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Principal Authors:

Eltron: Carl R. Evenson, Anthony F. Sammells, Richard T. Treglio, Jim Fisher

ANL: U. (Balu) Balachandran

CoorsTek: Richard N. Kleiner, James E. Stephan, Frank E. Anderson

Süd Chemie: Chandra Ratnasamy, Mahendra Sunkara, Jyothish Thangla

NORAM: Clive Brereton, Warren Wolfs, James Lockhart

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Name and Address of Submitting Organization:

Eltron Research Inc., 4600 Nautilus Court South, Boulder, CO 80301-3241

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ABSTRACT

During this quarter work was continued on characterizing the stability of layered composite membranes under a variety of conditions. Membrane permeation was tested up to 100 hours at constant pressure, temperature, and flow rates. In addition, design parameters were completed for a scale-up hydrogen separation demonstration unit. Evaluation of microstructure and effect of hydrogen exposure on BCY/Ni cermet mechanical properties was initiated. The fabrication of new cermets containing high permeability metals is reported and progress in the preparation of sulfur resistant catalysts is discussed. Finally, a report entitled "Criteria for Incorporating Eltron's Hydrogen Separation Membranes into Vision 21 IGCC Systems and FutureGen Plants" was completed.

EXECUTIVE SUMMARY

Eltron Research Inc. and team members CoorsTek, Süd Chemie, Argonne National Laboratory, and NORAM are developing an environmentally benign, inexpensive, and efficient method for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. This project was motivated by the National Energy Technology Laboratory (NETL) Vision 21 initiative, which seeks to economically eliminate environmental concerns associated with the use of fossil fuels. Currently, this project is focusing on four basic categories of dense membranes: i) mixed conducting ceramic/ceramic composites, ii) mixed conducting ceramic/metal (cermet) composites, iii) cermets with hydrogen permeable metals, and iv) layered composites containing hydrogen permeable alloys. Ultimately, these materials must enable hydrogen separation at practical rates under ambient and high-pressure conditions, without deactivation in the presence of feedstream components such as carbon dioxide, water, and sulfur.

This report contains results for composite layered membrane stability experiments, evaluation of cermet mechanical properties, high permeability metal cermet fabrication and sulfur tolerant catalyst testing. In addition progress is described on reactor engineering and design of a demonstration scale hydrogen separation unit.

INTRODUCTION

The objective of this project is to develop an environmentally benign, inexpensive, and efficient method for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. Currently, this project is focusing on four basic categories of dense membranes: i) mixed conducting ceramic/ceramic composites, ii) mixed conducting ceramic/metal (cermet) composites, iii) cermets with hydrogen permeable metals, and iv) layered composites with hydrogen permeable alloys. The primary technical challenge in achieving the goals of this project will be to optimize membrane composition to enable practical hydrogen separation rates and chemical stability. Other key aspects of this developing technology include catalysis, ceramic processing methods, and separation unit design operating under high pressure. To achieve these technical goals, Eltron Research Inc. has organized a consortium consisting of CoorsTek, Süd Chemie, Inc. (SCI), Argonne National Laboratory (ANL), and NORAM.

During this quarter composite layered membrane stability was characterized at intermediate temperature and high pressure. These results are presented in this report, in addition to progress with cermet fabrication and characterization, catalyst development, and reactor engineering.

EXPERIMENTAL

The Experimental Section of the first quarterly report (January 1, 2001) contained detailed descriptions of equipment and procedures to be used over the duration of this program. The specific aspects presented were: (a) preparation of ceramic powders, (b) preparation of composite materials, (c) fabrication of tube and disk membranes, (d) construction and operation of ambient-pressure hydrogen separation units, (e) construction and operation of high-pressure hydrogen separation units, (f) hydrogen transport and ambipolar conductivity measurements and calculations, and (g) fabrication of thin film ceramics. For brevity, these general issues will not be repeated. However, modification of equipment or methods, as well as any other experimentally relevant issues, will be reported in the Results and Discussion section under their corresponding Tasks as outlined in the original proposal.

RESULTS AND DISCUSSION

Tasks 1 & 2 Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes

Contributors: Eltron, CoorsTek, ANL

I. Composite Layered Membranes with High Hydrogen Permeability – Eltron

Composite layered membranes were tested under a variety of conditions to establish stability under optimal and expected operating conditions. Variables included temperature, pressure, flowrates, and a partial vs. 100% permeate hydrogen stream. Membranes were tested between 400 and 435°C and between 300 and 400 psig. **Figure 1** shows a plot of permeation vs. time for two membranes tested for 80 hours at 400°C, 300 psig feed stream pressure (40% H₂), and a 100% hydrogen permeation stream. For both membranes a slight decrease in permeation was observed during the first ten hours of the experiment. This initial loss of permeation has been observed at Eltron and in the literature and is attributed to the initial equilibration of hydrogen within the lattice vacancies of the composite membrane. Following this initial equilibration membrane permeation was very stable. The first membrane had a permeation of greater than 120 mL•min⁻¹•cm⁻² after 80 hours of testing, and the second membrane had a permeation of greater than 80 mL•min⁻¹•cm⁻². After 80 hours the membranes were characterized with X-ray diffraction. Results showed no surface contamination or undesired phase formation.

Figure 1. Graph of permeation vs. time for two composite layered membranes held at 400°C and 300 psig for 80 hours.

II. Multi-Phase Ceramics and Cermets – ANL, CoorsTek

Previous work at ANL showed that the microstructure of $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCY)/Ni cermet membranes affects hydrogen permeation through the membranes. The hydrogen flux was found to be higher for membranes with large Ni and BCY grains. ANL is now studying the effect of microstructure (Ni and BCY grain size) on the mechanical properties of BCY/Ni membranes. During this quarter, ANL prepared initial coarse-grained samples for fracture strength measurements, and performed a preliminary evaluation of the membrane microstructure. To evaluate the effect of operating conditions on the mechanical properties, the fracture strength of membranes will be measured after sintering without any additional heat treatments, and will be compared to the fracture strength of membranes that are exposed to hydrogen-containing gas mixtures after sintering.

Two groups of BCY/Ni membranes were prepared. First, a BCY/Ni mixture was made by using BCY powder from Praxair and Ni powder (40 Vol. %). Then, the powder mixture was uniaxially pressed into disks that were sintered at 1400°C in 200 ppm H_2 /balance N_2 . To study the effects of hydrogen exposure, one group of membranes was further exposed to $\approx 4\%$ H_2 /balance N_2 for 100 hr at 900°C. The other group of membranes will be tested in the as-sintered condition.

Figure 2 shows secondary electron images from polished cross-sections of BCY/Ni disks. **Figure 2A** shows the cross-section of a disk in the as-sintered condition; **Figure 2B** shows a disk after sintering and exposure to $\approx 4\%$ H_2 /balance N_2 for 100 h. The exposure to 4% H_2 had no apparent effect on the microstructure of the disks. Both types of disk exhibited dense and uniformly distributed Ni (dark phase) with a somewhat coarse Ni grain size (10–40 mm). Finer grained materials are in preparation.

Figure 2. Scanning electron micrographs of the polished fracture for Ni-BCY specimens sintered in 200 ppm H_2 /balance N_2 at 1400°C (A) before (B) after exposure to 4% H_2 /balance N_2 at 900°C for 100 hours.

Figure 3 shows secondary electron images of the surfaces of the BCY/Ni disks. **Figure 3A** shows an as-sintered disk, and **Figure 3B** a disk after sintering and exposure to $\approx 4\%$ H_2 /balance N_2 for 100 hours. As noted in the micrographs of polished cross-sections, the exposure to $4\% \text{H}_2$ did not have a dramatic effect on the microstructure, although it is possible that there is a slightly higher Ni concentration at the surface of the membrane after exposure to $4\% \text{H}_2$. This may indicate a preferential enrichment of Ni at the surface of the membrane during exposure to hydrogen-containing gases. To confirm this, it will be necessary to expose BCY/Ni membranes to $4\% \text{H}_2$ for time >100 hours or hydrogen concentration $>4\%$.

CoorsTek has begun preparation of new hydrogen separation cermets containing high permeability metals. Initial experiments explored three different ceramic phases combined with appropriate metals. Eleven different cermet compositions have been prepared and sintered. The volume percent of ceramic phase in the prepared cermets ranged from 40 to 60 volume percent (%). Sintering trials were performed at a variety of temperatures as shown in **Figure 4**. Porosity of the cermet was minimized by sintering at 1675°C . SEM analysis of the resulting cermets showed uniform composites with high densities and distinct phase separation, as shown in **Figure 5**.

Figure 3. Scanning electron micrographs of the surface for Ni-BCY specimens sintered in 200 ppm H_2 /balance N_2 at 1400°C (A) before (B) after exposure to $4\% \text{H}_2$ /balance N_2 at 900°C for 100 hours.

Figure 4. Densification curves for cermet containing 60 % ceramic and 40 % high permeability metal.

Figure 5. x100 SEM image of a 60 % ceramic 40 % high permeability metal cermet.

III. Membrane Coatings and Catalysts – SCI

SCI is currently developing sulfur tolerant catalysts for the retentate side of the hydrogen separation membrane. Palladium copper alloys have been discussed in the literature as sulfur tolerant alloys. Two Pd/Cu alloy samples were prepared using palladium nitrate and copper nitrate solutions. The preparation method involved two stages: (a) first the solution mixture was heated in air at 350°C for about two hours and (b) hydrogen treatment (reduction) of the resulting solid in a vacuum chamber at 500°C for about two hours. The resulting solid was analyzed for phase, composition and morphology using EDAX and SEM.

SEM images are shown in **Figure 6**. As shown in Figure 6a, the backscattered imaging does not show any difference between copper and palladium. This implies that there is an even mixture of both copper and palladium at the atomic level, which makes it difficult for the backscattering imaging to detect the difference between palladium and copper. This shows the formation of a Pd/Cu alloy. To confirm the presence of Cu/Pd after hydrogen treatment, EDAX analysis was performed on the same powder. As shown in **Figure 7**, there is a large presence of palladium along with copper. X-ray diffraction will be performed to confirm the correct alloy formation. Once characterized, the Pd/Cu catalyst will be tested on a commercially available hydrogen separation membrane.

Figure 6. SEM images showing Pd/Cu alloy. Image A shows the secondary electron image on the left and the backscattered image on the right. This image shows an even mixture of copper and palladium. Image B shows more palladium particles, along with the presence of copper.

Figure 7. EDAX analysis of the resulting Pd/Cu alloy prepared from initial solution mixture containing Pd nitrate and Cu nitrate solutions.

Task 3 *High Pressure Hydrogen Separation*

Contributors: Eltron

Key results for high pressure hydrogen separation are discussed under Task 1. Eltron is currently designing experiments for testing the mechanical stability of composite layered membranes up to 1000 psi.

Task 4 *Thin-Film Hydrogen Separation Membranes*

Contributors: CoorsTek, Eltron

As discussed in previous reports, CoorsTek has been developing a thin film deposition procedure for creating a dense thin film cermet membrane on a tubular support. In this process, Eltron prepared isopressed BCY / Ni closed one-end (COE) porous support tubes. Thin film slurry was then deposited on the inside diameter of the tubes and sintered by CoorsTek. Based on permeation data, testing of thin film BCY / Ni tubes will not be continued. The slurry thin film deposition techniques developed will continue to be evaluated at CoorsTek for future application to thin film cermet membranes containing high permeability metals.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: NORAM

Previous reports detailed NORAM's effort in drafting a report entitled "Criteria for Incorporating Eltron's Hydrogen Separation Membranes into Vision 21 IGCC Systems and FutureGen Plants." During this reporting period the report was modified to include:

- A discussion of recent advances in warm gas cleaning and the expected benefits for intermediate temperature membranes.
- Process flow sheets were prepared to illustrate the potential operating conditions for Eltron's membranes in different IGCC power plant configurations. The flow sheets explored the effect of cold, warm, and hot gas cleaning on high temperature and intermediate temperature composite membranes.
- Predictions for higher pressure separators in line with the 1000 psi gasifiers envisioned by DOE.

Once the completed report has been issued to Eltron Research, Inc., it will be delivered to DOE personnel as a separate document.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

Previous reports have detailed attempts at using hydrogen separation membranes for membrane-promoted alkane dehydrogenation. Several different hydrogen separation membranes were tested under a variety of different conditions. While some conversion of alkanes to olefins was observed, the membranes did not appear to promote this process. It is expected that under the correct pressures, flow rates, and in the presence of an appropriate catalyst, these membranes would promote alkane conversion. At this point in the project effort if focused on membrane stability and scale-up and therefore further experiments for membrane-promoted conversion of alkanes to olefins will not be pursued.

Task 7 Catalyst Membrane Compositions for Scale Up

Testing during the past year focused on layered composite membranes. Results for these materials were compiled and compared to all the categories of membranes developed under this program. Based on hydrogen permeation rates, mechanical stability, and economics, the results to date clearly indicated that the layered composites have the greatest potential for scale up and commercial viability. In terms of ceramics and cermets, effort now is being focused on new

cermets based on high permeability metals that have acceptably high permeation rates. In addition, cermets may provide chemical and mechanical stability advantages and have potential as protective/catalytic layers in the layered composite membranes.

Task 8 Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes

CoorsTek has developed a thin film deposition procedure for the application of BCY / Ni thin films ranging from 10 to 100 μm onto the inner surface of a tubular support. This process has been discussed on a research and development scale under Task 4. These procedures are easily adaptable to manufacturing scale; however, the permeability of BCY / Ni materials will limit its commercial potential. New cermets based on high permeability metals also have potential; however, these cermets are in an early stage of development. As mentioned under Task 7, composite layered membranes have the greatest potential for scale up. Therefore, current work in Task 8 is focused on identification of materials and manufacturing processes for composite layered membranes. Planar and tubular membrane configurations are under consideration.

Task 9 Fabrication and Evaluation of Demonstration-Scale Hydrogen Separation Unit

Work was begun on the design and construction of a scale-up hydrogen separation unit. The initial work plan described the modification of the research scale reactor for the demonstration unit. However, due to the high flow rates and operating conditions desired, careful design of a new reactor is necessary. Design parameters under consideration include membrane configuration, gas composition, flow rates, ultimate pressures, and temperature range of the unit. The membrane reactor will be designed to accommodate both a ten fold membrane scale-up and the possibility of larger scale-up steps. Conditions and equipment necessary for the demonstration-scale hydrogen separation unit are as follows:

- The reactor will have an operating temperature range of 320 to 440°C.
- The reactor will be designed to allow permeation testing using feed streams ranging from 300 to 1000 psi. Plumbing issues under these conditions include pressure rated tubing, appropriate gas regulators, and flow meters capable of the necessary flow rates at the desired operating pressure.
- The feed gas composition requires manifolding of four different gases plus an inert gas for reactor purging. The expected gas composition will be a simulated water gas shift mixture of H_2 , CO_2 , CO , and steam.
- The permeate side of the membrane will be designed for a variety of different conditions to allow complete characterization of membrane materials.

- A steam boiler and subsequent condensing tanks will be built to accommodate the required steam flow rates. The use of steam also requires the use of guard bed materials.
- Design of the reactor membrane itself includes sealing of the membrane, the potential use of a membrane support, flow characteristics to optimize feed stream residence time, and appropriate safety requirements.
- Reactor design also encompasses membrane configuration and choice of material(s) for housing the membrane. Both tubular and planar membrane designs are under consideration; however, it is expected that the initial scale-up step will utilize a single or multiple stack planar membrane module.
- Appropriate safety features are necessary and therefore included in the reactor design. Safety features include temperature and pressure sensors, relief valves, and hydrogen and carbon monoxide leak detectors. Both automated and manual safety shut down systems will be employed.

Careful design of the demonstration scale hydrogen separation unit as described above will maximize the versatility of the reactor and allow Eltron Research, Inc. to collect hydrogen separation data under a variety of different conditions and permeation rates.

SUMMARY AND CONCLUSIONS

Conclusions based on the work performed during this quarter are summarized as follows:

1. Permeation data was collected for 100 continuous hours on membranes exposed to varying temperature, pressure, and flow conditions to verify membrane stability.
2. BCY/Ni cermets were evaluated to determine the effect of microstructure on mechanical properties.
3. Fabrication of new cermets containing high permeability metals was initiated.
4. Sulfur tolerant hydrogen dissociation catalysts were prepared and characterized.
5. A report entitled "Criteria for Incorporating Eltron's Hydrogen Separation Membranes into Vision 21 IGCC Systems and FutureGen Plants" was completed.
6. A new scale-up hydrogen separation demonstration unit was designed.

OBJECTIVES FOR NEXT REPORTING PERIOD

During the next reporting period efforts will be continued on characterizing membrane stability. In addition a scale up hydrogen demonstration unit will be constructed. ANL will continue evaluation of the effect of grain size on the mechanical properties of BCY/Ni. CoorsTek will continue development of new cermet compositions, and SCI will further develop sulfur tolerant catalysts. NORAM will work on a preliminary report concerning the mechanical aspects of a hydrogen separation unit based on Eltron's membrane technology.

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

None.

TIME LINES

The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

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