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

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TABLE OF CONTENTS

DISCLAIMER

ABSTRACT

During this quarter, work was focused on testing layered composite membranes under varying feed stream flow rates at high pressure. By optimizing conditions, H_2 permeation rates in excess of 400 $mL\cdot min^{-1}\cdot cm^{-2}$ at 440°C were measured. Membrane stability was characterized by repeated thermal and pressure cycling. The effect of cermet grain size on permeation was determined. Finally, progress is summarized on thin film cermet fabrication, catalyst development, and H_2 separation unit scale up.

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 layered composite membranes with H_2 permeation rates in excess of 400 $mL\cdot min^{-1}\cdot cm^{-2}$ at 440°C. In addition, progress with cermets, thin film fabrication, catalyst development, and H_2 separation unit scale up is summarized.

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.

Hydrogen permeation rates in excess of 400 $mL\cdot min^{-1}\cdot cm^{-2}$ were achieved at 440°C and 450 psi differential pressure. Mass transport limitations were partially overcome by adjusting feed flow rates and the concentration of H_2 in the feed stream. These results are presented in this report, in addition to progress with cermets, thin film fabrication, catalyst development, and H_2 separation unit scale up.

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, SCI, ANL

I. Composite Layered Membranes with High Hydrogen Permeability – Eltron

During this quarter, one of Eltron's high pressure reactors was modified to increase the diameter of the feed and sweep lines. The objective was to allow increased flow rates of the feed and sweep gases without creating a back pressure within the gas lines. Figure 1 shows the hydrogen permeation for a composite layered membrane tested under this modified setup.

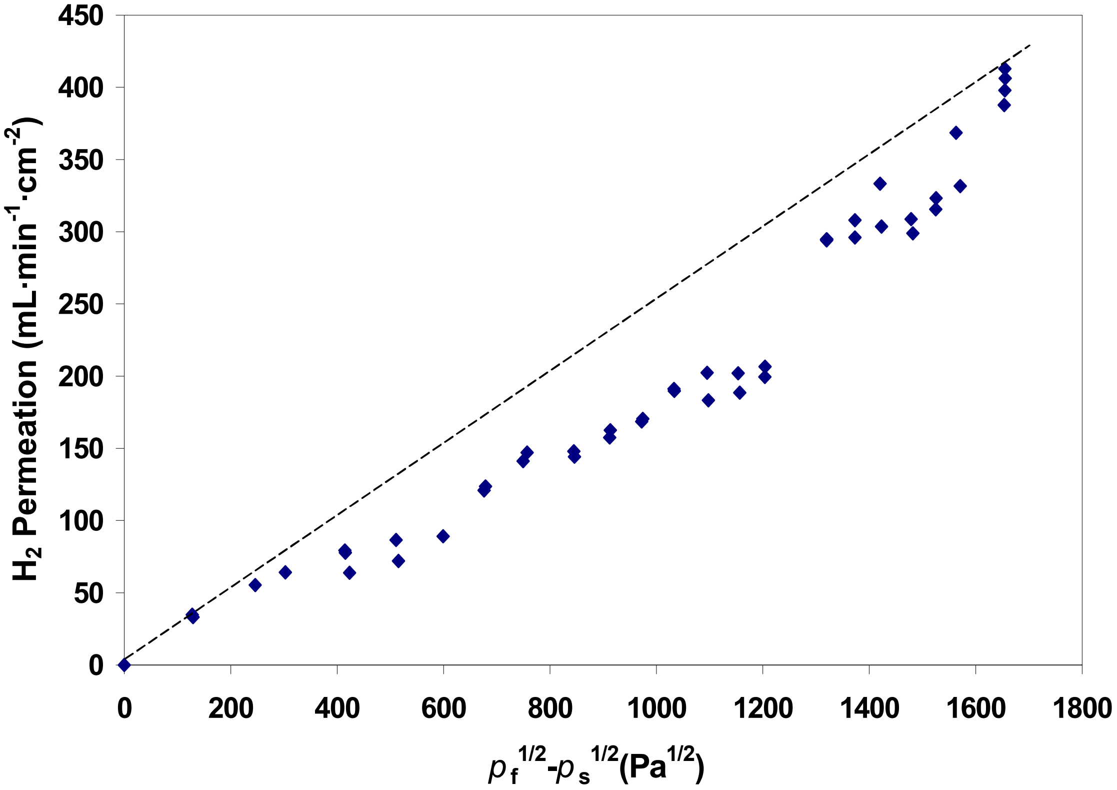


Figure 1. H_2 permeation at 440°C versus the partial pressure difference across the membrane. The feed flow rate was less than 2.5 L/min. The sweep flow rate was greater than 6.5 L/min, and the total pressure differential was 450 psi. The straight dashed line represents the flux predicted based on Sieverts' Law.

A high permeation rate of 413 ml/min/cm^2 was achieved in Figure 1 under a feed flow rate between 1.25 and 2.5 L/min. The concentration of H_2 in the feed stream was varied between 40 and 100%. The permeability of this membrane was 2.2 x 10^{-7} mol/m/s/Pa$^{1/2}$ at a hydrogen differential pressure of 450 psi. The concentration of H_2 in the feed stream was used to minimize mass transfer limitations, however, Figure 1 shows that permeation deviated from Sieverts' Law significantly over the course of the experiment.

As mentioned in previous reports, flow rate can be used to minimize mass transfer limitations. Figure 2 shows H_2 permeation data collected for two equivalent membranes. Both membranes were tested at 440°C using a feed stream containing 40% H_2. For the first membrane (open triangles) the H_2 feed rate was held constant at 1 L/min. Under this flow rate, permeation began to deviate from Sieverts' Law at approximately 330 Pa$^{1/2}$ differential hydrogen pressure. For the second membrane (filled squares) the H_2 feed rate was increased to 2 L/min. Under this increased flow rate permeation did not begin to deviate from Sieverts' Law until 460 Pa$^{1/2}$ differential hydrogen pressure. Increases in the hydrogen flow rate allow Sieverts' Law to be maintained up to higher differential hydrogen pressures.

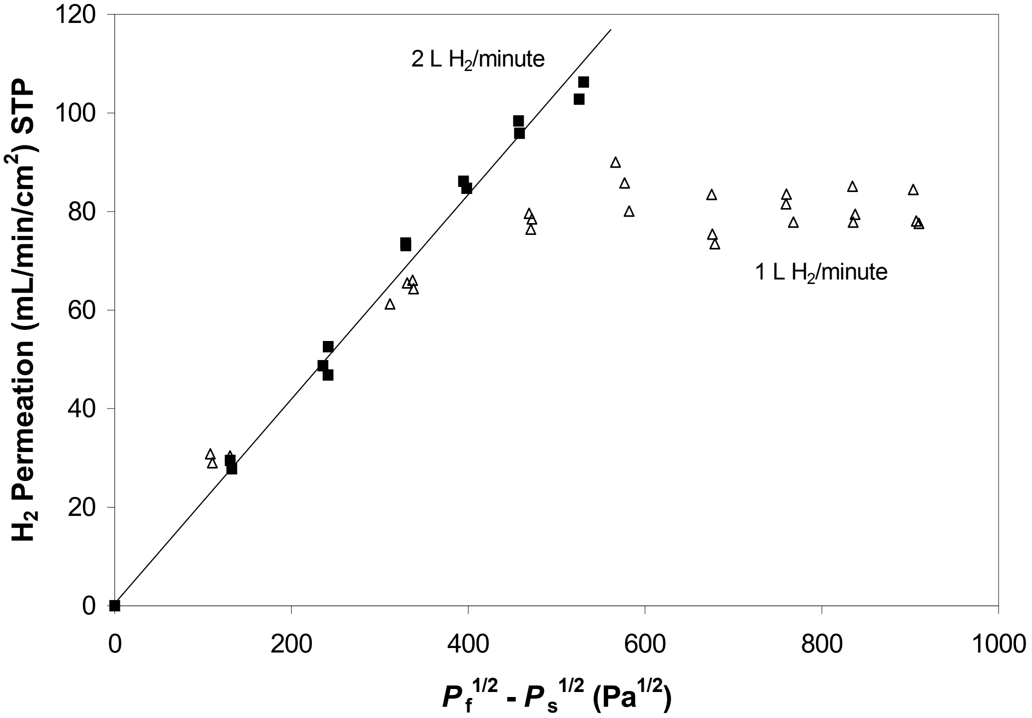


Figure 2. **H_2 permeation at 440°C versus the H_2 partial pressure difference across the membrane. Data was collected for two equivalent membranes with a feed gas stream of 40/60 H2/He and the sweep gas was Ar. For the membrane represented by open triangles the H_2 flow rate was 1 L/min. For the membrane represented by filled squares the H_2 flow rate was 2 L/min. The straight dashed line represents the flux predicted based on Sieverts' Law.**

Several further modifications were made to the reactor with the goal of improving membrane performance and stability. To improve the flow dynamics of hydrogen to the membrane surface the height of the compression flange used to secure the composite membrane was reduced to decrease the ‘dead space’ above the membrane. Also, the distance between the feed line and the membrane surface was minimized. These improvements allowed Sieverts’ law to be maintained at higher differential hydrogen pressures. Figure 3 shows the hydrogen permeation (filled diamonds) for a composite layered membrane under a feed stream containing 40% H_2 / 60% He. The dashed straight line represents flux predicted by Sieverts’ Law. Figure 3 shows that Sieverts’ Law is maintained up to 450 psi differential hydrogen pressure with only 40% hydrogen in the feed stream.

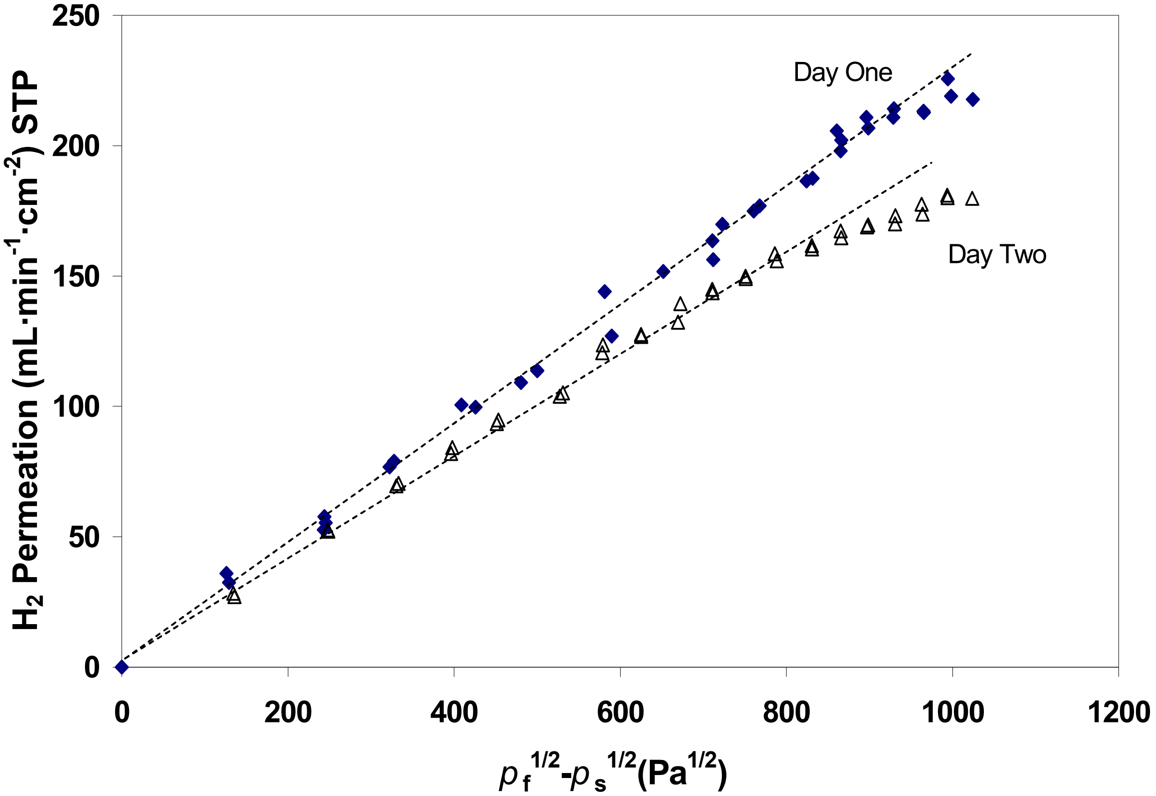


Figure 3. **H_2 permeation at 440/C versus the H_2 partial pressure difference across the membrane. The feed gas stream was 40/60 H_2/He and the sweep gas was Ar. The feed and sweep flow rates were between 2.5 and 6.25 L/min. The straight dashed lines represent the flux predicted based on Sieverts’ law.**

The membrane shown in Figure 3 was tested for two consecutive days to illustrate the stability of the membrane. On the first day a permeation greater than 200 mLAmin^{-1}Acm^{-2} was achieved at a differential pressure of 450 psi. After data were collected on the first day the reactor was returned to room temperature and ambient pressure conditions. The same membrane was used to collect hydrogen permeation data under equivalent conditions on the second day. Figure 3 shows that the permeation data began to deviate from Sieverts’ Law on the second day, however, a permeation of 180 mLAmin^{-1}Acm^{-2} was achieved under a differential pressure of 450 psi. The permeability of the membrane on the second day was slightly less than the permeability on the first day. This decrease in performance was likely due to surface contamination.

It is expected that both high permeation rates and long-term stability can be achieved using alloys within composite layered membranes. Eltron is in the process of constructing an arc melting furnace to produce a range of alloy compositions for permeation and stability testing under conditions representative of Vision 21 power plants.

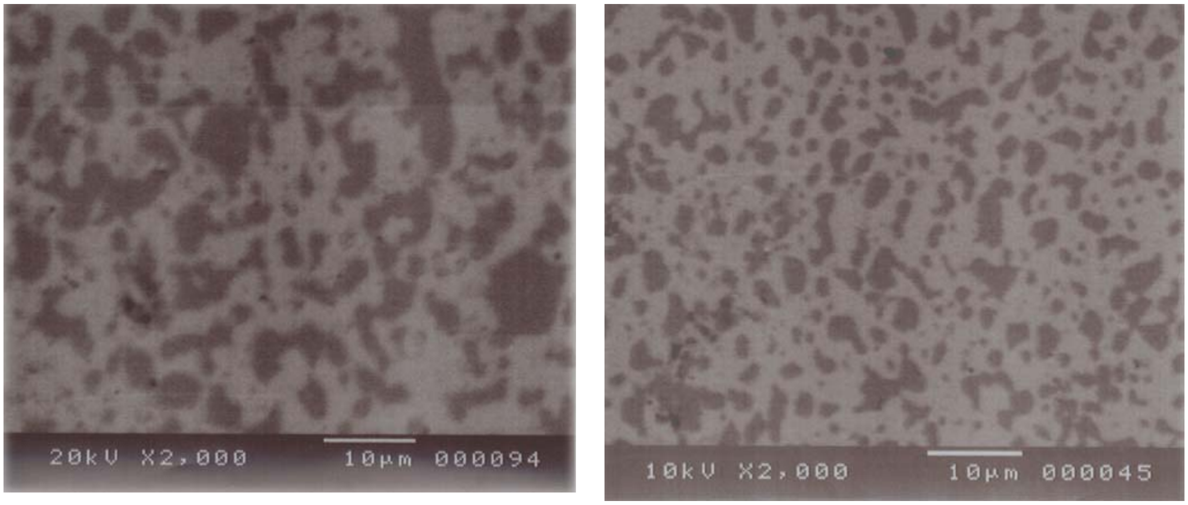
II. **Multi-Phase Ceramics and Cermets** – CoorsTek, ANL

Ceramic/ceramic composites consist of a proton conducting perovskite phase ($AB_{0.8}B^{c}_{0.2}O_{3-*}$) and an electron conducting transition metal oxide. Previously it was shown that these materials perform equivalently to analogous cermets, yet have higher corrosion resistance in water. It also was shown that a second ceramic phase could be added to cermets to improve corrosion resistance without dramatically affecting hydrogen permeation. CoorsTek has assembled the equipment necessary to measure corrosion in water vapor and other atmospheric conditions at temperatures up to 800/C. Results from these tests will enable assessment of membranes under more relevant conditions.

Previous work at ANL showed that the microstructure of the metal phase affects the hydrogen permeation through ANL-1a membranes. ANL-1a membranes with large-grained metal phase gave higher hydrogen flux than those with small-grained metal phase. In this quarter, ANL investigated the effect of the oxide phase grain size on the hydrogen permeation of ANL-1a membranes.

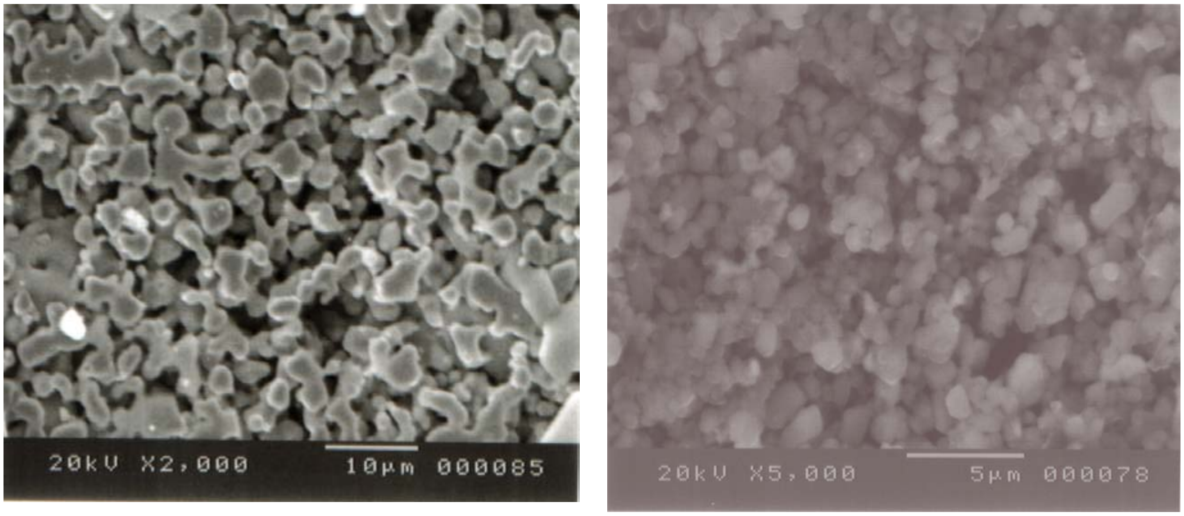
To vary the grain size of the oxide phase, ANL-1a membranes were prepared using $BaCe_{0.8}Y_{0.2}O_{3-*}$ (BCY) powder from Praxair that was treated in two different ways. As-received BCY, so-called “fine” powder, was used to prepare one type of membrane; the other type of membrane was made with “coarse” BCY powder, which was prepared by annealing the same as-received BCY powder for 10 h at 1200/C in air. Membranes were prepared by mixing the two types of BCY powder with Ni powder (40 vol.%), which was then uniaxially pressed into disks and sintered at 1400/C in 200 ppm H_2. The same batch of fine (avg. particle size . 0.08-0.18 :m) Ni powder was used to prepare both types of ANL-1a membrane.

Figure 4 shows scanning electron micrographs of the two types of ANL-1a membranes after sintering. The most notable difference in the two microstructures is that the average size of the metal phase (darker in color) is larger in the membrane prepared from BCY powder that had been pre-annealed. The difference in the BCY grain size is not obvious in these micrographs. In order to highlight differences in the BCY microstructure, the metal phase was removed by etching the membranes with nitric acid. SEM micrographs of the membranes after they were etched clearly show that the average BCY grain size is larger in the membrane made from pre-annealed powder (Fig. 5a) than in the membrane made with as-received powder (Fig. 5b). Because of its finer grain size, the membrane made with as-received BCY has a significantly larger grain boundary area. The difference in grain size was not as evident in Fig. 4, probably because individual grains were blended together during polishing of the membrane.



(a) (b)

Figure 4. **Back-scattered electron micrographs of ANL-1a membranes sintered in 200 ppm H_2 at 1400/C. Membrane made with: (a) pre-annealed BCY, (b) as-received BCY.**



(a) (b)

Figure 5. **SEM micrographs of ANL-1a membranes after being etched with HNO_3. Membrane made with: (a) pre-annealed BCY, (b) as-received BCY.**

Figure 6 shows the temperature dependence of the hydrogen flux for two ANL-1a membranes, one made with as-received BCY powder and one made with pre-annealed powder. The thickness for both membranes was . 0.35 mm. For both membranes, the flux reached a maximum at . 650/C, similar to previous results. It is thought that the hydrogen flux reaches a maximum as temperature increases due to competition between two effects: a decrease in the proton concentration and an increase in proton mobility. Over the entire temperature range, the hydrogen flux was lower for the membrane made with as-received powder. Considering that the BCY grain size is smaller in this membrane (Fig. 5b), its flux might be expected to be higher due to a larger triple-phase boundary area. The fact that the membrane made with as-received powder has a lower flux suggests that grain boundary resistance to proton diffusion may be a significant factor.

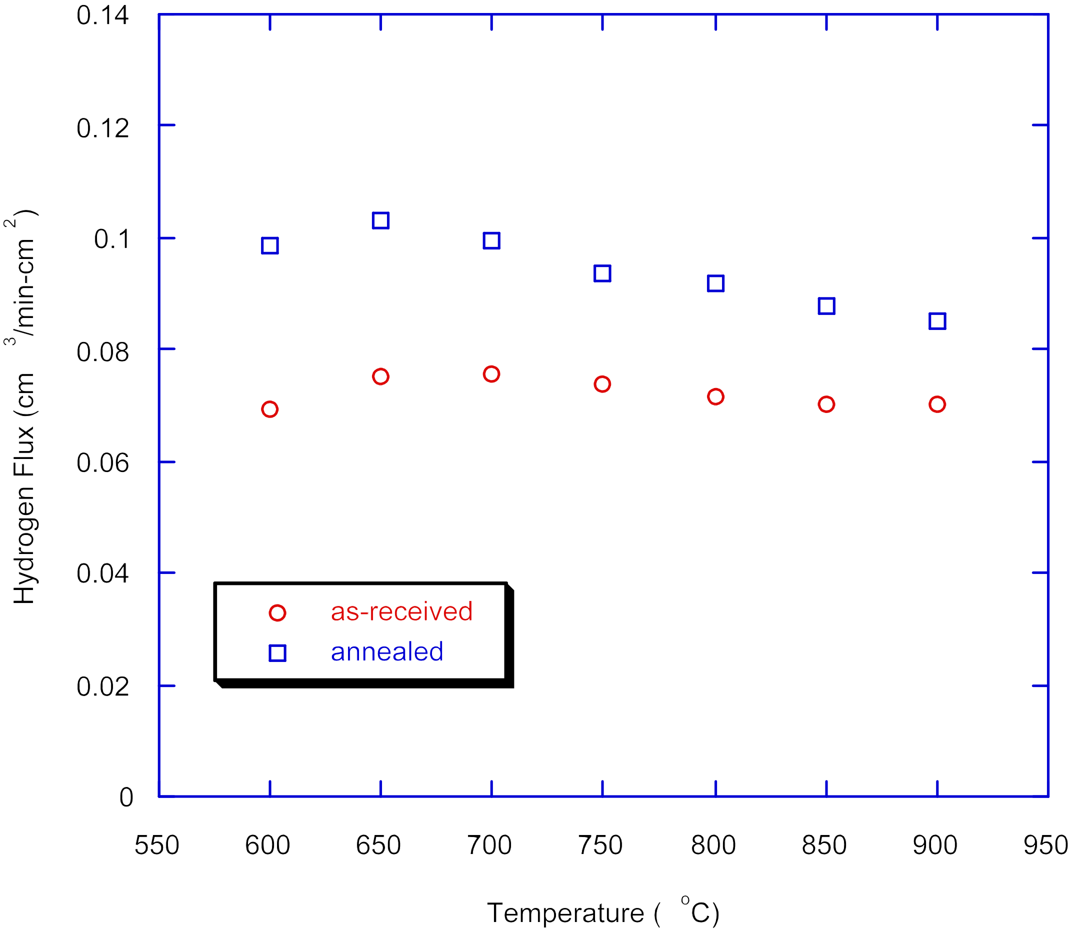


Figure 6. **Temperature dependence of the hydrogen flux of two ANL-1a membranes, one made with as-received powder, another made with annealed powder.**

These results are consistent with ANL's previous study into the effect of metal grain size on the hydrogen flux through ANL-1a membranes, which showed that the hydrogen flux was higher for membranes with large-grained metal phase. In the present study, the membrane made with pre-annealed powder had the higher hydrogen flux, and Fig. 4 shows that it had larger-grained metal phase. Although the effects of oxide grain size and metal grain size were not completely separated in the present study, the results show that higher hydrogen flux was obtained with larger-grained materials.

III. **Membrane Coatings and Catalysts** – Eltron, SCI

Eltron and SCI are developing membrane coatings that will dissociate H_2 and resist poisoning from common feedstream constituents of gasified coal. SCI used the reactor described in the previous report to test several catalyst compositions. Catalyst samples were heated to various temperatures on an alumina substrate and the gas phase composition was monitored using a Residual Gas Analyzer (RGA) to study the performance of the catalyst samples. 20 sccm of hydrogen and 50 sccm of deuterium gases were using for the present experiments. The testing was performed at four different temperatures, room temperature (25ºC), 140ºC, 240ºC and 375ºC. The pressure in the reactor under these conditions was approximately 410 mTorr. All the samples were tested under identical conditions for the purpose of comparing their performance. Experiments were repeated three times for each temperature and for each catalyst to verify the consistency of the results. Though hydrogen inflow is only 20 sccm compared to 50 sccm deuterium, the output showed more hydrogen for all catalysts tested, indicating a preferential adsorption of deuterium. Adsorption of H_2 on copper catalyst decreased above 140ºC. For the other catalysts tested hydrogen adsorption increased at higher temperatures.

During this quarter baseline catalyst studies under ambient pressure conditions were conducted at Eltron. Membranes were tested at 420ºC with an 80/20 mix of hydrogen and helium in the feed stream. Argon was used as the sweep gas. A statistical number of composite membranes were tested with the baseline palladium catalyst. Results showed average permeation of 22(2) $mL/min/cm^2$.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

During this quarter, all testing was performed using flat samples and a compression flange assembly with annealed copper seal rings. This assembly only is good for somewhat malleable planar membranes; however, seals routinely are achieved at differential pressures between 250 and 450 psi (zero leak rate). Provided the membrane mechanical characteristics are adequate, this type of seal is very scalable and now is the standard method for membrane evaluation. Key results for high pressure hydrogen separation are discussed under Task 1, and other issues associated with high-pressure H_2 separation are discussed under Task 5.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: CoorsTek, Eltron

Previous work concluded that thin film membranes deposited on isopressed tubes offered several advantages over thin films cast onto planar porous supports. During this quarter thin film membranes were produced on porous isopressed tubes. Closed One End (COE) isopressed green tubes were manufactured at Eltron with reduced porosity to increase tube strength. At CoorsTek, bisque fired tubes were used to optimize the slurry used to deposit thin films on the inside of the COE tube. Variables included viscosity, solids loading, and solvent/vehicle formulation. Figure 7 shows a cross section of a 42 μm thin film coated and fired on a bisque fired tube substrate.

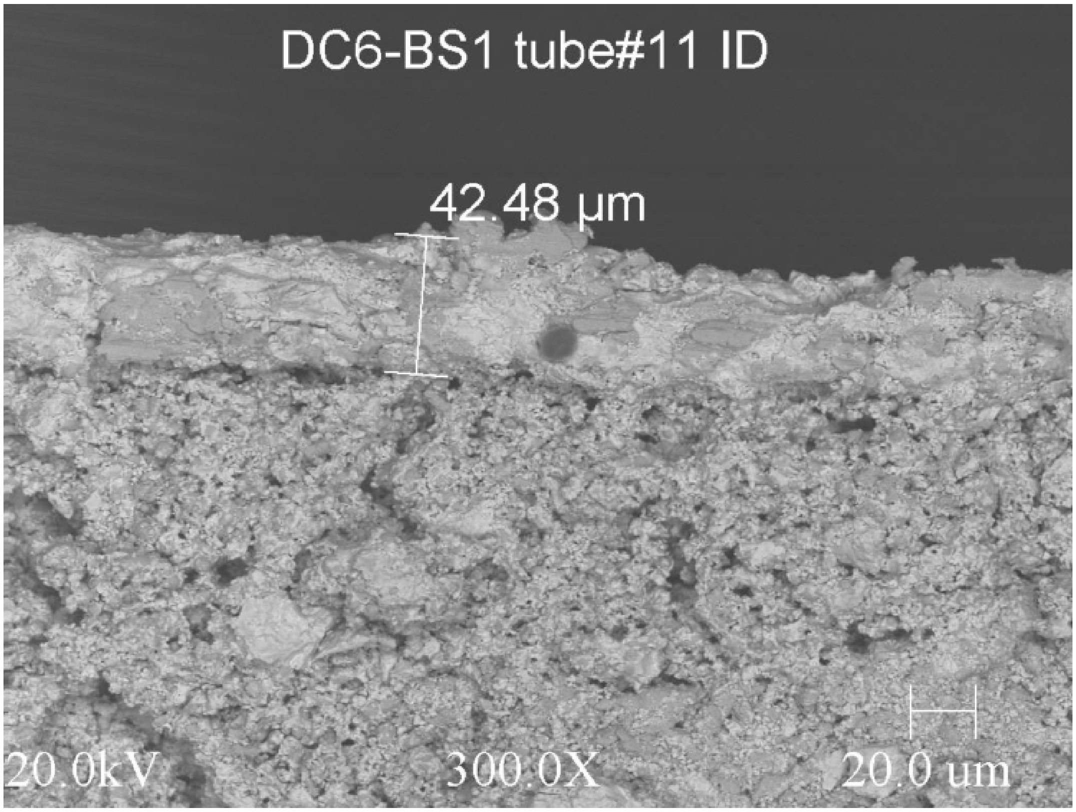


Figure 7. 300x SEM image of a dense perovskite membrane coated and fired on a bisque fired tube substrate.

During the next reporting period CoorsTek will further develop thin film deposition procedures, and will produce thin film tubes sealed onto 1/4" alumina tubes. Eltron will test the ambient pressure permeation of these thin film cermet membranes. Based on the high permeation results for intermediate temperature composite membranes, evaluation of thin film cermets will be switched to preparation and evaluation of cermets based on high permeation metals.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: Eltron, NORAM

As discussed above, engineering improvements were performed on the high-pressure reactors to maximize contact efficiency of the feed gas with the membrane surface, and to decrease sweep line back pressure. These modifications improved permeation rates, and will be incorporated into the demonstration-scale prototype design.

During this quarter, NORAM supplied Eltron with a report entitled "Criteria for Incorporating Eltron's Hydrogen Separation Membranes in Vision 21 IGCC Systems and Futuregen Plants." This report details the issues involved with insertion of ceramic - ceramic, cermet, and intermediate temperature composites into an IGCC plant. The main points of the report are summarized as follows:

- The type and location of an Eltron membrane depends on the type of IGCC plant, and the gas cleaning method employed.

- Ceramic - ceramic membranes must be in the form of thin film supported membranes to achieve the flux necessary for large scale applications. For insertion into a Vision 21 plant, ceramic - ceramic membranes must operate in the middle of the cooling train. There is very little gas treatment in this plant location. Therefore ceramic - ceramic membranes must be tolerant to fouling. In addition, at these temperatures there is no opportunity for water gas shift (WGS).

- Hot gas (>538°C) cleaning technology is relevant only to Eltron's ceramic - ceramic membranes. If ceramic membranes are sulfur tolerable, hot gas cleaning would prevent gas cooling / reheating cycles. However, Hg capture is difficult with hot gas cleaning and alkali metals foul turbine blades at these temperatures.

- Sulfur levels would be ~ 20 ppm using warm gas (260-427°C) cleaning technology. Therefore Eltron membranes must withstand this sulfur level to be included in an IGCC plant with warm gas cleaning.

- Cermet membrane use depends on tolerance to sulfur. If membranes can tolerate 20-50 ppm H_2S, warm gas cleaning can be used. If not, cold gas cleaning must be used. The lower end of the operating temperature for cermets (550°C) is consistent with WGS temperature ranges. The possibility exists to combine H_2 and WGS reactors.

- Intermediate temperature composite membranes (300-750°C) operate in a temperature range compatible with WGS reactors. If cold gas cleaning is required, gas flow reheat will be required, however, the reheat temperature is much lower than ceramic - ceramic membranes.

- For thin film intermediate composite membranes used in the form of tubes rather than disks, tubes should be ½ inch or greater in diameter. A ½ inch tube would require a 250 micron wall to withstand an internal pressure of 500 psi. Wall thickness would have to be greater to withstand 500 psi of external pressure.

- If 250 micron materials can be made, the size of the H_2 separation unit will be smaller than the competing Oak Ridge National Laboratory nano-porous technology (2002 Parsons report) and therefore will be extremely competitive. Even 500 micron membranes would be competitive.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

No activities were performed on this task during this quarter.

Task 7 Catalyst Membrane Compositions for Scale Up

Testing during the past three quarters 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. Effort now is being focused on identification of the most promising compositions within this category of membranes. A limited number of thin film ceramics also are being pursued since performance tests indicated that sufficiently thin films might have acceptably high permeation rates, and thin film cermets have good potential as protective/catalytic layers in the layered composite membranes.

Task 8 Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes

No actions were performed on this task during this quarter.

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

No actions were performed on this task during this quarter.

SUMMARY AND CONCLUSIONS

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

1. Mass transfer limitations were partially overcome through optimizing the design of the high pressure H_2 separation set-up. Under these conditions, H_2 permeation in excess of 400 ml/min/cm^2 was achieved.

2. Higher hydrogen flux results obtained in ANL-1 membranes with different ceramic grain sizes indicate that grain boundary resistance my significantly affect permeation.

3. Hydrogen adsorption onto potential dissociation catalysts was studied as a function of temperature. For all catalyst tested, increased hydrogen adsorption was observed at higher temperatures. Baseline studies evaluating catalyst performance as a function of permeation were completed.

4. The slurry used to prepare thin walled cermets on tubular porous supports was optimized.

5. NORAM produced a detailed report describing the key criteria for incorporation of Eltron hydrogen separation membranes into Vison 21 IGCC plants.

OBJECTIVES FOR NEXT REPORTING PERIOD

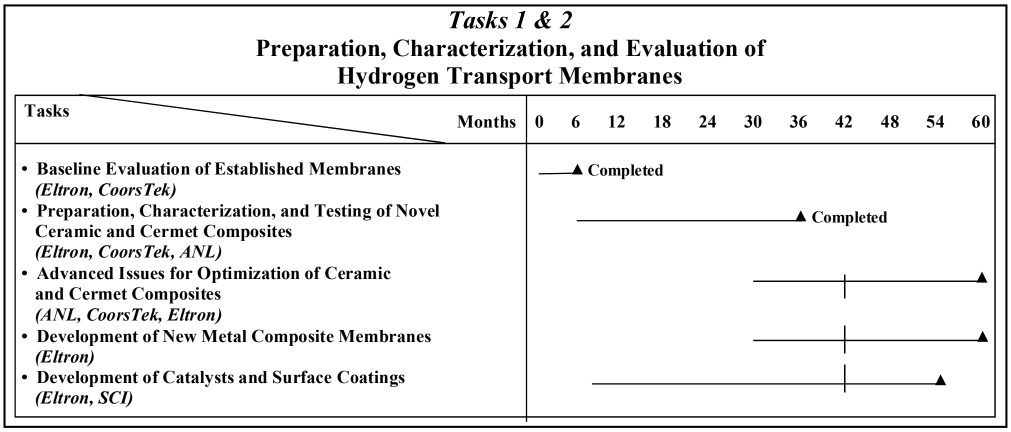
During the next reporting period new membrane compositions will be tested under high pressure and attempts will be made to further improve the stability of composite layered membranes under appropriate experimental conditions. Catalyst testing will continue at SCI and Eltron on a selected membrane compositions. ANL will conduct a detailed investigation of the grain boundary conductivity of the oxide phase of the ANL-1 cermet using impedance analysis, and CoorsTek will focus on production of thin cermet films onto the thin-walled tube supports for permeation testing. NORAM will review the current literature on warm gas clean up and begin putting together process flow diagrams for several different IGCC plant configurations.

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

None.

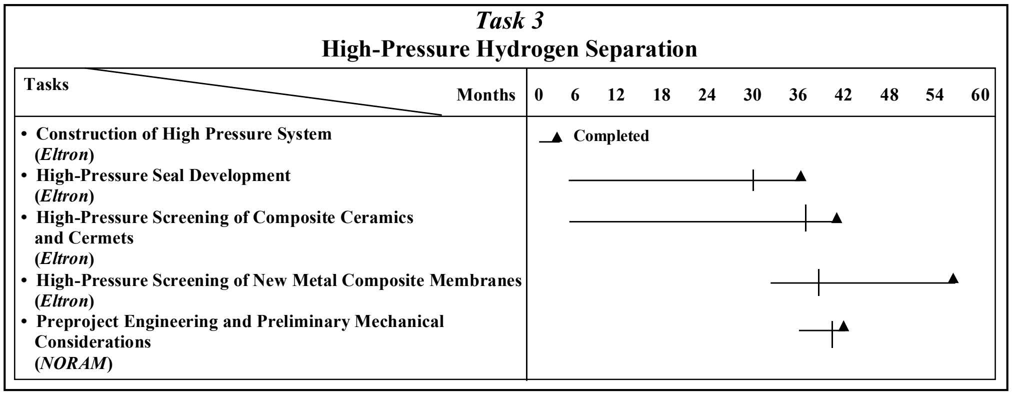
TIME LINES

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



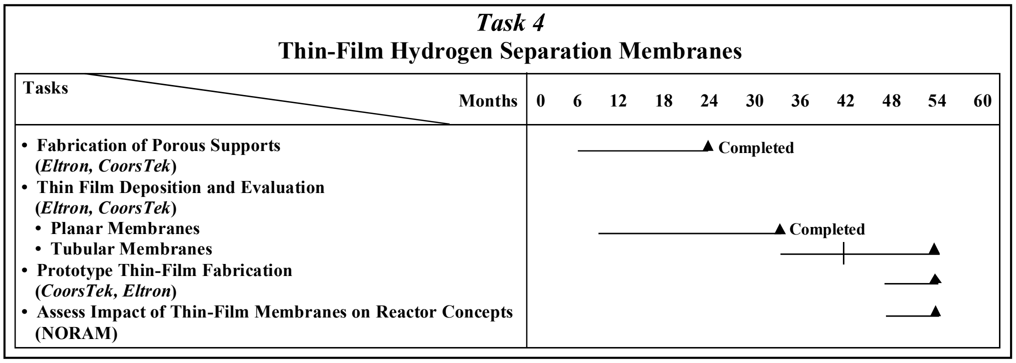
Tasks 1 & 2

Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes



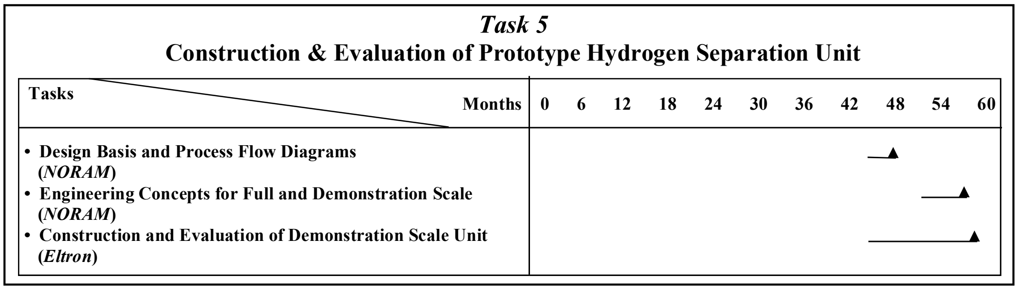
Task 3

High-Pressure Hydrogen Separation



Task 4

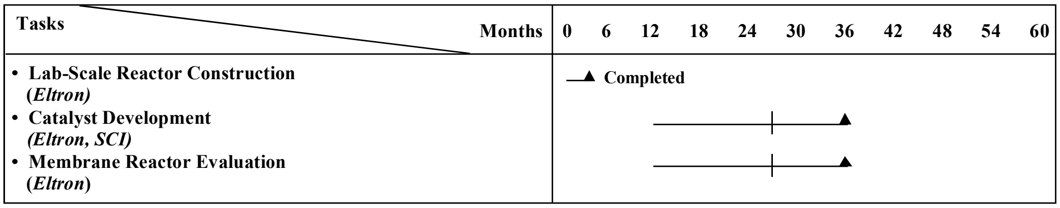
Thin-Film Hydrogen Separation Membranes



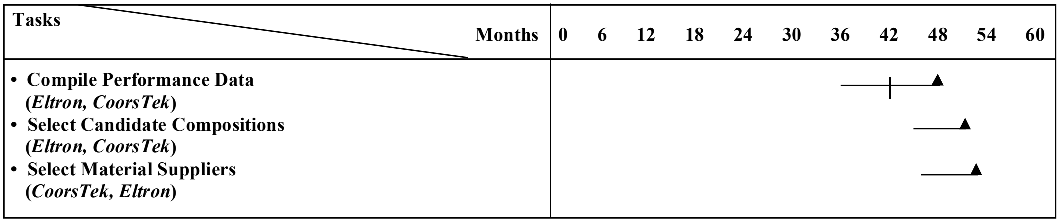
Task 5

Construction & Evaluation of Prototype Hydrogen Separation Unit

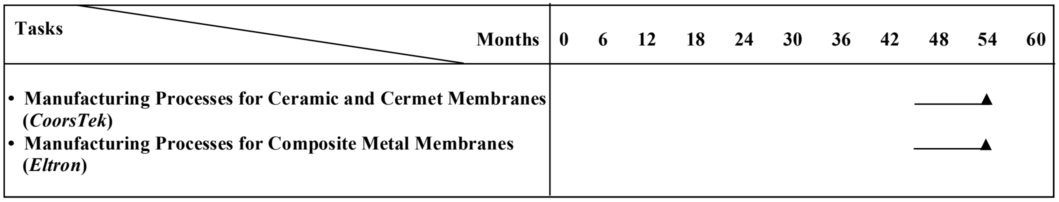
Task 6
Membrane-Promoted Conversion of Alkanes to Olefins



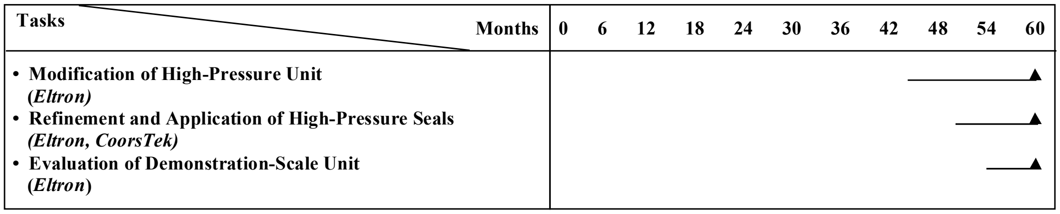
Task 7
Catalyst Membrane Compositions for Scale Up



Task 8
Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes



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



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