Title: Advanced Hydrogen Transport Membranes for Vision 21 Fossil Fuel Plants

Type of Report: Quarterly

Reporting Period Start Date: July 1, 2002

Reporting Period End Date: September 30, 2002

Principal Authors:
Eltron: Shane E. Roark, Anthony F. Sammells, Richard A. Mackay, Lyrik Y. Pitzman, Thomas A. Zirbel, Thomas F. Barton, Sara L. Rolfe
ANL: U. (Balu) Balachandran
CoorsTek: Richard N. Kleiner, James E. Stephan, Frank E. Anderson
MTI: George Farthing
ORNL: Tim R. Armstrong, Matt K. Ferber
Süd Chemie: Aaron L. Wagner, Jon P. Wagner

Date Report was Issued: October 25, 2002

DOE Award Number: DE-FC26-00NT40762

Name and Address of Submitting Organization:
Eltron Research Inc., 4600 Nautilus Court South, Boulder, CO 80301-3241

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do no necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Eltron Research Inc., and team members CoorsTek, McDermott Technology, Inc., Süd Chemie, Argonne National Laboratory, and Oak Ridge National Laboratory 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. This objective is being pursued using dense membranes based in part on Eltron-patented ceramic materials with a demonstrated ability for proton and electron conduction. The technical goals are being addressed by modifying single-phase and composite membrane composition and microstructure to maximize proton and electron conductivity without loss of material stability. 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.

During this quarter, additional cermet compositions were tested; however the performance was much lower than previous cermets. Ceramic/ceramic membranes also were evaluated, and decreasing membrane thickness resulted in a three-fold increase in H_2 permeation. The highest H_2 permeation for this category of membranes was ~0.03 mL/min/cm^2 at 800°C for a 0.21-mm thick sample. Although these permeation rates were roughly an order of magnitude lower than the best cermets, these results demonstrated the feasability of the approach and provided a good starting point for further development of this class of membranes. The highest H_2 separation rates were obtained for cermets containing a metal with high H_2 permeability. Moreover, permeation was improved by fabricating membranes with a graded metal content across the membrane thickness. Specifically, a 0.2-mm thick graded membrane achieved a H_2 permeation rate near 4 mL/min/cm^2 at 950°C, and 2.6 mL/min/cm^2 at only 650°C. A range of metals and metal alloys also were evaluated for possible inclusion in cermets for intermediate temperature H_2 separation and one metal composite achieved a H_2 permeation rate of ~20 mL/min/cm^2 at 400°C. Finally, a high-pressure seal has been maintained at 250 psi and 800°C for 2000 hours.

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. This objective will be accomplished by employing dense ceramic and composite membranes based in part on Eltron-patented materials[1-3] with a demonstrated ability for rapid hydrogen ion and electron conduction. The primary technical challenge in achieving the goals of this project will be to optimize membrane composition and microstructure 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, McDermott Technology, Inc. (MTI), Süd Chemie, Inc. (SCI), Argonne National Laboratory (ANL), and Oak Ridge National Laboratory (ORNL).

Currently two basic categories of membranes are under development: i) ceramic/metals (cermets) and ii) multi-phase ceramics. The cermets demonstrate several advantages, such as higher H_2 permeation rates, better structural stability, and the fact that the metal phase acts as an excellent catalyst for promoting the surface process. Unfortunately, the metal phase will be particularly susceptible to sulfur poisoning. Early sulfur stability measurements of multi-phase ceramics also demonstrated reactivity with sulfur, but conceivably it will be easier to design ceramics with some sulfur tolerance. By the end of this project it is anticipated that the final membrane compositions will include a cermet designed for maximum H_2 permeation and used only in concert with desulfurization, and a ceramic composite with greater chemical stability (sulfur tolerance, in particular), but lower H_2 permeation.

During this quarter, additional cermet compositions were tested; however the performance was much lower than previous cermets. Ceramic/ceramic membranes also were evaluated, and decreasing membrane thickness resulted in a three-fold increase in H_2 permeation. The highest H_2 permeation for this category of membranes was ~0.03 mL/min/cm^2 at 800°C for a 0.21-mm thick sample. Although these permeation rates were roughly an order of magnitude lower than the best cermets, these results demonstrated the feasability of the approach and provided a good starting point for further development of this class of membranes. The highest H_2 separation rates were obtained for cermets containing a metal with high H_2 permeability. Moreover, permeation was improved by fabricating membranes with a graded metal content across the membrane thickness. Specifically, a 0.2-mm thick graded membrane achieved a H_2 permeation rate near 4 mL/min/cm^2 at 950°C, and 2.6 mL/min/cm^2 at only 650°C. A range of metals and metal alloys also were evaluated for possible inclusion in cermets for intermediate temperature H_2 separation and one metal composite achieved a H_2 permeation rate of ~20 mL/min/cm^2 at 400°C. Finally, a high-pressure seal has been maintained at 250 psi and 800°C for 2000 hours.

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, MTI, SCI, ORNL, ANL

I. Cermet Membranes – Eltron, CoorsTek

In the previous report, H_2 permeation rate and ambipolar conductivity of cermets with the general composition $AB_{0.8}B^{d}_{0.2}O_{3-\delta}$/44 wt.% metal were presented and compared to earlier results for $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% metal analogs. For comparable membrane thicknesses of ~0.5 mm, both materials demonstrated equivalent results with permeation rates near ~0.2 mL/min/cm^2 and ambipolar conductivity of ~0.005 S/cm. This conductivity correlated very well with the known proton conductivity of the pure $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ and $AB_{0.8}B^{d}_{0.2}O_{3-\delta}$ ceramic phases. During this period an additional analog was tested with the general formula $AB_{0.8}B^{e}_{0.2}O_{3-\delta}$/44 wt.%. Despite the fact that the known proton conductivity of the $AB_{0.8}B^{e}_{0.2}O_{3-\delta}$ ceramic phase is equal to the other analogs, a 0.37-mm thick membrane only permeated 0.002 mL/min/cm^2 of H_2, corresponding to an ambipolar conductivity of less than 2×10^{-5} S/cm. Furthermore, unlike the other analogs, this material reached maximum permeation at 800°C, followed by a rapid drop as the temperature was increased to 950°C.

II. Ceramic/Ceramic Composite Membranes – Eltron, CoorsTek

Ceramic/ceramic composites also are under development as possible alternatives to cermets. It is anticipated that these composites might have greater mechanical stability due to similar characteristics between the two phases, and might have greater chemical stability in the presence of feedstream contaminants. In the last report, results were presented for a 0.94-mm thick preliminary composition represented as $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/CER1. Due to the thickness of the membrane, the highest H_2 permeation rate achieved was only 0.006 mL/min/cm^2, which corresponded to an ambipolar conductivity of 1.69×10^{-4} S/cm. A similarly prepared membrane of the same composition was ground down to 0.21 mm and results for this sample are presented in Figure 1. Both samples showed a maximum permeation at 800EC; however the thinner membrane demonstrate more than a three fold increase in performance. The highest permeation was 0.027 mL/min/cm^2, which correlated to a conductivity of 1.69×10^{-4} S/cm — exactly the same as the thicker sample.

Since the proton conducting ceramic phase of these ceramic/ceramic composites was the same as the above cermets, and simple ohmmeter measurements suggested comparable continuity of the electron conducting phase, the lower performance of these samples likely was due to cross diffusion of constituents from each phase. This assumption was supported by XRD patterns. Despite the fact that these results were lower than the best cermets tested to date, both feasibility and

reproducibility were demonstrated.

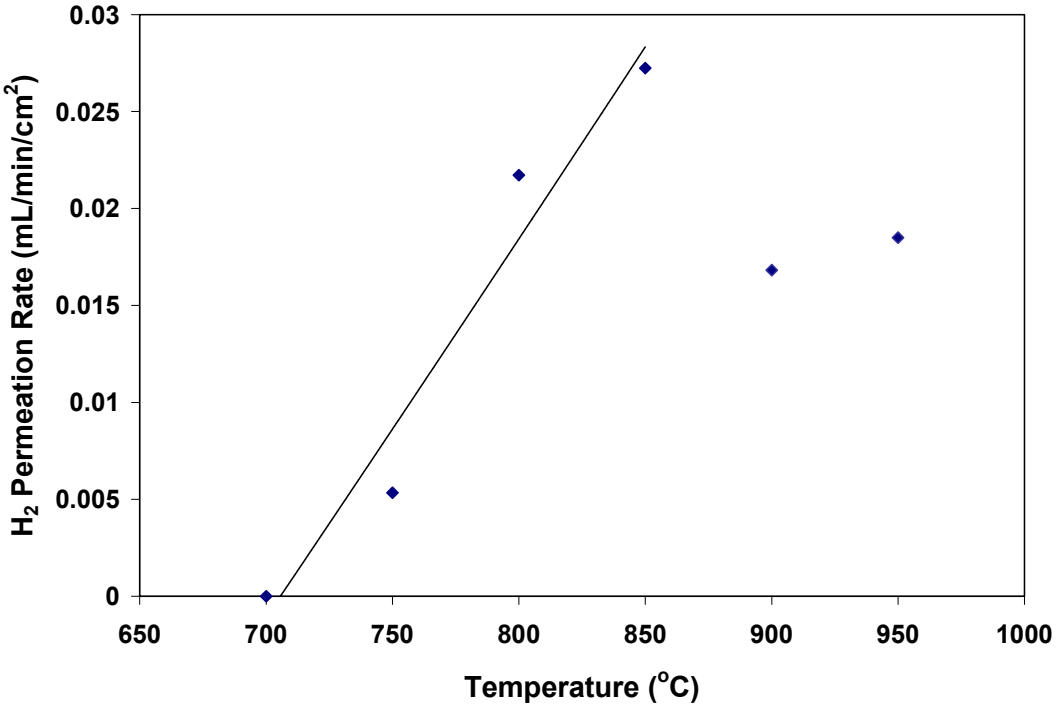


Figure 1. Plot showing H_2 permeation rate as a function of temperature for a ceramic/ceramic composite membrane. The feedstream was humidified 80 vol.% H_2 (bal. He). The sweep gas was Ar. Flow rates were between 80 and 120 mL/min.

III. Cermets Containing a H_2-Permeable Metal – Eltron

As an alternative to the above cermets, materials also are being developed with the general composition $AB_{1-x}B'_xO_{3-\delta}$/40 vol.% metal, where the metal phase has high H_2 permeability. These materials were described in previous reports, and analogous materials were described by others.[4,5] Despite several potential drawbacks of this category of H_2 separation membranes, permeation rates are significantly higher (at least one order of magnitude) and cover a wider temperature range than analogous membranes where permeation is limited by proton conductivity. Accordingly, efforts to develop these materials will continue and alternatives to overcome their limitations are being considered.

In an effort to minimize the thickness of the H_2 permeable phase, graded cermet membranes were fabricated as diagramed in Figure 2 and shown in the cross-section SEM micrograph in Figure 3. The concentration of the metal phase in these structures increased from one side to the other, with a corresponding decrease in ceramic phase content. The metal phase was continuous through the structure; however, the change in phase distribution was most severe at the outer edges, where the membrane was mostly metal. The metal "layer" shown in the micrograph in Figure 3 was between 10 and 15 Fm. The membrane was dense on the metal side, but the porosity of the mostly ceramic side has not yet been determined. It is anticipated that these structures will function

similarly to supported thin film membranes, except that in this case the film is thoroughly integrated with the support surface and any discontinuity in the metal film is filled with dense ceramic.

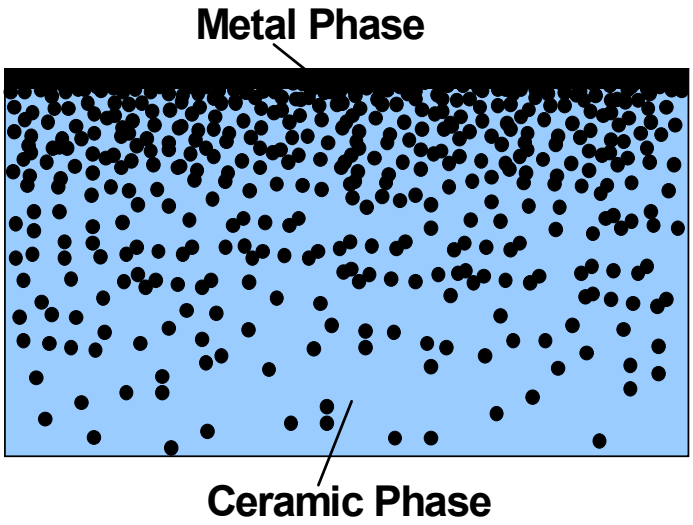


Figure 2. **Diagram of a graded cermet cross section used for H_2 separation.**

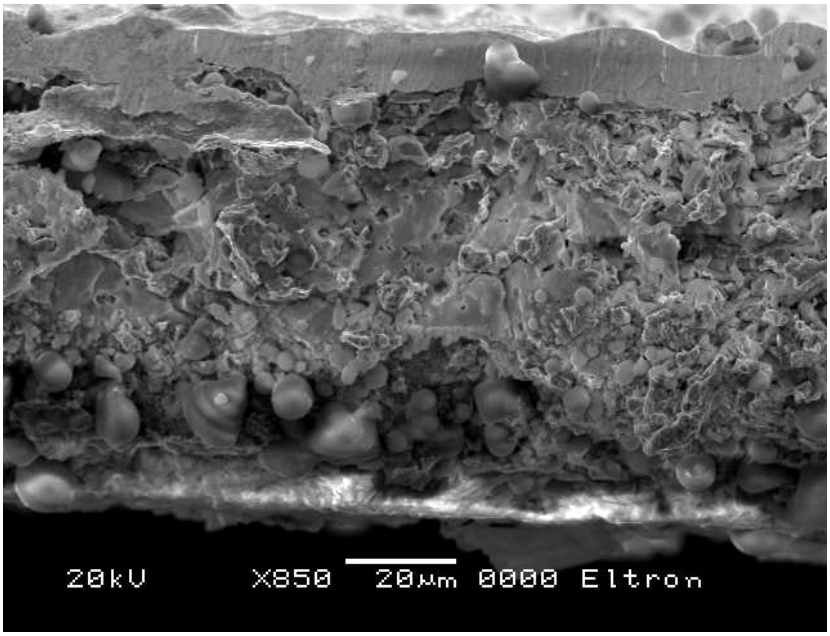


Figure 3. **SEM micrograph of a cross section of a graded cermet membrane.**

Preliminary results for this category of membranes are shown in Figure 4. The bottom two curves were for membrane samples prepared by sanding away both sides of the original structure. These samples did not contain the primarily metal layer, and were representative of the membrane bulk. Permeation for these samples increased from approximately 1 to 3 mL/min/cm^2 at 800 to 900°C as the membrane thickness decreased from 0.16 to 0.08 mm. The top curve in Figure 4 was from a membrane prepared by sanding away only one side of the original structure so that the metal surface layer remained. Despite being a much thicker membrane (0.2 mm), this sample achieved a maximum H_2 permeation of nearly 4 mL/min/cm^2 at 950°C, and 2.6 mL/min/cm^2 at only 650°C. It should be noted that these results were not corrected for standard pressure, which would lower permeation rates by 10 to 20%.

Measurements of H_2 permeation through a range of pure metals and metal alloys also are underway in an attempt to identify other metal candidates for inclusion in these cermets. In the absence of any detectable leak, H_2 permeation rates in excess of 20 mL/min/cm^2 at temperatures as low as 400°C were achieved. The goal now is to incorporate these metal phases into cermets, and several approaches are being tested. Specifically, traditional ceramic processing is being employed and the challenge is in achieving sufficiently small metal particles and overcoming high reactivity with oxygen. An alternative approach is to generate the metal phase from appropriate precursors within the ceramic phase in-situ during sintering. Early attempts at this method look promising and

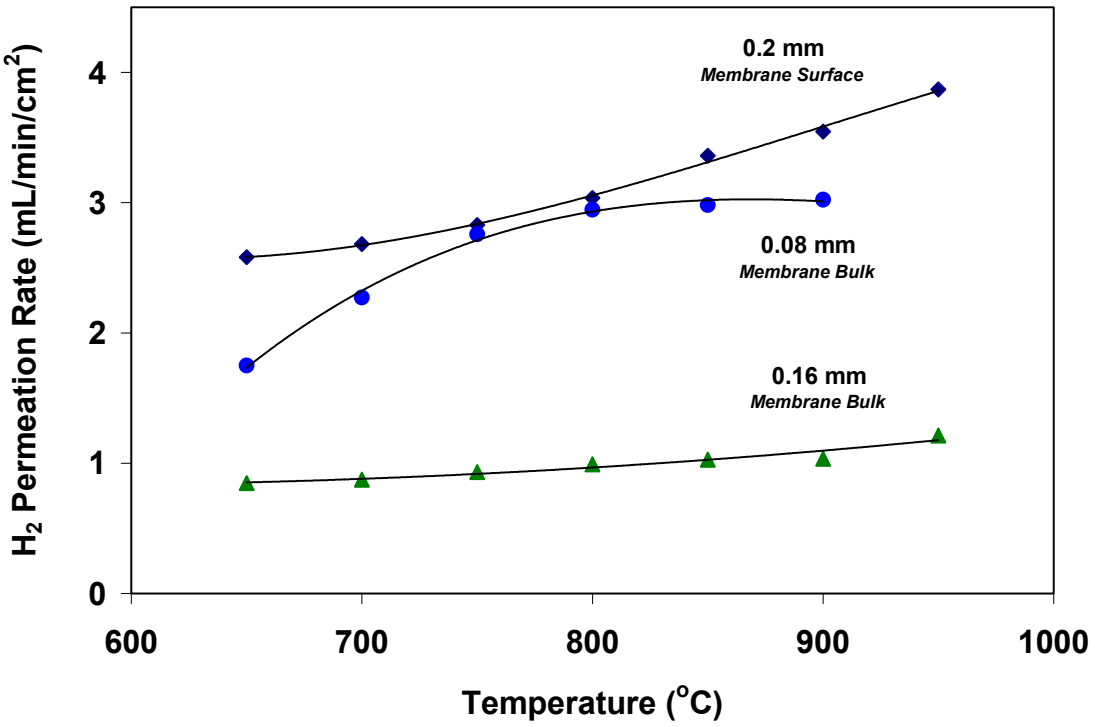


Figure 4. **Plot showing H_2 permeation for graded cermet membranes containing a H_2-permeable metal. The lower two curves show results for membrane sections from the center (bulk) of the structure shown in Figure 3. The top curve is from a membrane section that included the mostly metal surface. The feedstream was humidified H_2 (bal. He) and the sweep gas was Ar. Flow rates were between 80 and 120 mL/min.**

XRD patterns indicate formation of the desired metal phase.

IV. Manufacturing Issues and Relative Economics – CoorsTek, Eltron

Results below summarize work performed by CoorsTek during this reporting period. Additional work performed by CoorsTek is presented under Task 4.

A. Ceramic/Ceramic Composite: $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/CER1

The ceramic/ceramic composite $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/CER1 was prepared by combining 60 wt.% $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ with 40 wt.% CER1. After sintering, XRD analysis indicated excessive cross diffusion of constituents between the phases and the material was very brittle. Lowering the sintering temperature lowered membrane density, but did not eliminate cross diffusion.

An additional analog was prepared from 75 wt.% $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ and 25 wt.% CER1. This materials was less brittle, but cross diffusion was still evident. Again, lowering the sintering conditions decreased density without eliminating cross diffusion.

B. Ceramic/Ceramic Composite: $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/CER2

Samples of this composite were prepared from 65.6 wt.% $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ and 35.4 wt.% CER2. XRD analysis after sinter indicated that the desired CER2 phase remained, and the samples looked good upon visual inspection.

V. Mechanical Testing of Candidate Membrane Materials – ORNL

A range of candidate proton conducting ceramics were tested for mechanical properties and stability against carbonate formation. The samples demonstrated an average strength of 136 MPa and a Weibull modulus of 8.5. Dry machining of the sample surface reduced strength to 64 MPa, but increased the Weibull modulus to 14.3. This result suggested that the machining process could be used to improve device reliability with only a minor compromise in material strength. Sample failure typically was due to processing induced voids or hard agglomerates. Samples with ceramic A-site deficiency and/or a selectively substituted B site demonstrated greater resistance to carbonate formation.

VI. Membrane Surface Catalysis – SCI

Surface catalysis has not demonstrated an effect on H_2 permeation rates for any of the materials tested to date. Within the membrane thickness range evaluated, it is likely that for ceramic materials the permeation process was completely limited by diffusion through the bulk. Cermet membranes demonstrated much higher permeation; however, the metal phase had good catalytic properties and, again, no improvement in permeation was achieved by adding surface catalysts. During this reporting period, much thinner ceramic materials were modified with a range of catalysts and tested for permeation; however, the results were inconclusive.

The difficulty in preparing, handling, and testing thin film membranes makes routine evaluation of catalysts impractical. Accordingly, potential catalyst now are being evaluated by

performing temperature-programmed reduction (TPR) measurements on catalyst-impregnated membrane precursor powders.

Membrane materials were supplied from Eltron in powder form and then catalyzed with the same metals that were impregnated on the surfaces of previous membrane disks. TPR experiments exposed the powder to a stream of 5% H_2 in argon while the temperature was increased at a constant rate. A very sensitive thermal conductivity detector measured the changes brought about by this reduction and thereby provided a measurement of reduction or, in effect, hydrogen adsorption.

Pt, Pd, and Pt/Pd greatly increased the adsorption of H_2 relative to the unmodified powder precursors. Both Ni and Cr increased H_2 adsorption, but not to the same extent as the precious metals. Test results from the actual membranes catalyzed with these metals will validate the use of TPR as a tool for measuring the effectiveness of metals added to increase the rate of H_2 adsorption.

VII. Neutron Diffraction Studies – Eltron, ORNL

Scheduled upgrades on the diffractometer instrumentation needed for the proposed studies has taken much longer than originally forecasted. Current estimates suggest that the system will be operational by early next summer.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron, MTI

Operation of dense ceramic hydrogen separation membranes at high temperatures and pressures requires a chemically resistant seal with similar mechanical and expansion characteristics as the membrane material. Seal materials are being developed and tested using a closed-one-end tube configuration. Seal formation was achieved by ramping the cell assembly up to 1000°C in 10% H_2/90% N_2 and holding for a period of time. The assembly then was cooled to 800°C, for seal evaluation. A seal now has been maintained at a differential pressure of - 250 psi for 2000 hours. During the next reporting period, this seal will be evaluated at lower temperatures to determine the operational range. Other seal materials tested during this period maintained pressures greater than 100 psi.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: Eltron, CoorsTek

Efforts to fabricate thin films were continued using $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% metal cermet as a model material. Metal powder particle size was reduced to increase sinterability, and ceramic particle size was reduced to maintain a constant ratio between the metal and ceramic particle sizes. Agglomeration of metal particles in thin film slurries was minimized by employing a two-part dispersant system and varying the dispersant content. Dense agglomerate-free thin films were prepared between 30 and 150 Fm in thickness, but not with sufficient surface area or adherence to the support structure to enable sealing in the test apparatus.

CoorsTek also initiated work on supported thin film membranes, and outlined several improvements for Eltron's thin film processing. Additionally, CoorsTek was able to produce 50 Fm

thick cermet membranes using a Blanchard grinding process.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Preliminary actions related to prototype device design and identification of test conditions were continued.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

A new flange system was obtained that will enable improved membrane seals at the operation temperatures required for this Task. Additionally, a literature search was conducted to enable comparison of results from this project to other systems. The membrane-promoted dehydrogenation reactor is currently operating and steady-state conditions are being established.

SUMMARY AND CONCLUSIONS

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

- Cermet membranes with an alternative proton conducting phase generated H_2 permeation rates two orders of magnitude lower than previous cermets.
- Decreasing membrane thickness for ceramic/ceramic composites resulted in a three-fold increase in H_2 permeation. The highest H_2 permeation for this category of membranes was ~0.03 mL/min/cm^2 at 800°C for a 0.21-mm thick sample. This permeation rate corresponded to an apparent conductivity of 1.69 x 10^{-4} S/cm. Deleterious cross diffusion of ceramic constituents was apparent between the phases.
- H_2 permeation rates for a cermet containing a H_2-permeable alloy were improved by fabricating a membrane with a graded metal content. A relatively thick membrane (0.2 mm) achieved a H_2 permeation rate of nearly 4 mL/min/cm^2.
- Metal alloys with H_2 permeation in excess of 20 mL/min/cm^2 at intermediate temperatures (~400°C) were identified and will be incorporated in cermet structures.
- Preliminary mechanical testing of candidate proton conducting ceramics suggested that membrane reliability could be improved through dry machining.
- A membrane seal has been maintained at a differential pressure of 250 psi and 800°C for 2000 hours.

OBJECTIVES FOR NEXT REPORTING PERIOD

During the next reporting period, effort at Eltron will focus on incorporation of other H_2 permeable metals and alloys into cermets. This category of membranes will target the intermediate temperature range, which will be more compatible with gas cleanup technologies. Other tasks to be continued during the next quarter include:

- testing of multi-phase ceramics and cermets
- refining manufacturing of selected membrane compositions
- commercial concepting and market and forecast evaluation
- catalyst testing
- membrane stability studies
- testing catalytic membrane reactors for propane dehydrogenation
- outlining requirements for prototype and incorporation into a Vision 21 plant
- mechanical testing of candidate membrane compositions
- development of thin film membranes

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

The following modifications have been made to the project time line:

Task 1. Four subtasks were extended from 24 months to 30 months to accommodate development of intermediate-temperature H_2-separation cermets. Also, neutron diffraction studies were delayed pending completion of maintenance at the ORNL facility.

Task 2. Seven subtasks were extended from 24 months to 30 months to accommodate development of intermediate-temperature H_2-separation cermets.

Task 3. High-pressure seal development is on target, but was extended for the duration of the project along with composition refinement. Catalyst development for this task was moved to months 30 through 36. Compilation of high-pressure evaluation data was extended to month 30.

Task 4. Subtasks associated with thin film development were extended to 33 months. Fabrication of a prototype thin film membrane was move to months 30 through 36.

Task 5. Three subtasks were extended to month 30. Construction of a prototype device was moved to months 30 through 36.

Task 6. Four subtasks were extended to month 33. Design of prototype reactor was moved to months 30 through 33.

References

(1) White, J. H.; Schwartz, M.; Sammells, A. F.; Patent No. 5,821,185, Eltron Research, Inc.: USA, 1998.

(2) White, J. H.; Schwartz, M.; Sammells, A. F.; Patent No. 6,037,514, Eltron Research, Inc.: USA, 2000.

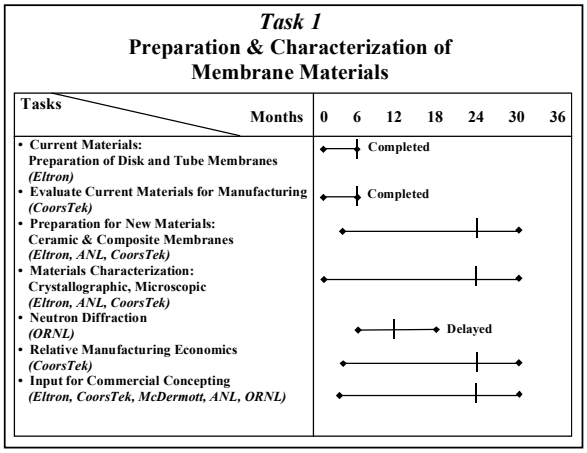
(3) White, J. H.; Schwartz, M.; Sammells, A. F.; Patent No. 6,281,403 B1, Eltron Research, Inc.: USA, 2001.

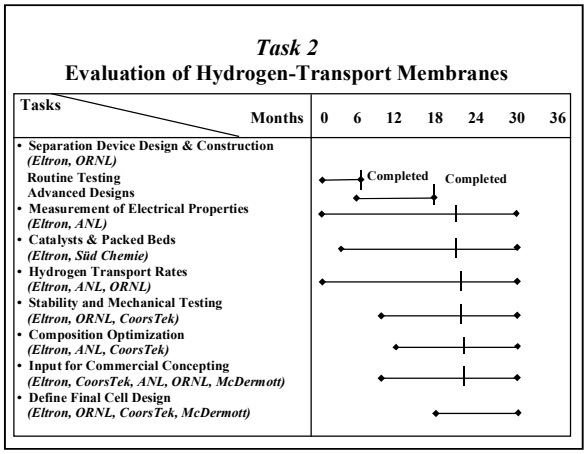
(4) Balachandran, U.; Lee, T. H.; Zhang, G.; Dorris, S. E.; Rothenberger, K. S.; Howard, B. H.; Morreale, B.; Cugini, A. V.; Siriwardane, R. V.; Jr., J. A. P.; Fisher, E. P. In *26th International Technical Conference on Coal Utilization and Fuel Systems*: Clearwater, FL, 2001, pp 751-761.

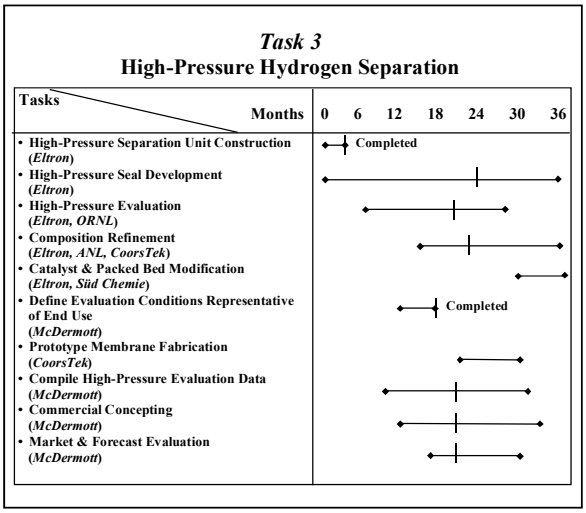
(5) Wachsman, E. D.; Naixiong, J.; Two-Phase Hydrogen Permeation Membrane. Patent No. 6,235,417, USA, 2001.

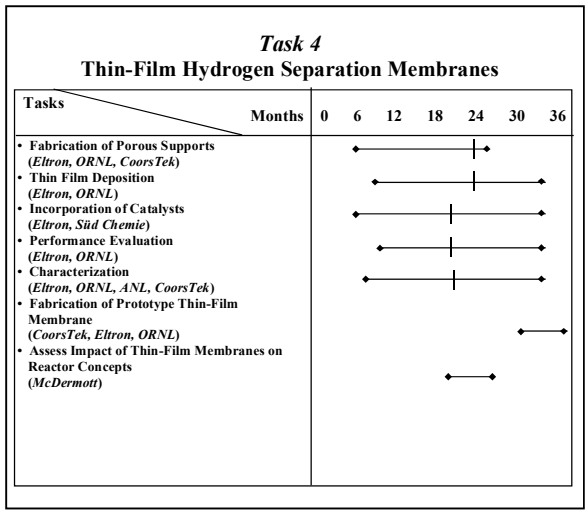
TIME LINES

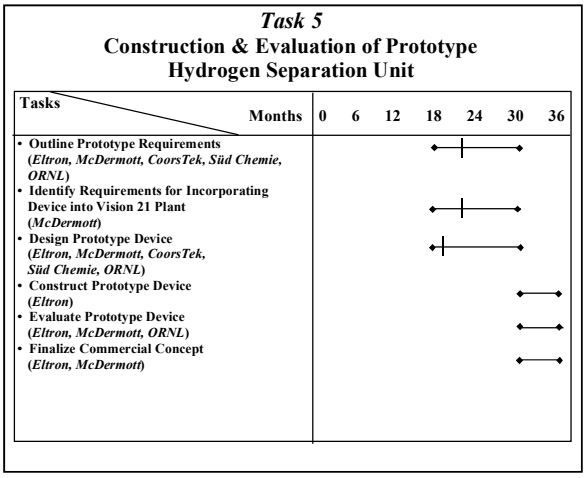
The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

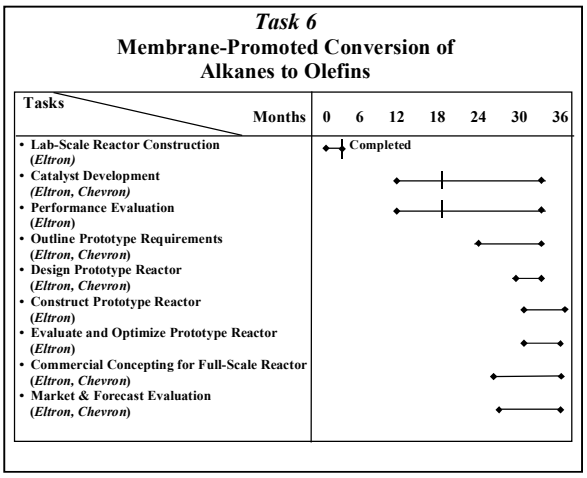












1022ser6.dsf