. 3. In this embodiment, seal assembly 301 is formed between flanged cylindrical pipes or vessels 303 and 305. The seal assembly utilizes a toroidal clamp element comprising first clamp segment 307, second clamp segment 309 opposite first clamp segment 307, and connecting segment 311 between clamp segments 307 and 309. The clamping element may be fabricated as a split ring to enable installation around the flanges. Axial clamping force may be applied by bolts 313.

[0093] Compensating spacer ring 315 is disposed between flange 317 of pipe 303 and flange 319 of pipe 305. Compliant seal ring 321 is disposed between compensating spacer ring 315 and flange 317, and compliant seal ring 323 is disposed between compensating spacer ring 315 and flange 319. Flanges 371 and 319 are integral parts of flanged pipes or vessels 303 and 305, respectively. Grooves (not shown) may be cut into the faces of compensating spacer ring 315 to locate and contain the compliant seal rings. Alternatively or additionally, grooves (not shown) may be cut into the faces of flange 317 and/or flange 319 to locate and contain the compliant seal rings. The compliant sealing rings may be, for example, suitable commercially-available compliant gaskets, O-rings, C-rings, or other sealing devices. For example, Metal C-Rings or Metal O-Rings manufactured by Advanced Products Company, Inc., may be used in this service.

[0094] The thickness of flange 317 is characterized by the dimension C1, the thickness of flange 319 is characterized by the dimension C2, and the dimension of compensating spacer ring 315 is characterized by the dimension B. The distance between opposing faces of clamp element 307 and clamp element 309 is D. The sum of C1, C2, and B differs from D by the sum of the distances between compensating spacer ring 315 and flanges 317 and 319.

[0095] Flanged cylindrical pipe 303 (including flange 321), flanged cylindrical pipe 305 (including flange 323), and compensating spacer ring 315 are made of different materials. First clamp element 307, second clamp element 309, and connecting element 311 form a single piece (the clamping element) and are made of a common material. Bolts 313 typically are made of the same material as the parts of the clamping element.

[0096] In one embodiment, flanged cylindrical pipe 303, the components of the clamp element, and bolts 313 are made of a first material; compensating spacer ring 315 is made of a second material; and flanged cylindrical pipe 305 is made of a third material. In this embodiment, the first material, the second material, the third material, the dimension B of compensating spacer ring 315 at a reference temperature (i.e., B_R), and the dimension C2 of flange 319 at the reference temperature (i.e., $C2_R$), are selected in the design of the seal element so that at any selected temperature

$$|A_T - (B_T + C2_T)| \leq 0.002 \text{ inch} \quad (8)$$

where the temperature-compensated dimensions A_T , B_T , and $C2_T$ at any selected temperature are defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R) \quad (9)$$

$$B_T = B_R(\alpha_B)(T - T_R) \quad (10)$$

$$C2_T = C2_R(\alpha_C)(T - T_R) \quad (11)$$

where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material of flanged cylindrical pipe 305 (including flange

321) and the clamp element (including connecting element 311 and bolts 313); α_B is the coefficient of thermal expansion of the second material of compensating spacer ring 315; α_C is the coefficient of thermal expansion of the third material of flanged cylindrical pipe 305 (including flange 309); and $A_R = B_R + C2_R$. The coefficient of thermal expansion of the first material typically is intermediate the coefficients of thermal expansion of the second and third materials.

[0097] In another embodiment, flanged cylindrical pipe 303 (including flange 321) is made of a first material, the components of the clamp element (including connecting element 311 and bolts 313) are made of a second material; flanged cylindrical pipe 305 (including flange 323) is made of a third material; and compensating spacer ring 315 is made of a fourth material.

[0098] In this embodiment, the first material, the second material, the third material, the fourth material, the dimension B of compensating spacer ring 315 at a reference temperature (i.e., B_R), the dimension C1 of flange 317 at the reference temperature (i.e., $C1_R$), and the dimension C2 of flange 319 at the reference temperature (i.e., $C2_R$), are selected in the design of the seal element so that at any selected temperature

$$|A_T - (B_T + C1_T + C2_T)| \leq 0.002 \text{ inch} \quad (12)$$

where the temperature-compensated dimensions A_T , B_T , and $C2_T$ at any selected temperature are defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R) \quad (13)$$

$$B_T = B_R(\alpha_B)(T - T_R) \quad (14)$$

$$C1_T = C1_R(\alpha_{C1})(T - T_R) \quad (15)$$

$$C2_T = C2_R(\alpha_{C2})(T - T_R) \quad (16)$$

where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material of flanged cylindrical pipe 303, the components of the clamp element, and bolts 313; α_B is the coefficient of thermal expansion of the second material of compensating spacer ring 315; α_{C1} is the coefficient of thermal expansion of the third material of flanged cylindrical pipe 303; α_{C2} is the coefficient of thermal expansion of the fourth material of flanged cylindrical pipe 305; and $A_R = B_R + C1_R + C2_R$. The coefficient of thermal expansion of the first material (the clamp element including connecting element 311 and bolts 313) is intermediate the highest and lowest of the coefficients of thermal expansion of the second material (compensating spacer ring 315), the third material (flanged cylindrical pipe 303 including flange 321), and the fourth material (flanged cylindrical pipe 305 including flange 323).

[0099] While this embodiment with four different materials requires a more complicated design procedure than the previous embodiment with three different materials, the designs of the embodiments utilize the same generic principle described above with reference to FIGS. 1 and 2. In any of the alternatives in the embodiments of FIG. 3, the clamp element of FIG. 2 may be used instead of the clamp element shown in FIG. 3.

[0100] Another embodiment is illustrated in FIG. 4 using an alternative method for applying axial force to the seal elements. In this embodiment, flanged pipe or vessel 401 is sealed to threaded pipe or vessel 403 by threaded clamp assembly 405. The threaded clamp assembly has a toroidal shape and comprises first clamp element 407, threaded clamp element 409, and connecting element 411 between first clamp

element **407** and threaded clamp element **409**. Threaded pipe or vessel **403** has threaded section **413** that engages the threads on threaded clamp element **409** and non-threaded extension **415** that extends beyond the threaded section.

[0101] The inner diameter of first clamp element **407** is greater than the outer diameter of the body section of flanged pipe or vessel **401** and the inner diameter of connecting element **411** is greater than the outer diameter of flange **417** of flanged pipe or vessel **401**. The inner diameter of the threaded section of threaded clamp element **409** is also greater than the outer diameter of flange **417** of flanged pipe or vessel **401**. The working seal is formed at interface **418** between the face of non-threaded extension **415** and the face of flange **417** and is provided by compliant seal ring **419**. Grooves (not shown) may be cut into the face of non-threaded extension **415** and/or the face of flange to locate and contain the compliant seal ring. The compliant sealing ring may be, for example, a suitable commercially-available compliant gasket, O-ring, C-ring, or other sealing device. For example, Metal C-Rings or Metal O-Rings manufactured by Advanced Products Company, Inc., may be used in this service. Axial clamping force is applied to press the faces of non-threaded extension **415** and flange **417** together against compliant seal ring **419** by turning the threaded clamp assembly to engage and move the threads on threaded pipe or vessel **403** and threaded clamp element **409**. The length of non-threaded extension **415** is characterized by dimension B and the thickness of flange **417** is characterized by the dimension C.

[0102] In this embodiment, threaded clamp assembly **405** (including connecting element **411**) is made of a first material, non-threaded extension **415** is made of a second material, and flanged pipe or vessel **401** and flange **417** is made of a third material. The first material, the second material, the third material, the dimension C of flange **417** at a reference temperature (i.e., C_R), and the dimension B of non-threaded extension **415** at the reference temperature (i.e., B_R), are selected in the design of the seal element so that at any selected temperature

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch} \quad (17)$$

where the temperature-compensated dimensions A_T , B_T , and C_T at any selected temperature are defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R) \quad (18)$$

$$B_T = B_R(\alpha_B)(T - T_R) \quad (19)$$

$$C_T = C_R(\alpha_C)(T - T_R) \quad (20)$$

where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material α_B is the coefficient of thermal expansion of the second material of flange **417**; and $A_R = B_R + C_R$. The coefficient of thermal expansion of the first material is intermediate the coefficients of thermal expansion of the second and third materials. The coefficient of thermal expansion of the first material may be less than the coefficient of thermal expansion of the second material.

[0103] In an alternative of this embodiment, threaded clamp assembly **405** (including connecting element **411**) and non-threaded extension **415** are made of a first material, and flanged pipe or vessel **401** (including flange **417**) is made of a second material. Pipe **403** including the threaded section may be the same material as threaded clamp assembly **405** (including connecting element **411**); alternatively, pipe **403** including the threaded section may be a different material than

threaded clamp assembly **405** (including connecting element **411**). In this alternative, the first material, the second material, the dimension C of flange **417** at a reference temperature (i.e., C_R), and a dimension C' at a reference temperature (i.e., C'_R) are selected in the design of the seal element so that at any selected temperature

$$|A_T - C_T| \geq 0.002 \text{ inch} \quad (21)$$

where the temperature-compensated dimensions A_T and C_T at any selected temperature are defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R) \quad (22)$$

$$C_T = C_R(\alpha_C)(T - T_R) \quad (23)$$

where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material; α_C is the coefficient of thermal expansion of the second material; and $A_R = C_R + C'_R$.

[0104] The dimension C' is defined as the distance between the face of non-threaded extension **415** and the face of flange **417** at interface **418**. When the seal assembly is assembled at the reference temperature, an initial axial load is placed on compliant seal ring **419** to slightly compress the ring. The distance between the face of non-threaded extension **415** and the face of flange **417** at interface **418** at the reference temperature then is the dimension C'_R . In this alternative, the coefficient of thermal expansion of the first material (threaded clamp assembly **405** including connecting element **411**) is less than the coefficient of thermal expansion of the second material (flange **417**).

[0105] In any the embodiments described above, components of the seal assembly may be metal and/or ceramic. In one embodiment, all components of the seal assembly may be metal, and the seal assembly may be used to seal two pipes or vessels made of different metals. Alternatively, the components of the seal assembly may be metal and ceramic, and the seal assembly may be used to seal a metal pipe or vessel to a ceramic pipe or vessel. In another alternative, the components of the seal assembly may be metal, and the seal assembly may be used to seal two ceramic pipes or vessels having different coefficients of thermal expansion. Exemplary metals that can be used for seal elements include Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels. Exemplary ceramic materials that can be used for seal elements include, but are not limited to, aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, and mixed metal perovskites including $(\text{La}_x\text{Sr}_{1-x})_z\text{CoO}_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral) and $(\text{La}_x\text{Ca}_{1-x})_z\text{FeO}_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral).

EXAMPLE 1

[0106] A ceramic-to-metal seal was developed for a ceramic material, $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-z}$, where the metallic clamping element was Haynes 230 and the compensating metallic spacer element was Incoloy 800H. The seal utilized a configuration similar to that of FIG. 2, except that a compliant gasket was used at interface **223** and a compressive

compliant ring was installed at interface 217 in a circular groove in first clamp segment or ring 203. The thermal expansion behavior on a unit length basis as a function of temperature for the three materials is given in Table 1.

TABLE 1

Thermal Expansion Behavior of Component Materials			
Thermal Expansion (Thermal strain expressed as $\Delta\text{length}/\text{length}$ in parts per million)			
Temperature, ° C.	Clamping element (Haynes 230)	Compensating element (Incoloy 800H)	Ceramic element ($\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-z}$)
0	0	0	0
100	982.5	1152	671
200	2327.5	2862	1638
300	3740	4536	2720
400	5287.5	6270	3891
500	6935	8064	5031
600	8740	9918	6151
700	10665	11900	7298

[0107] Using these expansion characteristics, the reference dimensions A_R , B_R , and C_R were selected so that the temperature-compensated dimensions satisfied equation (4) given above. The results are given in Table 2.

TABLE 2

Dimensions for Matched Length of Components (See FIG. 2)				
Temperature, ° C.	A Length of clamping element, in.	B Length of ceramic element, in.	C Length of compensating element, in.	A - (B + C) Net differential displacement, in.
Ambient	1.035	0.45	0.585	0
100	1.03598584	0.450302	0.58567392	9.97×10^{-6}
200	1.03735463	0.450737	0.58667427	-5.7×10^{-5}
300	1.03878551	0.451224	0.58765356	-9.2×10^{-5}
400	1.04031731	0.451751	0.58866795	-1.0×10^{-4}
500	1.04188275	0.452264	0.58971744	-9.9×10^{-5}
600	1.0435698	0.452768	0.59080203	-1.8×10^{-7}
700	1.04533965	0.453284	0.5919615	9.4×10^{-5}

[0108] In Table 2, the values of A, B, and C at ambient temperature are the reference dimensions A_R , B_R , and C_R , respectively. The values of A, B, and C at above-ambient temperature are the temperature-compensated dimensions A_T , B_T , and C_T , respectively.

[0109] As can be seen, the net differential displacement as defined by equation (4) never exceeds one ten thousandth of an inch, which is well within the dimensional compensating ability of commercial compliant elements such as metallic C-rings or O-rings.

EXAMPLE 2

[0110] A ceramic-to-metal seal was developed for for a ceramic material, $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-z}$, where the metallic clamping element was Inconel 600 and the compensating metallic spacer element was Haynes 230. The configuration of the seal assembly was identical to that of Example 1. The thermal expansion behavior on a unit length basis as a function of temperature for the three materials is given in Table 3.

TABLE 3

Thermal Expansion Behavior of Component Materials			
Thermal Expansion (thermal strain expressed as $\Delta\text{length}/\text{length}$ in parts per million)			
Temperature, ° C.	Clamping element (Inconel 600)	Compensating element (Haynes 230)	Ceramic element ($\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-z}$)
0	0	0	0
100	1064	982.5	1195
200	2484	2327.5	2818
300	3976	3740	4577
400	5510	5287.5	6453
500	7152	6935	8673
600	8874	8740	11351
700	10744	10665	14325

[0111] Using these expansion characteristics, the reference dimensions A_R , B_R , and C_R were selected so that the temperature-compensated dimensions satisfied equation (4) given above. The results are given in Table 4.

TABLE 4

Dimensions for Matched Length of Components (See FIG. 2)				
Temperature, ° C.	A Length of clamping element, in.	B Length of ceramic element, in.	C Length of compensating element, in.	A - (B + C) Net differential displacement, in.
Ambient	0.585	0.4	0.185	0
100	0.58562244	0.400490531	0.185176213	-0.000044
200	0.58645314	0.401153411	0.185420875	-0.000121
300	0.58732596	0.401816291	0.185676638	-0.000167
400	0.58822335	0.402472501	0.185950438	-0.000200
500	0.58918392	0.403129174	0.18623025	-0.000176
600	0.59019129	0.403784558	0.18653180	-0.000125
700	0.59128524	0.404439112	0.18684815	-0.000002

[0112] In Table 4, the values of A, B, and C at ambient temperature are the reference dimensions A_R , B_R , and C_R , respectively. The values of A, B, and C at above-ambient temperature are the temperature-compensated dimensions A_T , B_T , and C_T , respectively.

[0113] As can be seen, the net differential displacement as defined by equation (4) never exceeds two ten thousandths of an inch, which is well within the dimensional compensating ability of commercial compliant elements such as metallic C-rings or O-rings.

1. A seal assembly comprising

- two or more seal elements, each element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the seal elements are stacked such that adjacent faces are parallel and the axes are parallel or coincident, and wherein each of the seal elements is made of a material having a coefficient of thermal expansion; and
- a clamping element having a first segment, a second segment, and a connecting segment between and attached to the first and second segments, wherein the two or more seal elements are disposed between the first and second segments of the clamping element and the clamping element is adapted to exert axial clamping forces on the two or more seal elements, wherein the connecting segment has a central portion extending between a plane formed by the face of a seal element adjacent the first segment of the clamping element and a plane formed by the face of a seal element adjacent the

second segment of the clamping element, and wherein the connecting segment is made of a material having a coefficient of thermal expansion;

wherein the coefficient of thermal expansion of the material of the connecting segment is intermediate the largest and smallest of the coefficients of thermal expansion of the materials of the two or more seal elements.

2. The seal assembly of claim 1 further comprising a compliant sealing member disposed at any interfacial zone between adjacent seal elements and between a segment of the clamping element and an adjacent seal element.

3. A seal assembly comprising

(a) a first seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;

(b) a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the first seal element is made of a first material having a first coefficient of thermal expansion, and wherein the first face of the second seal element is in forcible contact with the second face of the first seal element; and

(c) a clamping element adapted to urge the first seal element axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the first seal element, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the first face of the first seal element and the second face of the second seal element, is generally parallel to the axes of the first and second seal elements, and is made of a third material having a third coefficient of thermal expansion;

wherein the third coefficient of thermal expansion is intermediate the first and second coefficients of thermal expansion.

4. The seal assembly of claim 3 wherein either of the first segment of the clamping element and the second segment of the clamping element is permanently attached to the connecting segment of the clamping element.

5. The seal assembly of claim 3 wherein either of the first segment of the clamping element and the second segment of the clamping element is removably attached to the connecting segment of the clamping element.

6. The seal assembly of claim 3 wherein the first material is selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

7. The seal assembly of claim 3 wherein the second material is selected from the group consisting of aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, mixed metal perovskites, $(\text{La}_x\text{Sr}_{1-x})_y\text{CoO}_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral), and $(\text{La}_x\text{Ca}_{1-x})_y\text{FeO}_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral).

8. The seal assembly of claim 3 wherein the third material is selected from the group consisting of Haynes 230, Haynes

188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

9. The seal assembly of claim 3 wherein the second seal element consists of a first subcomponent and a second subcomponent, each subcomponent having first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the first face of the first subcomponent is the first face of the second seal element, wherein the second face of the second subcomponent is the second face of the second seal element that is in forcible contact with the second segment of the clamping element.

10. The seal assembly of claim 9 wherein either of the first segment of the clamping element and the second segment of the clamping element is removably attached to the connecting segment of the clamping element.

11. The seal assembly of claim 3 further comprising a compliant sealing member disposed between the second segment of the clamping element and the second face of the second seal element.

12. The seal assembly of claim 3 further comprising a compliant sealing member disposed between the first segment of the clamping element and the first face of the first seal element.

13. The seal assembly of claim 3 wherein

(1) the second seal element is a flange attached to a first cylindrical pipe having an outer diameter, wherein the flange has an outer diameter;

(2) the clamping element comprises a torroidal body having a first ring that forms the first segment of the clamping element and has an inner and an outer diameter, a second ring that forms the connecting segment of the clamping element and has an inner and an outer diameter, and a third ring that forms the second segment of the clamping element and has an inner and an outer diameter;

(3) the first seal element is a compensating spacer ring having an inner and an outer diameter;

(4) the inner diameter of the first ring that forms the first segment of the clamping element is greater than the outer diameter of the first cylindrical pipe;

(5) the inner diameter of the compensating spacer ring is greater than the outer diameter of the first cylindrical pipe and the outer diameter of the compensating spacer ring is less than the inner diameter of the second ring that forms the connecting segment of the clamping element; and

(6) the outer diameter of the flange is less than the inner diameter of the second ring that forms the connecting segment of the clamping element.

14. The seal assembly of claim 13 wherein the flange and first cylindrical pipe are made of ceramic material, the clamping element is a metallic material, and the compensating spacer ring is a metallic material.

15. The seal assembly of claim 14 wherein the first material is selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

16. The seal assembly of claim 14 wherein the second material is selected from the group consisting of aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, mixed metal perovskites, $(\text{La}_x\text{Sr}_{1-x})_y\text{CoO}_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \geq y > 1.0$, and z is

a number which renders the composition of matter charge neutral), and $(La_xCa_{1-x})_yFeO_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral).

17. The seal assembly of claim 14 wherein the third material is selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

18. A seal assembly comprising

- (a) a first seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element has a first reference dimension defined by the axial distance between the first and second faces at a reference temperature, and wherein the first seal element is made of a first material having a first coefficient of thermal expansion;
- (b) a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the second seal element has a second reference dimension defined by the axial distance between the first and second faces at the reference temperature, wherein the first seal element is made of a first material having a first coefficient of thermal expansion, and wherein the first face of the second seal element is in contact with the second face of the first seal element; and
- (c) a clamping element adapted to urge the first seal element axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the first seal element, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the first face of the first seal element and the second face of the second seal element and is generally parallel to the axes of the first and second seal elements, and wherein the central portion is made of a third material having a third coefficient of thermal expansion;

wherein the first material, the reference thickness of the first seal element, the second material, the reference thickness of the second seal element, and the third material have values such that, at any selected temperature,

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch}$$

where

$$A_T = A_R(\alpha_A)(T - T_R),$$

$$B_T = B_R(\alpha_B)(T - T_R), \text{ and}$$

$$C_T = C_R(\alpha_C)(T - T_R),$$

and where T is the selected temperature, T_R is the reference temperature, A_R is the first reference dimension, B_R is the second reference dimension, A_R is the sum of B_R and C_R , α_A is the coefficient of thermal expansion of the a first material, α_B is the coefficient of thermal expansion of the second material, and α_C is the coefficient of thermal expansion of the third material.

19. A ceramic-to-metal seal assembly comprising

- (a) a toroidal compensating spacer ring having a first face, a second face generally parallel to the first face, an inner

diameter, an outer diameter, and an axis orthogonal to the first and second faces, wherein toroidal compensating spacer ring is made of a first metal having a first coefficient of thermal expansion;

- (b) a cylindrical ceramic tube having an inner diameter, an outer diameter, and a ceramic flange formed at an end of the cylindrical ceramic tube, the ceramic flange having an outer diameter, wherein

- (1) the inner diameter of the toroidal compensating spacer ring is greater than the outer diameter of the cylindrical ceramic tube and is disposed around the ceramic tube,

- (2) the ceramic flange forms a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the toroidal compensating spacer ring,

- (3) the first face of the second seal element is in forcible contact with the second face of the toroidal compensating spacer ring, and

- (4) the ceramic flange is made of a ceramic material having a second coefficient of thermal expansion; and

- (c) a toroidal clamping element adapted to urge the toroidal compensating spacer ring axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the toroidal compensating spacer ring, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment (1) has a central portion extending between planes formed by the first face of the toroidal compensating spacer ring and the second face of the second seal element, (2) is generally parallel to the axes of the toroidal compensating spacer ring and the second seal element, and (3) is made of a second metal having a third coefficient of thermal expansion;

wherein the third coefficient of thermal expansion is intermediate the first and second coefficients of thermal expansion.

20. The ceramic-to-metal seal assembly of claim 19 wherein the first metal is selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

21. The ceramic-to-metal seal assembly of claim 19 wherein the second metal is selected from the group consisting of Haynes 230, Haynes 188, Haynes 214, Incoloy 800H, Inconel 600, Inconel 625, Inconel 693, and 400-Series Stainless Steels.

22. The ceramic-to-metal seal assembly of claim 19 wherein the ceramic flange is made of a material selected from the group consisting of aluminum oxide, zirconium oxide, cerium oxide, magnesium oxide, silicon carbide, silicon nitride, mixed metal perovskites, $(La_xSr_{1-x})_yCoO_{3-z}$ (wherein $1.0 < x < 0.4$, $1.02 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral), and $(LaCa_{1-x})_yFeO_{3-z}$ (wherein $1.0 > x > 0.5$, $1.1 \geq y > 1.0$, and z is a number which renders the composition of matter charge neutral).

23. The ceramic-to-metal seal assembly of claim 19 wherein the ceramic tube is made of the same material as the ceramic flange, and wherein the ceramic tube and the ceramic flange form an integrated flanged ceramic tube.

24. A seal assembly comprising

- (a) a seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;
- (b) a compliant sealing member adjacent the second face of the seal element;
- (c) a clamping element having a first segment with a face in forcible contact with the first face of the seal element, a second segment having a face in forcible contact with the compliant seal member, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the face of the first segment and the face of the second segment, is generally parallel to the axis of the seal element, and is made of a second material having a second coefficient of thermal expansion, and wherein the a clamping element is adapted to urge the seal element axially toward the face of the second segment of the clamping element to compress the compliant seal member;

wherein the first coefficient of thermal expansion is greater than the second coefficient of thermal expansion.

25. A method of making and operating a seal assembly comprising

- (a) providing at a temperature equal to a reference temperature a seal assembly comprising
 - (1) a first seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;
 - (2) a second seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces that is parallel with or coincident with the axis of the first seal element, wherein the second seal element is made of a second material having a second coefficient of thermal expansion, and wherein the first face of the second seal element is in forcible contact with the second face of the first seal element; and
 - (3) a clamping element adapted to urge the first seal element axially toward the second seal element, wherein the clamping element has a first segment in forcible contact with the first face of the first seal element, a second segment in forcible contact with the second face of the second seal element, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the first face of the first seal element and the second face of the second seal element, is generally parallel to the axes of the first and second seal elements, and is made of a third material having a third coefficient of thermal expansion;
- (b) changing the temperature of the seal assembly to a selected temperature different than the reference temperature; and
- (c) maintaining the seal assembly at the selected temperature such that

$$|A_T - (B_T + C_T)| \leq 0.002 \text{ inch}$$

where A_T , B_T , and C_T are temperature-compensated dimensions defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R),$$

$$B_T = B_R(\alpha_B)(T - T_R), \text{ and}$$

$$C_T = C_R(\alpha_C)(T - T_R),$$

and where T is the selected temperature; T_R is the reference temperature; B_R is the axial distance between the faces of the first seal element at the reference temperature; C_R is the axial distance between the faces of the second seal element at the reference temperature; α_A is the coefficient of thermal expansion of the first material; α_B is the coefficient of thermal expansion of the second material; α_C is the coefficient of thermal expansion of the third material; and $A_R = B_R + C_R$.

26. A method of making and operating a seal assembly comprising

- (a) providing at a temperature equal to a reference temperature a seal assembly comprising
 - (1) a seal element having a first face, a second face generally parallel to the first face, and an axis orthogonal to the first and second faces, wherein the first seal element is made of a first material having a first coefficient of thermal expansion;
 - (2) a compliant sealing member adjacent the second face of the seal element;
 - (3) a clamping element having a first segment with a face in forcible contact with the first face of the seal element, a second segment having a face in forcible contact with the compliant seal member, and a connecting segment between and attached to the first and second segments, wherein the connecting segment has a central portion extending between planes formed by the face of the first segment and the face of the second segment, is generally parallel to the axis of the seal element, and is made of a second material having a second coefficient of thermal expansion, and wherein the a clamping element is adapted to urge the seal element axially toward the face of the second segment of the clamping element to compress the compliant seal member;
- (b) changing the temperature of the seal assembly to a selected temperature different than the reference temperature; and
- (c) maintaining the seal assembly at the selected temperature such that

$$|A_T - C_T| \leq 0.002 \text{ inch}$$

where A_T and C_T are temperature-compensated dimensions defined by the equations

$$A_T = A_R(\alpha_A)(T - T_R)$$

$$C_T = C_R(\alpha_C)(T - T_R)$$

where T is the selected temperature; T_R is the reference temperature; α_A is the coefficient of thermal expansion of the first material; α_C is the coefficient of thermal expansion of the second material; C_R is the axial distance between the first face and the second face of the seal element at the reference temperature; C'_R is the axial distance between the second face of the seal element and the face of the second segment of the clamping element at the reference temperature; and $A_R = C_R + C'_R$.

* * * * *

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PA (US)(21) Appl. No.: **11/838,477**(22) Filed: **Aug. 14, 2007****Related U.S. Application Data**(63) Continuation-in-part of application No. 11/028,124,
filed on Jan. 3, 2005.(57) **ABSTRACT**

Ion transport membrane system comprising (a) a pressure vessel comprising an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit; (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules; (c) a gas manifold having an interior surface wherein the gas manifold is in flow communication with the interior region of each of the planar ion transport membrane modules and with the exterior of the pressure vessel; and (d) a liner disposed within any of the inlet conduit, the outlet conduit, and the interior surface of the gas manifold.

FIG. 1

FIG. 2B

FIG. 2A

FIG. 3C

FIG. 3D

FIG. 4A

FIG. 4B

FIG. 5

FIG. 7

FIG. 6

FIG. 9

$$\frac{F}{G} \infty$$

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

FIG. 15

FIG. 16

FIG. 17

FIG. 18

FIG. 19

FIG. 20

FIG. 21

FIG. 22

FIG. 23

FIG. 24

LINERS FOR ION TRANSPORT MEMBRANE SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation-in-Part of U.S. patent application Ser. No. 11/028,124, filed on Jan. 3, 2005, the specification and claims of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with Government support under DOE Cooperative Agreement No. DE-FC26-97FT96052 between Air Products and Chemicals, Inc., and the U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0003] Ceramic membranes containing certain multicomponent metallic oxide compositions demonstrate mixed conducting (i.e., oxygen ion conductivity and electronic conductivity) at elevated temperatures. These compositions used in these ceramic membranes, known in the art as mixed conducting multicomponent metallic oxides, may be employed in ion transport membranes and ion transport membrane systems for use in gas separation applications and partial oxidation applications.

[0004] Oxygen stoichiometry of these mixed conducting multicomponent metallic oxides is a thermodynamic function of temperature and oxygen partial pressure wherein the equilibrium oxygen stoichiometry decreases with increasing temperature and with decreasing oxygen partial pressure. The materials are chosen to provide high rates of oxygen transport and thermodynamic stability under process conditions.

[0005] The structural components of ion transport membrane systems are typically fabricated from metal alloys that may contain chromium, silicon, tungsten and/or molybdenum; and oxides of each of these elements. Contaminants including vaporized species such as CrO_3 , $\text{CrO}_2(\text{OH})_2$, $\text{Si}(\text{OH})_4$, and $\text{WO}_2(\text{OH})_2$ are known to evolve from hot metallurgy under oxidizing and steam environments at elevated temperatures. These contaminants may adversely react with or deposit onto apparatus used in systems employing ion transport membranes. Such species are believed to be generated by the following reactions:

[0006] Vaporized species such as chromium-containing species are known to evolve from the interconnects of solid oxide fuel cells (SOFCs) and react with the perovskite cathode material used in such SOFCs (Steel Research 72 (2001) 11, 528-533; Proceedings-Electrochemical Society (2001), 2001-16 (Solid Oxide Fuel Cells VII), 793-802; US 2003/0096147 A1) resulting in diminished cell performance over time. The SOFC field teaches that interconnects may be coated to prevent chromium from vaporizing and subsequently reacting with the perovskite cathode material used in

such SOFCs. Such coatings must stay intact through repeated thermal cycles arising during operation of the SOFC to remain effective in preventing reaction between the vaporized species and the perovskite of the interconnects.

[0007] Ceramic membranes comprising a dense layer formed from mixed conducting multicomponent metallic oxides used in processes for producing synthesis gas (syngas) are known to experience flux decay and diminished flux performance when exposed to process streams containing elevated $\text{CrO}_2(\text{OH})_2$, CrO_3 , $\text{Si}(\text{OH})_4$ and $\text{WO}_2(\text{OH})_2$ partial pressures. Post-test analysis of these ceramic membranes revealed that the air-side surfaces of the membranes were coated with Cr-containing oxides while the syngas-side surfaces were coated with Si- or W-containing oxides. In some cases, the pores at the surface of the porous layer on the syngas-side of the ceramic membrane were almost completely plugged with such oxides.

[0008] Copending U.S. patent application Ser. No. 11/028,124, filed on Jan. 3, 2005, from which this application claims priority, teaches a method for gas purification comprising (a) obtaining a feed gas stream containing one or more contaminants selected from the group consisting of volatile metal oxy-hydroxides, volatile metal oxides, and volatile silicon hydroxide; (b) contacting the feed gas stream with a reactive solid material in a guard bed and reacting at least a portion of the contaminants with the reactive solid material to form a solid reaction product in the guard bed; and (c) withdrawing from the guard bed a purified gas stream. Suitable reactive solid material comprises one or more compounds selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites.

[0009] A need in the art exists for additional methods to minimize or substantially eliminate the presence of contaminants such as Si-, Cr-, Mo, and/or W-containing vapor species arising during operation of processes utilizing ceramic membranes formed from mixed conducting multicomponent metallic oxides and oxygen-conducting multicomponent metallic oxides. This need is addressed by the embodiments of the invention described below and defined by the claims that follow.

BRIEF SUMMARY OF THE INVENTION

[0010] An embodiment of the invention relates to an ion transport membrane system comprising

[0011] (a) a pressure vessel comprising an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;

[0012] (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules;

[0013] (c) a gas manifold having an interior surface wherein the gas manifold is in flow communication with the interior region of each of the planar ion transport membrane modules and with the exterior of the pressure vessel; and

- [0014] (d) a liner disposed within any of the inlet conduit, the outlet conduit, and the interior surface of the gas manifold.
- [0015] Another embodiment includes an ion transport membrane system comprising
- [0016] (a) a pressure vessel comprising an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
- [0017] (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules;
- [0018] (c) a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct (1) surrounds the plurality of planar ion transport membrane modules and the one or more guard beds and (2) is in flow communication with the inlet and the outlet of the pressure vessel;
- [0019] (d) a gas manifold having an interior surface wherein the gas manifold is in flow communication with the interior region of each of the planar ion transport membrane modules and with the exterior of the pressure vessel; and
- [0020] (e) a duct liner disposed within the flow containment duct.
- [0021] An alternative embodiment relates to an ion transport membrane system comprising
- [0022] (a) a pressure vessel having an axis, an interior, an interior surface, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
- [0023] (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules; and
- [0024] (c) a liner disposed adjacent the interior surface of the pressure vessel wherein any cross-section of the liner and pressure vessel taken perpendicular to the axis forms two concentric circles.
- [0025] A further embodiment of the invention includes an ion transport membrane system comprising
- [0026] (a) a pressure vessel having an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
- [0027] (b) a membrane stack or module assembly disposed in the interior of the pressure vessel, the assembly having a plurality of planar wafers comprising mixed metal oxide ceramic material, each wafer having an interior region and an exterior region, and a plurality of hollow ceramic spacers, wherein the stack or module assembly is formed by alternating wafers and spacers such that the interiors of the wafers are in flow communication via the hollow spacers, the wafers are oriented parallel to one another, and the alternating spacers and wafers are oriented coaxially to form the stack or module such that the wafers are perpendicular to the stack or module axis;

- [0028] (c) a gas manifold shroud assembly having an interior surface and disposed around the membrane stack or module assembly within the interior of the pressure vessel, wherein the shroud assembly (1) separates the stack or module into at least a first wafer zone and a second wafer zone, (2) places the inlet of the pressure vessel in flow communication with exterior regions of the wafers in the first wafer zone, (3) places exterior regions of the wafers in the first wafer zone in series flow communication with exterior regions of the wafers of the second wafer zone, and (4) places the outlet of the pressure vessel in flow communication with the exterior regions of the wafers in the second wafer zone or the wafers in a last wafer zone; and
- [0029] (d) a liner adjacent at least a portion of the interior surface of the gas manifold shroud assembly.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

- [0030] Embodiments of the invention are illustrated in the following drawings, which are not necessarily to scale and are not meant to limit these embodiments to any of the features shown therein.
- [0031] FIG. 1 is a schematic front view of a membrane wafer stack or module for use in oxygen recovery or in oxidation processes according to embodiments of the present invention. FIG. 2A is a side view of the membrane wafer stack or module of FIG. 1 for use in oxidation processes.
- [0032] FIG. 2B is a side view of the membrane wafer stack or module of FIG. 1 for use in oxygen recovery.
- [0033] FIG. 3A is a sectional view of a membrane wafer of FIGS. 1, 2A, and 2B.
- [0034] FIG. 3B is another sectional view of the membrane wafer of FIGS. 1, 2A, and 2B.
- [0035] FIG. 3C is a sectional view of an alternative membrane wafer of FIGS. 1, 2A, and 2B.
- [0036] FIG. 3D is another sectional view of the alternative membrane wafer of FIGS. 1, 2A, and 2B.
- [0037] FIG. 4A is a schematic side view of the interior of a membrane separator vessel for use in oxygen recovery.
- [0038] FIG. 4B is a cross sectional view of FIG. 4A.
- [0039] FIG. 5 is a schematic side view of the interior of a membrane reactor vessel for use in oxidation processes.
- [0040] FIG. 6 is a cross sectional view of FIG. 5.
- [0041] FIG. 7 is an embodiment of FIG. 4B showing the placement of insulation material.
- [0042] FIG. 8 is a second embodiment of FIG. 4B showing an alternative placement of thermal insulation material.
- [0043] FIG. 9 is a third embodiment of FIG. 4B showing an alternative placement of thermal insulation material.
- [0044] FIG. 10 is a fourth embodiment of FIG. 4B showing an alternative placement of thermal insulation material.
- [0045] FIG. 11 is a fifth embodiment of FIG. 4B showing an alternative placement of thermal insulation material.
- [0046] FIG. 12 is a sixth embodiment of FIG. 4B showing an alternative placement of thermal insulation material.
- [0047] FIG. 13 is a seventh embodiment of FIG. 4B showing the placement of insulation thermal material.
- [0048] FIG. 14 is a schematic side view of the interior of an alternative membrane vessel and module arrangement for use in oxygen recovery or in oxidation processes.
- [0049] FIG. 15 is a sectional plan view of a flow containment duct of FIG. 4A having coaxial parallel membrane modules.

[0050] FIG. 16 is a sectional plan view of a flow containment duct with offset banks of parallel membrane modules.

[0051] FIG. 17 is a schematic side view of the interior of a membrane separator vessel for use in oxygen recovery that includes guard beds for the removal of volatile contaminants from the feed gas to the vessel.

[0052] FIG. 18 is a schematic side view of the interior of a membrane reactor vessel for use in oxidation processes that includes guard beds for the removal of volatile contaminants from the feed gases to the vessel.

[0053] FIG. 19 is a sectional plan view of a flow containment duct of FIG. 4A having coaxial parallel membrane modules that includes guard beds for the removal of volatile contaminants in gases within the vessel.

[0054] FIG. 20 is a sectional plan view of a flow containment duct with offset banks of parallel membrane modules that includes guard beds for the removal of volatile contaminants in gases within the vessel.

[0055] FIG. 21 illustrates the equilibrium concentrations of CrO_3 over a Cr-containing alloy and over MgO between 850° C. and 900° C. at an oxygen partial pressure of 0.25 bara.

[0056] FIG. 22 illustrates the equilibrium concentrations of Si(OH)_4 over a Si-containing alloy and over MgO between 800° C. and 1000° C. at a water partial pressure of 8.0 bara.

[0057] FIG. 23 illustrates the equilibrium concentrations of $\text{WO}_2(\text{OH})_2$ over a W-containing alloy and over MgO between 800° C. and 950° C. at a water partial pressure of 8.0 bara.

DETAILED DESCRIPTION OF THE INVENTION

[0058] Embodiments of the present invention are directed toward the design of ion transport membrane systems that utilize multiple membrane modules operating in series for use in processes including but not limited to oxygen recovery and partial oxidation processes. The embodiments are more particularly drawn to methods for reducing or eliminating the degradation of multicomponent metallic oxides of the ion transport membranes that occurs by contact with volatile metallic species formed by the reaction of process gas components with the surfaces of alloy conduits, vessels, and other structural components during system operation. These embodiments comprise the installation of liners in the conduits and/or vessels of ion transport membrane systems to achieve this objective.

[0059] Prior to describing the embodiments of the present invention in detail, a discussion of suitable ion transport membrane systems is provided to enable one of ordinary skill in the art to understand the problems which arise during operation of these systems that are solved by the embodiments of the invention.

[0060] When oxygen transport across a membrane results in an exothermic reaction, for example in the production of synthesis gas from methane, the degree of reactant conversion across an individual membrane must be limited to prevent an excessive temperature gradient across the membrane. Moreover, when a membrane is transporting oxygen into a lower-pressure permeate stream, the amount of oxygen extraction across an individual membrane must be limited to prevent an excessive oxygen vacancy gradient in the membrane material between the leading edge and trailing edge of the membrane. Excessive temperature or oxygen vacancy gradients may cause excessive stresses in the membranes that could drastically limit the membrane life.

[0061] These problems may be alleviated by orienting multiple membrane modules or banks of modules in series so that

the amount of oxygen extracted across membranes in each module is sufficiently low to prevent an excessive oxygen vacancy gradient in the membrane material. The amount of oxygen extracted across each individual module may be limited by appropriate module sizing, and the total desired degree of oxygen extraction may be achieved by operating a selected plurality of modules in series. When oxygen transport across a membrane results in an exothermic reaction, the degree of reactant conversion across individual membranes in each module should be sufficiently low to prevent an excessive temperature gradient across the membrane in the flow direction. The degree of conversion across each individual module may be limited by appropriate module sizing, and the total desired conversion may be achieved by operating a plurality of selected modules in series.

[0062] The gas flowing over the outside of the membranes in each membrane module may be at a higher pressure than the gas on the inside of the membranes in the interior of the module as described below. In order to minimize gas-phase mass transfer resistance, the higher pressure gas should be directed across the outer surface of the membranes at high velocity and as uniformly as possible.

[0063] Because of the unique operating conditions of an ion transport membrane system, the system design may include a pressure vessel, an optional gas flow containment device, or duct disposed within the vessel and surrounding the series membrane modules, and thermal insulation within the vessel to allow the vessel wall to operate at a lower temperature than the membrane modules. The proper physical positioning of each of these components as described below improves the prospects for fabrication, installation, and long-term operability of the system. In addition, other internal design features are disclosed that may contribute to the long-term reliability of the overall ion transport membrane system.

[0064] The following definitions apply to terms used in the description of the embodiments of the invention presented herein.

[0065] An ion transport membrane module is an assembly of a plurality of membrane structures which has a gas inflow region and a gas outflow region disposed such that gas flows across the external surfaces of the membrane structures. Gas flowing from the inflow region to the outflow region of a membrane module changes in composition as it passes across the surfaces of the membrane structures in the module. Each membrane structure has an oxygen-containing gas feed side and a permeate side separated by an active membrane layer or region that allows oxygen ions to permeate therethrough. Each membrane structure also has an interior region and an exterior region. In one embodiment, in which the membrane module is operated as an oxygen separation device, the oxygen-containing gas feed side may be adjacent to the exterior region of the membrane structure and the permeate side may be adjacent to the interior region of the membrane structure.

[0066] In an alternative embodiment, in which the membrane module is operated as an oxidation reaction device, the oxygen-containing gas feed side may be adjacent to the interior region of the membrane structure and the permeate side may be adjacent to the exterior region of the membrane structure. In this alternative embodiment, a reactant feed gas flows through the exterior region of the membrane structure and reacts with the permeated oxygen. Thus in this embodiment the permeate side is also the reactant gas side of the membrane structure.

[0067] A membrane structure may have a tubular configuration in which an oxygen-containing gas flows in contact with one side of the tube (i.e., in either the interior region or the exterior region of the tube) and oxygen ions permeate through active membrane material in or on the tube walls to the other side of the tube. The oxygen-containing gas may flow inside or outside of the tube in a direction generally parallel to the tube axis, or conversely may flow over the outer side of the tube in a direction which is not parallel to the tube axis. A module comprises multiple tubes arranged in bayonet or shell-and-tube configurations with appropriate tube sheet assemblies to isolate the feed and permeate sides of the multiple tubes.

[0068] Alternatively, the membrane structure may have a planar configuration in which a wafer having a center or interior region and an exterior region is formed by two parallel planar members sealed about at least a portion of the peripheral edges thereof. Oxygen ions permeate through active membrane material that may be placed on either or both surfaces of a planar member. Gas can flow through the center or interior region of the wafer, and the wafer has one or more gas flow openings to allow gas to enter and/or exit the interior region of the wafer. Thus oxygen ions may permeate from the exterior region into the interior region, or conversely may permeate from the interior region to the exterior region.

[0069] Components of a membrane module include an active membrane layer that transports or permeates oxygen ions and may also transport electrons, structural components that support the active membrane layer, and structural components to direct gas flow to and from the membrane surfaces. The active membrane layer typically comprises mixed metal oxide ceramic material and also may comprise one or more elemental metals. The structural components of the membrane module may be made of any appropriate material such as, for example, mixed metal oxide ceramic materials, and also may comprise one or more elemental metals. Any of the active membrane layer and structural components may be made of the same material.

[0070] Single modules may be arranged in series, which means that a number of modules are disposed along a single axis. Typically, gas which has passed across the surfaces of the membrane structures in a first module flows from the outflow region of that module, after which some or all of this gas enters the inflow region of a second module and thereafter flows across the surfaces of the membrane structures in the second module. The axis of a series of single modules may be parallel or nearly parallel to the overall flow direction or axis of the gas passing over the modules in series.

[0071] Modules may be arranged in banks of two or more parallel modules wherein a bank of parallel modules lies on an axis that is not parallel to, and may be generally orthogonal to, the overall flow direction or axis of the gas passing over the modules. Multiple banks of modules may be arranged in series, which means by definition that banks of modules are disposed such that at least a portion of gas which has passed across the surfaces of the membrane structures in a first bank of modules flows across the surfaces of the membrane structures in a second bank of modules.

[0072] Any number of single modules or banks of modules may be arranged in series. In one embodiment, the modules in a series of single modules or in a series of banks of modules may lie on a common axis or common axes in which the number of axes equals one or equals the number of modules in each bank. In another embodiment described below, suc-

cessive modules or banks of modules in a series of modules or banks of modules may be offset in an alternating fashion such that the modules lie on at least two axes or on a number of axes greater than the number of modules in a bank, respectively. Both of these embodiments are included in the definition of modules in series as used herein.

[0073] The gas in contact with the outer surfaces in the exterior regions of the membrane modules may be at a higher pressure than the gas within the interior regions of the membrane modules.

[0074] A conduit is broadly defined as including but not limited to a pipe, tube, or channel through which a process fluid stream flows. A flow containment duct is defined as a conduit or closed channel surrounding a plurality of series membrane modules which directs flowing gas over modules in series.

[0075] A manifold is an assembly of pipes or conduits which directs gas to enter and/or exit the interior regions of the membrane modules. Two manifolds may be combined by installing a first or inner conduit within a second or outer conduit wherein the first conduit provides a first manifold and the annulus between the conduits provides a second manifold. The conduits may be concentric or coaxial, wherein these two terms have the same meaning. Alternatively, the conduits may not be concentric or coaxial but may have separate parallel or nonparallel axes. This configuration of inner and outer conduits to provide a combined manifold function is defined herein as a nested manifold.

[0076] The terms "flow communication" and "in flow communication with" as applied to a first and second region means that fluid can flow from the first region to the second region, and/or from the second region to the first region, through an intermediate region. The intermediate region may comprise connecting piping between the first and second regions or may comprise an open flow area or channel between the first and second regions. The term "flow communication" as applied to the series membrane modules described herein means that components of the membrane modules and vessel systems are oriented relative to one another such that gas can flow readily from one component to another component.

[0077] A wafer is a membrane structure having a center or interior region and an exterior region wherein the wafer is formed by two parallel planar members sealed about at least a portion of the peripheral edges thereof. Active membrane material may be placed on either or both surfaces of a planar member. Gas can flow through the center or interior region of the wafer, i.e., all parts of the interior region are in flow communication, and the wafer has one or more gas flow openings to allow gas to enter and/or exit the interior region of the wafer. The interior region of the wafer may include porous and/or channeled material that allows gas flow through the interior region and mechanically supports the parallel planar members. The active membrane material transports or permeates oxygen ions but is impervious to the flow of any gas.

[0078] Oxygen is the generic term for forms of oxygen comprising the element having an atomic number of 8. The generic term oxygen includes oxygen ions as well as gaseous oxygen (O₂ or dioxygen). An oxygen-containing gas may include, but is not limited to, air or gas mixtures comprising one or more components selected from the group consisting of oxygen, nitrogen, water, carbon monoxide, and carbon dioxide.

[0079] A reactant gas or reactant feed gas is a gas comprising at least one component which reacts with oxygen to form an oxidation product. A reactant gas may contain one or more hydrocarbons, wherein a hydrocarbon is a compound comprising primarily or exclusively hydrogen and carbon atoms. A hydrocarbon also may contain other atoms, such as, for example, oxygen.

[0080] Synthesis gas is a gas mixture containing at least hydrogen and carbon oxides.

[0081] An ion transport membrane, also referred to as a dense membrane comprising a mixed conducting multicomponent metallic oxide, is an active layer of dense, ceramic membrane material comprising mixed metal oxides capable of transporting or permeating oxygen ions at elevated temperatures having no connected through porosity. The ion transport membrane also may transport electrons as well as oxygen ions, and this type of ion transport membrane typically is described as a mixed conductor membrane. The ion transport membrane also may include one or more elemental metals thereby forming a composite membrane. The ion transport membranes suitable for use in this invention may include additional porous layers and structures as is well known in the art.

[0082] An ion transport membrane system is a generic term for an array of multiple ion transport membrane modules used for oxygen recovery or for oxidation reactions. An ion transport membrane separation system is an ion transport membrane system used for separating and recovering oxygen from an oxygen-containing gas. An ion transport membrane reactor system is an ion transport membrane system used for oxidation reactions.

[0083] The term “liner” is defined herein as a structure disposed within any portion of a system containing a process gas within a conduit, flow direction device, and/or vessel, wherein the process gas comes into contact with one or more ion transport membranes, and wherein the liner provides a barrier adapted to prevent or minimize contact of the process gas with the inner surfaces of the conduit, flow direction device, and/or vessel of the system. Alternatively or additionally, the liner may be adapted to prevent or minimize the diffusion into the process gas of volatile gaseous contaminants formed by reaction between process gas components and the structural metal of the conduit, flow direction device, and/or vessel. In some embodiments described herein, the liner is disposed adjacent the surface of the metal that forms a conduit, flow direction device, and/or vessel in the system. In other embodiments described herein, a flow channel may be formed by insulation material placed within a metal conduit, flow direction device, or vessel; a liner may be disposed adjacent the interior surface of this flow channel to protect membrane modules disposed within this flow channel. A liner is not a coating that adheres to and seals the interior metal surfaces of the conduit, flow direction device, and/or vessel.

[0084] The series membrane modules in the embodiments of the present invention may be fabricated in either tubular or planar configurations as described above. Planar configurations are preferred for many applications, and various configurations of planar membrane modules are possible. Planar membrane module configurations are described, for example, in copending U.S. patent application having Ser. No. 10/394,620 filed on Mar. 21, 2003, which application is incorporated herein by reference.

[0085] The use of the indefinite articles “a” and “an” means one or more when applied to any feature of the present inven-

tion described in the specification and claims. The use of “a” and “an” does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article “the” preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective “any” means one, some, or all indiscriminately of whatever quantity. The term “and/or” placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity.

[0086] An exemplary planar membrane module is illustrated in FIG. 1, which is a schematic front view of a membrane wafer stack or module for use in oxygen recovery or in oxidation processes according to embodiments of the present invention. The stack or module in this example comprises a plurality of planar wafers 1 separated by hollow spacers 3 and having an optional cap 5. The wafers and spacers are placed and joined in alternating fashion as shown and form stack or module axis 7. The wafers may be any shape in plan view, but square or rectangular shapes are generally preferred. The dimension of any side of a square or rectangular wafer may be between 2 and 45 cm. The number of wafers in a stack may range up to 1000.

[0087] The exterior region of the stack or module is that region surrounding the outer surfaces of the wafers and spacers. As described in detail below, wafers 1 have interior regions which are placed in flow communication with the interiors of spacers 3 wherein gas-tight seals are formed between the wafers and spacers. Opening 9 in bottom hollow spacer 11 allows gas to enter and/or exit the interior region of the stack or module wherein the interior region of the module is formed by the interior regions of the wafers and the openings in the hollow spacers. Thus opening 9 is in flow communication with the interior region of the module.

[0088] A side view of the module of FIG. 1 is shown in FIG. 2A, which illustrates an exemplary configuration for use in oxidation processes. In this example, spacers 201 between wafers 200 each have two separate sets of openings 203 and 205. Openings 203 in spacers 201, and additional openings in spacers disposed above and below spacers 201, form an internal manifold that is in flow communication with the interior regions of the wafers by way of appropriately placed openings (not shown) through the layers of the wafers at the left ends of the wafers. These openings through the layers of the wafers also place the internal openings 203 of spacers 201 and the internal openings in spacers above and below spacers 201 in flow communication with each other. Likewise, openings 205 in spacers 201, and additional openings in spacers disposed above and below spacers 201, form an internal manifold that is in flow communication with the interior regions of the wafers by way of appropriately placed openings (not shown) through the layers of the wafers at the right ends of the wafers. These openings through the layers of the wafers also place the internal openings 205 of spacers 201 and the internal openings in spacers above and below spacers 201 in flow communication with each other.

[0089] In this example configuration, gas stream 207 flows upward through the internal manifold formed by openings 203 and openings above them, and then flows horizontally through the interior regions of the wafers. Gas from the interior regions of the wafers then flows downward through the interior manifold formed by openings 205 and openings above them, and exits the module as gas stream 209. A second

gas 211 at the gas inflow region of the module flows through the exterior region of the module on either side of spacers 201 and in contact with the outer surfaces of wafers 200. Gas 213, after contacting the outer surfaces of wafers 200, flows through the gas outflow region of the module. The module may operate in a typical temperature range of 600 to 1100° C.

[0090] The module of FIG. 2A may be used as part of an oxidation reactor system wherein representative gas 211 is a reactant gas and representative gas 207 is an oxidant or oxygen-containing gas. The oxygen-containing gas 207 flows through the internal manifold via openings 203 and through the interior regions of the wafers, oxygen permeates the active membrane material in the planar members of the wafers, and oxygen-depleted gas 209 flows from the module via openings 205. Permeated oxygen reacts with reactant components in reactant gas or reactant feed gas 211 as the gas flows over the outer surfaces of the wafers and forms oxidation products. Exit gas 213 from the module contains the oxidation products and unreacted components. In one example embodiment, reactant gas 211 comprises methane or a methane-containing feed gas and exit gas 213 is a mixture of unreacted methane, hydrogen, carbon oxides, and water, oxygen-containing gas 207 is air, and oxygen-depleted gas 209 is enriched in nitrogen and depleted in oxygen relative to gas 207. Typically, the pressure of gases 211 and 213 is higher than the pressure of the gas in the interior region of the module.

[0091] An alternative side view of the module of FIG. 1 is shown in FIG. 2B, which illustrates an exemplary configuration for use in processes for the recovery of high purity oxygen from an oxygen-containing gas. In this example, spacers 215 between wafers 217 have openings 219 wherein openings 219 and additional openings in spacers disposed below spacers 215 form an internal manifold that is in flow communication with the interior regions of the wafers. Opening 221 thus places the interior region of the module in flow communication with a product gas conduit (not shown). Oxygen-containing gas 223, for example air, at the gas inflow region of the module flows through the exterior region of the module on either side of spacers 215 and in contact with the outer surfaces of wafers 217. After contacting the outer surfaces of wafers 217, oxygen-depleted gas 225 flows through the gas outflow region of the module. The module may operate in a typical temperature range of 600° C. to 1100° C.

[0092] As the oxygen-containing gas flows through the exterior region of the module and the gas contacts the outer surfaces of the wafers, oxygen permeates the active membrane material in the planar members of the wafers and high purity oxygen gas collects in the interior region of the module. High purity oxygen product gas 227 flows from opening 221. Typically, the pressure of oxygen-containing gases 223 and 225 is higher than the pressure of the high purity oxygen in the interior region of the module.

[0093] One possible exemplary configuration of the interior regions of the wafers in FIGS. 1, 2A, and 2B is illustrated in the sectional views of FIGS. 3A and 3B. Referring to FIG. 3A, which represents section 2-2 of FIG. 1, the wafer has outer support layers 301 and 303 of porous ceramic material that allows gas flow through the pores. Dense active membrane layers of 305 and 307 are in contact with outer support layers 301 and 303 and are supported by supporting ribs 321 and 329 which are part of flow channel layers 315 and 317. These ribs are in turn supported by slotted support layer 309 that has openings or slots 313 for gas flow. Open channels 319 and 325 are in flow communication via openings or slots 313.

Optionally, support layers 301 and 303 may not be required when the module of FIG. 2B is used for recovering oxygen from an oxygen-containing gas.

[0094] The term “dense” refers to a sintered or fired ceramic material through which a gas cannot flow. Dense fired ceramic material thus has no connected through porosity. Gas cannot flow through dense ceramic membranes made of mixed-conducting multi-component metal oxide material as long as the membranes are intact and have no cracks, holes, or imperfections which allow gas leaks. Oxygen ions can permeate dense ceramic membranes made of mixed-conducting multi-component metallic oxide material at elevated temperatures, typically greater than 600° C.

[0095] FIG. 3B, which represents section 4-4 of FIGS. 2A and 2B, illustrates a wafer section rotated 90 degrees from the section of FIG. 3A. This section shows identical views of outer support layers 301 and 303 and of dense active membrane material layers 305 and 307. This section also shows alternate views of slotted support layer 309 and flow channel layers 315 and 317. Open channels 331 are formed between alternating supporting ribs 333 and allow gas flow through the interior region of the wafer. The interior region of the wafer is therefore defined as the combined open volume within flow channel layer 315, flow channel layer 317, and slotted support layer 309.

[0096] The dense active membrane layers 305 and 307 preferably comprise a mixed metal oxide ceramic material containing at least one mixed-conducting multi-component metallic oxide compound having the general formula $(La Ca_{1-x})_y FeO_{3-\delta}$ wherein $1.0 > x > 0.5$, $1.1 \cong y > 1.0$, and δ is a number which renders the composition of matter charge neutral. Any appropriate material can be used for porous support layers 301 and 303, and this material may be, for example, a ceramic material having the same composition as that of active membrane layers 305 and 307. Preferably, porous support layers 301 and 303 are mixed-conducting multi-component metallic oxide material. Any appropriate material can be used for the structural members of slotted support layer 309 and flow channel layers 315 and 317, and this material may be, for example, a ceramic material having the same composition as that of active membrane layers 305 and 307. The material of channeled support layer preferably is a dense ceramic material. In one embodiment, active membrane layers 305 and 307, porous support layers 301 and 303, slotted support layer 309, and flow channel layers 315 and 317 all may be fabricated of material having the same composition.

[0097] Dense active membrane layers 305 and 307 optionally may include one or more oxygen reduction catalysts on the oxidant side. The catalyst or catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, ruthenium, gold, silver, bismuth, barium, vanadium, molybdenum, cerium, praseodymium, cobalt, rhodium and manganese.

[0098] Porous support layers 301 and 303 optionally may include one or more catalysts to promote hydrocarbon oxidation, reforming, and/or other reactions that occur in the porous layer. The catalyst or catalysts may be disposed on either or both surfaces of porous support layers 301 and 303, or alternatively may be dispersed throughout the layer. The one or more catalysts may comprise metals selected from or compounds containing metals selected from the group consisting of platinum, palladium, rhodium, ruthenium, iridium, gold, nickel, cobalt, copper, potassium and mixtures thereof. If desired for structural and/or process reasons, an additional

porous layer may be disposed between active membrane layers 305 and 307 and the adjacent flow channel layers 315 and 317 respectively.

[0099] Another possible configuration of the interior regions of the wafers for the oxygen recovery application in FIGS. 1, 2A, and 2B is illustrated in the sectional views of FIGS. 3C and 3D. Referring to FIG. 3C, which represents section 2-2 of FIG. 1, the wafer has outer dense layers 351 and 353. Porous ceramic layers of 355 and 357 are in contact with outer dense layers 351 and 353. Porous ceramic layer 355 is supported by supporting ribs 371, which are part of flow channel layer 365. Porous ceramic layer 355 is in contact with flow channels 366, which are part of flow channel layer 365. Porous ceramic layer 357 is in contact with flow channels 368, which are part of flow channel layer 367.

[0100] Ribs 371 are supported in turn by flow channel layer 358 that has openings or slots 363 for gas flow. Flow channel layer 367 is supported by ribs 373 of flow channel layer 359, and bridges 379 form the ends of flow channels 368. Bridges 372 form the ends of the flow channels 363 and flow channels 368 are in flow communication with flow channels 374 of flow channel layer 359. Open channels 374 and 363 are in flow communication.

[0101] FIG. 3D, which represents section 4-4 of FIGS. 2A and 2B, illustrates a section of the wafers rotated 90 degrees from the section of FIG. 3C. This section shows identical views of outer dense layers 351 and 353 and of porous ceramic layers 355 and 357. Porous ceramic layer 355 is supported by flow channel layer 365. Porous ceramic layer 355 is in contact with flow channels 366, which are part of flow channel layer 365. Porous ceramic layer 357 is supported by ribs 378 of flow channel layer 367. Porous layer 357 is in flow communication with flow channels 368, which are part of flow channel layer 367.

[0102] Ribs 378 are supported in turn by flow channel layer 359 that has openings or slots 374 for gas flow. Flow channel layer 365 is supported by ribs 375 of flow channel layer 358. Bridges 371 form the ends of flow channels 366. Bridges 376 form the ends of the flow channels 374 and flow channels 366 are in flow communication with flow channels 363 of flow channel layer 358. Open channels 374 and 363 are in flow communication.

[0103] The interior region of the wafer therefore is defined as the combined open volume within flow channel layer 365, flow channel layer 367, flow channel layer 358 and flow channel layer 359. The flow channels in layers 365 and 358 may be orthogonal to each other, as may be the flow channels in layers 367 and 359. Alternatively, flow channels 358 and 359 may be replaced by a single flow channel layer that comprises flow channels that radiate from the center of the wafer and are in flow communication with a central port in the center of the wafer.

[0104] Exemplary compositions for the dense active membrane are described in U.S. Pat. No. 6,056,807, which is incorporated herein by reference. Dense active membrane layers 351 and 353 preferably comprise a mixed metal oxide ceramic material containing at least one mixed-conducting multi-component metallic oxide compound having the general formula $(La_xSr_{1-x})Co_yO_{3-\delta}$ wherein $1.0 < x < 0.4$, $1.02 \leq y < 1.0$, and δ is a number which renders the composition of matter charge neutral. Any appropriate ceramic material can be used for porous support layers 355 and 357, and may be, for example, material of the same composition as that of active membrane layers 351 and 353. Preferably, porous

support layers 355 and 357 are mixed-conducting multi-component metallic oxide material. Any appropriate material can be used for the structural members of flow channel layers 365, 367, 358 and 359, and this material may be, for example, a ceramic material having the same composition as that of active membrane layers 351 and 353. The material of channeled flow layers preferably is a dense ceramic material. In one embodiment, active membrane layers 351 and 353, porous support layer 355 and 357, and channeled flow layers 358, 359, 365 and 367 all may be fabricated of material having the same composition.

[0105] Optionally, a porous layer may be applied on the outside surface of dense layers 351 and 353. Other exemplary configurations for the interior regions of the wafers for the oxygen generation application are given in U.S. Pat. No. 5,681,373, which is incorporated herein by reference.

[0106] Embodiments of the present invention utilize multiple membrane modules arranged in series as defined above. The series modules in turn may be installed in one or more vessels with appropriate gas flow containment ducts, conduits, and/or manifolds to direct gas streams to and from the modules. One of these embodiments is illustrated in FIG. 4A, which is a schematic side view of the interior of an exemplary membrane separator vessel for use in recovering a high purity oxygen product from an oxygen-containing gas. The high purity oxygen product may contain at least 99.9 vol % oxygen. Membrane modules 401, 403, 405, 407, and 409 are installed in series within pressure vessel 413 in optional flow containment duct 411. These membrane modules may be, for example, similar to the module described above with reference to FIGS. 1 and 2B. When used, optional flow containment duct 411 has inlet 415 to direct inlet gas stream 417 through the duct to contact the outer surfaces of the wafers in modules 401 to 409. Duct 411 is in flow communication with inlet conduits 416a and 416b where inlet conduit 416a is outside pressure vessel 413 and inlet conduit 416b is inside pressure vessel 413. Duct 411 is also in flow communication with outlet conduits 422a and 422b where outlet conduit 422a is outside pressure vessel 413 and outlet conduit 422b is inside pressure vessel 413. The inlet gas stream is a pressurized oxygen-containing oxidant gas, for example air, that has been heated by any appropriate method (not shown) to a temperature of 600° C. to 1100° C. The pressure of the gas within duct 411 may be in the range of 0.2 to 8 MPa. The flow containment duct preferably comprises an oxidation-resistant metal alloy containing iron and one or more elements selected from the group consisting of nickel and chromium. Commercially-available alloys that may be used for flow containment ducts include Haynes® 230, Incolloy 800H, Haynes® 214, and Inconel® 693 alloys.

[0107] The gas pressure in the interior of flow containment duct 411 may be greater than the gas pressure in the interior of pressure vessel 413 between the inner wall of the vessel and the outer wall of flow containment duct 411. The pressure differential between the interior and the exterior of duct 411 at any point between the inlet and outlet of pressure vessel 413 may be maintained at a value equal to or greater than zero, wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct. This may be accomplished, for example, by purging the space outside the duct with a gas at lower pressure than the process gas inside the duct; allowing flow communication between the space outside the duct and the process gas in the duct at process gas outlet 421; introducing a purge gas into the

space outside the duct, or withdrawing the purge gas through a purge gas outlet while using pressure controllers on a purge gas outlet to maintain a lower pressure in the space outside the duct than inside the duct.

[0108] As the oxygen-containing gas passes in series over the surfaces of the wafers in membrane modules **401** to **409**, oxygen permeates the dense active membrane layers and collects in the interior regions of the modules. Oxygen-depleted gas stream **419** exits the duct and pressure vessel through outlet **421** via outlet conduits **422a** and **422b**. High purity oxygen permeate product from the interior regions of the modules flows via primary manifolds **423**, **425**, **427**, **429**, and **431**, secondary manifolds **433**, **435**, **437**, **439**, and **441**, and main manifolds **445a** and **445b**, where **445a** is outside pressure vessel **413** and **445b** is inside pressure vessel **413**, and exits the system as high purity gas product stream **447**. At least two of membrane modules **401** to **409** define a module axis which may be parallel to or coincident with the axis of pressure vessel **413** or with the axis of flow containment duct **411**.

[0109] While the exemplary membrane separator vessel described above has a single inlet for feed gas to the membrane modules, a single flow containment duct, and a single outlet from the membrane modules, other embodiments are possible in which multiple inlets, multiple flow containment ducts, and/or multiple outlets may be used. For example, a pressure vessel may have two (or more) flow containment ducts, each having one or more inlets and one or more outlets. Generically, when a separator vessel is described as having an inlet and an outlet, this means that it has one or more inlets and one or more outlets. Generically, when a separator vessel is described as having a flow containment duct, this means that it has one or more flow containment ducts.

[0110] Another view of the exemplary membrane separator vessel of FIG. 4A is given by section 6-6 as shown in FIG. 4B. In this embodiment, a bank of three membrane modules **401a**, **401b**, and **401c** is installed in parallel in duct **411** and has three primary manifolds **423a**, **423b**, and **423c** that are connected to secondary manifold **433**. Secondary manifold **433** is connected in turn to main manifold **445b**. Alternatively, one membrane module, two parallel membrane modules, or more than three parallel membrane modules may be used in each bank.

[0111] While secondary manifolds **433**, **435**, **437**, **439**, and **441** and main manifold **445b** are located in the interior of pressure vessel **413** in the embodiments of FIGS. 4A and 4B, these manifolds may be located outside of the pressure vessel in an alternative embodiment. Primary manifolds **423**, **425**, **427**, **429**, and **431** would pass through the wall of pressure vessel **413** in this alternative embodiment.

[0112] In an alternative embodiment, planar membrane modules **401** through **409** may be replaced by tubular membrane modules placed in series relationship relative to the longitudinal flow of gas through optional duct **411**. These modules may utilize multiple single tubes or may utilize bayonet-type tubes, and the modules may be oriented such that gas flows across the tubes in crossflow or contacts the tubes in parallel flow. In this alternative embodiment, all manifolds are located inside the pressure vessel as shown in FIGS. 4A and 4B.

[0113] Another embodiment of the invention is illustrated in FIG. 5, which is a schematic side view of the interior of an exemplary membrane reactor vessel for use in oxidation processes. Membrane modules **501**, **503**, **505**, **507**, and **509** are

installed in series within pressure vessel **513** in optional flow containment duct **511**. These membrane modules may be, for example, similar to the module described above with reference to FIGS. 1 and 2A. When used, optional flow containment duct **511** has inlet **515** to direct inlet gas stream **517** through the duct to contact the outer surfaces of the wafers in modules **501** to **509**. Duct **511** is in flow communication with inlet conduits **516a** and **516b** where inlet conduit **516a** is outside pressure vessel **513** and inlet conduit **516b** is inside pressure vessel **513**. Duct **511** is also in flow communication with outlet conduits **558a** and **558b** where outlet conduit **558a** is outside pressure vessel **513** and outlet conduit **558b** is inside pressure vessel **513**. The inlet gas stream is a reactant feed gas containing one or more components which react with oxygen at elevated temperatures wherein the inlet reactant feed gas is heated by any appropriate method (not shown) to a temperature of 600° C. to 1100° C. The pressure of the gas within duct **511** may be in the range of 0.2 to 8 MPa. An example of a reactant feed gas is a mixture of steam and natural gas wherein the natural gas comprises mostly methane with smaller amounts of light hydrocarbons. The mixture may be prereformed at a temperature below about 800° C. to yield a reactant feed gas containing steam, methane, and carbon oxides. Other oxidizable reactant feed gases may include, for example, various mixtures of hydrogen, carbon monoxide, steam, methanol, ethanol, and light hydrocarbons.

[0114] The gas pressure in the interior of flow containment duct **511** may be greater than the gas pressure in the interior of pressure vessel **513** between the inner wall of the vessel and the outer wall of flow containment duct **511**. The pressure differential between the interior and the exterior of duct **511** at any point between the inlet and outlet of pressure vessel **513** preferably may be maintained at a value equal to or greater than zero, wherein the pressure in the interior of the duct is equal to or greater than the pressure in the pressure vessel exterior to the duct. This may be accomplished, for example, by purging the space outside the duct with a gas at lower pressure than the process gas inside the duct; allowing flow communication between the space outside the duct and the process gas in the duct at the process gas outlet **559** via outlet conduits **558a** and **558b**; introducing a purge gas into the space outside the duct, and withdrawing the purge gas through a purge gas outlet while using pressure controllers on a purge gas outlet to maintain a lower pressure in the space outside the duct than inside the duct.

[0115] The interior regions of membrane modules **501** to **509** are in flow communication with two manifold systems, one to introduce an oxygen-containing oxidant gas into the modules and the other to withdraw oxygen-depleted oxidant gas from the modules. The first of these manifold systems comprises main inlet manifold **519**, primary inlet manifolds **521**, **523**, **525**, **527**, and **529**, and secondary inlet manifolds **531**, **533**, **535**, **537**, and **539**. The second of these manifold systems comprises main outlet manifold **541** and primary outlet manifolds **543**, **545**, **547**, **549**, and **551**.

[0116] In an alternative configuration (not shown) to the configuration of FIG. 5, secondary inlet manifolds **531**, **533**, **535**, **537**, and **539** may be combined with primary outlet manifolds **543**, **545**, **547**, **549**, and **551**, respectively, when located within flow containment duct **511**. Two manifolds may be combined by installing a first or inner conduit within a second or outer conduit wherein the first conduit provides a first manifold and the annulus between the conduits provides a second manifold. The conduits may be concentric or

coaxial; alternatively, the conduits may not be concentric or coaxial and may have separate parallel or nonparallel axes. This configuration of inner and outer conduits to provide a combined manifold function is defined herein as a nested manifold.

[0117] In this alternative configuration, gas 553 would flow through the central conduit and gas 555 would flow through the annulus of each set of these nested manifolds. The nested manifolds would transition to separate manifolds exterior to flow containment duct 511, i.e., would transition to secondary inlet manifolds 531, 533, 535, and 539 and primary outlet manifolds 543, 545, 547, 549, and 551 as shown in FIG. 5. Optionally, primary outlet manifolds 543, 545, 547, 549, and 551 may be nested within secondary inlet manifolds 531, 533, 535, 537, and 539, respectively, within flow containment duct 511. In this option, gas 555 would flow through the central conduit and gas 553 would flow through the annulus of each set of these nested manifolds. In generic terms, therefore, the secondary inlet manifolds and the primary outlet manifolds may be nested when located within flow containment duct 511, and either a secondary inlet manifold or a primary outlet manifold may be provided by the annulus

[0118] Heated, pressurized oxygen-containing oxidant gas 553, for example, air that has been heated by any appropriate method (not shown) to a temperature of 600 to 1100° C., enters main inlet manifolds 519a and 519b and flows via primary inlet manifolds 521, 523, 525, 527, and 529 and secondary inlet manifolds 531, 533, 535, 537, and 539 to the inlets of membrane modules 501, 503, 505, 507, and 509. Inlet manifold 519a is outside pressure vessel 513 and inlet manifold 519b is inside pressure vessel 513. Oxygen from the oxidant gas in the interior regions of the membrane modules permeates the dense active membrane layers in the wafers of modules 501 to 509 and the permeated oxygen reacts with the reactive components in the exterior regions of the membrane modules. Oxygen-depleted oxidant gas exits the outlets of the interior regions of the membrane modules via primary outlet manifolds 543, 545, 547, 549, and 551 and main outlet manifold 541, and the final oxygen-depleted oxidant gas is withdrawn as gas stream 555. Outlet gas stream 557, which contains reaction products and unreacted feed components, is withdrawn from the reactor system through outlet 559 via outlet conduits 558a and 558b.

[0119] While the exemplary reactor vessel described above has a single inlet for reactant feed gas to the membrane modules, a single flow containment duct, and a single outlet from the membrane modules, other embodiments are possible in which multiple inlets, multiple flow containment ducts, and/or multiple outlets may be used. For example, a pressure vessel may have two or more flow containment ducts, each having one or more inlets and one or more outlets. Generically, when a reactor vessel is described as having an inlet and an outlet, this means that it has one or more inlets and one or more outlets. Generically, when a reactor vessel is described as having a flow containment duct, this means that it has one or more flow containment ducts.

[0120] Another view of the exemplary membrane reactor vessel of FIG. 5 is given in section 8-8 as shown in FIG. 6. In this embodiment, a bank of three membrane modules 503a, 503b, and 503c are installed in parallel in duct 511. Oxidant gas flows through main inlet manifold 519b, primary inlet manifold 523, and secondary inlet manifolds 533a, 533b, and 533c to the inlets of membrane modules 503a, 503b, and 503c. Oxygen-depleted oxidant gas exits membrane modules

503a, 503b, and 503c via primary outlet manifolds 545a, 545b, and 545c (located behind secondary inlet manifolds 533a, 533b, and 533c), secondary outlet manifold 561, and main outlet manifolds 541a and 541b. While three parallel membrane modules are shown in the embodiment of FIG. 6, one membrane module, two parallel membrane modules, or more than three parallel membrane modules may be used as desired.

[0121] Additional pressure vessels may be installed in series with pressure vessel 413 such that the outlet gas from one vessel feeds the other vessel. Additional pressure vessels may be placed in parallel wherein a plurality of pressure vessels operates in parallel and in series. Likewise, additional pressure vessels may be installed in series with pressure vessel 513 such that the outlet gas from one vessel feeds the other vessel. Additional pressure vessels may be placed in parallel wherein a plurality of pressure vessels operates in parallel and in series. Guard beds may be placed between any series pressure vessels as desired.

[0122] In the embodiments described above, it is desirable to use internal insulation to maintain the walls of pressure vessel 413 and 513 at temperatures lower than the temperatures of the respective membrane modules 401 to 409 and 501 to 509. This may be accomplished by various insulation alternatives in FIGS. 7 through 13, which illustrate insulation configurations for the embodiment of FIGS. 4A and 4B used for the recovery of oxygen from an oxygen-containing gas. Similar insulation configurations (not shown) may be used for the oxidation reactor embodiment of FIGS. 5 and 6.

[0123] The first of these alternatives is shown in FIG. 7 wherein insulation 701 is disposed within and may be in contact with the interior walls of pressure vessel 703. In this embodiment, a flow containment duct is not used; instead, cavity 705 is formed by the insulation itself and this cavity serves to direct gas flow over the exterior regions of the membrane modules. The insulation may be in contact with primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445b.

[0124] A second insulation configuration is shown in FIG. 8 wherein insulation 801 is disposed adjacent to and may be in contact with the inner wall of pressure vessel 413. In this embodiment, flow containment duct 411 is used and preferably is not in contact with insulation 801. The insulation preferably is not in contact with primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445b.

[0125] A third insulation configuration is shown in FIG. 9 wherein insulation 901 completely fills the interior region of the pressure vessel between the inner walls of the vessel and the exterior surfaces of flow containment duct 411, primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445b. The insulation may be in contact with the inner vessel walls and the exterior surfaces of flow containment duct 411, primary manifolds 423a, 423b, and 423c, secondary manifold 433, and main manifold 445b.

[0126] Another alternative insulation configuration is shown in FIG. 10 wherein insulation 1001 forms a cavity 1003 around the membrane modules and this cavity serves to direct gas flow over the exterior regions of the modules. Insulation 1001 may be in contact with primary manifolds 423a, 423b, and 423c, and typically is not in contact with the inner walls of pressure vessel 413.

[0127] FIG. 11 shows another alternative insulation configuration in which insulation 1101 surrounds flow contain-

ment duct **411**, which in turn surrounds the membrane modules as described above. Insulation **1101** may be in contact with primary manifolds **423a**, **423b**, and **423c**, and typically is not in contact with the inner walls of pressure vessel **413** and the outer surface of flow containment duct **411**.

[0128] Another insulation configuration is shown in FIG. **12** wherein insulation **1201** surrounds flow containment duct **411**, which in turn surrounds the membrane modules as described above. Insulation **1201** may be in contact with primary manifolds **423a**, **423b**, and **423c**, typically is in contact with the outer surface of flow containment duct **411**, and typically is not in contact with the inner walls of pressure vessel **413**.

[0129] A final insulation configuration is shown in FIG. **13** wherein insulation **1303** is placed within and typically in contact with the inner walls of flow containment duct **411**, wherein the insulation forms a cavity **1305** around the membrane modules and this cavity serves to direct gas flow over the exterior regions of the modules. Insulation **1303** may be in contact with primary manifolds **423a**, **423b**, and **423c**.

[0130] In any of the embodiments described above of FIGS. **7-13**, a metal-to-ceramic seal typically is used in primary manifolds **423a**, **423b**, and **423c** to transition from metal manifolds to the ceramic modules. Likewise, in the oxidation reactor embodiment of FIG. **6** and corresponding insulation embodiments similar to those of FIGS. **7-13**, a metal-to-ceramic seal typically is used in primary manifolds **533a**, **533b**, and **533c** to transition from metal manifolds to the ceramic modules. In the embodiments of FIGS. **10-13** (and similar embodiments for the oxidation reactor), these seals preferably are located within insulation **1001**, **1101**, **1201**, and **1303** (in contact with manifolds **423a**, **423b**, and **423c** but not with manifold **433**) to obtain desired seal operating temperatures.

[0131] In any of the embodiments of FIGS. **7-13**, additional insulation (not shown) may be placed around the external surface of the pressure vessel, for example to protect operating personnel from a potentially hot vessel surface. This additional insulation also may serve to ensure that the vessel interior is above the dew point of any gas within the vessel. In any of the embodiments of FIGS. **10-13**, additional insulation (not shown) may be placed adjacent to the inner surface of the pressure vessel. In any of the embodiments of FIGS. **4A**, **4B**, and **5-13**, any of the manifolds may be insulated internally and/or externally (not shown). This insulation would serve to improve the thermal expansion uniformity of flow containment duct **411** and the manifolds.

[0132] The insulation used in the embodiments of FIGS. **7-13** may contain alumina, alumino-silicate, silica, calcium silicate, or other conventional insulation materials suitable for use at elevated temperatures. The insulation may comprise, for example, one or more materials selected from the group consisting of fibrous alumina, fibrous alumino-silicate, porous alumina, and porous alumino-silicate. In the embodiments of FIGS. **7, 10**, and **13**, wherein the insulation itself forms a cavity around the membrane modules, the interior walls of the cavity may be coated or covered with a material which prevents volatile components from the insulation from contacting the membrane modules. For example, the cavity may be lined with a foil made of a metal such as Haynes 214 to prevent Si-containing vapor species, which may be generated from insulation materials, and/or Cr-containing vapor species, which may be generated from metal piping materials, from contacting the membrane modules.

[0133] The insulation may include one or more additional materials selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, strontium carbonate, sodium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites wherein these materials may be applied to the surface of the insulation and/or dispersed throughout the insulation. These additional materials may be used in place of or in addition to the guard bed or beds described above. These materials react with and remove contaminants that may be present in the inlet stream of reactant gas; these contaminants may include, for example, sulfur-, chromium-, silicon-, or oxygen-containing containing gaseous species.

[0134] An alternative embodiment for placing groups of wafers in a series flow configuration is shown in FIG. **14**. In this embodiment, a tall stack is formed of wafers and spacers as described above and the stack is installed in pressure vessel **1401**. Inlet **1403** and outlet line **1405** are connected to gas manifold shroud assembly **1407** which directs the flow of inlet gas **1408** to flow in alternating directions across groups of wafers and through outlet line **1405** as outlet stream **1409**. Inlet line or conduit **1404a** is the part of inlet **1408** that is outside of vessel **1401** and outlet line or conduit **1404b** is the part of inlet **1408** that is inside of vessel **1401**. In this embodiment, the stack is divided by the shroud assembly into first wafer zone **1411**, second wafer zone **1413**, and third wafer zone **1415**. Inlet gas **1408** thus flows in series across wafer zones **1411**, **1413**, and **1415** and exits via outlet line **1405**. While three wafer zones are shown here for illustration purposes, any number of wafer zones can be used as required.

[0135] The embodiment of FIG. **14** may be used as an oxygen recovery device or as an oxidation reactor device. When used as an oxygen recovery device, the stack is formed of wafers and spacers as earlier described with reference to FIGS. **1** and **2B**. In an oxygen recovery process, inlet gas **1408** is a heated, pressurized oxygen-containing gas (for example, air), outlet stream **1409** is an oxygen-depleted oxygen-containing gas, and stream **1417** flowing through outlet line **1419** is a high purity oxygen product stream typically at a lower pressure than the pressurized oxygen-containing gas. When used as an oxidation reactor system, the stack is formed of wafers and spacers as earlier described with reference to FIGS. **1** and **2A**. In an oxidation process, inlet gas **1408** is a heated, pressurized reactant gas and outlet gas **1409** is a mixture of oxidation reaction products and unreacted reactant gas components. Stream **1417** is an oxygen-depleted oxygen-containing gas stream typically at a lower pressure than the pressurized reactant gas. Fresh oxygen-containing oxidant gas (for example, air) flows into the stack through an internal stack manifold as described with reference to FIG. **2A**; the inlet to this manifold is not seen in FIG. **14** because it lies behind outlet line **1419**.

[0136] The embodiment of FIG. **14** can be operated with multiple pressure vessels in series and/or in parallel as desired. Multiple modules may be installed in a single pressure vessel if desired.

[0137] The series membrane modules may be arranged in banks of parallel modules as earlier described with reference to FIGS. **4A**, **4B**, **5**, and **6**. This is illustrated in FIG. **15**, which is a sectional plan view (not to scale) of flow containment duct **511** and the membrane modules within the duct. In this exemplary embodiment, five banks of three parallel modules are arranged such that each individual set of series modules lies on a common module axis, i.e., modules **501a**, **503a**, **505a**,

507a, and 509a lie on the same axis, modules 501b, 503b, 505b, 507b, and 509b lie on the same axis, and modules 501c, 503c, 505c, 507c, and 509c lie on the same axis. Thus in this example there are three axes, equal to the number of modules in each bank. Each bank comprises a plurality of modules in parallel; for example, modules 501a, 501b, and 501c constitute one bank of modules in parallel. A plurality of modules also may be arranged in series; for example, modules 501c, 503c, 505c, 507c, and 509c constitute modules in series. The definition of series modules also can include banks of modules; for example, the bank of modules 501a, 501b, and 501c is in series with the bank of modules 503a, 503b, and 503c. The module configuration in FIG. 15 thus includes modules in series and modules in parallel.

[0138] As a practical matter, it may be desirable to promote substantial radial mixing (i.e., gas flow in directions deviating from the axis of a series of modules) of gas between successive banks of modules to minimize the deleterious effect of gas bypassing around the membrane modules. The module configuration in FIG. 15 thus may be best described as including modules in parallel and banks of parallel modules operating in series. As in the design of many gas flow distribution systems, the degree of radial mixing can be maximized by proper selection of the axial and radial spacing between internal elements (i.e. membrane modules) and/or the use of flow baffles to promote gas mixing.

[0139] Inlet gas stream 1501 in inlet 1503 flows in series over each bank of radially-oriented (i.e., parallel) modules. With proper selection of the axial and radial spacing between modules, a small amount of gas may bypass modules 501a, 501b, and 501c, but eventually will contact downstream modules as it mixes or diffuses in a radial direction. Exit gas stream 1505 flows through outlet 1507. The gas flow over each successive bank of modules defines the series arrangement of this embodiment wherein all or nearly all of the gas from one bank of parallel modules contacts the next bank of parallel modules in the series of modules. Any desired number of modules may be used in parallel radially and any desired number of banks of parallel modules may be used in series axially.

[0140] In an alternative embodiment of the invention related to FIGS. 4A and 4B or to FIGS. 5 and 6, banks of parallel membrane modules may be oriented in a staggered or offset series arrangement such that a first bank of three modules is followed in series by an offset second bank of three modules which in turn is followed in series by an offset third bank of three modules, and so forth. This is illustrated in FIG. 16 wherein a first bank of three modules 502a, 502b, and 502c is followed in series by a second bank of three modules 504a, 504b, and 504c offset in a direction perpendicular to the axis of flow containment duct 511. A third bank of three modules 506a, 506b, and 506c is offset with respect to the second bank but the modules are coaxial with the modules in the first bank. This offset relationship may continue in similar fashion through the fourth bank of modules 508a, 508b, and 508c and the fifth bank of modules 510a, 510b, and 510c. Each bank may comprise a plurality of modules in parallel; for example, modules 502a, 502b, and 502c constitute one bank of modules in parallel. A plurality of modules also may be arranged in series; for example, modules 502c, 504c, 506c, 508c, and 510c may constitute modules in series. The definition of series modules also can include banks of modules; for example, the bank of modules 502a, 502b, and 502c is in series with the bank of modules 504a, 504b, and 504c. The

module configuration in FIG. 16 thus includes modules in series and modules in parallel.

[0141] The modules in FIG. 16 lie on six axes, i.e., modules 502c, 506c, and 510c lie on one axis, modules 504c and 508c lie on another axis, and so forth. These axes may be parallel to the overall flow direction of gas over the modules. In this embodiment, the number of axes is greater than the number of modules in each bank of modules.

[0142] In the embodiment of FIG. 16, inlet gas stream 1601 enters through inlet 1603, and flows over modules 502a, 502b, and 502c in the first bank. A portion of this gas may bypass module 502a but, in the absence of significant radial mixing, will at least contact offset module 504a. Gas that flows between modules 502a, 502b, and 502c, will at least contact the next series of offset modules 504b and 504c. Portions of the gas that flows from module 502a in the first bank will contact at least two modules (504a and 504b) in the second bank. In this way, such an offset arrangement prevents gas from bypassing straight through a gap between rows of modules on a common axis. Instead, gas bypassing any module in a bank of modules will impinge directly on a module in the next bank of modules. In the absence of significant radial mixing, at least a portion of the gas from one or more of the modules in a bank will contact one or more of the modules in the next bank, and this defines the series arrangement of modules in this embodiment.

[0143] The definition of modules arranged in series according to the present invention thus includes both embodiments described above with reference to FIGS. 15 and 16. In these embodiments, the axes of banks of modules and the axes of series modules may be generally orthogonal, and the axes of series modules may be generally parallel to the overall direction of gas flow through the vessel. Alternative embodiments are possible wherein the axes of banks of modules are not generally orthogonal to the axes of the series modules and/or wherein the axes of series modules are not generally parallel to the overall direction of gas flow through the vessel. In these alternative embodiments, the banks of modules lie at acute angles to the overall direction of gas flow through the vessel. These alternative embodiments are included in the definition of modules arranged in series according to the present invention.

[0144] The series reactor system described above may be used in oxidation service to produce synthesis gas from a hydrocarbon-containing feed gas such as natural gas. In this application, reforming catalyst may be disposed between any series modules, any parallel modules, any series and parallel modules, and/or following the final modules in a vessel. The reforming catalyst promotes the endothermic reactions of water and/or carbon dioxide with hydrocarbons, especially methane, to generate hydrogen and carbon monoxide. The catalyst may be used to complement or balance the exothermic oxidation reactions that occur between permeated oxygen and reactants adjacent to the surfaces of the active membrane material in the modules. By appropriate use of reforming catalyst at strategic locations between the modules in a multiple-module series reactor system, the temperature profiles across the reactor and the product gas composition may be controlled to achieve optimum reactor operation.

[0145] An embodiment of the present invention is illustrated by the exemplary placement of appropriate catalyst between the modules of a multiple-module series oxidation reactor system. For example, referring to FIG. 15, catalyst 501d, 501e, and 501f may be placed in series fashion in the

space between any modules in the first bank of modules **501a**, **501b**, and **501c** and the second bank of modules **503a**, **503b**, and **503c**. Alternatively, catalyst **501d**, **501e**, and **501f** may extend continuously between the inner walls of flow containment duct **511**. Likewise, catalyst may be placed between any or all of the second and third banks of modules, the third and fourth bank of modules, the fourth and fifth banks of modules, or following the fifth bank (not shown). Similarly, catalyst may be placed in series fashion between any or all of the offset banks of modules in the embodiment of FIG. 16. For example, referring to FIG. 16, catalyst **502d**, **502e**, and **502f** may be placed in series fashion in the space between the first and second banks of modules. Alternatively, catalyst **502d**, **502e**, and **502f** may extend continuously between the inner walls of flow containment duct **511**. In general, catalyst may be placed in series fashion between or downstream of any or all of the series banks of modules in FIGS. 15 and 16.

[0146] Additionally or alternatively, catalyst may be placed between the modules in a bank of parallel modules to promote reforming reactions in the gas passing between the modules. For example, in FIG. 15 catalyst **505d** and **505e** may be placed between modules **505a** and **505b** and between **505b** and **505c**. Alternatively, catalyst **505d**, and **505e** may extend continuously in the axial direction between the first through fifth banks of modules. For example, in FIG. 16 catalyst **506d** and **506e** may be placed between modules **406a** and **506b** and between **506b** and **506c**. In general, catalyst may be placed in parallel fashion between any or all of the parallel modules in FIGS. 15 and 16.

[0147] In the broadest application of this concept, therefore, catalyst may be placed in the space between any two adjacent modules in the embodiments of FIGS. 15 and 16, or in any other embodiments with both of series and parallel module placement. In addition, when pressure vessel **513** is operated in series with another similar pressure vessel, catalyst may be placed between the vessels such that the effluent gas from one pressure vessel passes through the catalyst before passing into the second pressure vessel.

[0148] The catalyst may be varied in type and/or amount depending on the axial or radial location among the modules in the pressure vessel. In one alternative, for example, the catalyst activity may be varied in the axial direction for optimal control of the module temperatures through the reactor. For example, catalyst sections near the inlet of the reactor may comprise catalyst which is active at lower temperature (i.e. a high Ni loading), whereas in higher temperature regions of the reactor the optimal catalyst composition may involve lesser activity and greater thermal stability (i.e. a low Ni loading). In this way, optimal catalyst activity can be achieved at every axial location in the reactor, while maintaining thermal stability of the catalyst. Other catalyst arrangements are possible and fall within the scope of embodiments of the claimed invention.

[0149] The catalyst for use in this embodiment may include one or more metals or compounds containing metals selected from the group consisting of nickel, cobalt, platinum, gold, palladium, rhodium, ruthenium, and iron. The catalyst may be supported on alumina or other oxide supports and may include additions such as lanthanum or potassium. The catalyst may be placed between modules by any known means including, for example, using monoliths or using granular catalysts in appropriate catalyst holders that fit in the spaces between the modules.

[0150] Structural components of the ion transport membrane systems described above, as in most chemical reactors, are made of metal alloys that may contain any of chromium, silicon, tungsten, molybdenum, and other elements, and oxides of these elements may form at the alloy surfaces at high operating temperatures. Structural components also may include oxide refractories that may contain compounds such as silica (silicon dioxide) or other temperature-resistant oxide materials. When these oxides are exposed to gas streams containing steam, such as, for example, hot synthesis gas or air preheated by direct firing, volatile contaminant compounds may form at the alloy or refractory surfaces and sublime into the hot gas stream. Even in the presence of dry oxygen-containing gas, volatile contaminant compounds containing chromium may form.

[0151] A contaminant is defined as any compound or element which reacts with components in the structure of the ion transport membrane system resulting in reduced performance of the system. For example, contaminants may react with the mixed conducting multicomponent metallic oxide materials used in the ion transport membrane wafers resulting in reduced oxygen permeability of the membranes. A volatile contaminant is a compound or element that exists as a gas at elevated temperatures in the range of 600° C. to 1100° C. A reactive solid material is any material that reacts with a volatile contaminant to form a non-volatile reaction product.

[0152] Typical volatile contaminants may include, for example, any of the gaseous oxy-hydroxide $\text{CrO}_2(\text{OH})_2$, the gaseous oxy-hydroxide $\text{WO}_2(\text{OH})_2$, and the gaseous hydroxide $\text{Si}(\text{OH})_4$. Similarly, when exposed to oxidizing gases such as air, certain metal oxides may form at the alloy surfaces and sublime into the hot gas stream. One of these volatile metal oxides which may be present is CrO_3 . Depending on the specific alloys or refractories used in the piping and vessels, other volatile hydroxides, volatile metal oxy-hydroxides, or volatile metal oxides may be present as contaminant compounds in the process gases in ion transport membrane reactors. Volatile sulfur-containing compounds such as SO_2 and H_2S may be present in these gas streams, and these compounds also may reduce the performance and operating life of the ion transport membranes. Other species that may be present in the gas streams include any of Cl_2 , Br_2 , I_2 , and compounds containing any of Cl, Br, and I. These compounds or elements also may reduce the performance and operating life of the ion transport membranes.

[0153] The partial pressures of these contaminants may be relatively low under some membrane operating conditions. Under other operating conditions, however, the partial pressures may be high enough for the contaminants to react with the ion transport membrane materials, thereby reducing membrane performance and operating life.

[0154] Ion transport membrane systems used for synthesis gas or oxygen production, when exposed to gas streams containing elevated $\text{CrO}_2(\text{OH})_2$, CrO_3 , $\text{Si}(\text{OH})_4$ and $\text{WO}_2(\text{OH})_2$ partial pressures at temperatures in the range of 700 to 950° C., experience oxygen flux decay and low oxygen flux performance. Post-test analyses of these membranes revealed that the air side surfaces of the membranes were coated with Cr-containing oxide while the synthesis gas side surfaces were coated with Si- or W-containing oxides. The pores at the surface of the porous layer on the synthesis gas side of the membrane experience plugging with contaminant reaction products.

[0155] The problems caused by these contaminants may be alleviated according to embodiments of the present invention by equipping the ion transport membrane system with one or more liners that reduce the contact of volatile metal oxide contaminants with the ion transport membrane surfaces. The liners may comprise a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, combinations thereof, and mixtures thereof, and the liners may be disposed within one or more portions or segments of any inlet conduit, outlet conduit, interior surface of the gas manifold, and interior surface of the flow duct of such systems. The liners need not cover the entire surface of the inlet conduit, the outlet conduit, the interior surface of the gas manifold, and/or the interior surface of the flow duct. The liners may be disposed within one or more selected portions of the conduits, manifolds, ducts, or vessels wherein process temperatures, alloy compositions, and the processes conducted in the system are likely to generate appreciable amounts of the Si-, Cr-, Mo, and/or W-containing metallic vapor species. The liner may create a diffusion barrier such that the vapor species cannot volatilize into the process gases within the ion transport membrane system and subsequently react with the multicomponent metallic oxides of the ion transport membranes to adversely affect process efficiency.

[0156] The partial pressures of the volatile contaminant species may be significantly reduced by placing the liners of the present embodiments in the flow path of process gases within the ion transport membrane system. The reduction may occur through one or more mechanisms including any of (1) reduction of the temperature of the contaminant source due to the liner insulating the metal surfaces from the hot process gas, (2) a mass transfer barrier provided by the liner where the liner hinders the transport of volatile contaminant species from the metal surfaces into the process stream, and (3) gettering of the volatile contaminants by reaction of the liner material with the volatile contaminant species to produce stable solid phases.

[0157] The liners in ion transport membrane systems used to separate oxygen from air may be advantageously situated within a segment of the inlet conduit or the entire length of the inlet conduit. The liners of ion transport membrane systems used to produce syngas or to perform partial oxidations reactions may be advantageously situated within a segment of the inlet conduit and/or a segment of the gas manifold. The liners may be incorporated into any conduit or structure in which process benefits may be obtained by substantially reducing or eliminating volatile species from entering the process gas streams of the ion transport membrane systems.

[0158] Exemplary locations for the liners may be described with reference to FIGS. 4A, 4B, and 5-14. In FIG. 4A, the liner may be placed adjacent the inner surfaces of any of duct 411 and conduits 416a, 416b, 422a, and 422b. In FIG. 4B, the liner may be placed adjacent the interior surface of duct 411. In FIG. 5, the liner may be placed adjacent the inner surfaces of any of the following: duct 511, conduits 516a, 516b, 558a, and 558b, conduits 519a and 519b, manifolds 521-529, and conduits 531-539. In FIG. 6, the liner may be placed adjacent the inner surfaces of any of the following: duct 511, conduits 533a, 533b, 533c, manifold 523, and conduit 519b. In FIG. 7, the liner may be placed adjacent the interior surface of vessel 703 and/or adjacent the interior surface of the flow channel formed around the membrane modules by insulation 701.

[0159] In FIGS. 8 and 9, the liner may be placed adjacent the interior surface of duct 411. In FIG. 10, the liner may be placed adjacent the inner surface of vessel 413, the outer surface of insulation 1001, and/or adjacent the interior surface of the flow channel formed around the membrane modules by insulation 1001. In FIGS. 11 and 12, the liner may be placed adjacent the interior surface of duct 411. In FIG. 13, the liner may be placed adjacent the interior surface of duct 411 and/or adjacent the interior surface of the flow channel formed around the membrane modules by insulation 1303. In FIG. 14, the liner may be placed adjacent any of the interior surfaces of inlet conduits 1404a and 1404b, gas manifold shroud assembly 1407, and outlet conduit 1405.

[0160] A liner may be placed adjacent the inner surface of duct 411 in FIG. 4A or duct 511 of FIG. 5, and this liner may be described specifically as a duct liner. A duct liner is defined herein as a structure disposed adjacent the inner wall of a duct and comprising a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, combinations thereof, and mixtures thereof. The duct liner composition does not contain compounds used in conventional insulation including but not limited to alumina, alumino-silicate, silica, and calcium silicate. The duct liner has the primary purpose of protecting multicomponent metallic oxides of the ion transport membranes from Si-, Cr-, Mo, and/or W-containing vapor species as described above. While the duct liner may affect heat transfer to or from the duct wall to a small degree, it does not have the primary purpose of insulation that significantly reduces heat transfer to or from the duct wall. If a significant reduction of heat transfer to or from the duct wall is needed, conventional insulation may be used in conjunction with the duct liner.

[0161] In the embodiment of FIG. 7, no duct is placed around the ion transport membrane modules and insulation is used to form a flow channel around the modules. In this case, a liner may be placed adjacent the inner wall of vessel 703 to reduce or eliminate the effects of the gaseous contaminants on the membrane surfaces as earlier described. The cross-section of this liner and pressure vessel taken perpendicular to the axis would form two concentric circles. A liner also may be placed adjacent the interior surface of the flow channel formed around the membrane modules by insulation 701. The embodiments of FIGS. 4A and 5 may be modified by eliminating optional flow ducts 411 and 511. In these alternative embodiments, a liner may be placed adjacent the inner wall of vessel 413 or 513 to reduce or eliminate the effects of the gaseous contaminants on the membrane surfaces as earlier described. Any cross-section of this liner taken perpendicular to the axis would form two concentric circles.

[0162] The liners of the present invention can be formed by conventional methods and may be introduced into a segment or the entire length of desired conduits of the ion transport membrane system. One method of introducing the liner into a conduit is to fabricate the liner in cylindrical sections that fit inside a cylindrical conduit. Linings for conduits with other cross sectional shapes may be similarly installed. Another method of introducing the lining is to cast the lining on the inside surface of the conduit by coating the inside surface of the conduit with an aqueous slurry comprising calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures thereof, and drying the applied coating.

[0163] The liners of the ion transport membrane systems of the claimed invention may further comprise alumina or zirconia wherein a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures or combinations thereof is deposited by conventional methods onto an alumina or a zirconia substrate. In another embodiment, the liners may be composite structures in which the liner material comprises (1) a base liner composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide and mixtures thereof and (2) materials having other compositions that provide improved mechanical properties of the liners.

[0164] One type of liner for use in the ion transport membrane systems described herein consists essentially of magnesium oxide wherein the liner is formed by conventional methods provided that additional additives and materials may be included in the liner that do not contribute or detract from the utility of the liners. Liners comprising magnesium oxide also may include one or more compositions selected from the group consisting of calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide. A liner may be fabricated from a mixture of magnesium oxide and calcium oxide.

[0165] Liners suitable for use as described herein may be formed from dense or porous compositions of matter recited in this specification. Thus, the liner may have no connected through porosity or the liner may have any desired degree of porosity provided that the liner maintains structural integrity during operation of the ion transport membrane system. Moreover, several segments of liner may be placed in desired portions of a conduit wherein each liner is formed of a different composition. Liners may be in the form of bricks which are stacked to line the walls of the conduit. Alternatively, liners may be in the form of rectangular plates.

[0166] Any conventional technique suitable for making conduits formed from multicomponent metallic oxides, alumina, and the like may be used to fabricate the liners of the present invention. The liners may be formed in segments of varying length to accommodate their fabrication and installation into the conduits and features of the ion transport membrane system. A cross-section of the liner taken perpendicular to the liner axis may form a concentric circle, a square, or any other shape, and the liner shape may be dictated by fabrication costs and other conventional engineering considerations. Segments of liners may be installed from end to end within the conduits of the system or may be separated by any axial distance depending upon the allowable amount of contaminants that may enter the system during process operation from unlined conduit interior surfaces.

[0167] The liners described herein should be fabricated with a thickness having sufficient structural strength for insertion into the desired conduit by pressure fitting or the like and a thickness sufficient to enable operation of the process in the ion transport membrane system, while retaining structural liner integrity during operation. Pressure fitting is an advantageous method of installing the liners in the conduits and other parts of the ion transport membrane system that may generate contaminants during operation of the system.

[0168] The required thickness of a liner segment may depend on the diameter of the liner segment, the mechanical properties of the liner segment, the stresses that occur in the

liner segment during process operation, and other process parameters. The liner thickness may be, for example, between 0.1 and 6 inches.

[0169] In order to provide additional protection of the membrane surfaces, guard beds may be utilized in combination with the liners described above. The guard beds remove any residual volatile contaminants from the process gases before the gases contact the membrane surfaces. These residual contaminants may be formed, for example, when the liners do not completely cover the metal surfaces of the system upstream of the membrane modules or when a liner failure occurs. The guard beds may be strategically located in the gas streams prior to or within the ion transport membrane reactor vessel as described below wherein the temperature of the guard beds may be between 600° C. and 1100° C.; typically, the temperature of the guard beds may be between 700° C. and 950° C. The guard beds should be located close to the membrane modules to minimize recontamination of the purified gas stream from the metal in the piping between the guard bed and membrane. A guard bed is defined as any vessel or enclosure which contains reactive solid material and is designed to allow flowing gas to contact the reactive solid material. A purified gas stream is defined as a process stream in which the concentration of contaminants has been reduced by contacting a contaminant-containing process stream with a reactive solid material in a guard bed.

[0170] In one embodiment, the reactor system of FIG. 4A used for the production of a high purity oxygen product may be modified as shown in FIG. 17 by installing guard bed 1701 in inlet 415 to treat inlet gas stream 417 prior to contact with membrane modules 401, 403, 405, 407, and 409. Guard bed 1701 is in flow communication with inlet conduits 416a and 416b where inlet conduit 416a is outside pressure vessel 413 and inlet conduit 416b is inside pressure vessel 413. Alternatively, guard bed 1703 may be installed within pressure vessel 413 prior to the inlet of flow containment duct 411 as shown. Guard bed 1703 is in flow communication with inlet conduits 416a and 416b where inlet conduit 416a is outside pressure vessel 413 and inlet conduit 416b is inside pressure vessel 413. The high purity oxygen product may contain at least 99.9 vol % oxygen.

[0171] In another embodiment, the reactor system of FIG. 5 used as an oxidation reactor may be modified as shown in FIG. 18 by installing guard bed 1801 in inlet 515 to treat inlet gas stream 517 prior to contact with membrane modules 501, 503, 505, 507, and 509. Guard bed 1801 is in flow communication with inlet conduits 516a and 516b where inlet conduit 516a is outside pressure vessel 513 and inlet conduit 516b is inside pressure vessel 513. Alternatively, guard bed 1803 may be installed within pressure vessel 513 prior to the inlet of flow containment duct 511. Guard bed 1803 is in flow communication with inlet conduits 516a and 516b where inlet conduit 516a is outside pressure vessel 513 and inlet conduit 516b is inside pressure vessel 513. Alternatively or additionally, guard bed 1805 may be installed in the exterior portion of main inlet manifold 519 to treat heated, pressurized oxygen-containing oxidant gas 553. Guard bed 1805 is in flow communication with inlet conduits 519a and 519b where inlet conduit 519a is outside pressure vessel 513 and inlet conduit 519b is inside pressure vessel 513. As an alternative to guard bed 1805, guard bed 1807 may be installed in main inlet manifold 519 within pressure vessel 513 as shown. Guard bed 1807 is in flow communication with main inlet manifolds 519a and 519b where main inlet manifold 519a is

outside pressure vessel **513** and main inlet manifold **519b** is inside pressure vessel **513**. Guard beds may be installed between any of membrane modules **501**, **503**, **505**, **507**, and **509** as described below.

[0172] In FIG. 17, the liners may be placed adjacent the inner surfaces of any of the following components: duct **411**, conduit **416a** upstream and/or downstream of guard bed **1701**, conduit **416b** upstream and/or downstream of guard bed **1703**, and conduits **422a**, and **422b**. In FIG. 18, the liners may be placed adjacent the inner surfaces of any of the following components: duct **511**, conduit **516a** upstream and/or downstream of guard bed **1801**, conduit **516b** upstream and/or downstream of guard bed **1803**, conduit **519a** upstream and/or downstream of guard bed **1805**, conduit **519b** upstream and/or downstream of guard bed **1807**, manifolds **521-529**, conduits **531-539**, and conduits **558a** and **558b**.

[0173] Another embodiment of the present invention is illustrated by the exemplary placement of appropriate guard beds between the modules of a multiple-module series oxidation reactor system to remove volatile contaminants. For example, the reactor of FIG. 15 may be modified as shown in FIG. 19 by placing guard beds **1901**, **1903**, and **1905** in series fashion in the space between any modules in the first bank of modules **501a**, **501b**, and **501c** and in the second bank of modules **503a**, **503b**, and **503c**. Alternatively, guard beds **1901**, **1903**, and **1905** may extend continuously between the inner walls of flow containment duct **511**. Likewise, guard beds (not shown) may be placed between any or all of the second and third banks of modules, the third and fourth bank of modules, the fourth and fifth banks of modules, or following the fifth bank. Similarly, guard beds may be placed in series fashion between any or all of the offset banks of modules by modifying the embodiment of FIG. 16 as shown in FIG. 20. For example, guard beds **2001**, **2003**, and **2005** may be placed in series fashion in the spaces between any of the first bank of modules **502a**, **502b**, and **502c** and any of the second bank of modules **504a**, **504b**, and **504c** as shown. Alternatively, guard beds **2001**, **2003**, and **2005** may extend continuously between the inner walls of flow containment duct **511**. In general, guard beds may be placed in series fashion between or downstream of any or all of the series banks of modules in FIGS. 19 and 20.

[0174] Additionally or alternatively, guard beds may be placed between the modules in a bank of parallel modules to remove contaminants from the gas passing between the modules. For example, in FIG. 19 guard beds **1907** and **1909** may be placed between modules **505a** and **505b** and between **505b** and **505c**, respectively. Alternatively, guard beds **1907** and **1909** may extend continuously in the axial direction between the first through fifth banks of modules. In FIG. 20, guard beds **2007** and **2009** may be placed between modules **506a** and **506b** and between **506b** and **506c**. In general, guard beds may be placed in parallel fashion between any or all of the parallel modules in FIGS. 19 and 20.

[0175] In the broadest application of this concept, therefore, guard beds may be placed in the space between any two adjacent modules in the embodiments of FIGS. 19 and 20, or in any other embodiments with both series and parallel module placement. In addition, when pressure vessel **513** is operated in series with another similar pressure vessel, guard beds may be placed between the vessels such that the effluent gas from one pressure vessel passes through the guard bed before passing into the second pressure vessel.

[0176] Guard beds may be used in the embodiment of FIG. 14 wherein a guard bed (not shown) is installed in inlet line **1403**, either outside or inside of vessel **1401**. Alternatively or additionally, guard beds (not shown) may be installed at any of the wafer discharge side of first wafer zone **1411**, the wafer inlet or discharge sides of second wafer zone **1413**, and the wafer inlet side of third wafer zone **1415**.

[0177] In the guard bed embodiments described above, the reactive material may be contained in parallelepiped-shaped or disk-shaped porous containers, wherein the porous containers are designed to fit between the modules as shown. The guard beds advantageously may have axial cross-sections of similar size and shape as the axial cross-sections of the membrane modules; alternatively, the guard beds may extend continuously between the inner walls of flow containment duct **511**.

[0178] Other embodiments are possible in which the reactor systems of FIGS. 19 and 20 are modified by adding guard beds such that both catalyst and guard beds are disposed between the membrane modules in any desired configuration. For example, catalyst and guard beds may be alternated in the axial direction between successive banks of membrane modules in series. Alternatively, both catalyst and guard beds may be placed between series membrane modules as required.

[0179] Each guard bed in the embodiments described above contains reactive material which reacts with volatile contaminants. The reactive material or materials may be placed in the guard bed in any form selected from porous pellets, beads, rods, extrudates, porous foams, tubes, and solid honeycombs or monoliths. The guard bed may be a typical pressure vessel having an inlet and an outlet wherein the reactive material is supported within the reactor by screens or other porous supports as known in the art. Alternatively, a disc-shaped or parallelepiped-shaped porous container may be used to hold the reactive material, wherein the porous container may be designed to fit within a length of piping or within the interior of a reactor vessel as described below.

[0180] The guard bed may contain, for example, one or more reactive materials selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites. The alkaline-earth-containing perovskites have the general formula $A_xA'_xB_yB'_yO_{3-d}$ where A comprises one or more of lanthanum, yttrium, and one of the lanthanide elements; A' comprises one or more of Ca, Sr, and Ba; B and B' comprise one or more of the first row transition metals Mg, Ga, and Al; $0.9 < x+x' < 1.1$; $0.9 < y+y' < 1.1$; $x' > 0$; and d is a number that makes the compound charge neutral.

[0181] In one embodiment, MgO may be used in the guard beds to remove these volatile contaminant compounds from the gases prior to contact with the membranes in the membrane modules. MgO is an effective reactive material for this service, and it is safe, easily handled, and inexpensive. The partial pressures of the volatile gas-phase contaminants can be reduced by up to several orders of magnitude, which may significantly reduce or eliminate membrane contamination and damage.

[0182] The MgO may be placed in the guard bed in any form selected from porous pellets, beads, rods, extrudates, porous foams, tubes, porous honeycombs, and porous and solid honeycombs or monoliths. The MgO will react with the chromium-, silicon-, and/or tungsten-containing gas phase

contaminants to form MgCr_2O_4 (magnesium chromite), Mg_2SiO_4 (magnesium silicate) and MgWO_4 (magnesium tungstate), respectively. These reaction products are very stable, safe to handle, and environmentally benign; disposal of spent guard bed material therefore should be simple and inexpensive.

[0183] Exemplary reactions which take place at the interface of the gas phase and the solid oxides to form the volatile contaminants described above are as follows:

[0184] The reactions which take place in a guard bed filled with MgO are as follows:

[0185] Thermodynamic equilibrium calculations for these reactions predict that the partial pressures of the contaminant phases in the gas streams can be decreased by an order of magnitude or more by reaction with MgO, which will reduce or eliminate contamination of the membrane materials. This is illustrated by comparing the calculated partial pressures of the contaminant compounds in equilibrium with piping metal alloys and in equilibrium with the guard bed material according to equations 2, 3, 4, 5, 7, and 8 above.

[0186] FIG. 21 demonstrates the equilibrium concentrations of CrO_3 over a Cr-containing alloy and over the MgO guard bed material between 850° C. and 900° C. at an oxygen partial pressure of 0.25 bara, and indicates an order of magnitude reduction in the gas phase partial pressure of CrO_3 by the guard bed. The calculation of the vapor pressure over the alloy assumes that the surface of the alloy is pure Cr_2O_3 .

[0187] FIG. 22 demonstrates the equilibrium concentrations of $\text{Si}(\text{OH})_4$ over a Si-containing alloy and over the MgO guard bed material between 850° C. and 900° C. at a water partial pressure of 8.0 bara, and it indicates a reduction of nearly three orders of magnitude in the gas phase partial pressure of $\text{Si}(\text{OH})_4$ by the guard bed. The calculation of the vapor pressure over the alloy assumes that the surface of the alloy is pure SiO_2 .

[0188] FIG. 23 demonstrates the equilibrium concentrations of $\text{WO}_2(\text{OH})_2$ over a W-containing alloy and over the MgO guard bed material between 850° C. and 900° C. at a water partial pressure of 8.0 bara, and it indicates a reduction of greater than two orders of magnitude in the gas phase partial pressure of $\text{WO}_2(\text{OH})_2$ by the guard bed. The calculation of the vapor pressure over the alloy assumes that the surface of the alloy is pure WO_3 .

[0189] The MgO in the guard beds may be in the form of porous pellets, beads, or rods to provide high surface area for the reactions and to enhance turbulent flow through the guard bed to minimize any gas phase mass transfer resistances. For example, the guard beds may be filled with MgO rods having a purity of 99.8 wt %, an average diameter of 0.2 cm, an

average length of 0.4 cm, and an open porosity of 30%. Other particle shapes, sizes, and porosities may be used as desired. Alternatively, a honeycomb of porous MgO may be used to provide a lower pressure drop. Other configurations for the guard bed include porous foams, structured packing, and random packing. Magnesium is a relatively small cation and a fast diffuser, and should provide the lowest possible solid phase mass transfer resistance if the MgO surface becomes encased with reaction product. The size of the guard bed will be determined by the rate limiting processes for the transport and reaction of the volatile species with the MgO. These processes include the gas phase diffusion of the volatile species to the surface of the MgO, reaction of MgO with the volatile species, and diffusion of Mg or the volatile species through any reaction product that may form on the MgO.

[0190] The embodiments of the invention are described above for the removal of exemplary volatile contaminants formed by the reaction of water with the oxides of chromium, silicon, molybdenum, and/or tungsten. These embodiments also may be applied to similar volatile contaminants formed from the oxides of any other alloying elements or from any oxide refractories when the hot surfaces are exposed to steam-containing gas streams such as hot synthesis gas or air preheated by direct firing. For example, these other alloying elements may include molybdenum and/or vanadium; oxide refractories may include oxides of molybdenum and/or oxides of vanadium.

[0191] In addition to the removal of volatile contaminants described above, embodiments of the invention also may be used to remove other volatile contaminants that may be present in the process gases. These may include, for example, any of Cl_2 , Br_2 , I_2 , and compounds containing any of Cl, Br, and I. Embodiments of the invention also may be applied to the removal of volatile sulfur-containing contaminants such as sulfur dioxide and/or hydrogen sulfide. Embodiments of the invention also may be applied to the removal of oxy-hydroxides of molybdenum.

[0192] The guard bed embodiments of the invention therefore may be applied to the removal of one or more volatile contaminant compounds from a gas stream at elevated temperatures, for example, in the range of 600 to 1100° C., by contacting the gas stream with one or more reactive solid materials. The gas stream may contain one or more components selected from the group consisting of water, oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, and methane. The one or more reactive materials may be selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and alkaline-earth-containing perovskites.

[0193] While the guard beds and liners described above are described for use in ion transport membrane systems, these guard beds and liners may be used in any application in which similar volatile contaminants must be removed from a high-temperature gas stream. For example, the guard beds may be used in solid oxide fuel cells to protect the fuel cell material from damage by the gaseous contaminants.

[0194] Although illustrated and described herein with reference to certain specific embodiments, the present invention is nevertheless not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the spirit of the invention.

1. An ion transport membrane system comprising
 - (a) a pressure vessel comprising an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
 - (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules;
 - (c) a gas manifold having an interior surface wherein the gas manifold is in flow communication with the interior region of each of the planar ion transport membrane modules and with the exterior of the pressure vessel; and
 - (d) a liner disposed within any of the inlet conduit, the outlet conduit, and the interior surface of the gas manifold.
2. The ion transport membrane system of claim 1 wherein the liner comprises a composition selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, combinations thereof, and mixtures thereof.
3. The ion transport membrane system of claim 2 wherein the liner comprises alumina and/or zirconia.
4. The ion transport membrane system of claim 1 wherein the liner comprises magnesium oxide.
5. The ion transport membrane system of claim 4 wherein the liner further comprises alumina.
6. The ion transport membrane system of claim 1 wherein the liner consists essentially of magnesium oxide.
7. The ion transport membrane system of claim 1 wherein the liner comprises magnesium oxide and a composition selected from the group consisting of calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide.
8. The ion transport membrane system of claim 1 wherein the liner comprises magnesium oxide and calcium oxide.
9. The ion transport membrane system of claim 1 comprising a guard bed in flow communication with the inlet of the pressure vessel.
10. The ion transport membrane system of claim 9 wherein the guard bed contains a reactive solid material selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures thereof.
11. The ion transport membrane system of claim 1 comprising a guard bed in flow communication with the gas manifold.
12. The ion transport membrane system of claim 11 wherein the guard bed contains a reactive solid material selected from the group consisting of magnesium oxide, calcium oxide, copper oxide, calcium carbonate, sodium carbonate, strontium carbonate, zinc oxide, strontium oxide, and mixtures thereof.
13. The ion transport membrane system of claim 1 comprising a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct surrounds the plurality of planar ion transport membrane modules and is in flow communication with the inlet and the outlet of the pressure vessel.
14. The ion transport membrane system of claim 13 comprising a duct liner disposed within the flow containment duct.
15. An ion transport membrane system comprising
 - (a) a pressure vessel comprising an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
 - (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules;
 - (c) a flow containment duct disposed in the interior of the pressure vessel, wherein the flow containment duct (1) surrounds the plurality of planar ion transport membrane modules and the one or more guard beds and (2) is in flow communication with the inlet and the outlet of the pressure vessel;
 - (d) a gas manifold having an interior surface wherein the gas manifold is in flow communication with the interior region of each of the planar ion transport membrane modules and with the exterior of the pressure vessel; and
 - (e) a duct liner disposed within the flow containment duct.
16. The ion transport membrane system of claim 15 comprising a liner disposed within any of the inlet conduit, the outlet conduit, and the interior surface of the gas manifold.
17. An ion transport membrane system comprising
 - (a) a pressure vessel having an axis, an interior, an interior surface, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
 - (b) a plurality of planar ion transport membrane modules disposed in the interior of the pressure vessel and arranged in series, each membrane module comprising mixed metal oxide ceramic material and having an interior region and an exterior region, wherein the inlet and the outlet of the pressure vessel are in flow communication with exterior regions of the membrane modules; and
 - (c) a liner disposed adjacent the interior surface of the pressure vessel wherein any cross-section of the liner and pressure vessel taken perpendicular to the axis forms two concentric circles.
18. The ion transport membrane system of claim 17 comprising a gas manifold having an interior surface wherein the gas manifold is in flow communication with the interior region of each of the planar ion transport membrane modules and with the exterior of the pressure vessel.
19. The ion transport membrane system of claim 17 comprising a liner disposed within any of the inlet conduit, the outlet conduit, and the interior surface of the gas manifold.
20. An ion transport membrane system comprising
 - (a) a pressure vessel having an interior, an exterior, an inlet, an inlet conduit, an outlet, and an outlet conduit;
 - (b) a membrane stack or module assembly disposed in the interior of the pressure vessel, the assembly having a plurality of planar wafers comprising mixed metal oxide ceramic material, each wafer having an interior region and an exterior region, and a plurality of hollow ceramic spacers, wherein the stack or module assembly is formed by alternating wafers and spacers such that the interiors of the wafers are in flow communication via the hollow spacers, the wafers are oriented parallel to one another,

and the alternating spacers and wafers are oriented coaxially to form the stack or module such that the wafers are perpendicular to the stack or module axis;

(c) a gas manifold shroud assembly having an interior surface and disposed around the membrane stack or module assembly within the interior of the pressure vessel, wherein the shroud assembly (1) separates the stack or module into at least a first wafer zone and a second wafer zone, (2) places the inlet of the pressure vessel in flow communication with exterior regions of the wafers in the first wafer zone, (3) places exterior regions of the wafers in the first wafer zone in series flow communica-

tion with exterior regions of the wafers of the second wafer zone, and (4) places the outlet of the pressure vessel in flow communication with the exterior regions of the wafers in the second wafer zone or the wafers in a last wafer zone; and

(d) a liner adjacent at least a portion of the interior surface of the gas manifold shroud assembly.

21. The ion transport membrane system of claim **20** comprising a liner disposed within the inlet conduit and/or the outlet conduit of the pressure vessel.

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(19) **United States**(12) **Patent Application Publication****Repasky et al.**(10) **Pub. No.: US 2008/0302013 A1**(43) **Pub. Date: Dec. 11, 2008**(54) **STAGED MEMBRANE OXIDATION
REACTOR SYSTEM****Publication Classification**(51) **Int. Cl.**
C01B 3/24 (2006.01)(52) **U.S. Cl.** **48/127.9; 48/198.1**(57) **ABSTRACT**

Ion transport membrane oxidation system comprising (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages and adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair; and (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas.

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FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

Percent of ITM Syngas Reactor

FIG. 6

FIG. 7

Percent of ITM Syngas Reactor

FIG. 8

STAGED MEMBRANE OXIDATION REACTOR SYSTEM

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] This invention was made with government support under Contract Number DE-FC26-97FT96052 between Air Products and Chemicals, Inc. and the U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0002] The permeation of oxygen ions through ceramic ion transport membranes is the basis for the design and operation of high-temperature oxidation reactor systems in which permeated oxygen is reacted with oxidizable compounds to form oxidized or partially-oxidized reaction products. The practical application of these oxidation reactor systems requires membrane assemblies having large surface areas, flow passages to contact oxidant feed gas with the oxidant sides of the membranes, flow passages to contact reactant feed gas with the reactant sides of the membranes, and flow passages to withdraw product gas from the permeate sides of the membranes. These membrane assemblies may comprise a large number of individual membranes arranged and assembled into modules having appropriate gas flow piping to introduce feed gases into the modules and withdraw product gas from the modules.

[0003] Ion transport membranes may be fabricated in either planar or tubular configurations. In the planar configuration, multiple flat ceramic plates are fabricated and assembled into stacks or modules having piping means to pass oxidant feed gas and reactant feed gas over the planar membranes and to withdraw product gas from the permeate side of the planar membranes. In tubular configurations, multiple ceramic tubes may be arranged in bayonet or shell-and-tube configurations with appropriate tube sheet assemblies to isolate the oxidant and reactant sides of the multiple tubes.

[0004] The individual membranes used in planar or tubular module configurations typically comprise very thin layers of active membrane material supported on material having large pores or channels that allow gas flow to and from the surfaces of the active membrane layers. The ceramic membrane material and the components of the membrane modules can be subjected to significant mechanical stresses during normal steady-state operation and especially during unsteady-state startup, shutdown, and upset conditions. These stresses may be caused by thermal expansion and contraction of the ceramic material and by dimensional variance caused by chemical composition or crystal structure changes due to changes in the oxygen stoichiometry of the membrane material. These modules may operate with significant pressure differentials across the membrane and membrane seals, and stresses caused by these pressure differentials must be taken into account in membrane module design. In addition, membrane modules have upper temperature limits above which membrane degradation and/or module damage may occur. The relative importance of these phenomena may differ depending on the specific oxidation reactions and operating conditions used. The potential operating problems caused by these phenomena may have a significant negative impact on the conversion efficiency and membrane operating life of the system.

[0005] There is a need in the field of high temperature ceramic membrane reactors for new membrane module and reactor system designs that address and overcome these potential operating problems. Such designs should include features to allow long membrane life, minimum capital cost, and efficient operation over wide ranges of production rates. Embodiments of the invention disclosed and defined herein address these needs by providing improved module and reactor designs for use in membrane oxidation systems.

BRIEF SUMMARY OF THE INVENTION

[0006] One embodiment of the invention relates to an ion transport membrane oxidation system comprising (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; and (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas.

[0007] Another embodiment includes a method for generating an oxidation product gas comprising (a) providing an ion transport membrane oxidation system having (1) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (2) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; and (3) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas. The method includes introducing one or more reactant feed gases into the reactant gas inlet region of a first stage of the two or more membrane oxidation stages; (c) introducing an oxidant gas into any of the oxidant gas inlet regions of the two or more membrane oxidation stages; (d) introducing a reactant interstage feed gas into any of the interstage reactant gas flow paths disposed between adjacent membrane oxidation stage or into any reactant zone of any stage receiving interstage reactant gas; and (e) withdrawing an oxidation gas product from the reactant gas outlet region of a last stage of the two or more membrane oxidation stages.

[0008] A related embodiment of the invention provides an ion transport membrane oxidation system comprising

[0009] (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a

reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;

[0010] (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of the second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage;

[0011] (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;

[0012] (d) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages;

[0013] (e) a reactant gas supply manifold in flow communication with one of the reactant gas feed lines to the first stage and in flow communication with any of the reactant interstage feed gas lines; and

[0014] (f) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

[0015] Another related embodiment of the invention relates to a method for generating an oxidation product gas comprising (a) providing an ion transport membrane oxidation system that includes (1) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (2) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; (3) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas; (4) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages; (5) a reactant gas supply manifold in flow communication with one of the reactant gas feed lines to the first stage and in flow communication with any of the reactant interstage feed gas lines; and (6) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

[0016] This embodiment includes the steps of (b) providing a reactant gas via the reactant gas supply manifold, introducing reactant feed gas from the manifold into the reactant zone of the first stage, and introducing reactant gas from the manifold as reactant interstage feed gas into any of the one or more reactant interstage feed gas lines; (c) introducing an oxidant gas into any of the oxidant gas inlet regions of the two or more membrane oxidation stages; and (d) withdrawing an oxidation gas product from the reactant gas outlet region of the last stage of the two or more membrane oxidation stages.

[0017] A further embodiment of the invention includes an ion transport membrane oxidation system comprising (a) two

or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas; (d) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages; (e) a reactant interstage feed gas supply manifold in flow communication with any of the reactant interstage feed gas lines; and (f) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

[0018] A further related embodiment of the invention provides an ion transport membrane oxidation system comprising (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas.

[0019] This embodiment includes (d) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages; (e) a reactant interstage feed gas supply manifold in flow communication with any of the reactant interstage feed gas lines; (f) a reactant gas supply manifold in flow communication with any of (1) any of the reactant interstage feed gas lines and (2) any of the one or more reactant gas feed lines; and (g) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

[0020] An optional embodiment of the invention relates to a method for generating an oxidation product gas comprising (a) providing an ion transport membrane oxidation system that includes (1) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region; (2) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair

in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; (3) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas; (4) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages; (5) a reactant interstage feed gas supply manifold in flow communication with any of the reactant interstage feed gas lines; and (6) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

[0021] This embodiment includes the steps of (b) introducing a reactant feed gas into the reactant zone of the first stage of the two or more membrane oxidation stages; (c) providing reactant interstage feed gas via the reactant interstage feed gas supply manifold into any of the one or more reactant interstage feed gas lines; (d) introducing an oxidant gas into any of the oxidant gas inlet regions of the two or more membrane oxidation stages; and (e) withdrawing an oxidation gas product from the reactant gas outlet region of the last stage of the two or more membrane oxidation stages.

[0022] Another embodiment provides a method for the operation of an ion transport membrane oxidation system comprising (a) introducing one or more reactant gases into a reactant zone of the ion transport membrane oxidation system, wherein the one or more reactant gases comprise at least methane and carbon dioxide; (b) introducing an oxygen-containing gas into an oxidant zone of the ion transport membrane oxidation system; (c) permeating oxygen from the oxidant zone through an ion transport membrane into the reactant zone and reacting the oxygen therein with one or more components in the reactant gases; and (d) maintaining the partial pressure of carbon dioxide in the reactant gas flowing into the reactant zone to be less than a critical threshold carbon dioxide partial pressure, $p_{CO_2}^*$, wherein $p_{CO_2}^*$ is defined as a carbon dioxide partial pressure above which the material in the ion transport membrane reacts with carbon dioxide and decomposes.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0023] FIG. 1 is a schematic flow diagram of a generic embodiment of the present invention.

[0024] FIG. 2 is a schematic flow diagram of an embodiment of the invention.

[0025] FIG. 3 is a schematic flow diagram for a specific configuration of the embodiment of FIG. 2.

[0026] FIG. 4 is a schematic flow diagram of another embodiment of the invention.

[0027] FIG. 5 is a plot of $p_{CO_2}^*$ vs. temperature at various equilibrium O_2 partial pressures for the mixed conducting metal oxide membrane material $La_{0.9}Ca_{0.1}FeO_{3-\delta}$.

[0028] FIG. 6 is a plot of the temperature of the reactant gas as a percentage of a group of 100 reaction stages from the reactant feed inlet (0) to the product outlet (100) for Example 1.

[0029] FIG. 7 is a plot of the temperature of the reactant gas as a percentage of a group of 100 reaction stages from the reactant feed inlet (0) to the product outlet (100) for Example 2.

[0030] FIG. 8 is a plot of the temperature of the reactant gas as a percentage of a group of 100 reaction stages from the reactant feed inlet (0) to the product outlet (100) for Example 3.

DETAILED DESCRIPTION OF THE INVENTION

[0031] Membrane oxidation reactor systems typically utilize partial oxidation, complete oxidation, steam reforming, carbon dioxide reforming, water-gas shift, and/or various combinations of these reactions to produce synthesis gas. Certain of these reactions are strongly exothermic and others are endothermic. Because ceramic membrane systems generally require a narrow operating temperature range, proper control of the exothermic and endothermic reactions is required. This need is addressed by embodiments of the present invention directed toward the design and operation of ion transport membrane (ITM) systems that utilize multiple reactant-staged membrane modules operating in series for use in oxidation processes. It has been found that when exothermic reactions occur between permeated oxygen and reactive components, for example in the production of synthesis gas from methane, the degree of reactant conversion across an individual membrane must be limited to prevent an excessive temperature gradient across the membrane. It also has been found that when a membrane is transporting oxygen, the amount of oxygen extraction across an individual membrane must be limited to prevent an excessive oxygen vacancy gradient in the membrane material between the leading edge and trailing edge of the membrane. Excessive temperature or oxygen vacancy gradients may cause excessive stresses in the membranes that could seriously limit the membrane life. In addition, it has been found that the concentration of certain components in the reactant gas, particularly carbon dioxide, must be maintained below certain critical partial pressures to avoid damage to the membrane material.

[0032] The embodiments of the present invention address these problems by utilizing multiple reactor stages so that the reactant conversion in each stage can be controlled, the amount of oxygen extracted across membranes in each module can be kept sufficiently low to prevent an excessive oxygen vacancy gradient in the membrane material, and the partial pressure of carbon dioxide in contact with the membranes can be maintained below a critical partial pressure. A reactor stage may comprise multiple membrane modules arranged in parallel and/or series. The amount of oxygen extracted across each individual module may be limited by appropriate module sizing, and the total desired degree of oxygen extraction within a stage may be achieved by operating a selected plurality of modules within a stage.

[0033] The total desired conversion in the system may be achieved by utilizing a plurality of reactor stages in series wherein each stage is operated so that the degree of reactant conversion in each stage is controlled at a selected value and may approach chemical equilibrium. This may be accomplished by introducing portions of the reactant gas into two or more stages of a multiple-stage reactor system wherein each stage may comprise multiple membrane modules arranged in series and/or parallel. The degree of reactant conversion across each individual module in a stage may be controlled by appropriate module sizing and/or feed gas flow rate. Recycle gas from downstream synthesis gas conversion processes or reactant gas from other sources may be introduced into the membrane reactor system as additional reactant gas to increase overall conversion and/or to control temperatures in

selected stages. This recycle gas often contains carbon dioxide, and the partial pressure of this carbon dioxide at any point in the reactor may be controlled to prevent membrane degradation as described in detail below.

[0034] The following definitions apply to terms used in the description and claims for the embodiments of the invention presented herein.

[0035] An ion transport membrane module is an assembly of a plurality of ion transport membrane structures that has a gas inflow region and a gas outflow region disposed such that gas can flow across the external surfaces of the membrane structures. The plurality of ion transport membrane structures also may have a gas inflow region and a gas outflow region disposed such that gas can flow across the internal surfaces of the membrane structures. Gas flowing from the inflow region to the outflow region of a membrane module may change in composition as it passes across the surfaces of the membrane structures in the module. Each membrane structure has an oxidant gas feed side or zone, also described as the oxidant or cathode side, and a reactant, permeate, or anode side or zone separated by an active membrane layer or region that allows oxygen ions to permeate through the membrane and react with reactive components on the reactant side. In one exemplary type of membrane module design, each module has an interior region and an exterior region wherein the oxidant gas feed flows through the interior region and the reactant gas flows through the exterior region of the membrane structure.

[0036] An ion transport membrane comprises an active layer of ceramic membrane material comprising mixed metal oxides capable of transporting or permeating oxygen ions at elevated temperatures. The ion transport membrane also may transport electrons in addition to oxygen ions, and this type of ion transport membrane typically is described as a mixed conductor membrane. The ion transport membrane also may be a composite membrane comprising a layer of dense active membrane material and one or more layers of porous or channeled support layers.

[0037] The terms “stage”, “reaction stage”, and “reactor stage” in a multi-stage membrane oxidation system are equivalent and are defined as an assembly of one or more membrane modules arranged in parallel and/or series within the stage wherein each stage comprises (1) a reactant side or zone (these terms are equivalent), (2) an oxidant side or zone, (3) one or more ion transport membranes separating the oxidant zone from the reactant zone, (4) a reactant gas inlet or inlet region in flow communication with the reactant zone, and (5) a reactant gas outlet or outlet region in flow communication with the reactant zone. More specifically, each stage may have a reactant feed gas inlet or inlet region (if it is the first stage), an interstage reactant gas stream inlet or inlet region (if it is not the first stage), an interstage reactant gas stream outlet or outlet region (if it is not the last stage), and a product gas outlet or outlet region (if it is the last stage). Each stage also has one or more oxidant gas inlets or inlet regions in flow communication with the oxidant zone and one or more oxygen-depleted oxidant gas outlets or outlet regions in flow communication with the oxidant zone.

[0038] The one or more ion transport membranes separating the oxidant zone from the reactant zone allow the permeation of oxygen ions through the membrane, and the dense active membrane material does not allow any substantial bulk flow of gas between the oxidant and reactant zones of the stage. Small but acceptable leaks in the membrane may occur in some cases.

[0039] A stage may have any number of individual membrane modules arranged in series and/or parallel flow arrangement with respect to the reactant gas streams. Reactant gas is introduced into the stage inlet, is distributed among the modules in the stage, and passes through the reactant sides of the modules. The effluent gas from the modules is withdrawn via the stage outlet. A stage may include one or more catalysts to enhance the reactions occurring therein; catalysts may include any of oxidation catalyst, steam reforming catalyst, carbon dioxide reforming catalyst, and water gas shift catalyst. Catalyst may be disposed (1) following the reactant zone of any stage and/or (2) downstream of any membrane module within any stage and/or (3) upstream of any membrane module within any stage and/or (4) within or between the modules within any stage in any desired configuration.

[0040] A reactant gas is defined as a gas comprising one or more reactive components that participate in any of the reactions (1) that occur in the reactant zone of a membrane oxidation reactor stage and (2) that may occur in a catalyst region following or preceding the reactant zone of the membrane oxidation reactor stage. The reactions in the reactant zone may occur (1) between oxygen permeated through the membrane and any of the reactive components and (2) among any of the reactive components. These reactions form reaction products that may be withdrawn as outlet or product gas from any stage of a staged reactor system.

[0041] The term “hydrocarbon” is defined as a compound comprising at least hydrogen and carbon atoms. The term “oxygenated hydrocarbon” is defined as a compound comprising at least hydrogen, carbon, and oxygen atoms.

[0042] The term “pre-reformed natural gas” means the reaction products from the catalytic reforming of a portion of the hydrocarbons in a natural gas stream. Pre-reformed natural gas typically comprises methane, carbon monoxide, carbon dioxide, hydrogen, and water. Pre-reforming of natural gas may be carried out to convert and decompose hydrocarbons heavier than methane for the purpose of eliminating coking in downstream reforming or partial oxidation processes. The terms “pre-reforming” and “pre-reformed” mean the partial reforming of a hydrocarbon-containing stream prior to further reaction in a membrane reactor system. The terms “pre-reforming” or “pre-reformed” also may be defined as the catalytic reaction of water and/or carbon dioxide with a portion of the hydrocarbons in a hydrocarbon-containing stream, particularly hydrocarbons heavier than methane, to form reformed products.

[0043] In one embodiment of the invention, a staged reactor system is operated to generate a synthesis gas product comprising hydrogen and carbon monoxide. This embodiment utilizes a first reactant gas comprising one or more hydrocarbons and a second reactant gas comprising steam (vaporized water). A typical first reactant gas is natural gas comprising mostly methane and smaller concentrations of hydrocarbons having 2 to 6 carbon atoms; another typical first reactant gas is methane-rich gas resulting from pre-reforming natural gas with steam; other carbonaceous reactant gases may be used in alternative applications. Optionally, a third reactant gas may be used that comprises one or more components selected from the group consisting of oxygen, nitrogen, hydrogen, water, methane, other hydrocarbons, carbon monoxide, and carbon dioxide. The third reactant gas may be provided, for example, by offgas from a downstream process that uses the synthesis gas product as feed gas. When three reactant gases are used in this embodiment, the chief reactive components

are any of methane, other hydrocarbons, water, hydrogen, carbon monoxide, and carbon dioxide.

[0044] An oxidant gas is defined as a gas comprising oxygen and other components from which oxygen can be extracted by permeation through an ion transport membrane to react with reactive components in the reactant zone. An oxygen-containing gas is a type of reactant gas that comprises one or more compounds that contain oxygen atoms such as, for example, water, carbon monoxide, and carbon dioxide.

[0045] A reactant feed gas is defined as a reactant gas introduced into the reactant zone or side of the first stage of a multi-stage membrane reactor system. An interstage reactant gas is defined as reactant gas flowing between stages, i.e., from the outlet region of the reactant zone of one stage and into the inlet region of the reactant zone of the next stage; this gas comprises reaction products and may include unreacted reactive components. The relative amounts of reactive components and oxidation products in an interstage reactant gas stream entering a given stage may depend on (1) the degree to which chemical equilibrium is approached in the previous stage and (2) the amount and composition of reactant interstage feed gas (if any) that is introduced into the interstage reactant gas to the reaction zone of the given stage.

[0046] A reactant interstage feed gas is defined as a reactant gas that is (1) introduced into the reactant zone of any stage other than the first stage or (2) mixed with an interstage reactant gas prior to entering that reactant zone. The reactant interstage feed gas may have the same composition as the reactant feed gas to the first stage or may have a different composition than the reactant feed gas. A reactant feed gas or reactant interstage feed gas typically comprises high concentrations of reactive components. A product gas is the reactant gas effluent from the reactant zone of the last stage of a multi-stage membrane reactor system, wherein the product gas comprises one or more oxidation products and also may comprise unreacted reactive components. The product gas may be, for example, synthesis gas containing at least hydrogen and carbon oxides.

[0047] A reactant-staged membrane reactor system is defined as a system comprising two or more membrane stages arranged in series with respect to the flow of reactant gases through the system wherein the reactant gas effluent flows from the outlet region of one stage into the inlet region of another stage immediately downstream. Reactant feed gas enters the first stage, product gas is withdrawn from the last stage, and an interstage reactant gas stream flows between each pair of series stages. A reactant interstage feed gas comprising additional reactant gas may be introduced into at least one interstage reactant gas stream and may be introduced into any of the interstage reactant gas streams in the multi-stage reactor system.

[0048] A membrane module may have a configuration of multiple planar wafers in which each wafer has a center or interior region and an exterior region, wherein the wafer is formed by two parallel planar members sealed about at least a portion of the peripheral edges thereof. Oxygen ions permeate through active membrane material that may be placed on either or both surfaces of a planar wafer. Gas can flow through the center or interior region of the wafer, and the wafer has one or more gas flow openings to allow gas to enter and/or exit the interior region of the wafer. Thus oxygen ions may permeate from the exterior region into the interior region, or conversely may permeate from the interior region to the exterior region. In one embodiment, the gas in contact

with the outer surfaces in the exterior regions of the membrane modules may be at a higher pressure than the gas within the interior regions of the membrane modules. Representative membrane compositions and planar membrane module configurations that may be used in the embodiments of the present invention are described in U.S. Pat. No. 7,179,323 and U.S. Patent Publication 2004/0186018(A1), which are incorporated herein by reference.

[0049] Alternatively, the membrane module may have a tubular configuration in which an oxidant gas flows in contact with one side of the tube (i.e., in either the interior region or the exterior region of the tube) and oxygen ions permeate through active membrane material in or on the tube walls to the other side of the tube. The oxidant gas may flow inside or outside of the tube in a direction generally parallel to the tube axis, or conversely may flow over the outer side of the tube in a direction which is not parallel to the tube axis. A module may comprise multiple tubes arranged in bayonet or shell-and-tube configurations with appropriate tube sheet assemblies to isolate the oxidant and reactant sides of the multiple tubes.

[0050] Modules may be arranged in series within a reactor stage wherein a number of modules are disposed along a single axis. Typically, reactant gas which has passed across the surfaces of the membrane structures in a first module flows from the outflow region of that module, after which some or all of this gas enters the inflow region of a second module and thereafter flows across the surfaces of the membrane structures in the second module. The axis of a series of single modules may be parallel or nearly parallel to the overall flow direction or axis of the gas passing over the modules in series.

[0051] Modules may be arranged within a stage in banks of two or more parallel modules wherein a bank of parallel modules lies on an axis that is not parallel to, and may be generally orthogonal to, the overall flow direction or axis of the gas passing over the modules. Multiple banks of modules may be arranged in series, which means by definition that banks of modules are disposed such that at least a portion of reactant gas which has passed across the surfaces of the membrane structures in a first bank of modules flows across the surfaces of the membrane structures in a second bank of modules.

[0052] Any number of single modules or banks of modules may be arranged in series and/or parallel within a stage. In one embodiment, the modules in a series of single modules or in a series of banks of modules may lie on a common axis or common axes in which the number of axes equals one or equals the number of modules in each bank. In another embodiment, successive modules or banks of modules in a series of modules or banks of modules may be offset in an alternating fashion such that the modules lie on at least two axes or on a number of axes greater than the number of modules in a bank, respectively. Both of these embodiments are included in the definition of modules in series as used herein.

[0053] The term "in flow communication with" as applied to a first and second region means that fluid can flow from the first region to the second region, through an intermediate region. The intermediate region may comprise connecting piping between the first and second regions or may comprise an open flow area or channel between the first and second regions. The term "connected to" as applied to a first and second region means that fluid can flow from the first region

directly to the second region or through connecting piping to the second region. The term “direct flow communication” and the term “directly” as applied to a flowing fluid mean that the fluid can flow from a first region to a second region, and/or from the second region to the first region, wherein the flow path between the regions is not in flow communication with any vessel, storage tank, or process equipment, except that the fluid flow path may include piping and/or one or more flow control devices selected from orifices, valves, and other flow restriction devices.

[0054] The indefinite articles “a” and “an” as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of “a” and “an” does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article “the” preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective “any” means one, some, or all indiscriminately of whatever quantity. The term “and/or” placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity.

[0055] A schematic flow diagram of a generic embodiment of the invention is illustrated in FIG. 1. The exemplary membrane oxidation system comprises first stage 1, second stage 3, third stage 5, and last or n^{th} stage 7. Any desired number of stages may be used as long as there are at least two stages. Each stage is illustrated schematically as a generic module having an oxygen permeable membrane that divides the module into an oxidant side and a permeate or reactant side. As explained above, a stage can comprise any number of membrane modules arranged in series and/or parallel and may include one or more catalysts.

[0056] First stage 1 comprises oxidant side or zone 1a, membrane 1b, reactant side or zone 1c, optional catalyst 1d, and appropriate gas inlet and outlet regions. Optional catalyst 1d is shown here as immediately following the module. Alternatively or additionally catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Similarly, second stage 3 comprises oxidant side 3a, membrane 3b, reactant side 3c, appropriate gas inlet and outlet regions, and optional catalyst 3d, which is shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Similarly, third stage 5 comprises oxidant side 5a, membrane 5b, reactant side 5c, appropriate gas inlet and outlet regions, and optional catalyst 5d. Optional catalyst 5d is shown here as immediately following the module. Alternatively or additionally catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Last or n^{th} stage 7 comprises oxidant side 7a, membrane 7b, reactant side 7c, appropriate gas inlet and outlet regions, and optional catalyst 7d, shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Product gas from last stage 7 is withdrawn via product line 7e.

[0057] In the illustration of FIG. 1, interstage reactant gas flows from stage 1 via flow path 1e, from stage 3 via flow path 3e, and from stage 5 via flow path 5e. In one embodiment, each of stages 1, 3, and 5 may be enclosed in a separate pressure vessel; in this case, flow paths 1e, 3e, and 5e are pipes, conduits, or closed channels between the vessels. In another embodiment, stages 1, 3, 5, and 7 may be enclosed in a single pressure vessel (not shown) such that reactant gas can flow through the reactant zones of each stage in succession; in this case, flow paths 1e, 3e, and 5e are open regions between stages through which gas can flow from the reactant gas outlet region of one stage into the reactant gas inlet region of the following stage. Each stage is adjacent a downstream stage and/or an upstream stage; the first stage is adjacent a downstream stage, the last stage is adjacent an upstream stage, and all other stages are adjacent an upstream stage and a downstream stage. The terms “upstream” and “downstream” are defined relative to the flow direction of reactant gas.

[0058] The oxidant zone and the reactant zone in each stage are isolated from each other so that the bulk flow of oxidant gas through the oxidant zone and the bulk flow of reactant gas through the reactant zone are separate and independent. The membrane or membranes separating the oxidant zone from the reactant zone prevents any substantial bulk gas flow between the zones and allows the permeation of oxygen through the membrane from the oxidant zone to the reactant zone. In some cases, small but acceptable leaks may occur through imperfections in the membrane.

[0059] An oxidant gas, for example, preheated air or oxygen-containing combustion products from a combustor operated with excess air, is introduced via oxidant inlet line 9 into oxidant side 1a of first stage 1 and contacts the oxidant side of membrane 1b, a portion of the oxygen permeates through membrane 1b, and oxygen-depleted gas exits first stage 1 via oxygen-depleted oxidant outlet line 11. Similarly, additional oxidant gas streams may be introduced via lines 13, 15, and 19 into stages 3, 5, and 7, respectively, and oxygen-depleted gas may exit the stages via lines 21, 23, and 25, respectively. Alternatively, some or all of the oxidant gas may flow through two or more stages in series via lines 27, 29, and 31. In one embodiment, for example, oxidant gas may flow through lines 9, 27, and 21 such that stages 1 and 3 operate in series with respect to oxidant gas; similarly, a single oxidant stream may provide oxidant to a pair of downstream stages. Thus the stages may be operated individually with respect to the flow of oxidant gas, may be operated in series with respect to the flow of oxidant gas, or may utilize any combination of individual and series operation with respect to the flow of oxidant gas. Oxidant gas inlet and outlet manifolds (not shown) may be used to introduce oxidant gas into the oxidant zones of the multiple stages and withdraw oxygen-depleted oxidant gas from the oxidant zones of the multiple stages.

[0060] Other oxidant gas flow configurations are possible as alternatives to that described above. For example, the oxidant gas may flow counter-current to the reactive gas flow, cross-flow to the reactive gas flow, or in any other arrangement such that sufficient oxidant gas is provided to the oxidant zone side of the membranes.

[0061] Reactant gas may enter the multi-stage reactor system via manifold 27, a first portion may be withdrawn via line 29 and combined with another reactant gas (for example, steam) provided in line 31, and the combined gas may be introduced via reactant gas inlet line 33 into reactant side 1c of first stage 1. Additional portions of reactant gas may be

withdrawn from manifold 27 via any of reactant interstage feed gas lines 35, 37, and 39 and introduced as reactant interstage feed gas into any of interstage reactant gas flow paths 1e, 3e, and 5e, respectively. Alternatively, the reactant interstage feed gas may be introduced directly into the reactant side of any stage and/or upstream of any of the catalysts 1d, 3d, 5d, and 7d. The reactant gas in manifold 27 may comprise one or more hydrocarbons and also may comprise any of the components water, carbon monoxide, carbon dioxide, and hydrogen. For example, the reactant gas in manifold 27 may be pre-reformed natural gas comprising methane, carbon monoxide, carbon dioxide, hydrogen, and water. The reactant gas provided via line 31 may be, for example, vaporized water (steam).

[0062] Additional reactant gas may be provided via manifold 41 from a source different than the source of the reactant gas in line 27 and the source of reactant gas provided via line 31. This additional reactant gas may be introduced via any of lines 29, 43, 45, and 47 into any of first stage 1, the interstage reactant gas in line 1e, the interstage reactant gas in line 3e, and the interstage gas entering last or n^{th} stage 7. Alternatively, the additional reactant gas may be introduced upstream of any of catalysts 1d, 3d, 5d, and 7d. This additional reactant gas may be, for example, an oxygen-containing gas comprising carbon dioxide obtained from a downstream process that uses product gas from line 7e. The additional reactant gas may comprise unreacted offgas from a downstream process that uses product gas from line 7e and/or may comprise partially-reformed unreacted offgas from a downstream process that uses product gas from line 7e. Any number of additional stages may be utilized between stage 5 and last stage 7 as desired.

[0063] The gas flow rates in any of the lines described above may be regulated by control valves or other flow devices (not shown) known in the art. Alternatively or additionally, the temperatures of any of the gas streams may be controlled by heating and/or cooling (not shown) by methods known in the art.

[0064] Various combinations of reactant gas types including oxygen-containing gas may be introduced into the reactant sides of the modules in the staged membrane oxidation reactor system of FIG. 1. In one embodiment, for example, pre-reformed natural gas may be introduced into the reactor stages via manifold 27 and lines 29, 35, 37, and 39, and steam may be introduced via lines 31 and 33 into first stage 1. No additional reactant gas is provided via manifold 41 and lines 29, 43, 45, and 47 in this embodiment. In another exemplary embodiment, pre-reformed natural gas and steam may be introduced into the first stage via lines 31 and 33, and carbon dioxide-containing gas (for example, a recycle gas from a downstream process) may be introduced into the system via manifold 41 and any of lines 43, 45, and 47. The downstream process may be a hydrocarbon synthesis process (e.g., a Fischer-Tropsch process) or an oxygenated hydrocarbon synthesis process (e.g., an alcohol synthesis process). The downstream process may utilize synthesis gas produced by the staged oxidation reactor system of FIG. 1. Manifold 27 and lines 29, 35, 37, and 39 are not used in this embodiment. Other embodiments are possible in which combinations of reactant gas from different sources are introduced into the reactor stages. For example, pre-reformed natural gas may be provided to the staged reactor system via manifold 27 and lines 29, 35, 37, and 39, steam may be introduced into the system via line 31, and carbon dioxide-containing gas (for example,

a recycle gas from a downstream process) may be introduced into the system via manifold 41 and any of lines 43, 45, and 47. In another example, a reactant gas comprising pre-reformed natural gas, a carbon dioxide-containing additional reactant gas, and steam are provided to the staged reactor system via manifold 27 and lines 29, 35, 37, and 39, and steam may be introduced into the system via line 31. Manifold 41 and lines 43, 45, and 47 are not used in this case.

[0065] Another embodiment of the invention is illustrated in the schematic flowsheet of FIG. 2 wherein a membrane oxidation system comprises first stage 201, second stage 203, third stage 205, and last or n^{th} stage 207. Any number of stages may be used as long as there are at least two stages. Each stage is illustrated schematically as a generic module having an oxygen permeable membrane that divides the module into an oxidant side or zone and a permeate or reactant side or zone. As explained above, a stage can comprise any number of membrane modules arranged in series and/or parallel and may include one or more catalysts selected from oxidation catalyst, steam reforming catalyst, carbon dioxide reforming catalyst, and water gas shift catalyst.

[0066] First stage 201 comprises oxidant side 201a, membrane 201b, reactant side 201c, optional catalyst 201d, and appropriate gas inlet and outlet regions. Optional catalyst 201d is shown here as immediately following the module, but alternatively or additionally catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Similarly, second stage 203 comprises oxidant side 203a, membrane 203b, reactant side 203c, appropriate gas inlet and outlet regions, and optional catalyst 203d, which is shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Similarly, third stage 205 comprises oxidant side 205a, membrane 205b, reactant side 205c, appropriate gas inlet and outlet regions, and optional catalyst 205d. Optional catalyst 205d is shown here as immediately following the module, but alternatively or additionally catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Last or n^{th} stage 207 comprises oxidant side 207a, membrane 207b, reactant side 207c, appropriate gas inlet and outlet regions, and optional catalyst 207d, shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Product gas from last stage 207 is withdrawn via product line 207e. Interstage reactant gas flows from stage 201 via line 201e, from stage 203 via line 203e, and from stage 205 via line 205e.

[0067] An oxidant gas, for example, preheated air or oxygen-containing combustion products from a combustor operated with excess air, is introduced via line 209 into oxidant side 201a of first stage 201 and contacts the oxidant side of membrane 201b, a portion of the oxygen permeates through membrane 201b, and oxygen-depleted gas exits first stage 201 via line 211. Similarly, additional oxidant gas streams may be introduced via lines 213, 215, and 219 into stages 203, 205, and 207, respectively, and oxygen-depleted gas may exit the stages via lines 221, 223, and 225, respectively.

[0068] Natural gas is provided as a reactant gas via line 227, is mixed with steam from line 229, the mixture is heated in

pre-heater 231, and the heated mixture flows via line 233 to steam-methane reformer 235. Hydrogen may be added via line 237 for use within the reformer for feed gas desulfurization (not shown) as is normally practiced in the steam-methane reforming art. Partially-reformed or pre-reformed gas exits the reformer via line 239 and optionally is mixed with reactant gas in line 241 (for example, a recycle gas from a downstream process) to form a reactant feed gas flowing through manifold 243. The downstream process may be a hydrocarbon synthesis process (e.g., a Fischer-Tropsch process) or an oxygenated hydrocarbon synthesis process (e.g., an alcohol synthesis process). The downstream process may utilize synthesis gas produced by the staged oxidation reactor system of FIG. 2. Reactant feed gas may be at a temperature of 600 to 1150° C. and a pressure of 2 to 40 atma, and the gas typically comprises methane, water, hydrogen, carbon dioxide, and carbon monoxide.

[0069] A first portion of the reactant gas feed via line 245 is mixed with steam provided in line 247 and the mixed reactant feed gas flows into reactant side 201c of first stage 201, reacts therein with oxygen permeated through membrane 201b, passes through optional catalyst 201d, and flows via flow path 201e as an interstage reactant gas. A second portion of the reactant gas feed from manifold 243 is withdrawn via line 249 to provide a reactant interstage feed gas that is mixed with the interstage reactant gas in flow path 201e. The mixed gas then flows into reactant side 203c of second stage 203, reacts therein with oxygen permeated through membrane 203b, passes through optional catalyst 203d, and flows via flow path 203e as an interstage reactant gas. Alternatively, the reactant interstage feed gas in line 249 may be introduced directly into the reactant side or zone of stage 203 and/or upstream of catalyst 201d.

[0070] A third portion of the reactant gas feed from manifold 243 is withdrawn via line 251 to provide a reactant interstage feed gas that is mixed with the interstage reactant gas in flow path 203e. The mixed gas then flows into reactant side 205c of third stage 205, reacts therein with oxygen permeated through membrane 205b, passes through optional catalyst 205d, and flows via flow path 205e as an interstage reactant gas. Alternatively, the reactant interstage feed gas in line 251 may be introduced directly into the reactant side of stage 205 and/or upstream of catalyst 203d.

[0071] A fourth or nth portion of the reactant gas feed from manifold 243 is withdrawn via line 253 to provide a reactant interstage feed gas that is mixed with the interstage reactant gas in flow path 205e. The mixed gas then flows into reactant side 207c of last or nth stage 207, reacts therein with oxygen permeated through membrane 207b, passes through optional catalyst 207d, and flows via line 207e as a product synthesis gas. Alternatively, the reactant interstage feed gas in line 253 may be introduced directly into the reactant side of stage 207 and/or upstream of catalyst 205d.

[0072] The product gas may be at a temperature of 600 to 1150° C. and a pressure of 2 to 40 atma, and the gas may typically comprise hydrogen, carbon monoxide, water, carbon dioxide, and methane. Any number of additional stages may be utilized between third stage 205 and last stage 207 as desired.

[0073] In the illustration of FIG. 2 described above, interstage reactant gas flows from stage 201 via flow path 201e, from stage 203 via flow path 203e, and from stage 205 via flow path 205e. In one embodiment, each of stages 201, 203, 205, and 207 may be enclosed in a separate pressure vessel; in

this case, flow paths 201e, 203e, and 205e are pipes, conduits, or closed channels between the vessels. In another embodiment, stages 201, 203, 205, and 207 may be enclosed in a single pressure vessel (not shown) such that reactant gas can flow through the reactant zones of each stage in succession; in this case, flow paths 201e, 203e, and 205e are open regions between stages through which gas can flow from the reactant gas outlet region of one stage into the reactant gas inlet region of the following stage.

[0074] A selected embodiment of the system of FIG. 2 is illustrated in FIG. 3. In this exemplary embodiment, twenty reactor stages are used and are arranged for control purposes into two groups of ten stages each such that stages 301 through 319 are in a first group and stages 321 through 341 are in a second group. Pre-reformed natural gas is introduced as a reactant feed gas via line 343 and is analogous to the reactant feed gas in line 243 as described above with reference to FIG. 2. The reactant feed gas flows via primary manifold 345 and is split to flow through secondary manifolds 347 and 349. Steam is fed into first stage 301 via line 351.

[0075] The reactant feed gas flows through the reactant side of first stage 301, and interstage reactant gas flows between successive stages through stage 319 as described above with reference to FIG. 2. Interstage reactant gas from the first group of stages 301-319 flows via line 353 and then flows through the reactant sides of the successive stages in the second group of stages 321-341. Synthesis gas product flows from the system via line 355. The first group of stages 301-319 may be installed in a single pressure vessel (not shown) wherein interstage reactant gas flows through open flow regions between stages and reactant gas from manifold 347 is injected into the respective flow regions between the stages.

[0076] The reactant feed gas in manifold 347 is divided into ten individual streams, and the first of these streams provides a reactant feed gas in line 357 that is mixed with the steam feed in line 351. The remaining nine reactant gas streams provide reactant interstage feed gas streams that are mixed with the corresponding interstage reactant gas streams between pairs of adjacent stages 301 through 319 as shown. Similarly, the reactant feed gas in manifold 349 is divided into ten individual streams to provide reactant interstage feed gas streams that are mixed with the corresponding interstage reactant gas streams between pairs of adjacent stages 321 through 341 as shown. The second group of stages 321-341 may be installed in a single pressure vessel (not shown) wherein interstage reactant gas flows through open flow regions between stages and reactant gas from manifold 349 is injected into the respective flow regions between the stages.

[0077] Manifold 347 may be designed to provide generally equal flow rates of reactive gas into stages 301 to 319; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages for reaction control purposes. Likewise, manifold 349 may be designed to provide generally equal flow rates of reactive gas into stages 321 to 341; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages for reaction control purposes.

[0078] A first preheated oxidant gas is introduced via line 359 into manifold 361 and is divided into ten portions to provide oxidant gas to the oxidant sides of stages 301 to 319 as shown. A second preheated oxidant gas is introduced via line 363 into manifold 365 and is divided into ten portions to provide oxidant gas to the oxidant sides of stages 321 to 341 as shown. The first and second preheated oxidant gas streams

may be provided from a common upstream heater (not shown) and may be air heated to a temperature of 600 to 1150° C. Oxygen permeates through the membranes in the stages and reacts with the reactive components on the reactant sides of the stages as described earlier above. Oxygen-depleted non-permeate gas is withdrawn from stages 301-319 via lines feeding into manifold 367 and the gas is discharged via line 369. Similarly, oxygen-depleted non-permeate gas is withdrawn from stages 321-341 via lines feeding into manifold 371 and the gas is discharged via line 373. Heat and/or pressure energy may be recovered from the withdrawn non-permeate gas by any of the known methods described in the art.

[0079] Manifold 361 may be designed to provide generally equal flow rates of oxidant gas into stages 301 to 319; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages, for example, for reaction and/or temperature control purposes. Likewise, manifold 365 may be designed to provide generally equal flow rates of oxidant gas into stages 321 to 341; alternatively, the manifold may be designed to provide a different flow rate to each stage or groups of stages, for example, for reaction and/or temperature control purposes.

[0080] The temperatures in the stages and the reactions through the stages can be regulated by controlling the flow rates of reactant and oxidant gases to the stages and the operating conditions within the stages. This may be accomplished, for example, by controlling the flow rates of reactant gas into manifolds 347 and 349 by control valves 375 and 377, respectively, and/or by controlling the flow rates of oxidant gas into manifolds 361 and 365 by control valves 379 and 381, respectively. For example, control of the reactant gases to the group of stages 301 to 319 may be effected by temperature indicator/controller 383, which sends control signals via control line 385 to control valve 375. Likewise, control of the reactant gases to the group of stages 321 to 341 may be effected by temperature indicator/controller 389, which sends control signals via control line 391 to control valve 377. In another example, temperature indicator/controller 383 may be located on oxygen-depleted non-permeate gas manifold 367 (not shown) and/or on oxygen-depleted non-permeate gas discharge line 369 (not shown). Likewise, temperature indicator/controller 389 may be located on oxygen-depleted non-permeate gas manifold 371 (not shown) and/or on oxygen-depleted non-permeate gas discharge line 373 (not shown). Control of oxidant gases to the group of stages 301 to 319 may be, for example, effected by control valve 379 located on the oxidant gas stream upstream of the stages (as shown), or located on the oxygen-depleted non-permeate gas stream downstream of the stages (not shown). Likewise, control of oxidant gases to the group of stages 321 to 341 may be, for example, effected by control valve 381 located on the oxidant stream upstream of the stages (as shown), or located on the oxygen-depleted non-permeate gas stream downstream of the stages (not shown). In a typical embodiment, flow rates of oxidant gases fed to the stages may be varied to maintain target oxygen concentration in oxygen-depleted non-permeate gas withdrawn from the stages, for example through manifolds 367 and 371. For example, oxygen concentration may be monitored by an oxygen analyzer/indicator controller (not shown) located on manifold 367 and/or discharge 369, which may send control signals via a control line (not shown) to control valve 379. Likewise, oxygen concentration may be monitored by an oxygen analyzer/indicator controller (not shown) located on manifold 371 and/or dis-

charge 373, which may send control signals via a control line (not shown) to control valve 381. Flow rate of permeated oxygen through the membranes may also be affected by the operating conditions (e.g. pressure and/or temperature) within the stage, particularly in the vicinity of the membrane permeation surface. In another embodiment, any or all feed gases (e.g. reactant feed gas, reactant interstage feed gas, and/or oxidant gas) to a stage or series of stages may be omitted from or bypassed around the stage or series of stages to affect temperatures and/or reactions.

[0081] The staged ITM reactor systems described above utilize reactant gas streams that may include any of oxygen, steam, hydrocarbons, pre-reformed mixtures of steam and hydrocarbon feed gas, hydrogen, carbon monoxide, carbon dioxide, and/or carbon dioxide containing gas. Reactions that occur in the staged reactor systems may include, for example, partial oxidation, complete oxidation, steam reforming, carbon dioxide reforming, water-gas shift, and combinations thereof to produce synthesis gas. Certain of these reactions are strongly exothermic and others are endothermic. Because ITM systems generally require a narrow operating temperature range, proper control of the exothermic and endothermic reactions is required. The embodiments described above enable inherently stable operation in which the temperatures of the membrane system can be controlled within the required ranges.

[0082] The multiple reactant-staged membrane oxidation systems described above utilize at least two stages in series and may utilize up to 10 stages, up to 20 stages, up to 100 stages, or even greater than 100 stages in series depending on specific operating and product requirements. The embodiments are designed for the generation of synthesis gas, but may be applied to any oxidation or partial oxidation processes utilizing oxygen provided by permeation through ion transport membranes. When utilized for the generation of synthesis gas, the oxidant gas typically is preheated air and steam is introduced into the reactant side of the first reactor stage. The reactant gas, for example pre-reformed natural gas, is divided into multiple streams (not necessarily equal), which are subsequently introduced into the multiple reactor stages. In some embodiments, it is preferable that the reactant gas in each stage approach chemical equilibrium with respect to the steam reforming reaction, carbon dioxide reforming reaction, and/or the water gas shift reaction when catalysts for these reactions are provided in each stage. The reactant gas entering a stage, exiting a stage, and/or exiting optional catalyst (e.g. catalyst 1d on FIG. 1) thus may be at or near chemical equilibrium with respect to these reactions.

[0083] A flow of steam may be introduced into the reactant side of the first stage as shown in FIGS. 2 and 3 for the purpose of minimizing temperature excursions and enabling the process to operate at or near equilibrium in each of the stages. The term "temperature approach to equilibrium" for a given gas mixture is herein defined as the absolute value of the temperature difference between the actual temperature of the gas mixture and a calculated temperature at which the given reactants in the gas mixture would be at chemical equilibrium. Temperature approach to equilibrium may be expressed with respect to the gas mixture as a whole or with respect to a specific reaction or reactions (e.g., steam reforming, carbon dioxide reforming, and/or water-gas shift reactions) between specific reactants in the gas mixture. A typical temperature approach to equilibrium may be on the order of 0 to 100° F., and typically may be on the order of 0 to 20° F. When the

catalyst is disposed on or adjacent the membranes, this approach will occur within the modules of the stage; when the catalyst is disposed following the membrane modules as shown in FIGS. 1 and 2, the approach to equilibrium will occur at the outlet of the catalyst module. When catalyst is disposed preceding the membrane modules, the approach to equilibrium will occur preceding the modules.

[0084] The temperature of the reactant side of the modules in each stage (and therefore the temperature of the entire stage) may be controlled by varying the amount and distribution of the reactant gas provided to each stage. The reactant side of each stage is generally reactant-rich (e.g., rich in oxidizable species) and the exothermic oxidation reactions which generate temperature rise are limited by the rates of oxygen permeation through the membrane. The endothermic reforming reactions which generate temperature drop are generally limited by both catalyst activity and by the amount of hydrocarbon, particularly methane, fed to each stage.

[0085] By conducting the overall reaction in multiple stages, sufficient catalyst may be provided within or between each of the stages such that the composition of the gas exiting a stage approaches equilibrium with respect to the reactions occurring in that stage prior to entering the next stage. This effectively tunes or regulates the catalyst activity such that endothermic reforming reactions and the associated temperature drop in each stage can be limited by the amount of hydrocarbon, particularly methane, fed to each stage as reactant interstage feed gas. Thus the hydrocarbon feed rate to each stage may be used to control the gas composition and temperature within and/or at the exit of the stage, and the composition and temperature of the gas can be made to approach equilibrium by controlling the hydrocarbon feed rate. A higher hydrocarbon feed rate will tend to cool the gas mixture via endothermic reforming, whereas a lower hydrocarbon feed rate will tend to yield higher temperatures by limiting the endothermic reforming that cools the reactant gas mixture.

[0086] If the oxidation reaction system is operated so that at least some of the reaction stages do not operate at or near equilibrium, varying the hydrocarbon feed rate to each stage also may be used to control the gas composition and temperature within and/or at the exit of the stage. A higher hydrocarbon feed rate and feed concentration will lead to increased rates of endothermic reforming reactions and thus tend to cool the gas mixture, whereas a lower hydrocarbon feed rate and feed concentration will lead to decreased rates of endothermic reforming reactions and thus tend to yield higher temperatures.

[0087] The membrane material used in the membrane oxidation reaction system must be operated within a specific temperature range. The upper temperature limit is established based on criteria including the kinetic decomposition of the material, the mechanical creep of the membranes, the degree of iron volatilization in systems using iron-containing oxides, membrane stability in a synthesis gas environment in the presence of volatilized iron, potential catalyst life issues, and other criteria. The lower temperature limit is established based on the potential for carbon dioxide-induced membrane degradation (discussed later), phase decomposition, and other criteria. The embodiments described above provide a membrane-based oxidation reaction system which provides for inherently stable performance during steady-state operation, startup, shutdown, turndown, and recovery from process upset conditions. This may be achieved by controlling the

system within the critical ranges of gas composition and temperature required for stable and reliable membrane operation.

[0088] Mixed conducting metal oxide membranes and membrane modules are mechanically fragile ceramic bodies. Mechanical stresses may accumulate as a result of temperature and composition gradients within the ceramic material, and these stresses can damage the membranes as well as joints and seals in the membrane modules. The use of reactant-staged membrane reactors allows for the minimization of these thermal and concentration gradients within the ceramic components of the reactor system.

[0089] Hydrocarbon-containing components in the feed gas may form elemental carbon (soot) at the operating temperatures of ITM oxidation reactors, which may operate in a typical range of 600 to 1150° C. (1112 to 2102° F.). Undesirable formation of soot in the ITM modules, control valves, and internal piping will occur at these temperatures in certain reactive gas composition ranges. The potential for soot formation decreases as temperature decreases, and soot formation may be substantially lower in the range 600 to 750° C. (1112 to 1382° F.) than at higher ITM operating temperatures of 850 to 1150° C. (1562 to 2102° F.). The potential for soot formation decreases further and becomes readily manageable at temperatures in the range 500 to 650° C. (932 to 1202° F.) and below. Operation to avoid soot formation may be accomplished by utilizing the reactant-staged ITM system described above with appropriate control of the distribution, composition, and temperature of the reactant feed gas and reactant interstage feed gas among the stages.

[0090] The use of a reactant-staged ITM reactor system allows the introduction of the reactant gases at temperatures significantly below the operating temperatures of the ITM modules, which allows operation of the reactant gas feed system at lower temperatures. As a result, expensive high-temperature alloys may not be required for components of the reactant gas feed system.

[0091] Other potential problems in the operation of ITM oxidation reactor systems may be minimized or eliminated by the use of the reactant-staged embodiments described above. For example, oxygen flux may vary among membrane modules due to variations in manufacturing, installation, and/or operation. By staging the reactor system with respect to the reactant gases, control schemes may be utilized so that the reactor system can tolerate reasonable variations in oxygen flux among the multiple membrane modules in the system. Flux variations among the modules may be compensated for by controlling the flow and/or composition of the reactant interstage feed gas among the stages. Reactant-staged operation also can be used to address operating problems associated with startup, turndown, process upsets, and shutdown of ITM oxidation reactor systems.

[0092] The reactant-staged membrane oxidation reactor systems are illustrated above for the generation of synthesis gas from natural gas. The systems alternatively may be used for other oxidation or partial oxidation processes such as, for example, combustion (e.g. for power, steam, or heat generation) or reforming of hydrocarbons heavier than methane.

[0093] It is well known in the field of synthesis gas production that the injection of CO₂ into the hydrocarbon feed to a steam-methane reformer effectively reduces the H₂/CO molar ratio in the synthesis gas product. This is often required to provide specific H₂/CO ratios in the synthesis gas feed to downstream chemical processes. CO₂ separated from the

synthesis gas product can be recycled to the reformer feed, or CO₂ can be imported for this purpose from an outside source. For example, CO₂-containing offgas from a downstream Fischer-Tropsch (F-T) hydrocarbon synthesis process may be recycled to the feed of the synthesis gas generation process to adjust the synthesis gas product H₂/CO molar ratio to about 2:1 as required for the F-T process. This external recycle step avoids the need for an acid gas removal system to remove CO₂ from the synthesis gas produced; instead, the F-T offgas containing about 60 vol % CO₂ is recovered at high pressure along with other useful components for recycle, including light hydrocarbons, H₂, and CO. This external recycle step also serves to reduce CO₂ emissions while increasing the efficiency of carbon conversion into useful products. Only a modest amount of compression is required to overcome pressure drop through the synthesis gas generation process and the F-T process.

[0094] For an ITM oxidation process operated with an overall reactant feed gas steam-to-carbon (S/C) molar ratio of 1.5, which is desirable to minimize methane slip (i.e. unreacted methane in the product synthesis gas) and carbon deposition, the product synthesis gas H₂/CO molar ratio would be about 3:1 (refer to Example 1 below). As described above, a Fischer-Tropsch (F-T) reactor system generally requires a H₂/CO ratio of about 2:1. Other processes require even lower H₂/CO ratios; for example, certain oxo-alcohol synthesis processes require a 1:1 H₂/CO ratio in the synthesis gas feed.

[0095] It has been found that in the production of synthesis gas by ITM oxidation reactors, high concentrations of CO₂ may react with and decompose the material used in the membranes. The terms “decompose” or “decomposed” mean that the original membrane composition or stoichiometry is changed, for example by the reaction with CO₂. Exemplary membranes are complex multi-component metal oxides consisting of alkaline earth metals (e.g., Ca), transition metals, and lanthanum or lanthanides. The driving force for the reaction of these materials with CO₂ is the large negative free energy of formation of the alkaline earth carbonates, for example, CaCO₃. A representative chemical reaction for the decomposition of a perovskite in the presence of CO₂ can be expressed in terms of the CO₂ partial pressure, p_{CO_2} , at equilibrium conditions, which may be defined as $p_{CO_2}^*$. At CO₂ partial pressures less than $p_{CO_2}^*$, decomposition via CO₂ reactions will not occur and the membrane material will be stable. At CO₂ partial pressures greater than $p_{CO_2}^*$, the membrane material will decompose via reaction with CO₂. The value of $p_{CO_2}^*$ is a function of temperature, oxygen partial pressure, and membrane composition, and $p_{CO_2}^*$ generally decreases as temperature decreases.

[0096] In addition, the membranes used in ITM oxidation reactors have an upper operating temperature limit defined by other phenomena such as, for example, kinetic decomposition, excessive material creep, reduction or volatilization of transition metal species (e.g. Fe), and potential catalyst life issues.

[0097] Embodiments of the present invention may be applied to eliminate the problem of membrane degradation by providing methods to recycle CO₂ in membrane reactor systems for controlling the product synthesis gas H₂/CO ratio while ensuring that p_{CO_2} remains less than $p_{CO_2}^*$ throughout the membrane reactor system. The use of reactant-staged membrane oxidation reactor systems allows the controlled interstage introduction of carbon dioxide so that p_{CO_2} remains less than $p_{CO_2}^*$ in all stages. Lower carbon dioxide

concentrations allow lower operating temperature limits, which in turn allow a larger operating temperature window, thereby easing constraints on process control and providing a more operable process.

[0098] As described in detail below, $p_{CO_2}^*$ is a strong function of temperature, and the introduction of CO₂-containing gas into the membrane reactor system may be accomplished advantageously by dividing the CO₂-containing gas into two or more reactant interstage feed gas streams for injection between selected stages of a reactant-staged ITM oxidation system. The CO₂-containing gas may be injected into one or more interstage points in the reactor system where higher temperatures lead to higher values of $p_{CO_2}^*$.

[0099] This embodiment is illustrated in the schematic flow diagram of FIG. 4. The exemplary reactant-staged membrane oxidation system comprises first stage **401**, second stage **403**, third stage **405**, and last or n^{th} stage **407**. Each stage is illustrated schematically as a generic module having an oxygen permeable membrane that divides the module into an oxidant side and a permeate or reactant side. As explained above, a stage can comprise any number of membrane modules arranged in series and/or parallel and may include one or more catalysts selected from oxidation catalyst, steam reforming catalyst, carbon dioxide reforming catalyst, and water gas shift catalyst. Any desired number of stages may be used as long as there are at least two stages.

[0100] First stage **401** comprises oxidant side **401a**, membrane **401b**, reactant side **401c**, optional catalyst **401d**, and appropriate gas inlet and outlet regions. Optional catalyst **401d** is shown here as immediately following the module, but alternatively or additionally catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Similarly, second stage **403** comprises oxidant side **403a**, membrane **403b**, reactant side **403c**, appropriate gas inlet and outlet regions, and optional catalyst **403d**, which is shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Similarly, third stage **405** comprises oxidant side **405a**, membrane **405b**, reactant side **405c**, appropriate gas inlet and outlet regions, and optional catalyst **405d**. Optional catalyst **405d** is shown here as immediately following the module, but alternatively or additionally catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Last stage **407** comprises oxidant side **407a**, membrane **407b**, reactant side **407c**, appropriate gas inlets and outlets, and optional catalyst **407d**, shown here as immediately following the module. Alternatively or additionally, catalyst may be disposed immediately preceding the module (not shown) or within or around the module in any desired configuration (not shown). Product gas from last or n^{th} stage **407** is withdrawn via product line **407e**. Interstage reactant gas flows from stage **401** via line **401e**, from stage **403** via line **403e**, and from stage **405** via line **405e**.

[0101] An oxidant gas, for example, preheated air or oxygen-containing combustion products from a combustor operated with excess air, is introduced via line **409** into oxidant side **401a** of first stage **401** and contacts the oxidant side of membrane **401b**, a portion of the oxygen permeates through membrane **401b**, and oxygen-depleted gas exits first stage **401** via line **411**. Similarly, additional oxidant gas streams

may be introduced via lines **413**, **415**, and **419** into stages **403**, **405**, and **407**, respectively, and oxygen-depleted gas may exit the stages via lines **421**, **423**, and **425**, respectively.

[0102] A reactant gas feed such as, for example, pre-reformed natural gas is provided via line **427** and is mixed with steam provided via line **429**, and the mixed reactant gas feed is introduced into reactant side **401c** of stage **401**. Another gas stream comprising reactant components is provided via line **431** from a source different than the source of the reactant gas feed provided via line **427**. The gas in line **431** may be, for example, offgas from a downstream process that utilizes synthesis gas produced by the staged oxidation reactor system of FIG. **4**. The downstream process may be a hydrocarbon synthesis process (e.g., a Fischer-Tropsch process) or an oxygenated hydrocarbon synthesis process (e.g., an alcohol synthesis process). In one embodiment described in more detail below, the gas in line **431** is offgas from a Fischer-Tropsch hydrocarbon synthesis reactor system that contains a major concentration of CO_2 , smaller concentrations of H_2 and CO , and some unreacted CH_4 . This gas in line **431** optionally may be combined with steam provided via line **433**, the mixture heated in pre-heater **435**, and the heated mixture introduced into steam-methane reformer **437** in which some of the unreacted methane is converted to additional H_2 and carbon oxides. In some situations, it may not be necessary to reform the offgas before recycle, and reformer **437** would not be required.

[0103] The partially reformed offgas stream flows via manifold **439**, is divided into separate streams in lines **441**, **443**, and **445**, and these streams are optionally heated in heat exchangers **447**, **449**, and **451** to provide reactant interstage feed gas in lines **453**, **455**, and **457**. The reactant gas feed in reactant side **401c** of first stage **401** reacts with permeated oxygen, reforming and/or shift reactions may be promoted by optional catalyst **401d**, and the first stage effluent flows via flow path **401e**. Reactant interstage feed gas is provided via line **453**, is mixed with first stage effluent in flow path **401e**, and the mixed interstage reactant gas flows into reactant side **403c** of second stage **403**. Alternatively, the reactant interstage feed gas in line **453** may be introduced directly into the reactant side of stage **403** and/or upstream of catalyst **401d**.

[0104] The gas in reactant side **403c** of second stage **403** reacts with permeated oxygen, reforming and/or shift reactions may be promoted by optional catalyst **403d**, and the second stage effluent flows via flow path **403e**. Reactant interstage feed gas is provided via line **455**, is mixed with second stage effluent in flow path **403e**, and the mixed interstage reactant gas flows into reactant side **405c** of third stage **405**. Alternatively, the reactant interstage feed gas in line **455** may be introduced directly into the reactant side of stage **405** and/or upstream of catalyst **403d**.

[0105] The gas in reactant side **405c** of third stage **405** reacts with permeated oxygen, reforming and/or shift reactions may be promoted by optional catalyst **405d**, and the third stage effluent flows via flow path **405e**. Reactant interstage feed gas is provided via line **457**, is mixed with third stage effluent in flow path **405e**, and the mixed interstage reactant gas flows into reactant side **407c** of last stage **407**. Alternatively, the reactant interstage feed gas in line **457** may be introduced directly into the reactant side of stage **407** and/or upstream of catalyst **405d**.

[0106] The gas in reactant side **407c** of last stage **407** reacts with permeated oxygen, reforming and/or shift reactions may be promoted by optional catalyst **407d**, and the last stage

effluent flows via line **407e** to provide a synthesis gas product. The product gas may be at a temperature of 600 to 1150° C. and a pressure of 2 to 40 atma, and the gas typically comprises hydrogen, carbon monoxide, water, carbon dioxide, and methane. Any number of additional stages may be utilized between third stage **405** and last stage **407** if desired.

[0107] In the illustration of FIG. **4** described above, interstage reactant gas flows from stage **401** via flow path **401e**, from stage **403** via flow path **403e**, and from stage **405** via flow path **405e**. In one embodiment, each of stages **401**, **403**, **405**, and **407** may be enclosed in a separate pressure vessel; in this case, flow paths **401e**, **403e**, and **405e** are pipes, conduits, or closed channels between the vessels. In another embodiment, stages **401**, **403**, **405**, and **407** may be enclosed in a single pressure vessel (not shown) such that reactant gas can flow through the reactant zones of each stage in succession; in this case, flow paths **401e**, **403e**, and **405e** are open regions between stages through which gas can flow from the reactant gas outlet region of one stage into the reactant gas inlet region of the following stage.

[0108] The embodiment of FIG. **4** is particularly useful when CO_2 -rich gas (for example, recycle gas from an external process) is utilized for the purpose of controlling the H_2/CO ratio in the product synthesis gas. As mentioned above, it has been found that the mixed conducting metal oxide materials used in the membranes may react with CO_2 and degrade or decompose when the CO_2 partial pressure in the reactive gas, p_{CO_2} , is greater than a critical threshold partial pressure defined as $p_{\text{CO}_2}^*$. The CO_2 partial pressures in the reactor stages therefore should be controlled as described below to minimize or eliminate membrane degradation.

[0109] In the process of FIG. **4**, a steam-to-carbon (S/C) molar ratio of about 1.5 in the reactant feed gas is desirable to minimize methane slip and carbon deposition in the system. With this reactant feed gas, the product synthesis gas H_2/CO molar ratio would be about 3:1. The injection of the CO_2 -rich gas stream into the reactant feed gas to first stage **401** would effectively reduce the product H_2/CO ratio to a level required for downstream chemical processes. For example, this ratio should be about 2:1 for a Fischer-Tropsch hydrocarbon synthesis process. At CO_2 partial pressures greater than the critical threshold, $p_{\text{CO}_2}^*$, however, the membrane material may react with the CO_2 and decompose. This can be avoided by operating the membrane reactor system so that p_{CO_2} is less than $p_{\text{CO}_2}^*$ throughout the system, thereby enhancing the operating life of the membrane. It may not be possible to maintain p_{CO_2} less than $p_{\text{CO}_2}^*$ when all of the recycled CO_2 is introduced into the reactant gas feed to the first stage.

[0110] FIG. **5** shows the behavior of $p_{\text{CO}_2}^*$ as a function of temperature and oxygen partial pressure for a typical material used in ITM reactor systems, $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$, wherein the value of δ makes the compound charge neutral. This plot was generated from thermodynamic calculations of the complex phase equilibria exhibited by these materials. The oxygen partial pressure, p_{O_2} , of the synthesis gas stream is itself determined from thermodynamic calculations rather than measured directly; it is also a strong function of temperature and synthesis gas composition.

[0111] Because $p_{\text{CO}_2}^*$ is a strong function of temperature, CO_2 injection is problematic at lower temperatures typical of the inlet conditions to a membrane reactor system. Since the synthesis gas generation process is net exothermic and the reactant gas temperature increases down the length of the reactor, it can be advantageous to inject the CO_2 at one or

more intermediate points in the reactor system where higher temperature leads to much higher values of $p_{CO_2}^*$. This is especially beneficial when the CO_2 injection stream is significantly cooler than the reactant feed stream to the membrane reactor and the injection itself causes a substantial drop in temperature. In this case, dividing the CO_2 injection stream into multiple intermediate injections as described above can mitigate the temperature drop at each injection point. A significant temperature drop is generally undesirable because it creates a locally depressed value of $p_{CO_2}^*$ and also leads to significant thermal stress in the membranes.

[0112] As pointed out above, maintaining $p_{CO_2} < p_{CO_2}^*$ throughout the system during operation is beneficial to long-term membrane life in an ITM reactor system. FIG. 5, which is a plot of $p_{CO_2}^*$ vs. temperature at various equilibrium O_2 partial pressures for the mixed conducting metal oxide membrane material $La_{0.9}Ca_{0.1}FeO_{3-\delta}$, shows that this task is most difficult at lower temperatures typical of the inlet conditions to an ITM synthesis gas generation process. Since the oxidation reactions in the process are net exothermic and the reactant gas temperature increases down the length of the reactor, injection of CO_2 -containing gas is best accomplished at one or more intermediate points in the staged reactor system where the higher temperature and corresponding oxygen partial pressure lead to much higher values of $p_{CO_2}^*$. As long as the cooling effects are mitigated properly, the cooling provided by CO_2 -containing gas will be beneficial to the process because of the upper operating temperature limit of the membranes imposed by other material requirements.

[0113] Cooling provided by CO_2 -containing gas follows several mechanisms, all of which are most beneficial when occurring in a higher temperature zone downstream from the inlet to the membrane reactor. Obviously, the CO_2 -containing gas stream can provide sensible cooling. In addition, the presence of CO_2 leads to the endothermic reverse shift reaction and the endothermic CO_2 reforming reaction; when these reactions occur on or near the membrane surfaces, they provide beneficial membrane cooling. Furthermore, any hydrocarbon components present in the CO_2 -containing gas stream may undergo the endothermic reforming reaction on the membranes, leading to further cooling. Finally, intermediate injection(s) of CO_2 -containing gas leads to less mass flow and lower pressure drop at the front end of the membrane reactor.

[0114] The embodiment described above illustrates the use of ITM reactor systems for the production of synthesis gas with controlled H_2/CO ratios. The embodiment may be applied to any partial oxidation reaction with introduction of a CO_2 -containing stream.

[0115] The following Examples illustrate embodiments of the present invention but do not limit embodiments of the invention to any of the specific details described therein.

EXAMPLE 1

[0116] An embodiment of the invention similar to FIGS. 2 and 3 was simulated using the process simulator Aspen Plus™ from Aspen Technology, Inc. The simulation utilized 100 membrane reactor stages in series wherein the reactant gas feed is divided into ten portions (not necessarily equal) and each portion is divided into ten equal sub-portions. Each sub-portion is fed to the inlet of a corresponding stage wherein the sub-portion to the first stage is mixed with steam and each of the remaining sub-portions is provided as a reactant interstage feed gas that is mixed with a corresponding interstage reactant gas stream.

[0117] The following specific process features and parameters were used in the simulation:

[0118] Total sum of oxygen permeation in all stages is 1000 kgmol/hr with an evenly-distributed oxygen flux of 10 kgmol/hr in each stage.

[0119] Overall steam-to-carbon molar ratio is 1.5 in the reactant feed to the system wherein the steam-to-carbon ratio is defined as total water divided by total organic carbon in the stream; carbon contained in carbon dioxide and carbon monoxide is not included.

[0120] Natural gas feed has the following composition: 94.73% methane, 3.16% ethane, 0.54% propane, 0.18% butane, 0.06% pentane, 0.04% hexane, 0.71% carbon dioxide, 0.58% nitrogen (compositions in mole %).

[0121] A small amount of hydrogen is added to the natural gas, as is typical for desulfurization, e.g. approximately 3% of the total carbon feed on a molar basis.

[0122] Reactant gas feed is provided by pre-reforming natural gas in an adiabatic pre-reformer with an inlet temperature of 510° C. to convert hydrocarbons heavier than methane.

[0123] Reactant gas pressure on the reactant sides of all stage membrane modules is 30.3 bara (440 psia) and the oxidant gas pressure on the oxidant sides of all stage membrane modules is 1.7 bara (25 psia).

[0124] Natural gas at 2142.9 kgmol/hr, 67.3 kgmol/hr hydrogen, and 1113.5 kgmol/hr steam are mixed and heated to 510° C. The heated mixture is pre-reformed in an adiabatic pre-reformer reactor and exits the adiabatic pre-reformer reactor at 474° C. The pre-reformed mixture is divided into the portions given in Table 1.

TABLE 1

Reactant Feed Distribution for Example 1			
Distribution of Pre-reformed		Flow to Stage Group	
Reactant Feed to Stage Groups	Portion	kgmol/hr	%
Stages 1 through 10	1	332.2	9.6
Stages 11 through 20	2	330.7	9.5
Stages 21 through 30	3	342.4	9.9
Stages 31 through 40	4	358.7	10.3
Stages 41 through 50	5	374.5	10.8
Stages 51 through 60	6	388.1	11.2
Stages 61 through 70	7	399.2	11.5
Stages 71 through 80	8	408.2	11.7
Stages 81 through 90	9	415.6	12.0
Stages 91 through 100	10	125.2	3.6
Total to all stages		3474.9	100.0

[0125] Each of portions 1-10 in Table 1 is divided into ten equal sub-portions. Steam at 2227.1 kgmol/hr is preheated to 875° C. and mixed with a first sub-portion of portion 1, and the mixture is introduced to the reactant side of the first stage. The other 99 sub-portions (all of the sub-portions except the first sub-portion of portion 1) are provided as reactant interstage feed gas streams, each of which is mixed with a respective interstage reactant gas stream and fed to the inlet of each of the respective 99 stages. Air is provided to the oxidant side of each stage at 855° C., and oxygen-depleted air is withdrawn from the oxidant side of each stage.

[0126] Sufficient catalyst is provided in this Example on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift

reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the 100-stage reactor system. A final synthesis gas product is withdrawn from stage **100** at 900° C. and 9442.2 kgmol/hr with a composition of 46.7% hydrogen, 3.0% methane, 6.7% carbon dioxide, 14.1% carbon monoxide, 29.4% water, and 0.1% nitrogen (compositions in mole %).

[0127] A summary of the simulation results is given in Table 2 showing the reactant gas temperature and composition from the first reactor stage and from each succeeding group of 10 stages. FIG. 6 shows the temperature of the reactant gas at the inlet and outlet of each stage plotted as a percentage of the group of 100 reaction stages from the reactant feed inlet (**0**) to the product outlet (**100**). It is seen that staged operation of the reactor system controls the reactant gas temperature within the preferred membrane temperature range of 850 to 900° C. The temperature of the reactant gas is generally flat at about 875° C. through the first 90 stages and rises to 900° C. in the last 10 stages. The saw-tooth temperature profile is attributed to quenching of the reactant gas by the introduction of cold (474° C.) pre-reformed reactant feed gas via the reactant interstage feed lines into the interstage reactant gas between each of the 100 stages.

TABLE 3

Reactant Feed Gas Distribution for Example 2			
Distribution of Pre-reformed Reactant Feed to Stage Groups	Portion	Flow to Stage Group	
		kgmol/hr	%
Stages 1 through 10	1	335.1	9.7
Stages 11 through 20	2	327.8	9.5
Stages 21 through 30	3	339.2	9.8
Stages 31 through 40	4	352.1	10.2
Stages 41 through 50	5	362.9	10.5
Stages 51 through 60	6	372.4	10.8
Stages 61 through 70	7	379.1	10.9
Stages 71 through 80	8	385.6	11.1
Stages 81 through 90	9	390.1	11.3
Stages 91 through 100	10	219.2	6.3
Total to all stages		3463.4	100.0

[0129] Each portion in Table 3 is divided into ten equal sub-portions. The preheated steam is mixed with a first sub-portion of portion 1, and the mixture is introduced to the reactant side of the first stage. The other 99 sub-portions (all

TABLE 2

Simulation Summary for Example 1														
	Pre- Ref'r	ITM Reactor	Total O ₂	Reactant Gas at Outlet of Reactor Stage No.										
	Feed	Feed	Permeate	1	10	20	30	40	50	60	70	80	90	100
Temp., ° C.	510	474		874	875	875	874	875	875	875	875	875	900	900
Press., bara	33.3	32.7		30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3
Flow, kgmol/hr	3324	3475	1000	2301.4	2969.5	3696.0	4424.5	5162.2	5910.2	6667.7	7433.2	8205.2	8982.7	9442.2
H ₂ , mol %	2.02	7.31		2.78	19.91	29.75	35.44	39.00	41.36	42.98	44.13	44.97	45.59	46.69
CH ₄ , mol %	61.08	61.91		0.00	0.02	0.20	0.60	1.14	1.76	2.40	3.01	3.59	4.13	2.98
CO ₂ , mol %	0.46	2.50		0.90	5.38	6.99	7.49	7.58	7.52	7.39	7.25	7.10	6.96	6.68
CO, mol %		0.11		0.03	1.82	4.38	6.58	8.33	9.70	10.80	11.67	12.38	12.97	14.09
H ₂ O, mol %	33.50	27.80		96.28	72.83	58.62	49.82	43.85	39.55	36.32	33.82	31.83	30.21	29.43
N ₂ , mol %	0.37	0.36		0.01	0.04	0.06	0.08	0.09	0.11	0.11	0.12	0.13	0.13	0.13
O ₂ , mol %			100											
C ₂ H ₆ , mol %	2.04													
C ₃ H ₈ , mol %	0.35													
C ₄ H ₁₀ , mol %	0.12													
C ₅ H ₁₂ , mol %	0.04													
C ₆ H ₁₄ , mol %	0.03													

EXAMPLE 2

[0128] Operation of the system of Example 2 was simulated using the same simulation method and the same specific process features and parameters as in Example 1, except that catalyst is not used within the membrane modules. Instead, an adiabatic catalyst bed is provided at the exit of each stage (see FIGS. 1 and 2) to equilibrate the steam reforming, carbon dioxide reforming, and water-gas shift reactions. 2219.7 kgmol/hr steam is preheated to 860° C. and introduced to the first reactor stage. 2135.8 kgmol/hr natural gas, 67.0 kgmol/hr hydrogen, and 1109.9 kgmol/hr steam are mixed and preheated to 510° C., pre-reformed in an adiabatic pre-reformer reactor, and withdrawn from the adiabatic pre-reformer reactor at 474° C. The pre-reformed mixture is divided into the portions given in Table 3.

of the sub-portions except the first sub-portion of portion 1) are provided as reactant interstage feed gas streams, each of which is mixed with a respective interstage reactant gas stream and fed to the inlet of each of the respective 99 stages. Air is provided to the oxidant side of each stage at 855° C., and oxygen-depleted air is withdrawn from the oxidant side of each stage. A final synthesis gas product is withdrawn from stage **100** at 900° C. and 9413.1 kgmol/hr with a composition of 46.7% hydrogen, 3.0% methane, 6.7% carbon dioxide, 14.1% carbon monoxide, 29.5% water, and 0.1% nitrogen (compositions in mole %).

[0130] A summary of the simulation results is given in Table 4 showing the reactant gas temperature and composition from the first reactor stage and from each succeeding group of 10 stages. FIG. 7 shows the temperature of the

reactant gas at the inlet and outlet of each stage plotted as a percentage of the group of 100 reaction stages from the reactant feed inlet (0) to the product outlet (100). It is seen that the temperature of the reactant gas is within the desired control range of 850 to 900° C. through the first 90 stages. The temperature of the reactant gas rises above 900° C. in the last 10 stages and exits the last stage at 900° C. The saw-tooth temperature profile is attributed to the exothermic partial and complete oxidation reactions occurring in each stage followed by net endothermic equilibration of the steam reforming, carbon dioxide reforming, and water-gas shift reactions in each adiabatic catalyst bed following the stage.

TABLE 4

Simulation Summary for Example 2														
	Pre- Ref'r	ITM Reactor	Total O ₂	Reactant Gas at Outlet of Reactor Stage No.										
	Feed	Feed	Permeate	1	10	20	30	40	50	60	70	80	90	100
Temp., ° C.	510	474		858	860	867	872	875	877	879	881	882	883	900
Press., bara	33.3	32.7		30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3
Flow, kgmol/hr	3313	3463	1000	2294.7	2968.2	3686.4	4407.3	5134.6	5868.0	6607.7	7351.5	8100.1	8851.7	9413.1
H ₂ , mol %	2.02	7.31		2.82	20.16	29.77	35.35	38.88	41.25	42.92	44.14	45.06	45.76	46.65
CH ₄ , mol %	61.08	61.91		0.00	0.03	0.23	0.63	1.13	1.66	2.19	2.68	3.14	3.56	2.97
CO ₂ , mol %	0.46	2.50		0.91	5.47	7.05	7.53	7.60	7.52	7.38	7.23	7.07	6.93	6.69
CO, mol %		0.11		0.03	1.79	4.32	6.52	8.28	9.70	10.84	11.76	12.53	13.17	14.08
H ₂ O, mol %	33.50	27.80		96.23	72.51	58.56	49.89	44.00	39.76	36.56	34.07	32.08	30.46	29.47
N ₂ , mol %	0.37	0.36		0.01	0.04	0.06	0.08	0.09	0.10	0.11	0.12	0.13	0.13	0.13
O ₂ , mol %			100											
C ₂ H ₆ , mol %	2.04													
C ₃ H ₈ , mol %	0.35													
C ₄ H ₁₀ , mol %	0.12													
C ₅ H ₁₂ , mol %	0.04													
C ₆ H ₁₄ , mol %	0.03													

EXAMPLE 3

[0131] Operation of the system of Example 3 was simulated using the same simulation method and the same specific process features and parameters as in Example 1. 1505.3 kgmol/hr natural gas, 47.3 kgmol/hr hydrogen, and 782.2 kgmol/hr steam are mixed and preheated to 510° C. The heated mixture is pre-reformed in an adiabatic pre-reformer reactor and exits the adiabatic pre-reformer reactor at 474° C. A stream of recycled offgas from a Fischer-Tropsch synthesis reactor at 2631.5 kgmol/hr and 38° C. having a composition of 38.1% hydrogen, 11.7% methane, 28.8% carbon dioxide, 19.10% carbon monoxide, 0.3% water, and 2.0% nitrogen is mixed with the pre-reformed reactant gas. The resulting mixed reactant feed gas at 282° C. is divided and distributed to the 100 ITM stages for temperature control, and the amount of recycle gas is used to control the H₂/CO ratio in the synthesis gas product from the reactor system. The mixed reactant feed gas is divided into portions as given in Table 5.

TABLE 5

Mixed Reactant Feed Gas Distribution for Example 3			
Distribution of Mixed Reactant Feed Gas to	Portion	Flow to Stage Group	
		kgmol/hr	%
Stages 1 through 10	1	492.9	9.7
Stages 11 through 20	2	497.1	9.8
Stages 21 through 30	3	522.0	10.3

TABLE 5-continued

Mixed Reactant Feed Gas Distribution for Example 3			
Distribution of Mixed Reactant Feed Gas to	Portion	Flow to Stage Group	
		kgmol/hr	%
Stages 31 through 40	4	543.4	10.7
Stages 41 through 50	5	558.6	11.0
Stages 51 through 60	6	569.0	11.2
Stages 61 through 70	7	576.4	11.4
Stages 71 through 80	8	581.6	11.5
Stages 81 through 90	9	585.5	11.5
Stages 91 through 100	10	145.9	2.9
Total to all stages		5072.5	100.0

[0132] Each portion in Table 5 is divided into ten equal sub-portions. 1564.5 kgmol/hr of steam is preheated to 875° C., mixed with the first sub-portion of portion 1, and the mixture is introduced to the reactant side of the first stage. The

other 99 sub-portions (all of the sub-portions except the first sub-portion of portion 1) are provided as reactant interstage feed gas streams, each of which is mixed with a respective interstage reactant gas stream and fed to the inlet of each of the respective 99 stages. Air is provided to the oxidant side of each stage at 855° C. and oxygen-depleted air is withdrawn from the oxidant side of each stage.

[0133] Sufficient catalyst is provided in this Example on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the 100-stage reactor system. A final synthesis gas product is withdrawn from stage **100** at 900° C. and 9702.2 kgmol/hr with a composition of 40.3% hydrogen, 3.0% methane, 9.8% carbon dioxide, 19.7% carbon monoxide, 26.7% water, and 0.6% nitrogen (compositions in mole %).

[0134] A summary of the simulation results is given in Table 6 showing the reactant gas temperature and composition from the first reactor stage and from each succeeding group of 10 stages. FIG. 8 shows the temperature of the reactant gas at the inlet and outlet of each stage plotted as a percentage of the group of 100 reaction stages from the reactant feed inlet (**0**) to the product outlet (**100**). It is seen that staged operation of the reactor system controls the reactant gas temperature within the preferred membrane temperature range of 850 to 900° C. The temperature of the reactant gas rises from nominally 870 to 900° C. in the last 10 stages. The saw-tooth temperature profile is attributed to quenching of the interstage reactant gas upon introduction of cold mixed reactant feed gas (i.e., pre-reformed feed gas plus recycle gas) into the interstage reactant gas between each of the 100 stages.

F-T offgas is recycled to the ITM reactor system to adjust the synthesis gas product H₂/CO molar ratio to about 2:1. In this example, a single stage reactor system operates at 30 bara and 800° C. Sufficient catalyst is provided in this Example on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the reactor system. The F-T offgas is mixed with natural gas feed and the combined feed is mixed with steam before being partially reformed in a pre-reformer. This pre-reformed gas provides reactant feed gas to the single stage ITM reactor system. The reactor inlet gas composition is 5.5% H₂, 0.4% CO, 16.3% CO₂, 46.6% H₂O, 30% CH₄, and 1.3% N₂ (compositions in mole %). At these feed conditions, the equilibrium partial pressure of oxygen is 2.5×10⁻¹⁹ bara and p_{CO₂}* is 1.7 bara (from FIG. 5). However, the actual equilibrium value of p_{CO₂} is 3.2 bara, well above p_{CO₂}*, indicating that decomposition of the reactor membranes would occur.

EXAMPLE 5

[0136] The ITM oxidation reactor system of FIG. 4 is operated with two stages **401** and **403**, and stages **405-407** and manifold **439** are not used. Sufficient catalyst is provided in this Example on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the reactor system. Pre-reformed natural gas in line **427** is mixed with steam via line **429** and the mixture flows via line **430** into first reactor stage **401**. The reactant stream is par-

TABLE 6

Simulation Summary for Example 3														
	Pre-Ref'r	ITM Reactor	Total O ₂	Reactant Gas at Outlet of Reactor Stage No.										
	Feed	Feed	Permeate	1	10	20	30	40	50	60	70	80	90	100
Temp., ° C.	510	282		875	875	875	875	875	875	875	875	875	875	900
Press., bara	33.3	32.7		30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3
Flow, kgmol/hr	2335	5073	1000	1649.1	2407.0	3230.6	4065.1	4912.1	5768.5	6631.6	7499.4	8370.6	9244.4	9702.2
H ₂ , mol %	2.02	23.28		3.98	23.58	31.50	35.07	36.90	37.92	38.53	38.90	39.15	39.31	40.30
CH ₄ , mol %	61.08	35.86		0.00	0.08	0.53	1.18	1.85	2.47	3.01	3.47	3.87	4.22	2.95
CO ₂ , mol %	0.46	16.15		1.76	8.64	10.31	10.69	10.74	10.67	10.58	10.48	10.39	10.30	9.79
CO, mol %		9.96		0.09	3.96	8.16	11.18	13.34	14.94	16.16	17.11	17.88	18.50	19.66
H ₂ O, mol %	33.50	13.54		94.13	63.48	49.13	41.43	36.67	33.45	31.15	29.42	28.09	27.02	26.67
N ₂ , mol %	0.37	1.21		0.04	0.25	0.37	0.45	0.51	0.55	0.58	0.61	0.63	0.64	0.63
O ₂ , mol %			100											
C ₂ H ₆ , mol %	2.04													
C ₃ H ₈ , mol %	0.35													
C ₄ H ₁₀ , mol %	0.12													
C ₅ H ₁₂ , mol %	0.04													
C ₆ H ₁₄ , mol %	0.03													

EXAMPLE 4

[0135] Consider an ITM oxidation reactor system with membranes having a composition that exhibits the p_{CO₂}* behavior characterized by FIG. 5. The oxidation system is integrated with a Fischer-Tropsch (F-T) process wherein the

tially converted in stage **401** and reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **401**. F-T offgas via line **431** is preheated in heat exchanger **435** and is reformed in pre-reformer **437** to convert heavier hydrocarbons in the F-T offgas. Steam is added via line **433**. The pre-reformed gas at 560° C. flows via lines **441**

and **453** (heater **447** is not used) and is mixed with the interstage reactant gas in line **401e**. The mixed gas flows via line **402** into second reactor stage **403**. Selected operating conditions and gas compositions are given in Table 7.

TABLE 7

Operating Conditions for Example 5		
	Pre-reformed feed (line 430)	Interstage feed to stage 403 (line 402)
Pressure (bara)	30	26
Temperature (° C.)	800	783
H ₂ (mol %)	8.0	36.1
CO (mol %)	0.1	11.4
CO ₂ (mol %)	3.2	16.4
H ₂ O (mol %)	52.6	28.8
CH ₄ (mol %)	35.7	6.3
N ₂ (mol %)	0.4	1.1

[0137] The equilibrium partial pressure of oxygen at the conditions in line **430** is 1.5×10^{-19} bara, $p_{CO_2}^*$ is 1.65 bara (from FIG. 5), and the actual equilibrium value of p_{CO_2} is 1.61 bara. Thus, the membranes are essentially at the limit of decomposition stability via CO₂ reaction at the inlet to stage **401**. In line **402** at the inlet to second stage **403**, the equilibrium partial pressure of oxygen is 1.9×10^{-19} bara and $p_{CO_2}^*$ is 1.5 bara (from FIG. 5). The actual equilibrium value of p_{CO_2} , however, is 3.9 bara, indicating that decomposition of the membranes in stage **403** would occur.

EXAMPLE 6

[0138] The ITM oxidation reactor system of FIG. 4 is operated with three stages **401**, **403**, and **405**. Stage **407** is not used. Sufficient catalyst is provided in this Example on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the reactor system. Pre-reformed natural gas in line **427** is mixed with steam via line **429** and the mixture flows via line **430** into first reactor stage **401**. The reactant stream is partially converted in stage **401** and reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **401**. F-T offgas via line **431** is preheated in heat exchanger **435** and is reformed in pre-reformer **437** to convert heavier hydrocarbons in the F-T offgas. Steam is added via line **433**. Half of the pre-reformed offgas at 560° C. flows via lines **441** and **453** (heater **447** is not used) and is mixed with the interstage reactant gas in line **401e**. The mixed gas flows via line **402** into second reactor stage **403**, the reactant stream is partially converted therein, and the stream reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **403**. The other half of the pre-reformed offgas at 560° C. flows via lines **443** and **455** (heater **449** is not used) and is mixed with the interstage reactant gas in line **403e**. The mixed interstage gas flows via line **404** into third reactor stage **405**. [0139] Selected operating conditions and gas compositions are given in Table 8.

TABLE 8

Operating Conditions for Example 6		
	Pre-reformed feed (line 430)	Interstage feed to stage 403 (line 402)
Pressure (bara)	30	28
Temperature (° C.)	800	829
H ₂ (mol %)	8.0	41.1
CO (mol %)	0.1	12.5
CO ₂ (mol %)	3.2	12.3
H ₂ O (mol %)	52.6	28.1
CH ₄ (mol %)	35.7	5.3
N ₂ (mol %)	0.4	0.8

[0140] Conditions at the inlet to first stage **401** are similar to those in Example 5 (above). The equilibrium partial pressure of oxygen is 1.2×10^{-18} bara in line **402** at the inlet to stage **403** and $p_{CO_2}^*$ is 2.9 bara (from FIG. 5). Since the actual equilibrium value of p_{CO_2} is 3.0 bara, however, decomposition of the membranes in stage **403** would occur.

EXAMPLE 7

[0141] The ITM oxidation reactor system of FIG. 4 is operated with four stages **401**, **403**, **405**, and **407**. Sufficient catalyst is provided in this Example on the reactant sides of all membrane modules such that the steam reforming, carbon dioxide reforming, and water-gas shift reactions occur within the modules and maintain essentially chemical equilibrium conditions throughout the reactor system. Pre-reformed natural gas in line **427** is mixed with steam via line **429** and the mixture flows via line **430** into first reactor stage **401**. The reactant stream is partially converted in stage **401** and reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **401**. F-T offgas via line **431** is preheated in heat exchanger **435** and is reformed in pre-reformer **437** to convert heavier hydrocarbons in the F-T offgas. Steam is added via line **433**.

[0142] One-third of the pre-reformed offgas at 560° C. flows via lines **441** and **453** (heater **447** is not used) and is mixed with the interstage reactant gas in line **401e**. The mixed gas flows via line **402** into second reactor stage **403**, the reactant stream is partially converted therein, and the stream reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **403**. Another one-third of the pre-reformed offgas at 560° C. flows via lines **443** and **455** (heater **449** is not used) and is mixed with the interstage reactant gas in line **403e**. The mixed interstage gas flows via line **404** into third reactor stage **405**, the reactant stream is partially converted therein, and the stream reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **405**.

[0143] The remaining one-third of the pre-reformed offgas at 560° C. flows via lines **445** and **457** (heater **451** is not used) and is mixed with the interstage reactant gas in line **405e**. The mixed interstage gas flows via line **406** into fourth reactor stage **407**, the reactant stream is partially converted therein, and the stream reaches equilibrium at the upper operating temperature limit of 900° C. at the outlet of stage **407**.

[0144] Selected operating conditions and gas compositions are given in Table 9.

TABLE 9

Operating Conditions for Example 7				
	Pre-reformed feed (line 430)	Interstage feed to stage 403 (line 402)	Interstage feed to stage 405 (line 404)	Interstage feed to stage 407 (line 406)
Pressure (bara)	30	28	28	27
Temperature (° C.)	800	849	856	862
H ₂ (mol %)	8.0	43.1	39.4	36.6
CO (mol %)	0.1	13.1	14.9	16.0
CO ₂ (mol %)	3.2	10.6	11.9	13.0
H ₂ O (mol %)	52.6	27.9	29.3	30.3
CH ₄ (mol %)	35.7	4.7	3.7	3.0
N ₂ (mol %)	0.4	0.6	0.9	1.1

[0145] Conditions at the inlet to first stage 401 are similar to those in Example 5 (above). In the interstage reactant gas in line 402, the equilibrium partial pressure of oxygen is 2.7×10^{-18} bara, $p_{CO_2}^*$ is 3.7 bara, and the actual equilibrium value of p_{CO_2} is only 2.6 bara. In the interstage reactant gas in line 404, the equilibrium partial pressure of oxygen is 4.3×10^{-18} bara, $p_{CO_2}^*$ is 4.3 bara, and the actual equilibrium value of p_{CO_2} is only 3.0 bara. Finally, in the interstage reactant gas in line 406, the equilibrium partial pressure of oxygen is 7.9×10^{-18} bara, $p_{CO_2}^*$ is 5.2 bara, and the actual equilibrium value of p_{CO_2} is only 3.4 bara.

[0146] It is seen from these results that p_{CO_2} remains below $p_{CO_2}^*$ at all locations in the reactor system. Thus, multiple stages, in this example four stages with three interstage injection points, enable the injection of this particular CO₂-containing pre-reformed F-T offgas while maintaining $p_{CO_2} < p_{CO_2}^*$ throughout the ITM reactor system.

EXAMPLE 8

[0147] For membranes with compositions having less robust $p_{CO_2}^*$ behavior than shown in FIG. 5, the stream of pre-reformed F-T offgas can be divided and injected at a greater number of interstage injection points to mitigate temperature depression and corresponding decrease in $p_{CO_2}^*$ at each injection point. Alternatively, the pre-reformed F-T offgas streams can be heated before injection, for example by heaters 447, 449, and 451 of FIG. 4 or in a common heater (not shown) downstream of pre-reformer 437. The number of stages and the heating of the intermediate pre-reformed F-T offgas streams may be selected to optimize the membrane reactor operation and equipment cost for specific feed gas compositions and product synthesis gas H₂/CO ratio requirements.

[0148] As an example, if the F-T off-gas recycle stream in line 441 of FIG. 4 in Example 6 were heated from 560° C. to 650° C. in heater 447, the combined stream in line 402 would be at 847° C. At this temperature, the equilibrium partial pressure of oxygen would be 2.6×10^{-18} bara, $p_{CO_2}^*$ would be 3.7 bara, and the actual equilibrium value of p_{CO_2} would be only 2.9 bara. If the F-T off-gas recycle stream in line 443 of Example 6 were heated from 560° C. to 650° C. in heater 449, the combined stream in line 404 would be at 857° C. At this temperature, the equilibrium partial pressure of oxygen would be 5.0×10^{-18} bara, $p_{CO_2}^*$ would be 4.5 bara, and the actual equilibrium value of p_{CO_2} would be only 3.3 bara. Thus the use of two intermediate injection points and a three-stage reactor system would maintain $p_{CO_2} < p_{CO_2}^*$ throughout the ITM reactor system. The choice of reheating versus addi-

tional reactor stages would depend on the cost tradeoff between high temperature heat exchanger tubing for the reheat duty and the cost of providing stages required for the injection and mixing points.

1. An ion transport membrane oxidation system comprising

- two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;
- an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; and
- one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas.

2. The system of claim 1 comprising one or more catalysts disposed within any reactant zone and/or in the interstage reactant gas flow path between any pair of membrane oxidation stages.

3. The system of claim 2 wherein the one or more catalysts are selected from the group consisting of oxidation catalyst, steam reforming catalyst, carbon dioxide reforming catalyst, and water gas shift catalyst.

4. The system of claim 1 comprising between 2 and 100 stages, inclusive.

5. The system of claim 1 comprising greater than 100 stages

6. The system of claim 1 comprising a pressure vessel in which the two or more membrane oxidation stages are disposed.

7. The system of claim 6 wherein the two or more membrane oxidation stages comprise a first stage and a last stage, and wherein the pressure vessel has a reactant feed inlet in flow communication with the reactant gas inlet region of the first stage, a product gas outlet in flow communication with the reactant gas outlet region of the last stage, an oxidant gas inlet in flow communication with the oxidant gas inlet regions of the two or more membrane oxidation stages, an oxidant gas outlet in flow communication with the oxidant gas outlet regions of the two or more membrane oxidation stages, and an interstage reactant gas inlet in flow communication with the interstage reactant gas flow path disposed between any two adjacent membrane oxidation stages.

8. A method for generating an oxidation product gas comprising

- providing an ion transport membrane oxidation system comprising
 - two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;
 - an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place

the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage; and

- (3) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;
 - (b) introducing one or more reactant feed gases into the reactant gas inlet region of a first stage of the two or more membrane oxidation stages;
 - (c) introducing an oxidant gas into any of the oxidant gas inlet regions of the two or more membrane oxidation stages;
 - (d) introducing a reactant interstage feed gas into any of the interstage reactant gas flow paths disposed between adjacent membrane oxidation stage or into any reactant zone of any stage receiving interstage reactant gas; and
 - (e) withdrawing an oxidation gas product from the reactant gas outlet region of a last stage of the two or more membrane oxidation stages.
9. The method of claim 8 wherein a first reactant feed gas comprises methane and a second reactant feed gas comprises steam.

10. The method of claim 9 wherein the reactant interstage feed gas and the first reactant feed gas are provided as portions of the same reactant gas stream.

11. The method of claim 9 wherein the reactant interstage feed gas and the first reactant feed gas are obtained from different sources.

12. The method of claim 11 wherein the reactant interstage feed gas comprises carbon dioxide.

13. An ion transport membrane oxidation system comprising

- (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;
- (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of the second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage;
- (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;
- (d) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages;
- (e) a reactant gas supply manifold in flow communication with one of the reactant gas feed lines to the first stage and in flow communication with any of the reactant interstage feed gas lines; and
- (f) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

14. The system of claim 13 comprising one or more catalysts disposed within any reactant zone and/or in the interstage reactant gas flow path between any pair of membrane oxidation stages.

15. The system of claim 14 wherein the one or more catalysts are selected from the group consisting of oxidation catalyst, steam reforming catalyst, carbon dioxide reforming catalyst, and water gas shift catalyst.

16. A method for generating an oxidation product gas comprising

- (a) providing an ion transport membrane oxidation system comprising
 - (1) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;
 - (2) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage;
 - (3) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;
 - (4) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages;
 - (5) a reactant gas supply manifold in flow communication with one of the reactant gas feed lines to the first stage and in flow communication with any of the reactant interstage feed gas lines; and
 - (6) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages;
- (b) providing a reactant gas via the reactant gas supply manifold, introducing reactant feed gas from the manifold into the reactant zone of the first stage, and introducing reactant gas from the manifold as reactant interstage feed gas into any of the one or more reactant interstage feed gas lines;
- (c) introducing an oxidant gas into any of the oxidant gas inlet regions of the two or more membrane oxidation stages; and
- (d) withdrawing an oxidation gas product from the reactant gas outlet region of the last stage of the two or more membrane oxidation stages.

17. The method of claim 16 wherein the reactant gas provided via the reactant gas supply manifold is pre-reformed natural gas and the oxidation gas product is synthesis gas comprising hydrogen and carbon monoxide.

18. The method of claim 17 comprising introducing steam into one of the reactant gas feed lines in flow communication with the reactant zone of the first stage of the two or more membrane oxidation stages.

19. The method of claim **16** wherein the reactant gas provided via the reactant gas supply manifold comprises pre-reformed natural gas and a reactant gas comprising carbon dioxide.

20. The method of claim **16** wherein the reactant gas provided via the reactant gas supply manifold comprises a pre-reformed mixture of natural gas and a reactant gas comprising at least one of methane and carbon dioxide.

21. An ion transport membrane oxidation system comprising

- (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;
- (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage;
- (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;
- (d) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages;
- (e) a reactant interstage feed gas supply manifold in flow communication with any of the reactant interstage feed gas lines; and
- (f) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

22. The system of claim **21** comprising one or more catalysts disposed within any reactant zone and/or in the interstage reactant gas flow path between any pair of membrane oxidation stages.

23. The system of claim **22** wherein the one or more catalysts are selected from the group consisting of oxidation catalyst, steam reforming catalyst, carbon dioxide reforming catalyst, and water gas shift catalyst.

24. An ion transport membrane oxidation system comprising

- (a) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;
- (b) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage;
- (c) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;

(d) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages;

(e) a reactant interstage feed gas supply manifold in flow communication with any of the reactant interstage feed gas lines;

(f) a reactant gas supply manifold in flow communication with any of (1) any of the reactant interstage feed gas lines and (2) any of the one or more reactant gas feed lines; and

(g) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages.

25. A method for generating an oxidation product gas comprising

(a) providing an ion transport membrane oxidation system comprising

(1) two or more membrane oxidation stages, each stage comprising a reactant zone, an oxidant zone, one or more ion transport membranes separating the reactant zone from the oxidant zone, a reactant gas inlet region, a reactant gas outlet region, an oxidant gas inlet region, and an oxidant gas outlet region;

(2) an interstage reactant gas flow path disposed between each pair of membrane oxidation stages, wherein the interstage reactant gas flow path is adapted to place the reactant gas outlet region of a first stage of the pair in flow communication with the reactant gas inlet region of a second stage of the pair such that interstage reactant gas can flow from the first stage to the second stage;

(3) one or more reactant interstage feed gas lines, each line being in flow communication with any interstage reactant gas flow path or with the reactant zone of any membrane oxidation stage receiving interstage reactant gas;

(4) one or more reactant gas feed lines in flow communication with the reactant zone of a first stage of the two or more membrane oxidation stages;

(5) a reactant interstage feed gas supply manifold in flow communication with any of the reactant interstage feed gas lines; and

(6) a product withdrawal line adapted to withdraw an oxidation product from the reactant zone of the last stage of the two or more membrane oxidation stages;

(b) introducing a reactant feed gas into the reactant zone of the first stage of the two or more membrane oxidation stages;

(c) providing reactant interstage feed gas via the reactant interstage feed gas supply manifold into any of the one or more reactant interstage feed gas lines;

(d) introducing an oxidant gas into any of the oxidant gas inlet regions of the two or more membrane oxidation stages; and

(e) withdrawing an oxidation gas product from the reactant gas outlet region of the last stage of the two or more membrane oxidation stages.

26. The method of claim **25** wherein the reactant feed gas and the reactant interstage feed gas comprise pre-reformed natural gas and the oxidation gas product is synthesis gas comprising hydrogen and carbon monoxide.

27. The method of claim **26** comprising introducing steam into one of the reactant gas feed lines in flow communication with the reactant zone of the first stage of the two or more membrane oxidation stages.

28. The method of claim **25** wherein the reactant interstage feed gas comprises methane and/or carbon dioxide.

29. The method of claim **28** comprising maintaining the partial pressure of carbon dioxide in the interstage reactant gas flowing into any membrane oxidation stage to be less than a critical threshold carbon dioxide partial pressure, $p_{CO_2}^*$, wherein $p_{CO_2}^*$ is defined as a carbon dioxide partial pressure above which the material in the ion transport membranes reacts with carbon dioxide and decomposes.

30. The method of claim **28** wherein the oxidation gas product is synthesis gas comprising hydrogen and carbon monoxide.

31. The method of claim **30** wherein the reactant interstage feed gas is provided by pre-reforming a reactant gas comprising carbon dioxide, methane, and one or more hydrocarbons heavier than methane.

32. The method of claim **30** wherein the synthesis gas comprising hydrogen and carbon monoxide is utilized as feed gas to a hydrocarbon synthesis process or an oxygenated hydrocarbon synthesis process that generates a process offgas comprising carbon dioxide, and wherein some or all of the process offgas provides at least a portion of the reactant interstage feed gas.

33. The method of claim **31** wherein the synthesis gas comprising hydrogen and carbon monoxide is utilized as feed gas to a hydrocarbon synthesis process or an oxygenated hydrocarbon synthesis process that generates a process offgas comprising carbon dioxide, and wherein some or all of the process offgas provides at least a portion of the reactant gas that is pre-reformed to provide the reactant interstage feed gas.

34. A method for the operation of an ion transport membrane oxidation system comprising

- (a) introducing one or more reactant gases into a reactant zone of the ion transport membrane oxidation system, wherein the one or more reactant gases comprise at least methane and carbon dioxide;
- (b) introducing an oxygen-containing gas into an oxidant zone of the ion transport membrane oxidation system;
- (c) permeating oxygen from the oxidant zone through an ion transport membrane into the reactant zone and reacting the oxygen therein with one or more components in the reactant gases; and
- (d) maintaining the partial pressure of carbon dioxide in the reactant gas flowing into the reactant zone to be less than a critical threshold carbon dioxide partial pressure, $p_{CO_2}^*$, wherein $p_{CO_2}^*$ is defined as a carbon dioxide partial pressure above which the material in the ion transport membrane reacts with carbon dioxide and decomposes.

* * * * *

TITLE OF THE INVENTION:

FABRICATION OF CATALYZED
ION TRANSPORT MEMBRANE SYSTEMS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

[0001] This invention was made in part with Government support under Cooperative Agreement No. DE-FC26-97FT96052 between Air Products and Chemicals, Inc., and the
5 U.S. Department of Energy. The Government has certain rights to this invention.

BACKGROUND OF THE INVENTION

[0002] Ceramic materials containing certain mixed metal oxide compositions possess both oxygen ion conductivity and electronic conductivity at elevated temperatures.
10 These materials, known in the art as mixed conducting metal oxides, may be used in applications including gas separation membranes and membrane oxidation reactors. Ceramic membranes are made of selected mixed metal oxide compositions and have been described as ion transport membranes (ITM). Catalysts may be used, for example, to promote the oxidation and/or reforming reactions that take place in membrane
15 oxidation reactors.

[0003] A characteristic property of these materials is that their oxygen stoichiometry is a thermodynamic function of temperature and oxygen partial pressure wherein the equilibrium oxygen stoichiometry decreases with increasing temperature and with decreasing oxygen partial pressure. It is known that the dimensions of all materials
20 change with changing temperature due to thermal expansion and contraction. In addition to these thermal dimensional changes, mixed conducting metal oxide materials undergo chemical dimensional changes that are functions of the metal oxide oxygen stoichiometry. At isothermal conditions, an article made of mixed conducting metal oxide material will increase in dimensions with decreasing oxygen stoichiometry. At isothermal
25 conditions, the oxygen stoichiometry decreases with decreasing oxygen partial pressure. Since the equilibrium oxygen stoichiometry increases with decreasing temperature, an

article made of mixed conducting metal oxides will contract due to both thermal and chemical dimensional changes as the temperature decreases at a constant oxygen partial pressure. Conversely, an article made of mixed conducting metal oxides will expand by both thermal and chemical dimensional changes as the temperature

5 increases at a constant oxygen partial pressure. This is described in an article entitled "Chemical Expansivity of Electrochemical Ceramics" by S. B. Adler in *J. Am. Ceram. Soc.* 84 (9) 2117-19 (2001).

[0004] Dimensional changes therefore result from equilibrium oxygen stoichiometry changes in mixed conducting metal oxide materials. Changing the temperature at a
10 constant oxygen partial pressure or changing the oxygen partial pressure at a constant temperature will change the equilibrium oxygen stoichiometry of the mixed conducting metal oxide material. When a mixed conducting metal oxide is used as an ion transport membrane, for example, an oxygen partial pressure difference across the membrane creates a difference in the equilibrium oxygen stoichiometry at each of the two surfaces
15 of the membrane, which in turn creates the thermodynamic driving force for oxygen ions to diffuse through the membrane.

[0005] It is known that temperature gradients in a mixed conducting metal oxide ceramic structure can create differential strains due to differential thermal expansion and contraction. Similarly, oxygen stoichiometry gradients in a ceramic structure can create
20 differential strains due to differential chemical expansion and contraction. This gradient in oxygen stoichiometry may be sufficiently large to create a correspondingly large differential chemical expansion, and therefore large mechanical stresses, that lead to failure of the ceramic structure. It is desirable, therefore, to avoid differential chemical expansion or at least to control the differential chemical expansion to below maximum
25 allowable values.

[0006] There is a need in the art for improved methods to reduce the potential for mechanical damage due to dimensional changes during the heating and cooling of mixed conducting metal oxide membrane systems, particularly in the operation of membrane reactor systems under transient conditions of temperature, pressure, and gas
30 composition that may occur during membrane and module fabrication as well as subsequent startup and shutdown of the membrane systems. These needs are addressed by embodiments of the invention disclosed below and defined by the claims that follow.

BRIEF SUMMARY OF THE INVENTION

[0007] An embodiment of the invention relates to a process for fabricating a catalyzed ion transport membrane comprising

5 (a) providing an ion transport membrane comprising a dense mixed conducting multicomponent metallic oxide layer having a first side, a second side, and a porous mixed conducting multicomponent metallic oxide layer contiguous with the first side;

10 (b) contacting the ion transport membrane with a non-reducing gaseous stream having a first oxygen partial pressure while heating the ion transport membrane to a temperature and for a time period sufficient to provide an ion transport membrane possessing anion mobility;

15 (c) contacting the ion transport membrane possessing anion mobility with a first reducing gaseous stream having a second oxygen partial pressure that is less than the first oxygen partial pressure for a time period sufficient to provide an ion transport membrane having anion mobility and essentially constant oxygen stoichiometry;

20 (d) cooling the ion transport membrane having anion mobility and essentially constant oxygen stoichiometry while contacting the membrane with the first reducing gaseous stream to provide an ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility; and

25 (e) applying a catalyst to at least one of the second side of the dense mixed conducting multicomponent metallic oxide layer and the porous mixed conducting multicomponent metallic oxide layer of the ion transport membrane that has essentially constant oxygen stoichiometry and no anion mobility, thereby providing the catalyzed ion transport membrane.

[0008] In an alternative embodiment, a process for fabricating a catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility comprises

30 (a) providing an ion transport membrane comprising a dense mixed conducting multicomponent metallic oxide layer having a first side, a second side,

and a porous mixed conducting multicomponent metallic oxide layer contiguous with the first side;

5 (b) applying a catalyst to at least one of the second side of the dense mixed conducting multicomponent metallic oxide layer and the porous mixed conducting multicomponent metallic oxide layer to provide the catalyzed ion transport membrane;

10 (c) contacting the catalyzed ion transport membrane with a non-reducing gaseous stream having a first oxygen partial pressure while heating the catalyzed ion transport membrane to a temperature and for a time period sufficient to provide a catalyzed ion transport membrane possessing anion mobility;

15 (d) contacting the catalyzed ion transport membrane possessing anion mobility with a first reducing gaseous stream having a second oxygen partial pressure that is less than the first oxygen partial pressure for a time period sufficient to provide a catalyzed ion transport membrane having anion mobility and essentially constant oxygen stoichiometry; and

20 (e) cooling the catalyzed ion transport membrane having anion mobility and essentially constant oxygen stoichiometry while contacting the membrane with the first reducing gaseous stream to provide a catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility.

DETAILED DESCRIPTION OF THE INVENTION

25 **[0009]** During startup or shutdown of an oxidation reactor system using mixed conducting metal oxide membranes, the temperature is increased or decreased, the oxygen partial pressure on the oxidant side of the membrane may change, and the reactive gas composition on the reactant side of the membrane may change. The equilibrium oxygen stoichiometry of the membrane material will change in response to the changes in temperature, oxygen partial pressure, and reactant gas composition. Oxygen anions will diffuse into or out of the membrane material and the membrane material will approach its equilibrium oxygen stoichiometry value.

30 **[0010]** As the oxygen stoichiometry and temperature change, the dimensions of the membrane will change. The time required for the membrane to reach chemical

equilibrium with the oxygen partial pressures on the surfaces of the membrane will depend on the oxygen anion diffusion rate into or out of the membrane. The time required for equilibration to occur is a function of the material composition, the temperature, and the dimensions of the membrane modules.

- 5 **[0011]** Different membrane compositions will have different oxygen anion diffusivities, and compositions with higher diffusivities will equilibrate with the gas phase faster, all other factors being equal. For a given membrane composition, the oxygen anion diffusivity increases exponentially with temperature. Therefore, equilibration times decrease with increasing temperature. Finally, the equilibration time increases
- 10 approximately with the square of the characteristic dimension (e.g., length or thickness) of the parts in the membrane modules. Thus thinner parts will equilibrate faster than thicker parts, all other factors being equal. As the thickness of a part increases and as the temperature decreases, it becomes increasingly difficult to keep the interior of the part in equilibrium with the gas phase due to sluggish diffusion of oxygen anions into or
- 15 out of the part.

- [0012]** Catalyst may be used to promote the oxidation and/or reforming reactions that take place in ion transport membrane oxidation reactors for the production of synthesis gas. In these reactors, the catalyst may be applied in contact with the reactant sides of the dense oxygen ion-permeable membranes and/or in contact with a porous layer
- 20 contiguous with the reactant side of the dense layer. Alternatively or additionally, catalyst may be applied to the oxidant side of the dense membrane to promote the rate of the surface reaction wherein oxygen anions are produced from oxygen at the surface of the membrane from gas phase species such as molecular oxygen. The catalyst on the oxidant side may be applied in contact with the oxidant side of the dense oxygen ion-
- 25 permeable membrane and/or in contact with a porous layer contiguous with the oxidant side of the dense layer.

- [0013]** It has been found that catalytic ion transport membranes may fail during start-up because the membrane catalyst can catalyze the reduction of certain compounds in the membrane material by small amounts of oxidizable impurities or fuels in the gas in
- 30 contact with the membranes during heating to operating temperatures. These oxidizable impurities or fuels may be generated, for example, during heating to operating temperatures by the decomposition of residual contaminants in the membrane reactors. These residual contaminants typically are materials that remain in the membrane

modules after fabrication and may include, for example, oil, grease, cleaning compounds, and other organic materials. Alternatively or additionally, oxidizable impurities may be present in the gas introduced into the modules during heating.

5 **[0014]** Uncontrolled reduction of the membrane material may cause failure of the catalytic membranes due to excessively large oxygen stoichiometry gradients in the membrane structure. This may cause an excessive differential chemical expansion between the reduced, catalyzed porous layer and the non-reduced, non-catalyzed dense layer and other non-reduced components, thereby causing the membrane structure to fail.

10 **[0015]** The elimination of these residual contaminants and oxidizable impurities during fabrication becomes increasingly difficult as the scale of membrane oxidation reactors increases to commercially-sized systems. These contaminants and impurities are likely to exist, therefore, in all large-scale membrane reactor systems after initial fabrication, and also may exist in the systems after subsequent modification or maintenance
15 procedures.

[0016] The problem of destructive uncontrolled catalytic reduction by oxidizable impurities can be avoided by utilizing embodiments of the present invention wherein the materials in the membrane structures are reduced under controlled conditions prior to use of the membranes in reactor vessels under operating conditions. This reducing
20 pretreatment or preconditioning procedure reduces the oxygen stoichiometry uniformly throughout the membrane components such that subsequent exposure of the catalyzed membrane modules to oxidizable impurities will not produce excessive further reduction of membrane material. As discussed in more detail below, the prereduction procedure may be carried out during membrane fabrication either before or after the introduction of
25 catalyst into the membrane structure.

[0017] The following definitions apply to terms used in the description and claims for the embodiments of the invention presented herein.

[0018] An ion transport membrane is defined as an active dense layer of ceramic membrane material comprising mixed metal oxides capable of transporting or
30 permeating oxygen anions at elevated temperatures. The ion transport membrane also may transport electrons in addition to oxygen ions, and this type of ion transport membrane typically is described as a mixed conductor membrane. The ion transport

membrane also may be a composite membrane comprising a layer of dense active membrane material and one or more layers of porous and/or channeled support layers.

[0019] A catalyzed ion transport membrane is defined as an ion transport membrane comprising catalyst disposed in contact with the reactant side of the active dense layer and/or in contact with a porous layer contiguous with the reactant side of the dense layer and/or in contact with the oxidant side of the active dense layer. A catalyst is defined as one or more elements and/or compounds that promote (1) reactions that occur on the reactant side of the dense layer and/or in the porous layer contiguous with the reactant side of the dense layer, including the oxidation of species such as hydrogen, carbon monoxide and hydrocarbons, and/or (2) the formation of oxygen anions from gaseous oxygen on the oxidant side of the dense layer. A catalytic material is defined as a material that contains the catalyst and also may include non-catalytic support material that supports the catalyst.

[0020] The term "dense" refers to a sintered or fired ceramic material that is impervious to bulk gas flow. Gas cannot flow through dense ceramic membranes made of mixed-conducting multi-component metal oxide material as long as the membranes are intact and have no cracks, holes, or imperfections which allow gas leaks. Oxygen ions can permeate dense ceramic membranes made of mixed-conducting multi-component metal oxide material. The one or more ion transport membranes separating the oxidant zone from the reactant zone allow the permeation of oxygen ions through the membranes, and the membranes do not allow bulk flow of gas between the oxidant and reactant zones of the stage.

[0021] The term "anion mobility" is defined as the condition in dense ceramic membrane material wherein oxygen anions can diffuse readily under an oxygen activity gradient, typically when the oxygen ion conductivity is at least 0.001 S/cm, where S the conductivity in siemens expressed as ohm^{-1} . The term "a temperature sufficient to provide anion mobility" is defined as a temperature at which the oxygen ion conductivity is greater than about 0.001 S/cm and more specifically greater than about 0.01 S/cm. A time period sufficient to provide anion mobility is defined as at least one diffusion time constant, and typically more than two diffusion time constants, where the diffusion time constant is defined as L^2/D_v where L is the solid state diffusion distance and D_v is the oxygen vacancy diffusivity.

[0022] The term "essentially constant oxygen stoichiometry" is defined by an oxygen vacancy fraction that does not vary by more than 3% of the mean value and typically does not vary by more than 0.5% of the mean value.

[0023] As used herein, the generic term "oxygen" includes all forms of oxygen comprising the element or moiety having an atomic number of 8. The generic term oxygen therefore includes oxygen ions, gaseous oxygen (dioxygen or O₂), and oxygen that exists in compounds in the gaseous, liquid, or solid state. The term "oxygen partial pressure" as used herein is the usual thermodynamic definition of the partial pressure of dioxygen or O₂ in a gas mixture containing O₂ and/or other gaseous compounds containing oxygen.

[0024] The reactant side of catalyzed ion transport membrane is defined as the side that is in contact with a reactant gas. A reactant gas is defined as a gas comprising one or more reactive components that participate in any of the reactions that occur on or adjacent the reactant side of the membrane. The reactions in the reactant zone may occur (1) between oxygen permeated through the membrane and any of the reactive components and (2) among any of the reactive components or reaction intermediates. These reactions form reaction products that may be withdrawn as product gas from the reactor system. In one embodiment of the invention, for example, the catalyzed membranes may have catalyst on the reactant sides of the membranes and may be used in an oxidation reactor system for generation of a synthesis gas product comprising hydrogen and carbon monoxide from a hydrocarbon-containing feed gas.

[0025] A reducing gas or reducing gaseous stream is defined as a gas comprising one or more oxidizable components that can react with components in a mixed conducting metal oxide material to reduce the oxygen stoichiometry or composition of the mixed conducting metal oxide material. An example of a reducing gas is a gas comprising one or more reducing components selected from the group consisting hydrogen, carbon monoxide, methane, ethane, and mixtures thereof. Any of these components can react with a mixed conducting metal oxide material to reduce the oxygen stoichiometry. A non-reducing gas or non-reducing gaseous stream is a gas that contains essentially no reducing components.

[0026] The term "contacting" as applied to a gas stream and an ion transport membrane means passing or flowing the gas stream over the surfaces of the ion transport membrane in any appropriate reaction vessel having at least a gas inlet and a

gas outlet. The reaction vessel may have a heating system adapted to heat the vessel and contents of the vessel under controlled conditions, e.g., heating at one or more temperature ramp rates, maintaining the temperature at a desired level, and cooling at one or more temperature ramp rates. Chemical reactions may take place between components in the gas stream and components in the membrane material; alternatively, the gas stream may be inert and serve to protect the membrane material during heating or cooling.

[0027] The terms "calcine" and "calcining" are defined as a heating step to produce a chemical change such as decomposing a precursor metal salt or metal compound to a metal or metal oxide. The adjective "calcined" describes a catalyzed ion transport membrane that has been subjected to a calcining step.

[0028] The indefinite articles "a" and "an" as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of "a" and "an" does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article "the" preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective "any" means one, some, or all indiscriminately of whatever quantity. The term "and/or" placed between a first entity and a second entity means one of (1) the first entity, (2) the second entity, and (3) the first entity and the second entity.

[0029] The catalyzed ion transport membranes described herein may be used in any type of mixed conducting multicomponent metallic oxide ion transport membrane module or system known in the art. Exemplary types of known ion transport membrane modules may include but are not limited to the ion transport membrane module and vessel systems described in United States Patent No. 7,179,323 and the planar ceramic membrane assembly and oxidation reactor systems described in United States Patent No. 7,279,027. Ion transport membrane modules that may be used with catalyzed ion transport membranes according to embodiments of the present invention include but are not limited to the mixed conducting membranes described in United States Patent No. 6,492,290. The complete disclosures United States Patent Nos. 6,492,290, 7,179,323, and 7,279,027 are incorporated herein by reference.

[0030] Embodiments of the present invention may be applied, for example, to the planar ceramic membrane modules described in United States Patent No. 7,279,027 cited above. Each of these modules comprises a plurality of membrane wafers assembled in a stack or module, and a plurality of the modules may be installed in a reactor pressure vessel with appropriate manifolds for introducing oxidant gas and reactant gas to the modules and withdrawing oxygen-depleted oxidant gas and reaction products from the modules.

[0031] Each of the wafers comprises a dense layer of mixed-conducting multi-component metal oxide material that has a first side and a second side, a porous layer of mixed-conducting multi-component metal oxide material in contact with the first side of the dense layer, and a ceramic channeled support layer in contact with the second side of the dense layer. The composite layers form an individual ion transport membrane. Two layers are joined and sealed around the edges such that a cavity is formed between the second sides of the two layers with the channeled support layers disposed within the cavity. The first sides of the dense layers have respective contiguous layers of porous mixed-conducting multi-component metal oxide material. The internal cavity has appropriate inlet and outlet ports formed by the particular structures of the two respective composite layers. This assembly of layers thus forms a wafer having an internal cavity or internal region adjacent the first sides of the layers and an external region covered with the contiguous porous layers. The internal cavity or region of the wafer has appropriate inlet and outlet ports formed by the particular structures of the two respective composite layers.

[0032] A plurality of wafers is assembled into a stack or module with formed internal manifolds adapted to introduce oxidant gas into the interior regions of the wafers and to withdraw oxygen-depleted oxidant gas from the interior regions. As described below, catalyst that promotes the reactions taking place in the exterior regions may be applied to the first sides of the dense layers and/or the adjacent porous layers in selected steps in the wafer and stack fabrication procedure. When used in reaction systems for making synthesis gas comprising hydrogen and carbon monoxide from a hydrocarbon feed gas, for example, air is introduced into the internal regions of the wafers in the module and hydrocarbon reactant gas is passed over the exterior regions (i.e., the reactant or process sides of the membranes) of the wafers in the module. Oxygen selectively diffuses through the dense layers and reacts with the hydrocarbon feed gas on the reactant sides of the wafers to produce synthesis gas components, the catalyst promotes

the reactions taking place on the reactant sides of the wafers, oxygen-depleted air is withdrawn from the interior regions of the wafers in the module, and synthesis gas and possibly unreacted hydrocarbons are withdrawn from the reactant sides of the wafers in the module.

- 5 **[0033]** The modules described above may be fabricated according to several different embodiments of the invention. These are summarized below.

10 (1) Fabricate the wafers, apply catalyst to the exterior regions of the wafers, assemble a stack or module comprising a plurality of the catalyzed wafers, and treat the module with a reducing gas to yield an essentially constant oxygen stoichiometry of the mixed-conducting multi-component metal oxide material in the module.

15 (2) Fabricate the wafers, assemble a stack or module comprising a plurality of wafers, apply catalyst to the exterior regions of the wafers, and treat the module with a reducing gas to yield an essentially constant oxygen stoichiometry of the mixed-conducting multi-component metal oxide material in the module.

20 (3) Fabricate the wafers, assemble a stack or module comprising a plurality of wafers, treat the module with a reducing gas to yield an essentially constant oxygen stoichiometry of the mixed-conducting multi-component metal oxide material in the module, and apply catalyst to the exterior regions of the wafers in the module.

[0034] In the fabrication options described above, the application of catalyst and the reduction treatment of each membrane to yield an essentially constant oxygen stoichiometry may be carried out by either of the following procedures.

25 (A) Reduction followed by catalyst application:

(1) contact each ion transport membrane with a non-reducing gaseous stream having a first oxygen partial pressure while heating the ion transport membrane to a temperature and for a time period sufficient to provide an ion transport membrane possessing anion mobility;

30 (2) contact each ion transport membrane possessing anion mobility with a first reducing gaseous stream having a second oxygen partial pressure that is less than the first oxygen partial pressure for a time

period sufficient to provide an ion transport membrane having anion mobility and essentially constant oxygen stoichiometry;

5 (3) cool each ion transport membrane having anion mobility and essentially constant oxygen stoichiometry while contacting the membrane with the first reducing gaseous stream to provide an ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility; and

10 (4) apply a catalyst to at least one of the second side of the dense mixed conducting multicomponent metallic oxide layer and the porous mixed conducting multicomponent metallic oxide layer of each ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility, thereby providing the catalyzed ion transport membrane.

(B) Catalyst application followed by reduction:

15 (1) apply a catalyst to at least one of the second side of the dense mixed conducting multicomponent metallic oxide layer and the porous mixed conducting multicomponent metallic oxide layer of each membrane to provide a catalyzed ion transport membrane;

20 (2) contact each catalyzed ion transport membrane with a non-reducing gaseous stream having a first oxygen partial pressure while heating the catalyzed ion transport membrane to a temperature and for a time period sufficient to provide a catalyzed ion transport membrane possessing anion mobility;

25 (3) contact each catalyzed ion transport membrane possessing anion mobility with a first reducing gaseous stream having a second oxygen partial pressure that is less than the first oxygen partial pressure for a time period sufficient to provide a catalyzed ion transport membrane having anion mobility and essentially constant oxygen stoichiometry; and

30 (4) cool each catalyzed ion transport membrane having anion mobility and essentially constant oxygen stoichiometry while contacting the membrane with the first reducing gaseous stream to provide a

catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility.

[0035] After completing (A) or (B), a final step may be effected by contacting each catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility with a second reducing gaseous stream and calcining the catalyzed ion transport membrane at a temperature ranging from 200°C to 500°C to provide a calcined catalyzed ion transport membrane.

[0036] In the above embodiments, the first non-reducing gaseous stream may comprise a component selected from the group consisting of oxygen, nitrogen, argon, helium, carbon dioxide, and mixtures thereof. The first non-reducing gaseous stream, for example, may be air. The first reducing gaseous stream and/or the second reducing gaseous stream may comprise a reducing component selected from the group consisting of hydrogen, carbon monoxide, methane, ethane, and mixtures thereof.

[0037] The catalyst applied to the membrane may comprise a metal or an oxide of a metal selected from Groups II, III, IV, V, VI, VII, VIII, IX, X, XI, XV and the F block lanthanides of the Periodic Table of the Elements. In particular, the metal or the oxide of the metal may be selected from the group consisting of bismuth, barium, cerium, yttrium, zirconium, vanadium, molybdenum, cerium, manganese, praseodymium, platinum, palladium, rhodium, iron, ruthenium, iridium, gold, nickel, cobalt, copper, silver and mixtures thereof.

[0038] The catalyst may be applied to a membrane or wafer by any method of catalyst impregnation known in the art. For example, the catalyst may be applied as a solution of soluble metal salts, metal organic compounds, metallic oxide and mixtures thereof followed by calcination of the membrane or wafer. In one embodiment, this may include contacting a catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility with a second reducing gaseous stream and calcining the catalyzed ion transport membrane at a temperature ranging from 200°C to 500°C to provide a calcined catalyzed ion transport membrane. The second reducing gaseous stream may comprise a reducing component selected from the group consisting of hydrogen, carbon monoxide, methane, ethane and mixtures thereof.

[0039] The mixed conducting multicomponent metallic oxide in either or both of the dense layer and the porous layer may comprise at least one mixed conducting multicomponent metallic oxide represented by the formula $(La_xCa_{1-x})_yFeO_{3-\delta}$, wherein

$1.0 > x > 0.5$, $1.1 \geq y \geq 1.0$, and δ is a number which renders the composition of matter charge neutral.

[0040] Embodiments of the invention described above are illustrated by, but are not limited by, the following Examples.

5

EXAMPLE 1

Fabrication and Reduction of an ITM Module
and Test Bars Made of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$

[0041] An ion transport membrane (ITM) module was constructed according to methods described in earlier-cited U.S. Patent 7,279,027, and all components of the module were formed of material having a composition of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ where δ is a number to make the compound charge neutral. The module was 3.5 inches wide, 5 inches long, and 2 inches thick, and was fitted with an inlet line adapted to introduce air into the interior region of the module and an outlet line to withdraw oxygen-depleted air from the interior region.

[0042] The porous layers of the module were impregnated with a suspension of nanoparticles of $\text{CeO}_2\text{-ZrO}_2$ in water (Nanophase Technologies Corporation) and dried at 300°C in N_2 ; the layers were then impregnated with a solution of Rh nitrate and tetra amine Pd nitrate, calcined at 500°C at $0.5^\circ\text{C}/\text{min}$ in N_2 , and cooled to room temperature at $0.5^\circ\text{C}/\text{min}$. The catalyst content of the entire module was 259 mg CeO_2 , 139 mg ZrO_2 , 47.6 mg Rh, and 47.6 mg Pd.

[0043] Thirty-nine dense bars of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ with dimensions of 50 mm x 3 mm x 4 mm were made by pressing powder of the same composition into a bar shape and sintering at 1400°C in air for 5 hours, followed by cooling in air to room temperature at $1^\circ\text{C}/\text{min}$. Fifteen of the bars were coated with a suspension of nanoparticles of $\text{CeO}_2\text{-ZrO}_2$ in water (Nanophase Technologies Corporation) and dried at 300°C in N_2 . The coated bars were then dipped in a solution of Rh nitrate and tetra amine Pd nitrate in water, calcined at 500°C at $0.5^\circ\text{C}/\text{min}$ in N_2 , and cooled to room temperature at $0.5^\circ\text{C}/\text{min}$. The remaining twenty-four bars did not have catalyst applied to them.

[0044] The membrane module, five of the catalyzed bars, and three of the bars that were not catalyzed were placed in a gas-tight retort in a furnace and processed as described below. Ten of the catalyzed bars were not processed. The module and test bars were heated in dry air at $0.5^\circ\text{C}/\text{min}$ to 900°C and held at 900°C for 5 hours in air at 500 sccm.

Nitrogen Equilibration

[0045] The air flow to the retort was ramped or decreased linearly from 500 sccm to 0 sccm, and nitrogen flow was ramped or increased linearly from 0 to 1000 sccm over a time period of 7 hours. During this time period, the air and nitrogen gas flows were bubbled through water at room temperature to humidify the gases before introduction into the retort. The bars and module then were held in the nitrogen atmosphere at 900°C for 18 hours.

100 ppm Hydrogen Equilibration

[0046] The nitrogen flow was ramped or decreased linearly from 1000 sccm to 0 sccm, and flow of a reducing gas mixture of 100 ppm H₂/balance N₂ was ramped or increased linearly from 0 to 500 sccm over 5 hours. The nitrogen and H₂/N₂ gas mixtures were bubbled through water at room temperature to humidify the gases before introduction into the retort. The bars and module then were held in the 100 ppm H₂/balance N₂ gas mixture for 19 hours at 900°C. The term "ppm" as used in all Examples herein means parts per million by volume.

1000 ppm Hydrogen Equilibration

[0047] The 100 ppm H₂/balance N₂ gas flow was ramped or decreased linearly from 500 sccm to 0 sccm, and flow of a reducing gas mixture of 1000 ppm H₂/balance N₂ was increased linearly from 0 to 500 sccm over 5 hours. The H₂/N₂ gas was bubbled through water at room temperature to humidify the gas before introduction into the retort. After the 5 hours, the bars and module were held in the 1000 ppm H₂/balance N₂ gas mixture for 19 hours at 900°C.

5000 ppm Hydrogen Equilibration

[0048] The 1000 ppm H₂/balance N₂ gas flow was ramped or decreased linearly from 500 sccm to 0 sccm, and flow of a reducing gas mixture of 5000 ppm H₂/balance N₂ was ramped or increased linearly from 0 to 5000 sccm over 5 hours. The H₂/N₂ gas was bubbled through water at room temperature to humidify the gas before introduction into the retort. After the 5 hours, the bars and module then were held in the 5000 ppm H₂/balance N₂ gas mixture for 19 hours at 900°C. The bars and module then were ramped or cooled linearly to room temperature at 0.5°C/min in humidified 5000 ppm H₂/bal N₂ gas and were removed from the retort.

[0049] The bars and module made by this method may be described as preconditioned, prereduced, or pretreated articles.

EXAMPLE 2

Start-up of a Preconditioned Catalyzed ITM Module for Syngas Production

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[0050] After completion of the preconditioning reduction process described in Example 1, the module was installed in a laboratory reactor vessel for use as an ITM syngas reactor with gas inlet and gas outlet piping connected to the oxidant inlet and oxidant outlet lines of the module. Since air typically is the oxidant gas in ITM syngas reactors, the oxidant side of the membrane module will be described here as the air side. The reactor was fitted with inlet and outlet lines for gas flow over the exterior region, i.e., the reactant or process side, of the module. The reactant side and air side of the reactor then were purged with nitrogen long enough to reduce the oxygen concentration in the purge outlet of both streams to less than 50 ppm. Water bubblers were installed on the air feed and reactant side inlet piping and purged with nitrogen to remove dissolved oxygen and any air trapped in the head space.

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[0051] A 500 sccm flow of 1000 ppm H₂/balance N₂ was bubbled through water and passed through the reactant or process side of the module, and the pressure on the process side was increased to 60 psig. A 500 sccm flow of 5000 ppm H₂/balance N₂ was bubbled through water and passed through the air side of the module. The module then was heated at 0.5°C/min to 900°C and held at 900°C.

20

Air Side Gas Composition Change No. 1

[0052] The gas composition on the air side of the module was changed over 5 hours by blending out the 5000 ppm H₂/balance N₂ bubbled through water and blending in 1000 ppm H₂/balance N₂ bubbled through water. The total flow rate on the air side of the module remained at 500 sccm. At the end of the gas change or ramp, the module was held at these conditions for 19 hours at 900°C.

25

Air Side Gas Composition Change No. 2

[0053] The gas composition on the air side was then changed over 5 hours by blending out the 1000 ppm H₂ bubbled through water and blending in 100 ppm H₂ bubbled through water. The total flow rate on the air side of the module remained at 500 sccm.

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At the end of the gas change or ramp, the module was held at these conditions for 19 hours at 900°C.

Air Side Gas Composition Change No. 3

5 [0054] The gas composition on the air side of the module was then changed over 5 hours by blending out the 100 ppm H₂ bubbled through water and blending in nitrogen bubbled through water. The total flow rate on the oxidant fed side of the module remained at 500 sccm. At the end of the gas change or ramp, the gas feed was switched to dry nitrogen by bypassing the bubbler. The module was held for 19 hours at 900°C with dry nitrogen flowing through the air side.

10 Air Side Gas Composition Change No. 4

[0055] The gas composition on the air side of the module then was changed over 15 hours by blending out the nitrogen and blending in 1000 ppm O₂/balance N₂. The total flow rate on the air side of the module remained at 500 sccm. At the end of the gas change, the module was held at those conditions for 19 hours at 900°C.

15 Air Side Gas Composition Change No. 5

[0056] Over 1 hour, air was blended in to the 1000 ppm O₂/balance N₂ flow to achieve a 4000 ppm O₂ mix. The total flow rate on the air side of the module remained at 500 sccm.

Air Side Gas Composition Change No. 6

20 [0057] The gas composition on the air side of the module then was changed over 5 hours by blending out the 1000 ppm O₂/balance N₂ gas mix and blending in air. The total flow rate on the air side of the module remained at 500 sccm. At the end of the gas change or ramp, the module was held at those conditions for 19 hours at 900°C.

25 [0058] During the entire process described above, the module remained leak tight and did not suffer any mechanical breakage or damage.

EXAMPLE 3

Start-up of a Non-Preconditioned Catalyzed ITM Module
for Syngas Production

30 [0059] A module identical to the module that was preconditioned in Example 1 and used in Example 2 was fabricated and cooled from a joining temperature of 1200°C in air

at 0.5°C/min. The ITM syngas module then was impregnated with catalyst in the same manner as the module of Example 1, but it was not preconditioned by contact with reducing gas. After the catalyst was applied, the module was installed in the ITM syngas reactor with gas inlet and gas outlet piping connected to the air inlet and air outlet lines of the module.

[0060] The process side and air side of the module were purged with nitrogen long enough to reduce the oxygen concentration in the outlet of both streams to less than 50 ppm. Water bubblers were installed on the oxidant and reactant side inlet piping and were purged with nitrogen to remove dissolved oxygen and any air trapped in the head space. A 500 sccm flow of 1000 ppm H₂/balance N₂ was bubbled through water and passed through the process side of the module, and the pressure therein was increased to 60 psig. A 500 sccm flow of 5000 ppm H₂/balance N₂ was bubbled through water and passed through the air side of the module.

[0061] The module was then heated from room temperature at 0.5°C/min under continuing gas flow. When the temperature reached about 90°C, the module failed by breaking into numerous pieces.

EXAMPLE 4 Strength Testing of Bars

[0062] Strength testing was carried out for the following test bars of Example 1: the 10 catalyzed but not preconditioned bars, the 5 catalyzed and preconditioned bars, the 3 preconditioned but not catalyzed bars, and the 21 bars that were neither preconditioned nor catalyzed. The strengths of the bars were measured using a standard 4-point flexure geometry using the protocol of ASTM C1161-94 and ASTM C1211-92. The outer load point span was 40 mm and the inner load point span was 20 mm. The 10 catalyzed but not preconditioned bars, the 5 catalyzed and preconditioned bars, and the 3 preconditioned but not catalyzed bars were heated to 450°C in an atmosphere of 2.5% H₂O, 5% H₂, balance Ar. The hydrogen in this atmosphere represented oxidizable impurities in the gas phase. The strength of each bar was measured at 450°C after holding the bars in this atmosphere for 18 hours. The strengths of the 21 bars that were neither catalyzed nor pretreated were measured at room temperature.

[0063] The strength test results given in Table 3 below. The bars that were catalyzed but not pretreated had strengths below the resolution of the measuring device, which is

approximately 20 MPa, and therefore were untestable. The catalyzed bars that were pretreated had a measured strength that was within 1 standard deviation of the room temperature strength of the bars that were neither catalyzed nor pretreated. These results show that the preconditioning of catalyzed bars of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-x}$ preserves the strength of the material as measured when the material is contacted with dilute oxidizable impurities in the gas phase.

Table 3
Strength of Test Bars of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-x}$

Test Bars		Strength Test Temperature (°C)	Average Strength (MPa)	Std. Deviation (MPa)
Description	Number of bars			
Not catalyzed and not preconditioned	21	Room temperature	201	26
Not catalyzed and not preconditioned	3	450	139	27
Catalyzed and not preconditioned	10	450	Not testable	--
Catalyzed and preconditioned	5	450	191	20

EXAMPLE 5

Preconditioning Prior to Catalyst Impregnation

[0064] An ITM syngas module was constructed according to methods described in earlier-cited U.S. Patent 7,279,027, and all components of the module were formed of material having a composition of $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_{3-\delta}$ where δ is a number to make the compound charge neutral. The module was 3.5 inches wide, 5 inches long, and 2 inches thick, and was fitted with an inlet line adapted to introduce air into the interior region of the module and an outlet line to withdraw oxygen-depleted air from the interior region. The module was placed in a gas tight retort in a furnace, heated in dry air at 0.5°C/min to 900°C, and held at 900°C for 5 hours in air.

Nitrogen equilibration

[0065] The air flow to the retort was ramped from 500 sccm to 0 sccm and nitrogen flow was ramped from 0 to 1,000 sccm over 7 hours. During this time, the combined air and nitrogen gas flows were bubbled through water. After the 7 hours the module was held in the nitrogen atmosphere at 900°C for 18 hours.

100 ppm H_2 equilibration

[0066] The nitrogen flow was ramped from 1,000 sccm to 0 sccm and a gas mixture of 100 ppm H₂/balance N₂ was ramped from 0 to 500 sccm over 5 hours. The combined nitrogen and H₂/N₂ gas mixture was bubbled through room temperature water. After the 5 hours, the module was held in the 100 ppm H₂/balance N₂ gas mixture for 19 hours.

5 1000 ppm H₂ equilibration

[0067] The 100 ppm H₂/bal N₂ flow was next ramped from 500 sccm to 0 sccm and a gas mixture of 1,000 ppm H₂/balance N₂ was ramped from 0 to 500 sccm over 5 hours. The combined H₂/N₂ gas mixtures were bubbled through room temperature water. After the 5 hours, the bars and module were held in the 1,000 ppm H₂/balance N₂ gas mixture for 19 hours.

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5,000 ppm H₂ equilibration

[0068] The 1,000 ppm H₂/bal N₂ flow was next ramped from 500 sccm to 0 sccm and a gas mixture of 5,000 ppm H₂/balance N₂ was ramped from 0 to 500 sccm over 5 hours. The combined H₂/N₂ gas mixtures were bubbled through room temperature water. After the 5 hours, the module was held in the 5000 ppm H₂/balance N₂ gas mixture for 19 hours.

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[0069] The module then was ramped to room temperature at 0.5°C/min in humidified 5000 ppm H₂/bal N₂. The reduced preconditioned module was removed from the retort.

[0070] The porous layers of the preconditioned module were impregnated with a suspension of nanoparticles of CeO₂-ZrO₂ in water (Nanophase Technologies Corporation) and dried at 300°C in a gas tight retort in an atmosphere of 5000 ppm H₂ in a balance of N₂. The porous layers of the module then were impregnated with a solution of Rh nitrate and tetra amine Pd nitrate, calcined at 500°C at 0.5 cc/min in a gas tight retort in an atmosphere of 5000 ppm H₂/balance N₂ and cooled to room temperature at 0.5°C/min. The weights of the catalyst components impregnated on the module were 259 mg CeO₂, 139 mg ZrO₂, 47.6 mg Rh, and 47.6 mg Pd.

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EXAMPLE 6

Start-up of a Catalyzed Preconditioned ITM Syngas Module

[0071] The ITM syngas module that was preconditioned in Example 5 was installed in an ITM Syngas reactor. Since air typically is the oxidant gas in ITM syngas reactors, the oxidant side of the membrane module is described here as the air side. The module was

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fitted with an inlet line adapted to introduce air into the interior region of the module and an outlet line to withdraw oxygen-depleted air from the interior region. Gas inlet and gas outlet piping of the reactor was plumbed to the air inlet and air outlet of the module. The reactant or process side and the air feed side of the reactor then were both purged with
5 nitrogen long enough to lower the oxygen concentration in the outlet of both streams to less than 50 ppm.

[0072] Water bubblers on the air feed and process side inlet piping were also purged with nitrogen to remove dissolved oxygen and any air trapped in the head space.

[0073] A 500 sccm flow of 1,000 ppm H₂/balance N₂ bubbled through water was
10 established on the process side. The process side pressure was increased to 60 psig and a 500 sccm flow of 5,000 ppm H₂/balance N₂ bubbled through water was established through the air feed side of the module. The module then was heated at 0.5°C/min to 900°C and then held at 900°C

Air Side Change No. 1

15 **[0074]** The gas composition on the air feed side of the module was then changed over 5 hours by blending out the 5,000 ppm H₂/balance N₂ bubbled through water and blending in 1,000 ppm H₂/balance N₂ bubbled through water. The total flow rate on the air feed side of the module remained at 500 sccm.

[0075] At the end of the ramp, the module was held for 19 hours.

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Air Side Change No. 2

[0076] The gas composition on the air feed side of the module was then changed over 5 hours by blending out the 1,000 ppm H₂ bubbled through water and blending in 100 ppm H₂ bubbled through water. The total flow rate on the air feed side of the module remained at 500 sccm.

25 **[0077]** At the end of the ramp, the module was held for 19 hours.

Air Side Change No. 3

[0078] The gas composition on the air feed side of the module was then changed over 5 hours by blending out the 100 ppm H₂ bubbled through water and blending in nitrogen
30 bubbled through water. The total flow rate on the air feed side of the module remained at 500 sccm.

[0079] At the end of the ramp, the gas feed was switched to dry nitrogen by bypassing the bypass bubbler and the module was held for 19 hours.

Air Side Change No. 4:

5 [0080] The gas composition on the air feed side of the module was then changed over 15 hours by blending out the nitrogen and blending in 1000 ppm O₂/balance N₂. The total flow rate on the air feed side of the module remained at 500 sccm.

[0081] At the end of the ramp, the module was held for 19 hours.

Air Side Change No. 5

10 [0082] Over 1 hour, air was blended into the 1,000 ppm O₂/balance N₂ flow to achieve a 4,000 ppm O₂ mix. The total flow rate on the air feed side of the module remained at 500 sccm.

Air Side Change No. 6

15 [0083] The gas composition on the air feed side of the module was then changed over 5 hours by blending out the 1,000 ppm O₂/balance N₂ gas mix and blending in air. The total flow rate on the air feed side of the module remained at 500 sccm. At the end of the ramp, the module was held for 19 hours.

[0084] During the entire process carried out in this Example, the module remained leak tight and did not suffer any damage.

20 [0085] The above Examples illustrate that the problem of destructive uncontrolled catalytic reduction in ion transport membrane modules by oxidizable impurities can be avoided by utilizing embodiments of the present invention wherein the materials in the membrane modules are reduced under controlled conditions prior to use of the modules in reactor vessels under operating conditions.

CLAIMS

1. A process for fabricating a catalyzed ion transport membrane comprising

(a) providing an ion transport membrane comprising a dense mixed
conducting multicomponent metallic oxide layer having a first side, a second side,
5 and a porous mixed conducting multicomponent metallic oxide layer contiguous
with the first side;

(b) contacting the ion transport membrane with a non-reducing gaseous
stream having a first oxygen partial pressure while heating the ion transport
membrane to a temperature and for a time period sufficient to provide an ion
10 transport membrane possessing anion mobility;

(c) contacting the ion transport membrane possessing anion mobility with
a first reducing gaseous stream having a second oxygen partial pressure that is
less than the first oxygen partial pressure for a time period sufficient to provide an
ion transport membrane having anion mobility and essentially constant
15 oxygen stoichiometry;

(d) cooling the ion transport membrane having anion mobility and
essentially constant oxygen stoichiometry while contacting the membrane with
the first reducing gaseous stream to provide an ion transport membrane having
essentially constant oxygen stoichiometry and no anion mobility; and

(e) applying a catalyst to at least one of the second side of the dense
mixed conducting multicomponent metallic oxide layer and the porous mixed
conducting multicomponent metallic oxide layer of the ion transport membrane
that has essentially constant oxygen stoichiometry and no anion mobility, thereby
providing the catalyzed ion transport membrane.

2. The process of Claim 1 wherein the first non-reducing gaseous stream comprises a
component selected from the group consisting of oxygen, nitrogen, argon, helium,
carbon dioxide, and mixtures thereof.

3. The process of Claim 1 wherein the first non-reducing gaseous stream is air.

4. The process of Claim 1 wherein the first reducing gaseous stream comprises a reducing component selected from the group consisting of hydrogen, carbon monoxide, methane, ethane, and mixtures thereof.
- 5 5. The process of Claim 1 wherein the catalyst comprises a metal or an oxide of a metal selected from Groups II, III, IV, V, VI, VII, VIII, IX, X, XI, XV and the F block lanthanides of the Periodic Table of the Elements.
6. The process of Claim 5 wherein the metal or the oxide of the metal is selected from
10 the group consisting of bismuth, barium, cerium, yttrium, zirconium, vanadium, molybdenum, cerium, manganese, praseodymium, platinum, palladium, rhodium, iron, ruthenium, iridium, gold, nickel, cobalt, copper, silver and mixtures thereof.
7. The process of Claim 5 or 6 wherein the catalyst is applied as a solution comprising a
15 component selected from the group consisting of soluble metal salts, metal organic compounds, metallic oxides, and mixtures thereof.
8. The process of Claim 1 further comprising:
- 20 (f) contacting the catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility with a second reducing gaseous stream and calcining the catalyzed ion transport membrane at a temperature ranging from 200°C to 500°C to provide a calcined catalyzed ion transport membrane.
- 25 9. The process of Claim 8 wherein the second reducing gaseous stream comprises a reducing component selected from the group consisting of hydrogen, carbon monoxide, methane, ethane and mixtures thereof.
10. The process of Claim 1 wherein at least one of the dense mixed conducting
30 multicomponent metallic oxide layer and the porous mixed conducting multicomponent

metallic oxide layer comprises at least one mixed conducting multicomponent metallic oxide represented by the formula $(La_xCa_{1-x})_yFeO_{3-\delta}$, wherein $1.0 > x > 0.5$, $1.1 \geq y \geq 1.0$, and δ is a number which renders the composition of matter charge neutral.

- 5 11. A process for fabricating a catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility comprising

10 (a) providing an ion transport membrane comprising a dense mixed conducting multicomponent metallic oxide layer having a first side, a second side, and a porous mixed conducting multicomponent metallic oxide layer contiguous with the first side;

(b) applying a catalyst to at least one of the second side of the dense mixed conducting multicomponent metallic oxide layer and the porous mixed conducting multicomponent metallic oxide layer to provide the catalyzed ion transport membrane;

15 (c) contacting the catalyzed ion transport membrane with a non-reducing gaseous stream having a first oxygen partial pressure while heating the catalyzed ion transport membrane to a temperature and for a time period sufficient to provide a catalyzed ion transport membrane possessing anion mobility;

20 (d) contacting the catalyzed ion transport membrane possessing anion mobility with a first reducing gaseous stream having a second oxygen partial pressure that is less than the first oxygen partial pressure for a time period sufficient to provide a catalyzed ion transport membrane having anion mobility and essentially constant oxygen stoichiometry; and

25 (e) cooling the catalyzed ion transport membrane having anion mobility and essentially constant oxygen stoichiometry while contacting the membrane with the first reducing gaseous stream to provide a catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility.

12. The process of Claim 11 wherein the first non-reducing gaseous stream comprises a component selected from the group consisting of oxygen, nitrogen, argon, helium, carbon dioxide, and mixtures thereof.

5 13. The process of Claim 11 wherein the first non-reducing gaseous stream is air.

14. The process of Claim 11 wherein the first reducing gaseous stream comprises a reducing component selected from the group consisting of hydrogen, carbon monoxide, methane, ethane and mixtures thereof.

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15. The process of Claim 11 wherein the catalyst comprises a metal or an oxide of a metal selected from Groups II, III, IV, V, VI, VII, VIII, IX, X, XI, XV and the F block lanthanides of the Periodic Table of the Elements.

15 16. The process of Claim 15 wherein the metal or the oxide of the metal is selected from the group consisting of bismuth, barium, cerium, yttrium, zirconium, vanadium, molybdenum, cerium, manganese, praseodymium, platinum, palladium, rhodium, iron, ruthenium, iridium, gold, nickel, cobalt, copper, silver and mixtures thereof.

20 17. The process of Claim 15 or 16 wherein the catalyst is applied as a solution comprising a component selected from the group consisting of soluble metal salts, metal organic compounds, metallic oxides, and mixtures thereof.

18. The process of Claim 11 further comprising:

25 (f) contacting the catalyzed ion transport membrane having essentially constant oxygen stoichiometry and no anion mobility with a second reducing gaseous stream and calcining the catalyzed ion transport membrane at a temperature ranging from 200°C to 500°C to provide a calcined catalyzed ion transport membrane.

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19. The process of Claim 18 wherein the second reducing gaseous stream comprises a reducing component selected from the group consisting of hydrogen, carbon monoxide, methane, ethane and mixtures thereof.

- 5 20. The process of Claim 11 wherein at least one of the dense mixed conducting multicomponent metallic oxide layer and the porous mixed conducting multicomponent metallic oxide layer comprises at least one mixed conducting multicomponent metallic oxide represented by the formula $(La_xCa_{1-x})_yFeO_{3-\delta}$, wherein $1.0 > x > 0.5$, $1.1 \geq y \geq 1.0$, and δ is a number which renders the composition of matter charge neutral.

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ABSTRACT OF THE DISCLOSURE

Process for fabricating a catalyzed ion transport membrane (ITM). In one embodiment, an uncatalyzed ITM is (a) contacted with a non-reducing gaseous stream
5 while heating to a temperature and for a time period sufficient to provide an ITM possessing anion mobility; (b) contacted with a reducing gaseous stream for a time period sufficient to provide an ITM having anion mobility and essentially constant oxygen stoichiometry; (c) cooled while contacting the ITM with the reducing gaseous stream to provide an ITM having essentially constant oxygen stoichiometry and no anion
10 mobility; and (d) treated by applying catalyst to at least one of (1) a porous mixed conducting multicomponent metallic oxide (MCMO) layer contiguous with a first side of a dense layer of MCMO and (2) a second side of the dense MCMO layer. In another embodiment, these steps are carried out in the alternative order of (a), (d), (b), and (c).

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