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

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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 as high as 423 mLAmin^{-1}Acm^{-2} at 440/C were measured. Membrane stability was investigated by comparison to composite alloy membranes. Permeation of alloyed membranes showed a strong dependance on the alloying element. Impedance analysis was used to investigate bulk and grain boundary conductivity in cermets. Thin film cermet deposition procedures were developed, hydrogen dissociation catalysts were evaluated, and hydrogen separation unit scale-up issues were addressed.

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 up to 423 mL•min^{-1}•cm^{-2} at 440/C. In addition, progress is summarized on cermet characterization, cermet thin film fabrication, catalyst development, and H_2 separation unit scale up.

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 up to 423 $mL \cdot min^{-1} \cdot cm^{-2}$ were achieved at 440/C and 475 psi differential pressure. Membrane stability was investigated by determining the permeation of layered alloy composites. 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, high pressure permeation experiments were performed up to 475 psi differential pressure. Figure 1 shows the hydrogen permeation for a composite layered membrane tested at 440/C.

A permeation rate of 423 ml/min/cm^2 was achieved in Figure 1 under a feed flow rate between 2.5 and 2.8 L/min. The concentration of H_2 in the feed stream was varied between 40 and 100%. The permeability of this membrane was 2.3 x 10^{-7} mol/m/s/Pa$^{1/2}$ at a differential pressure of 475 psi. Figure 1 shows that permeation data fit well with the permeation predicted by Sieverts' Law.

Membrane long term stability is essential for separation of hydrogen under conditions present in coal gasification power plants. During this reporting period several different alloy layered composites membrane were tested. Three different alloys were tested under similar high pressure hydrogen separation conditions. It was found that the alloying element(s) and concentration significantly affect H_2 separation. Figure 2 shows H_2 permeation for 3 different alloys tested under similar conditions.

All three alloys were annealed prior to testing. During permeation testing, H_2 flow rates varied between 1 and 2 L/min. In addition the sweep flow rate was 1 to 2 L/min. Figure 2 shows that the permeation varied significantly depending on the alloy. For Alloy A a maximum permeation of 75 mL·min^{-1}·cm^{-2} was measured. In addition, Alloy A

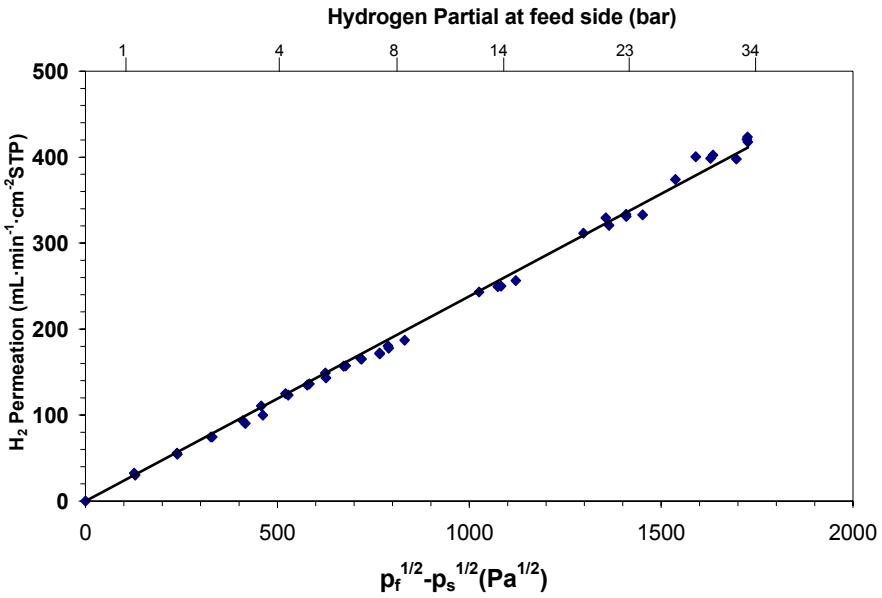


Figure 1. **H_2 permeation at 440/C versus the partial pressure difference across the membrane. The feed flow rate was less than 3 L/min. The sweep flow rate was greater than 7 L/min, and the total pressure differential was 475 psi. The straight line represents the flux predicted based on Sieverts' Law.**

could only be tested up to pressure differential of 75 psi. The permeability of Alloy A was 4.0 x 10^{-7} mol/m/s/$Pa^{1/2}$. The maximum permeation for Alloy B was 76 mL·min^{-1}·cm^{-2}. This was very similar to the maximum permeation measured for Alloy A, except at a much higher partial pressure difference, as shown in Figure 2. The difference was that Alloy B had a lower permeability of 1.4 x 10^{-7} mol/m/s/$Pa^{1/2}$. Finally, Alloy C had a maximum permeation of 33 mL·min^{-1}·cm^{-2} and a permeability of 6.0 x 10^{-8} mol/m/s/$Pa^{1/2}$ at a total pressure differential of 433 psi.

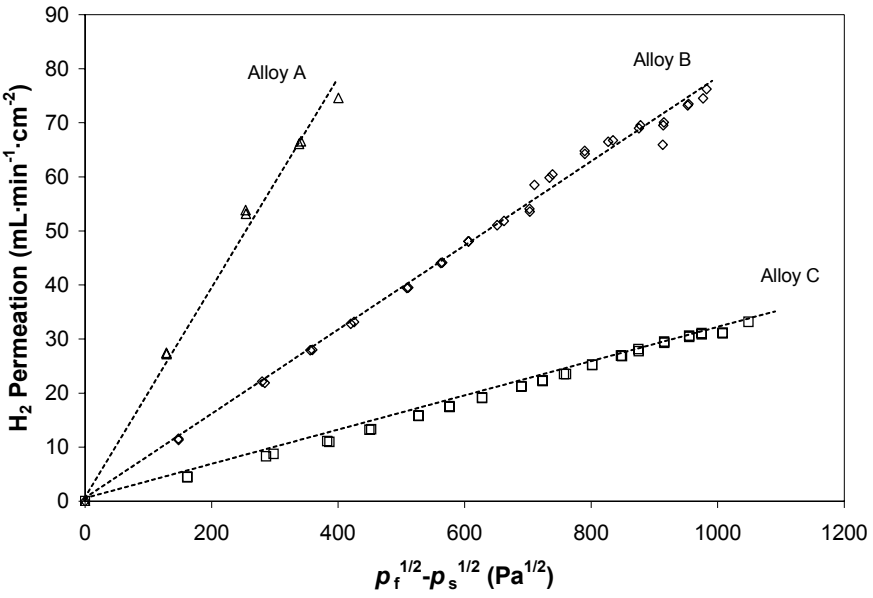


Figure 2. H_2 permeation at 440ºC versus the partial pressure difference across the membrane for three different alloys. The dashed lines represent the flux for each membrane based on Sieverts' Law.

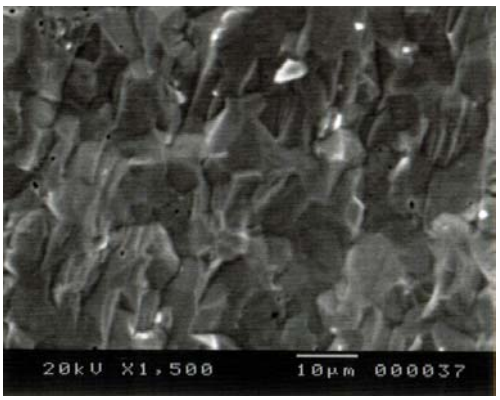
II. Multi-Phase Ceramics and Cermets – ANL

Previous work at ANL showed that the grain boundary resistance of ANL-1a membranes might significantly affect hydrogen permeation. In this quarter, ANL used impedance analysis to conduct a detailed investigation of the bulk/grain boundary conductivity of the oxide phase in ANL-la cermet membranes.

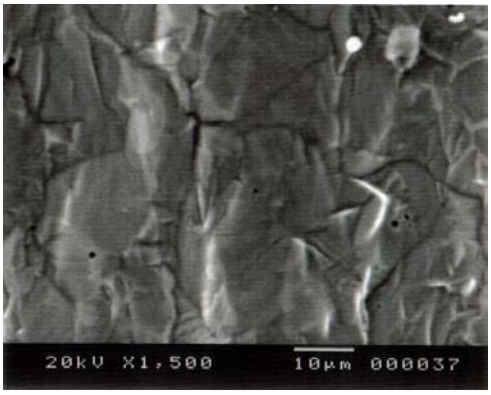
To study the effect of microstructure on proton conductivity, BCY powder from Praxair was used to sinter two specimens in air for 10 h, one at 1500/C (specimen I) and the other at 1600/C (specimen II). The fracture scanning electron micrographs of the specimens after sintering are shown in Figure 3. The sample sintered at higher temperature (Specimen II) showed larger grains and less grain boundary length per unit area.

The electrical response of the BCY samples below 300/C typically showed three semicircles in the Nyquist plot: one at high frequencies corresponding to the bulk characteristics; one at medium frequencies related to the grain boundary resistance, and one at low frequencies associated with the electrode response. Comparing the impedance diagrams for specimens I and II shows that the medium frequency semicircle (associated with grain boundary resistance) was larger for specimen I than for specimen II. This result indicates that specimen I had a larger grain boundary resistance, which is reasonable because the mobile charge carriers encounter more boundaries in specimen I. Assuming a bricklayer model with an equivalent circuit of three parallel RC circuits connected in series, the impedance diagrams were fitted to obtain the resistance, characteristic frequency, and capacitance of bulk, grain boundary, and electrodes. The Arrhenius plot of the

electrical conductivity is shown in Figure 4. The bulk conductivity was . two orders of magnitude higher than the grain boundary conductivity over the temperature range (100–300/C) in feed gas of 4% H_2/balance He (pH_2O = 0.03 atm). The significantly lower grain boundary conductivity indicates that larger-grained materials might be more suitable for proton transport.



(a)



(b)

Figure 3.Scanning electron micrographs of BCY specimens sintered in air for 10 h at (a) 1500/C, (b) 1600/C.

As temperature increases, the semicircle associated with grain boundary resistance becomes extremely small even for small-grained specimen I, therefore the grain boundary resistance cannot be separated from bulk resistance. Above 600/C, both the bulk and grain boundary response are incorporated into the high frequency offset, leaving the electrode response as the only semicircles. Figure 5 shows the Arrhenius plot of total conductivity in 4% H_2 (pH_2O = 0.03 atm) feed gas from 300–900/C. Specimen II, with larger grains, showed higher conductivity at 900/C (5.31 x 10^{-2} S-cm^{-1}) than did specimen I (2.68 x 10^{-2} S-cm^{-1}) with smaller grains. Because the two specimens have the same macroscopic geometry, and their bulk and grain boundary conductivities are expected to be identical, the difference in total conductivity should mainly reflect a difference in their microstructures. This suggests that the grain boundaries may not provide a pathway for fast proton transport, and that bulk transport makes a major contribution to the total conductivity at higher temperature.

These results are consistent with ANL's previous study into the effect of oxide grain size on the hydrogen flux through ANL-1a membranes, which showed that the hydrogen flux was higher for large-grained membranes due to higher proton conductivity for the bulk than for the grain boundaries.

III. Membrane Coatings and Catalysts – Eltron, SCI

Catalyst development at Eltron focused on developing catalysts that maintain high permeation in the presence of H_2S. Layered composite membranes containing the baseline catalyst were tested in four different ambient pressure reactors. The average permeation measured at 420/C

was 21(2) mLÅmin^{-1}Åcm^{-2}. Sulfur tolerance of the baseline catalyst was determined by introducing hydrogen sulfide into the feed stream. A sample membrane was heated to 420/C and exposed to a hydrogen / helium feedstream. Three to four data points were taken at three hour intervals to establish an initial permeation. Hydrogen sulfide was then introduced into the feed stream to produce a H_2S concentration of 8 ppm. Permeation data was collected at 10 minute intervals for one hour to measure the rate of degradation. Additional data points were then taken at three hour intervals. Results showed that layered composite membranes containing the baseline catalyst degraded rapidly in the presence of 8 ppm H_2S. Within 20 minutes of exposure to H_2S, permeation decreased 30–40%, and after two hours permeation had dropped to 50% of each membrane's original permeation value.

The current literature has shown that palladium copper alloys exhibit sulfur tolerance.[1-4] Within the palladium / copper alloy system, two different Pd/Cu crystal lattices are found depending on the temperature and composition of the alloy. The alloy composed of 60%Pd and 40%Cu by weight has been studied extensively. Below 500/C this alloy exists in a body-centered cubic (bcc) structure. Above 500/C, the

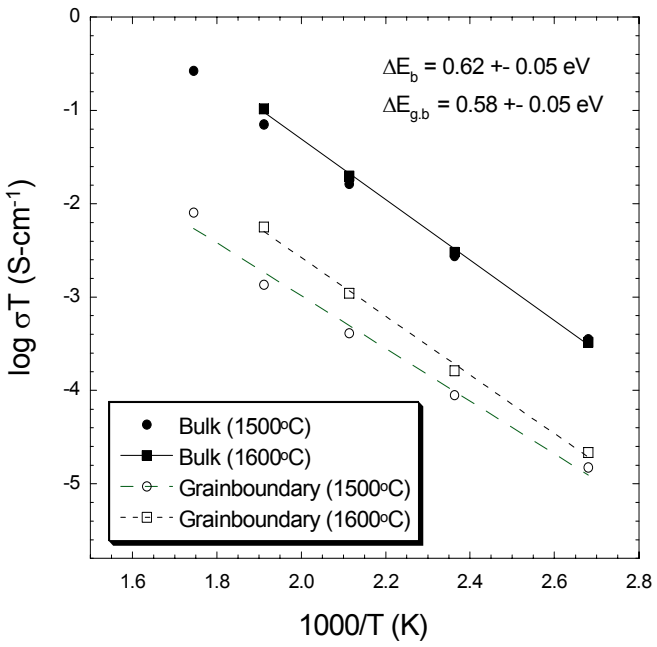


Figure 4. Arrhenius plot of bulk and grain boundary conductivity of two BCY specimens sintered in air for 10 h, one at 1500/C, the other at 1600/C.

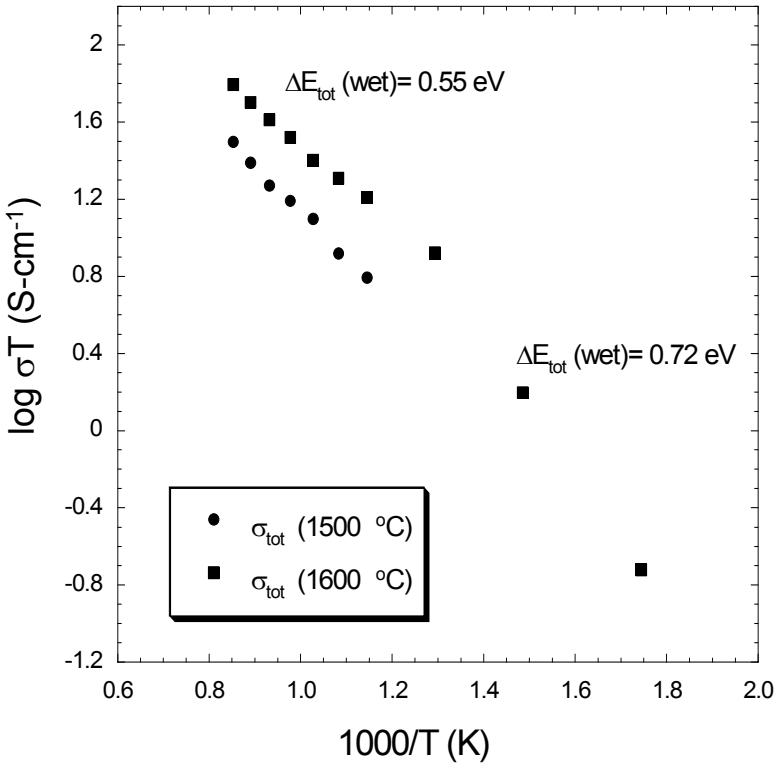


Figure 5. Temperature dependence of total electrical conductivity of two BCY specimens sintered for 10 h in air, one at 1500/C, the other at 1600/C.

60/40 alloy is found in a face-centered cubic (fcc) structure. Alternatively, the 80%Pd / 20%Cu alloy is found in a fcc lattice at all temperatures. The literature suggests that the bcc structure has a high permeability, but poor sulfur tolerance. The fcc structure has a lower permeability, but good sulfur tolerance. Eltron has used vapor deposition to deposit palladium and copper alloy catalysts in an effort to verify the sulfur tolerance of both fcc and bcc palladium copper alloys. Figure 6 shows the X-ray diffraction patterns for catalysts deposited on glass substrates. The bottom pattern shows the X-ray pattern following vapor deposition of palladium and copper. Diffraction peak corresponding to palladium and copper are present. The top X-ray pattern in Figure 6 shows the catalyst surface after heating at 400/C for 12 hours in a nitrogen atmosphere. Individual Pd and Cu are no longer found. Peaks corresponding to an alloy were found, although, based on the presence of doublets, it is clear that the catalyst has not completely alloyed. It is expected heating at 400/C for a longer period of time will produce a uniform alloy. During the next reporting period Eltron will produce fcc and bcc palladium / copper alloys. Alloy formation will be verified with X-ray diffraction and alloy composition will be determined with energy dispersive X-ray analysis. Once formed, palladium / copper alloys will be characterized for permeation in a hydrogen / helium feedstream and in the presence of H_2S

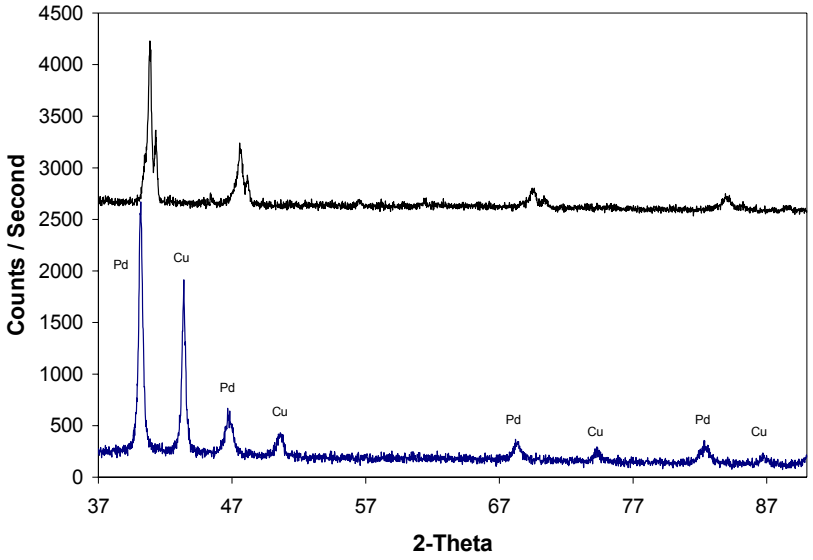


Figure 6. X-ray diffraction patterns for palladium / copper alloy formation. Bottom: X-ray pattern for palladium and copper as deposited on glass using vapor deposition. Top: Pd/Cu alloy formed at 400/C for 12 hours.

Catalyst development at Süd Chemie focused on evaluating three hydrogen dissociation catalyst samples. Catalysts were tested in the setup mentioned in the previous report. Alumina was impregnated with the metal(s) and the samples were placed on a substrate heater and heated to various temperatures. Gas phase composition was monitored using the RGA mentioned previously to study the performance of the catalyst samples. 20 sccm of hydrogen and 50 sccm of deuterium gas was used for the present experiments. The testing was performed at four different temperatures, room temperature (25/C), 140/C, 240/C and 375/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 samples were scanned three times for each temperature and for each catalyst to verify the consistency of the results. The samples were then treated in hydrogen at a temperature of 500/C for 90 minutes and the above performance testing was repeated. This was done to reduce some of the metal oxide to active metal on the catalyst sample surfaces. The reduced metal was intended to be more representative of the conditions that catalyst will be exposed to in a gasified coal feed stream.

Of the samples tested, the performance of the binary metal catalysts were observed to be the

best before hydrogen treatments at all temperatures. Similar trends were observed after hydrogen treatment of the samples.

Hydrogen treatment had an effect on all three samples. Hydrogen treatment improved catalyst performance at lower temperatures. At high temperatures (375/C) the performance of the catalysts before and after hydrogen treatment was similar.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

During this quarter, all testing was performed using a room temperature mechanical seal. Leak free seals are consistently achieved at differential pressures between 250 and 475 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.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: CoorsTek, Eltron

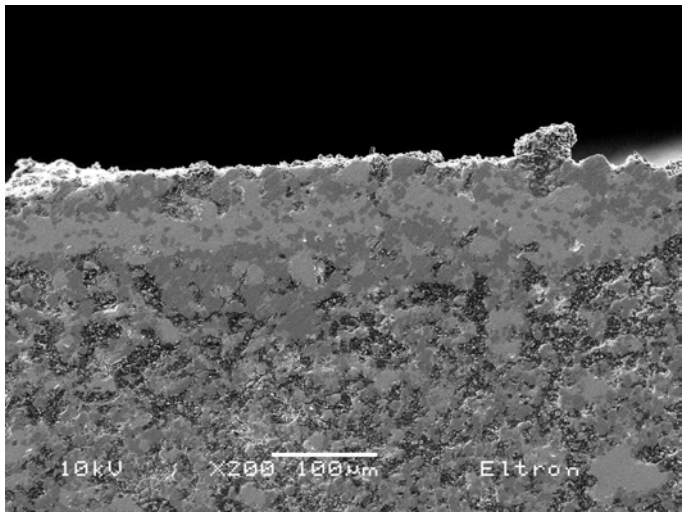


Figure 7. x200 SEM image of a thick dense BCY/Ni film applied to the inside diameter of a porous closed-one-end tube.

Twelve green BCY/Ni isopressed closed one-end (COE) tubes were prepared at Eltron Research Inc. Thin film slurry was deposited on the inside diameter of the tubes by CoorsTek. Coated tubes were sintered at 1360/C for 4 hours in a forming gas atmosphere. A SEM image of a cross-section of a sintered tube is shown in Figure 7. A dense coating was found with a highly variable thickness of 99(23) µm. Further development of the thin film slurry allowed deposition of a thinner dense layer as shown in Figure 8. Figure 8 clearly shows the inner curvature of the thin film tube. The average thickness of the dense thin film in was 15(3) µm. The inside diameter of sintered tubes will be ground to 0.24" for sealing to a 0.250" outer diameter alumina tube. A precious metal seal has

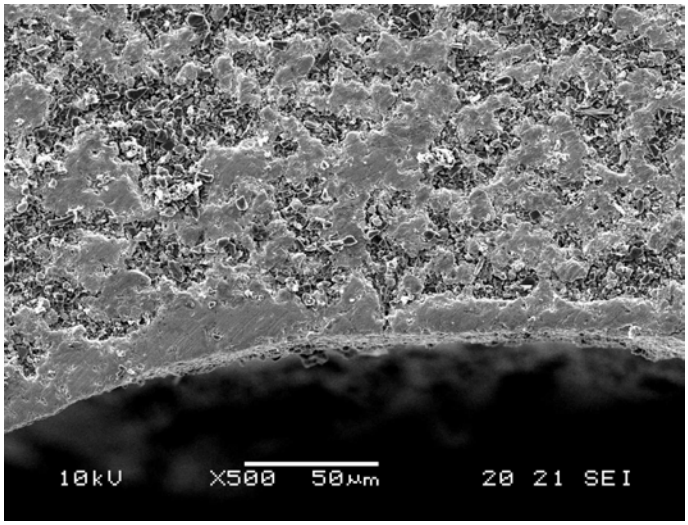


Figure 8. x500 SEM image of a thin BCY/Ni dense film applied to a porous closed-one-end tube.

been developed for sealing the BCY/Ni COE tube to alumina tubing to allow leak-free permeation testing at Eltron Research Inc.

During the next reporting period CoorsTek will finish producing thin film BCY/Ni 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 thin film cermets based on high permeation metals.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: NORAM

In the past quarter work at NORAM was focused in three areas:

1. Minor clarifications and additions were made to the preliminary report presented to Eltron describing the preliminary sizing and location options for hydrogen permeable membranes in an IGCC application.
2. Work was continued on preliminary mechanical concepts and sizing for tubular metal based separators based on bayonet heat exchanger concepts. Other layout types were also evaluated.
3. Conceptualizing of process flow diagrams for IGCC cases with membrane extraction. Detailed flow diagrams will be produced next quarter.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

Alkane dehydrogenation experiments were performed using the experimental set-up described in previous reports. A composite layered membrane was brought up to 500/C under a feed stream flow rate of 60 ml/min of a 10% propane / balance argon. 120 ml/min of Ar was used as the sweep gas. Helium was added to the feed stream to check for leaks. No hydrogen was observed permeating through the membrane, although propene was detected in the feed out of the reactor. It is possible that the catalyst had decomposed prior to use. During the next reporting period new catalyst will be made, and alkane dehydrogenation will be monitored as a function of catalyst surface area.

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. A record high permeation of 423 $mL \cdot min^{-1} \cdot cm^{-2}$ was achieved at 440/C and a total pressure difference of 475 psi.
2. Three different layered composite alloy membranes were tested. It was found that the permeability varied significantly depending on the alloying elements.
3. Impedance spectroscopy was used to show that bulk transport is higher than grain boundary transport in the ceramic phase of hydrogen conducting cermets.
4. Several different type of catalysts were evaluated. Hydrogen dissociation catalysts were evaluated at several temperatures. In addition, palladium / copper alloys were formed using vapor deposition for testing as sulfur resistant catalysts for hydrogen separation membranes.
5. Dense thin films of BCY/Ni were deposited on the inner surface of porous BCY/Ni closed-one end tubes. Thicknesses between 20 and 100 μm were found depending on the thin film deposition process.
6. Mechanical concepts and sizing for tubular metal based separators were evaluated.

OBJECTIVES FOR NEXT REPORTING PERIOD

During the next reporting period efforts will be made to further improve the stability of composite layered membranes under appropriate experimental conditions. ANL will continue to investigate grain boundary conductivity of the oxide phase of the ANL-1 cermet using impedance analysis, and CoorsTek will focus on production of high permeability thin cermet films. SCI will deposit potential catalysts on a hydrogen separation membrane and evaluate their performance. NORAM will produce process flow diagrams for several different IGCC plant configurations.

References:

1. Edlund, D.; "A Membrane Reactor for H_2S Decomposition," http://www.netl.doe.gov/publications/ proceedings/96/96ps/ps_pdf/96pspb14.pdf.
2. Howard, B.H.; Killmeyer, R.P; Rothenberger, K.S.; Ciocco, M.V.; Morreale, B.D.; Enick, R.M.; Bustamante, F.; "Hydrogen Permeability of Palladium-Copper Alloy Composite Membranes over a Wide Range of Temperatures and Pressures," http://www.netl.doe.gov/coalpower/gasification/projects/gas-sep/docs/03Mar%20NHA%

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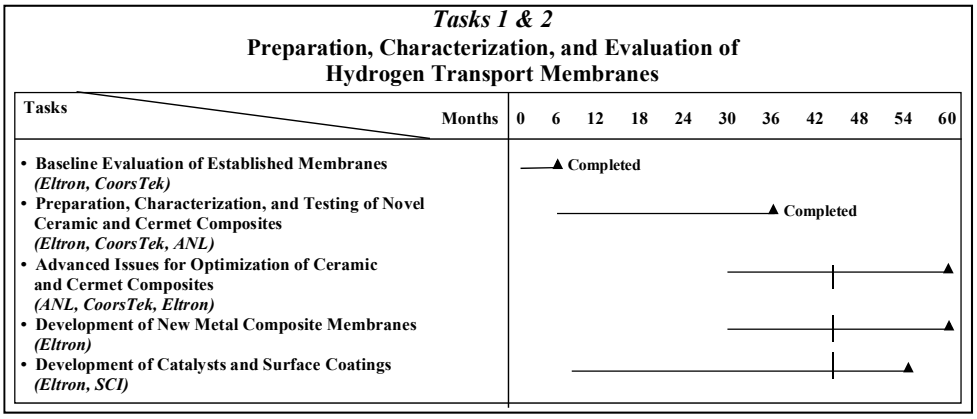
3. Way, Douglas J.; McCormick, Robert L.; "Palladium/Copper Alloy Composite Membrane for High Temperature Hydrogen Separation from Coal-derived Gas Streams," http://www.netl.doe.gov/publications/proceedings/01/ucr-hbcu/McCormick2.pdf.
4. Ciocco, M.V.; Morreale; A.V., Killmeyer, R.P.; Howard, B.H.; "Sulfur Resistance of Palladium-Copper Membranes," The Proceedings of the 29th International Technical Conference on Coal Utilization and Fuel Systems, April 18, 2004.

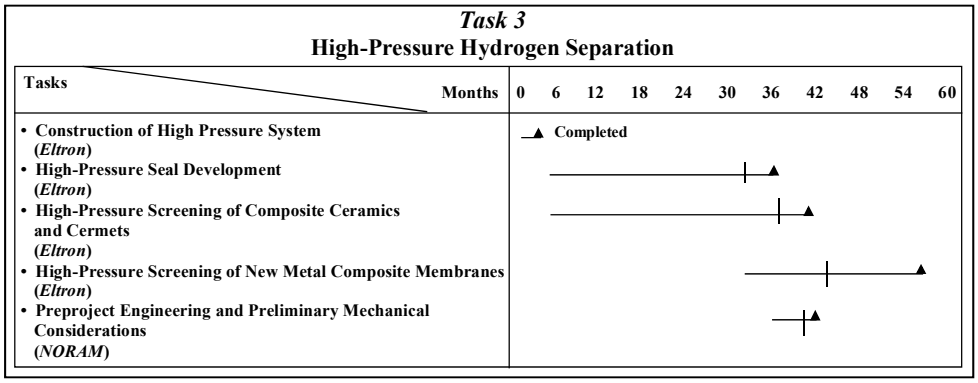
OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

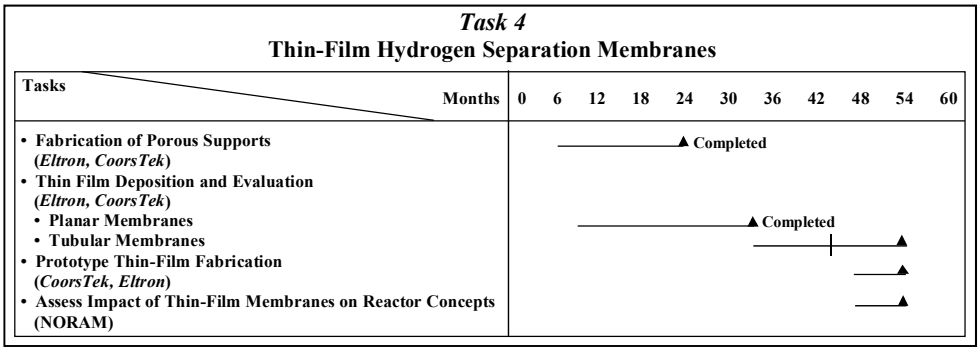
None.

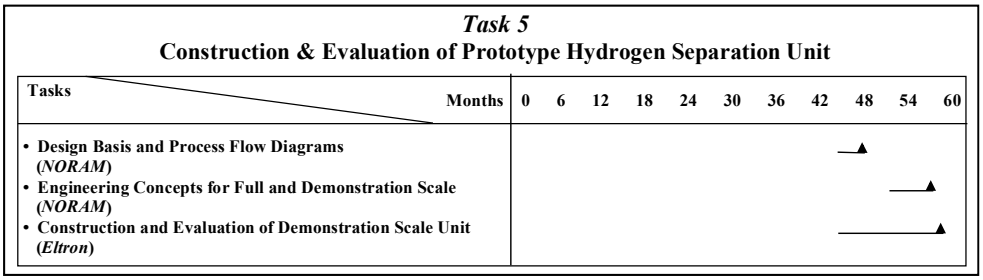
TIME LINES

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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