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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 between 50 and 350 $mL{\cdot}min^{-1}{\cdot}cm^{2}$ 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 50 mLAmin^{-1}Acm^{2} at ~440/C were routinely achieved under less than optimal experimental conditions using a range of membrane compositions. Factors that limit the maximum permeation attainable were determined to be mass transport resistance of H_2 to and from the membrane surface, as well as surface contamination. Mass transport resistance was partially overcome by increasing the feed and sweep gas flow rates to greater than five liters per minute. Under these experimental conditions, H_2 permeation rates in excess of 350 mLAmin^{-1}Acm^{2} at ~440/C were attained. 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

Figure 1 shows hydrogen permeation over nine months of continuous operation for a layered metal/ceramic composite membrane at 320/C. The total thickness of the membrane structure was approximately 2 mm, with only 0.13 mm from the metal phase. Over the first 500 hours of operation, permeation remained steady at approximately 11.5 mLAmin^{-1}Acm^{-2} with permeability greater than 6 x 10^{-8} molAmAm^{-2}As^{-1}APa$^{-0.5}$. There was a slow loss of performance between 500 and 1700 hours, which stabilized at roughly 8 mLAmin^{-1}Acm^{-2} until 4000 hours. Over the remaining 2000 hours, permeation decreased steadily to approximately 6 mLAmin^{-1}Acm^{-2}. An attempt was made to restore performance by applying an oxidation cycle using flowing air at 320/C for 24 hours. As evident in the figure, permeation increased to nearly 9 mLAmin^{-1}Acm^{-2} before stabilizing at approximately 8 mLAmin^{-1}Acm^{-2}. This result suggested that at least some of the deactivation was from surface contamination, and that the membrane was sufficiently rugged to tolerate strongly oxidizing conditions.

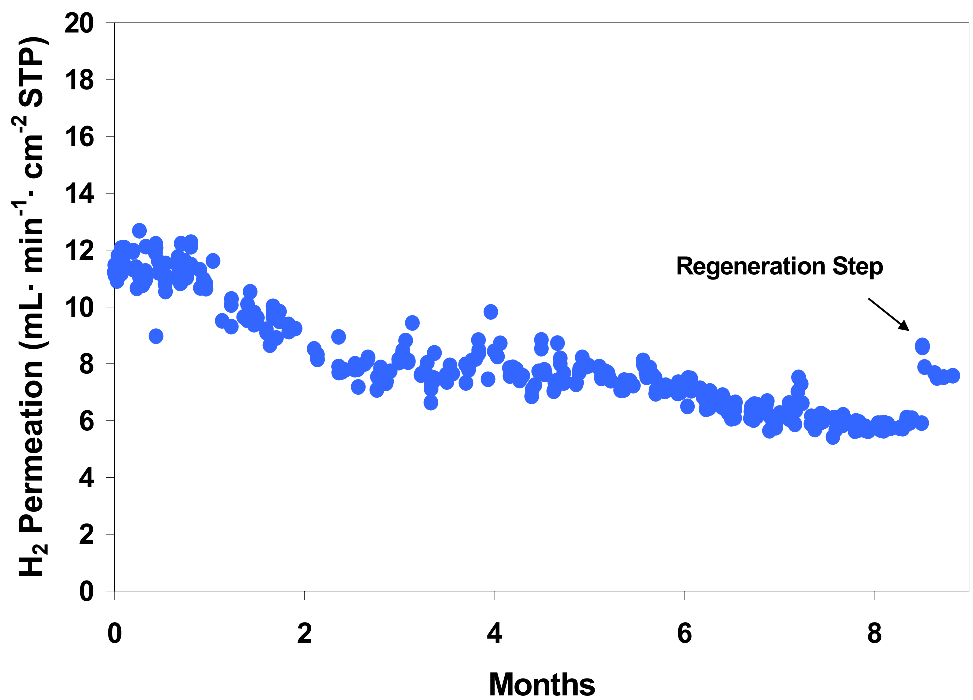


Figure 1. Hydrogen permeation over time at 320/C for a layered metal/ceramic composite membrane. The feed gas was 80 mL/min 80/20 H_2/He, and the sweep gas was 250 mL/min Ar.

During this quarter, a total of 39 composite membranes were tested at differential pressures as high as 450 psi. Ten of these membranes enabled a H_2 flux in excess of 50 mL·min^{-1}·cm^{-2} near 440/C using less than optimum experimental conditions. Figure 2 shows results for three membranes that varied only in the relative concentrations of the two major membrane constituents (*i.e.*, 90%/10%, 85%/15%, and 80%, 20%). As the concentration of the minor constituent increased, there was an increase in H_2 permeability from 2.5 to 3.0 x 10^{-7} mol·m^{-1}·s^{-1}·Pa^{½}. However, the membranes also became more brittle and the maximum total differential pressured achieved decreased from 450 to 126 psi. As a result, the highest flux for this series (78 mL·min^{-1}·cm^{-2}) was obtained for the 90/10 analog, despite the lower permeability.

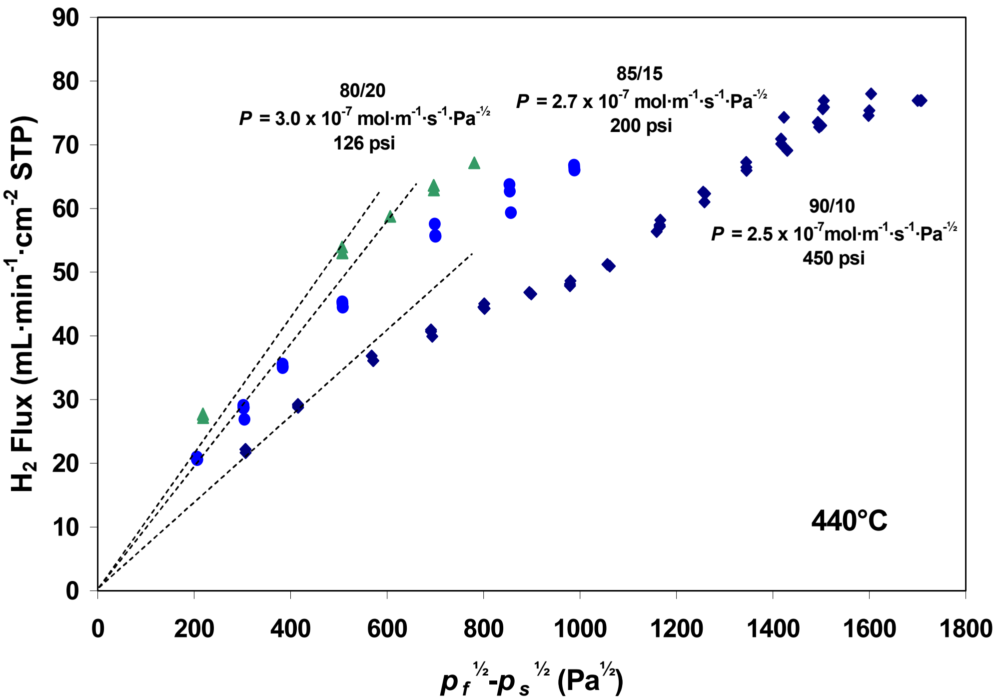


Figure 2. **H_2 permeation at 440/C verus the H_2 partial pressure difference across the membrane. The feed gas was ~80/20 H_2/He and the sweep gas was Ar. The feed and sweep flow rates were between 1 and 1.5 L/min. The straight dashed lines represent the flux predicted based on Sieverts' Law.**

The dashed lines in Figure 2 represent the predicted flux based on Sieverts' Law. For each sample, the permeation curve deviated from Sieverts' law at a H_2 partial pressure differential of ~ 500 Pa^{½}. This deviation likely was from a combination of surface contamination and mass transfer limitation of H_2 to and from the membrane surface on the feed and sweep sides, respectively. It was determined that agreement with Sieverts' Law and maximum permeation could be improved by substantially increasing gas flow rates. An example is shown in Figure 3 for a selected membrane at 435/C and a total differential pressure of 450 psi. In this example, the feed and sweep gas flow rates were in excess of 5 L/min, which was roughly four times higher than those used for the data in Figure 2. As a result, relatively good agreement with Sieverts' Law was maintained, and a

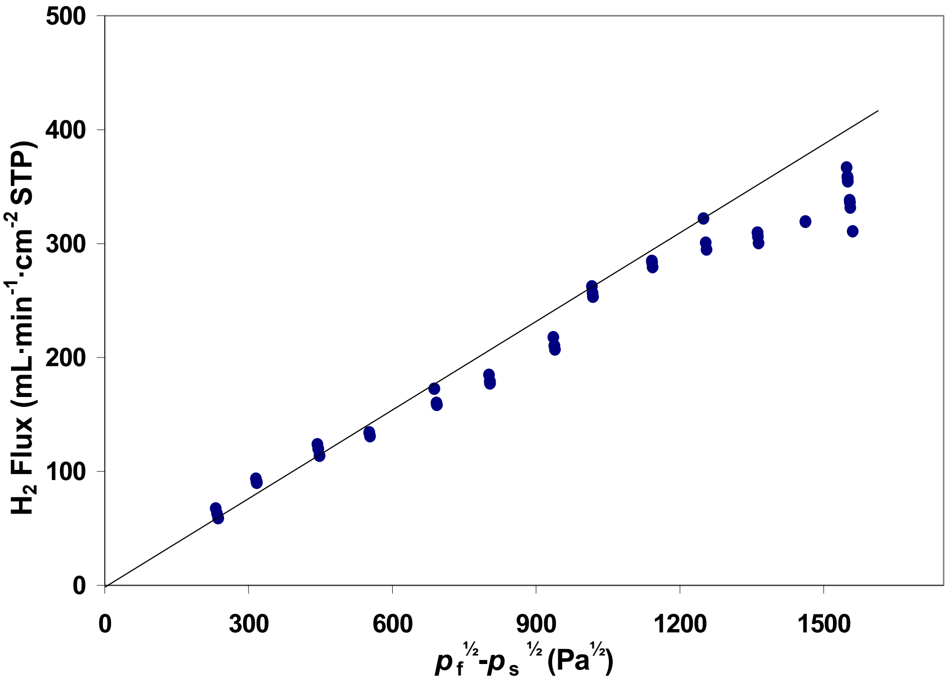


Figure 3. **H_2 permeation at 435°C versus the H_2 partial pressure gradient across the membrane. The feed gas was ~80/20 H_2/He and the sweep gas was Ar. The feed and sweep flow rates were greater than 5 L/min, and the total pressure differential was 450 psi. The straight line represent the flux predicted based on Sieverts' Law.**

maximum H_2 permeation greater than 350 mL·min^{-1}·cm^{-2} was achieved, although the calculated permeability was only 2.2 x 10^{-7} mol·m^{-1}·s^{-1}·Pa^{½}.

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 is in the final stage of assembly of equipment 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 in cermets affects hydrogen permeation through ANL-1a membranes. ANL-1a membranes with large-grain metal phase gave a higher hydrogen flux than ANL-1a membranes with small-grain metal phase. ANL also reported that the electrical properties of ANL-1a membranes change dramatically with sintering conditions. In this quarter, ANL continued to investigate the effect of microstructure on hydrogen permeation. Figure 4 shows the temperature dependence of the hydrogen flux of two ANL-1a membranes, one that was conductive after sintering in 200 ppm H_2 and another that was insulating after sintering in 4% H_2. For both types of membranes, the H_2 flux increased as temperature increased, but the flux through the conductive membrane was ~5-10 times higher than that through the insulating membrane. This result confirmed that the electronic conductivity of ANL-1a membranes limits the hydrogen permeation through its oxide phase.

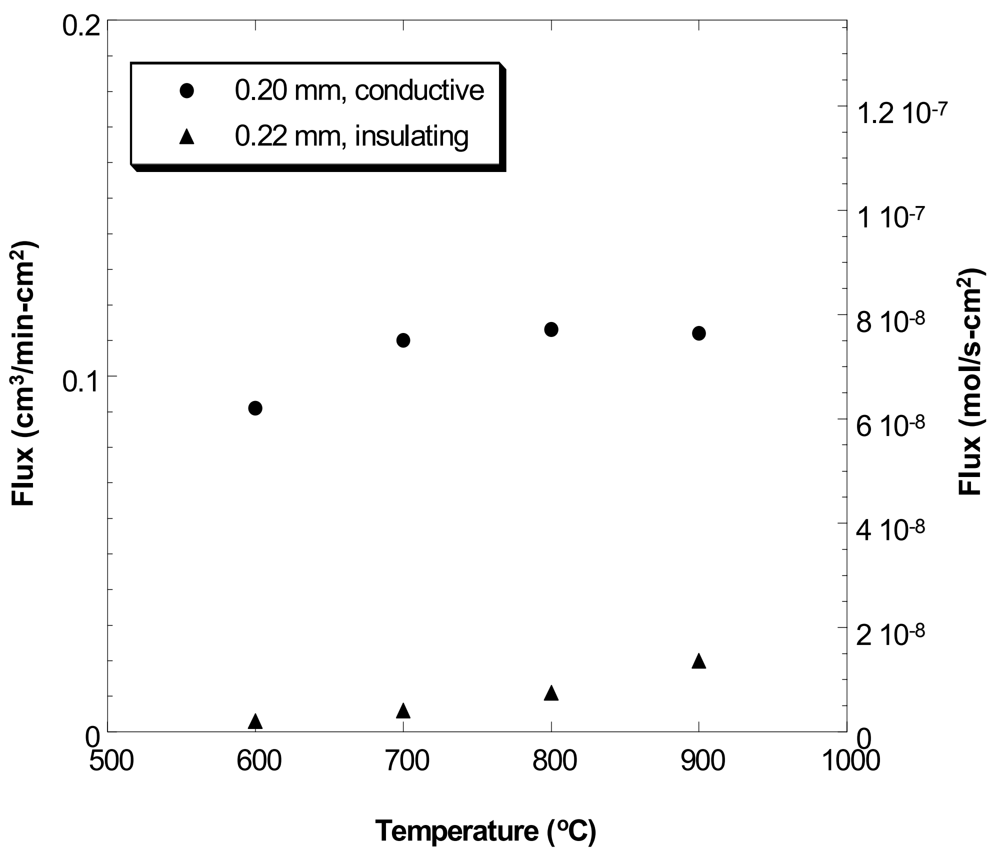


Figure 4. **Temperature dependence of hydrogen flux for ANL-1a membranes in feed gas of 4% H_2/He (containing ~3% H_2O). Membrane thickness given in inset.**

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 is using the apparatus shown schematically in Figure 5 to test potential candidates by measuring the exchange between H_2 and deuterium. The apparatus consists of a flow reactor equipped with a turbo pump (Turbo pump (Edwards Model ETP 100) and a mechanical pump (Edwards Model E2V8). The flow rates of the gases are controlled using two mass flow controllers (Horiba STEC Model SEC 4400, Max. Flow rate = 100 sccm). The setup includes a substrate heater (GE HTR1001 Boron Nitride heater, max. temperature 900/C). The temperature of the catalyst sample is measured using a K-type

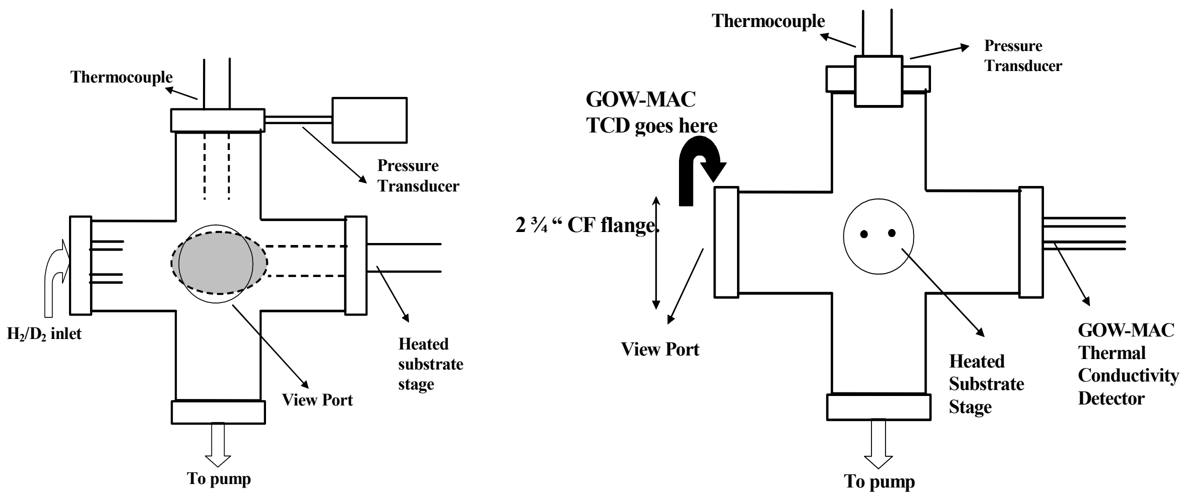


Figure 5. Schematic diagram of the apparatus used by SCI for catalyst evaluation. Figure on left is a front view, and the figure on the right is a side view.

thermocouple, capable of measuring temperature up to 980/C. The pressure inside the chamber is monitored and controlled using a pressure transducer (MKS Baratron Model 629, capable of measuring up to 1 mTorr) in conjunction with a pressure control valve. In addition, it is also equipped with a residual gas analyzer (RGA, Kurt Lesker Co.) capable of detecting the composition of the gases in the gas phase from pressures 10^{-6} Torr to as low as 10^{-11} Torr. The entire setup is enclosed in a chamber for cooling purposes and to test the samples at low temperatures. Thermal conductivity detectors (GOW-MAC Model 10-077 WX), capable of detecting up to 200 ppm of H_2 in deuterium, will be installed shortly in the setup for further testing of the performance of the catalyst.

Four catalysts were tested in the setup described above. The catalyst samples were made by impregnating high surface area alumina with the metal precursor solutions. The samples were placed on the substrate heater and heated to various temperatures while the gas phase composition was monitored using the RGA. A feed gas consisting of 20 sccm of H_2 and 50 sccm of deuterium was used for the present experiments. The testing was performed at three different temperatures: 25/C, 140/C, and 240/C. The pressure in the reactor under these conditions was approximately 490 mTorr. All the samples were tested under identical conditions for the purpose of comparing their performance. The scans were repeated three times for each temperature and for each catalyst to verify the consistency of the results.

Preliminary data indicated that the RGA unit was capable of resolving HD from H_2 and D_2. At both 25 and 140/C, a selected new catalyst composition produced greater H_2/D_2 exchange than the base-case Pd catalyst. However, at higher temperatures Pd had the best performance. Also, H_2 adsorption by the alumina support increased with increasing temperature.

Catalyst testing at Eltron will employ the standard membrane evaluation apparatus, and differences in H_2 permeation will be used as the performance metric. Approximately 40 catalyst compositions were outlined for comparison to the base-case Pd. Several Pd-coated analogs were prepared to determine the inherent reproducibility of sample fabrication, and to establish a baseline for assessing new compositions. Testing will be initiated during the next quarter.

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. Other issues associated with high-pressure H_2 separation are discussed under Task 5.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: CoorsTek, Eltron

It was concluded that problems with tape casting thin films onto planar supports were associated with uncontrolled variables during precursor preparation rather than the binder burnout and sintering cycles. Based on results to date, CoorsTek suggested coating thin membranes on thin-walled (0.5 mm) isopressed tubes. Effort during this quarter focused on fabrication of a selected thin-walled tube cermet composition.

The objective for thin film fabrication is to produce a 50-micron thick membrane tape cast on a porous substrate of the same composition. Green, isopressed tubes were provided to CoorsTek by Eltron. Some of these tubes were used for a bisque firing optimization study, and some of the bisque fired tubes were high fired. Membrane coatings will be applied to all three of these series to determine which condition of the tube yields the best substrate for the membrane.

The current study is being carried out at CoorsTek on open both end (OBE) cut segments of the isopressed tubes. The three processes that will be considered for manufacturing these supports are: i) isopressed closed one end (COE) tubes, ii) extruded OBE tubes, and iii) extruded COE tubes.

Unfired tubes are relatively strong since they still contain the binder for shrinkage matching with the membrane. Binder burnout could be problematic resulting in defects in the membranes. The isopressed mandrels provided by Eltron to CoorsTek were re-machined and polished to remove dents or other irregularities. These mandrels are anticipated to improve the ID quality of pressed tubes and, hence, the membrane thickness uniformity.

The optimal bisque firing temperature appeared to be 1100ºC. The corresponding shrinkage was 13% out of a total shrinkage of ~20%. The bisque tube in this condition appears to have the minimum amount of strength required for handling. The fired tubes have excellent strength and no binder burnout issues, however, they have no shrinkage left to match that of the membrane and may result in stresses or even cracking of the membrane.

Two dispersion systems were used to suspend the membrane. The system based on a slower drying solvent yielded better results than the faster drying system on bisque-state tubes. The viscosity and solids loading of the membrane will need to be optimized to minimize the membrane thickness. A digital Brookfield computer interface rheometer was ordered to better understand the complex rheology in characterizing membrane slip viscosity. Understanding and controlling membrane thickness and uniformity in a defect-free state is underway.

Bisque fired tubular supports were tested first with the thin film deposition. The resulting membranes deposited on the 1100/C bisque fired tubes did not coat uniformly. This result was attributed to excessive porosity of the bisque fired tubes. SEM measurements indicated that the membrane thickness was 70 :m. CoorsTek will work with Eltron to modify the isopressing formulation with a decreased amount of pore former to reduce the porosity and increase the strength of the bisque fired support. CoorsTek will then optimize the viscosity and percent solids to further reduce the thickness of this membrane.

Initial green tube supports were fired at 1390/C in forming gas and the metal phase migrated to the surface and formed beads. The firing temperature was reduced to 1360/C and the beading was mostly eliminated. The dispersion techniques also were improved to reduce the possibility of metal agglomerates. SEM images of these samples indicated that the resulting membrane was 73 :m thick. CoorsTek will optimize the viscosity and percent solids to further reduce the thickness of this membrane.

Conclusion from the thin film fabrication efforts to date are as follows: i) The thin wall tubes have shown excellent potential as a support for the membranes and will greatly simplify achieving gas tight seals, ii) the amount of open porosity in the porous support tube is excessive and needs to be reduced, which will increase the strength of the support, iii) CoorsTek confirmed that the out-of-roundness condition for the thin wall (~0.5mm) isopressed tubes is caused by slumping (high temperature creep) during firing, iv) the out of roundness on thin wall tubes (~0.5 mm) tubes ~ 2.5 inches long sintered in a vertical upright position was ~0.004-0.006 inches compared to 0.030 inches on tubes fired in the horizontal position, and v) thick and thin wall tubes yielded very similar out of roundness on vertical firing.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: NORAM

During this quarter, NORAM focused on compiling information needed for H_2 separation unit scale up and outlined preliminary mechanical considerations. NORAM's efforts are summarized as follows:

- Reports to the DOE on hydrogen production from gasification have been downloaded and summarized. These reports have sufficient information on practical IGCC cycles to define the conditions under which hydrogen separation membranes must function (pressure, temperature and composition) if they are to be realistically incorporated into IGCC cycles.

- Gas cleaning options, hot, warm and cold have been studied, and summarized together with the realistic levels of contaminants that they can hope to achieve. In the context of Eltron's family of membranes, the current state of gas cleaning technology restricts where some types of membranes can be incorporated into IGCC.

- A simple spreadsheet model has been written which predicts the area requirement for a hydrogen membrane separator as a function of the membrane properties. It is suitable for prediction of area requirements both for membranes characterized by ambipolar conductivity (those where flux is driven by a Nernst potential), and membranes characterized by permeability.

- The mechanical properties of an intermediate temperature composite membrane have been developed and used to predict the allowable internal and external pressures on unsupported tubes fabricated from this composite structure. Based on this, some preliminary design concepts for large membrane separators have been developed. Both tubular and plate type designs have been considered. Fabricators of tube type structures based on this composite have been identified.

- For ceramic-ceramic membranes some criteria have been developed for maximum thickness to produce workable designs. It is clear that for these membranes thin films must be supported on a permeable substrate.

- The entire body of work to date is currently being summarized in a first stage report which will be issued to Eltron. We hope that this report will result in a video-conference where we can discuss the preliminary findings and focus the ongoing effort.

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 two 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:

- Deviation from Sieverts' Law for layered membranes was a result of mass transfer limitations and surface contamination.
- Mass transfer limitations in the experimental setup were partially overcome by maximizing the gas feed and sweep rates. Under these experimental conditions, H_2 permeation in excess of 350 $mL\cdot min^{-1}\cdot cm^{-2}$ now are achieved routinely with layered membranes.
- The electronic conductivity of ANL-1a membranes was limited by the hydrogen permeation through the oxide phase.
- Strategies for development of improved surface catalysts were outlined by SCI and Eltron. Catalyst testing apparatus were constructed, and a list of candidate catalysts were prepared. Preliminary catalyst testing was performed by SCI.
- Fabrication of thin-walled tubes was optimized, and these structures appear to have excellent potential as thin film supports.
- NORAM has completed roughly 70% of the preliminary tasks associated with information gathering and preliminary mechanical considerations for H_2 separation unit scale up.
- The range of candidate membrane compositions for scale up was narrowed to selected compositions within the layered composite category.

OBJECTIVES FOR NEXT REPORTING PERIOD

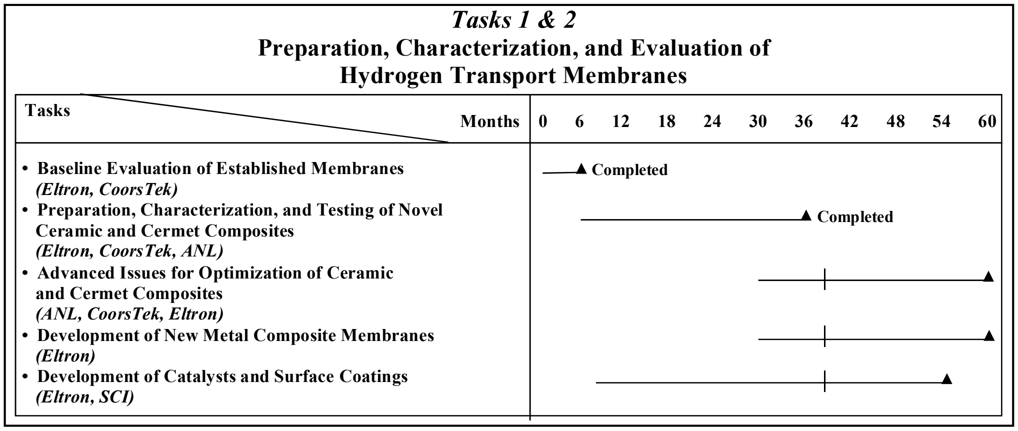
During the next reporting period new membrane compositions will be tested under high pressure and attempts will be made to further improve the experimental conditions to maximize H_2 permeation. Catalyst testing will continue at SCI and Eltron will establish a catalyst baseline performance for Pd on a selected membrane compositions. ANL will study the effect of oxide phase grain size on hydrogen permeation through ANL-1a membranes, and CoorsTek will focus on deposition of thin cermet films onto the thin-walled tube supports. NORAM will complete the compilation and analysis of relevant information for engineering scale up.

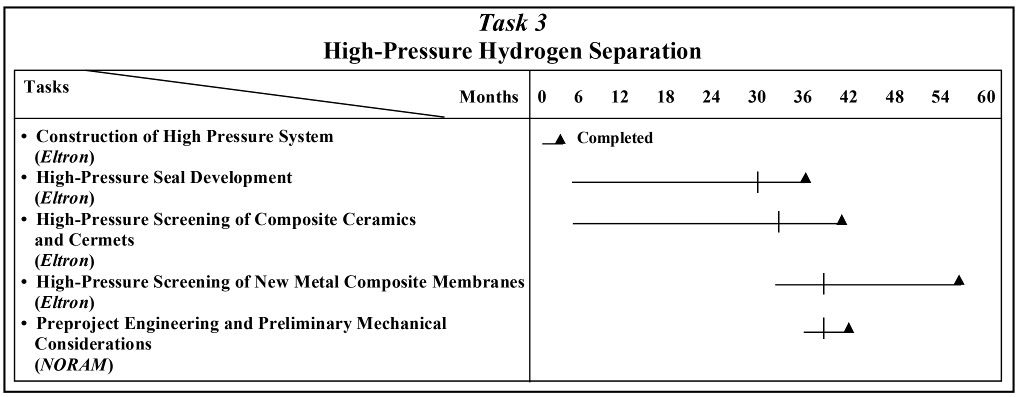
OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

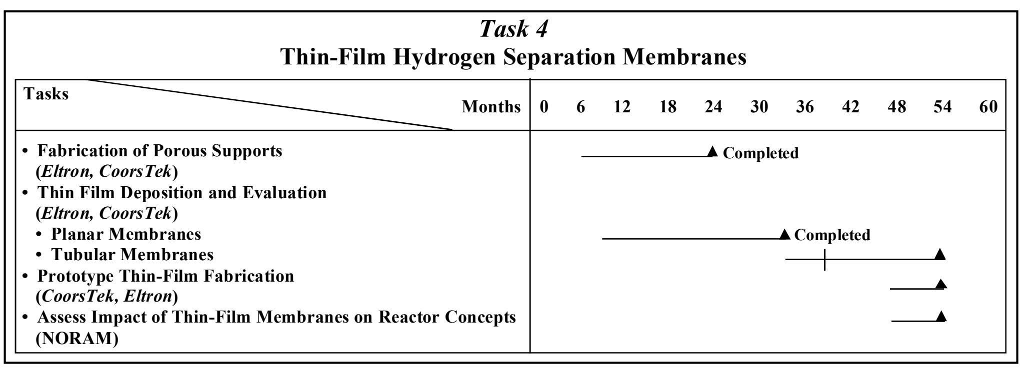
None.

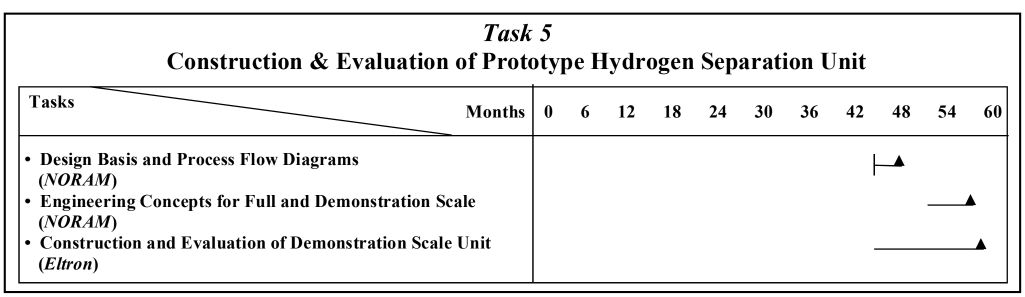
TIME LINES

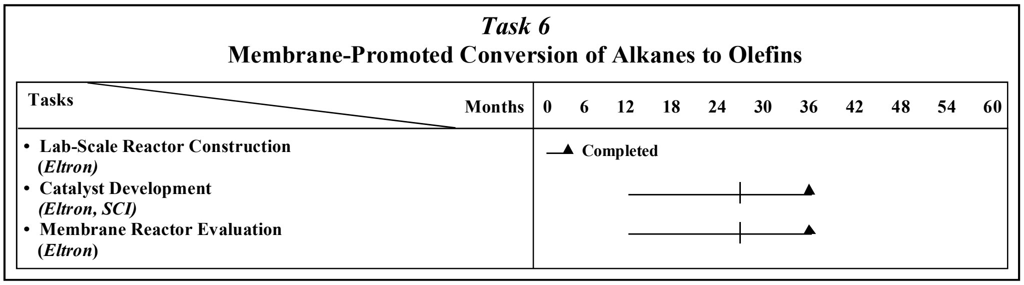
The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

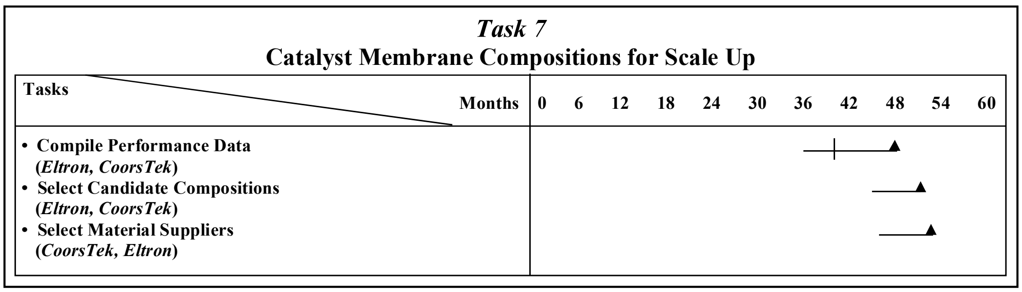


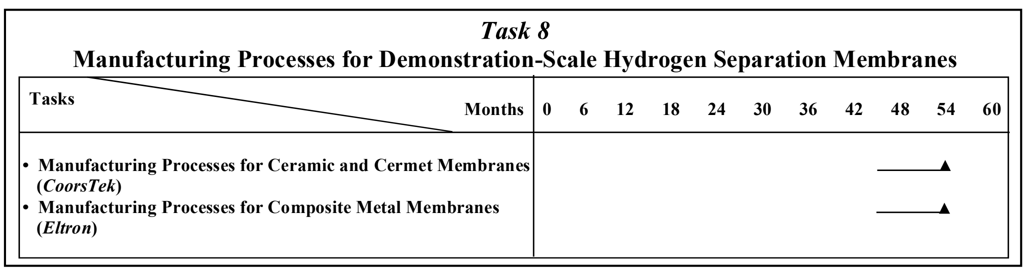


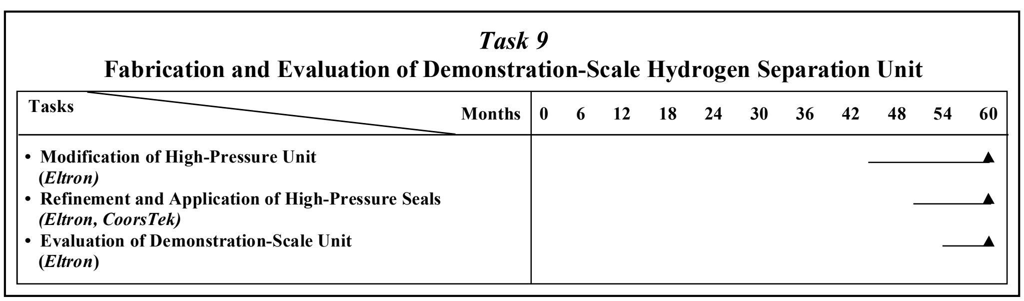





Task 6
Membrane-Promoted Conversion of Alkanes to Olefins
Tasks
Months
0 6 12 18 24 30 36 42 48 54 60
• Lab-Scale Reactor Construction (Eltron)
Completed
• Catalyst Development (Eltron, SCI)
• Membrane Reactor Evaluation (Eltron)


Task 7
Catalyst Membrane Compositions for Scale Up
Tasks
Months
0 6 12 18 24 30 36 42 48 54 60
• Compile Performance Data (Eltron, CoorsTek)
• Select Candidate Compositions (Eltron, CoorsTek)
• Select Material Suppliers (CoorsTek, Eltron)


Task 8
Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes
Tasks
Months
0 6 12 18 24 30 36 42 48 54 60
• Manufacturing Processes for Ceramic and Cermet Membranes (CoorsTek)
• Manufacturing Processes for Composite Metal Membranes (Eltron)


Task 9
Fabrication and Evaluation of Demonstration-Scale Hydrogen Separation Unit
Tasks
Months
0 6 12 18 24 30 36 42 48 54 60
• Modification of High-Pressure Unit (Eltron)
• Refinement and Application of High-Pressure Seals (Eltron, CoorsTek)
• Evaluation of Demonstration-Scale Unit (Eltron)

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