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ABSTRACT

Eltron Research Inc. and team members CoorsTek, Süd Chemie, and Argonne 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. 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) 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 describes resent results for long-term hydrogen permeation and chemical stability measurements, new mixed conducting cermets, progress in cermet, thin film, and thin-walled tube fabrication, hydrogen absorption measurements for selected compositions, and membrane facilitated alkane to olefin conversion.

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) 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), and Argonne National Laboratory (ANL).

Long-term H_2 permeation measurements and chemical stability tests were performed on layered metal/ceramic composite membranes. Permeation at 320°C decreased by 17% from 11.4 to 9.5 $mL{\cdot}min^{-1}{\cdot}cm^{-2}$ (STP) during 1300 hours of continuous operation. These membranes were not affected by high levels of CO_2; however, 3 vol.% CO reduced permeation to 75% of its original value. Similarly, addition of 5 to 10 vol.% steam dropped permeability to roughly 50% of its original value. Cermets incorporating 40 to 60 vol.% of the same H_2-permeable metals as the layered structures had much lower permeation, showing a maximum of only 0.65 $mL{\cdot}min^{-1}{\cdot}cm^{-2}$ (STP) at 800°C.

New mixed proton/electron conducting cermets achieved a maximum permeation of approximately 0.17 $mL{\cdot}min^{-1}{\cdot}cm^{-2}$, corresponding to an apparent ambipolar conductivity of 0.003 S/cm. These results were slightly lower than previous analogs. Replacing the metal phase with an electron-conducting ceramic reduced permeation to 0.025 $mL{\cdot}min^{-1}{\cdot}cm^{-2}$ and ambipolar conductivity to below 0.001 S/cm. However, these ceramic/ceramic composites demonstrated very high corrosion resistance under extreme conditions. Combining these metal and electron-conducting ceramic phases with thin film membranes might yield very stable materials with adequate H_2 permeation.

Also described in this report is progress in cermet, thin film, and thin-walled tube fabrication, additional H_2 absorption measurements for selected compositions, and membrane facilitated alkane to olefin conversion.

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. Layered Composites Containing Metals with High Hydrogen Permeability – Eltron

In the previous report, composite membranes based on metals with high hydrogen permeability were presented. These materials enabled hydrogen permeation at rates ranging from approximately 2 to a maximum of 27 mL·min^{-1}·cm^{-2} for structures on the order of 0.15 mm thick at temperatures between 300° and 500°C. These results were very consistent with those presented in the literature for similar materials.

Figure 1 shows the long-term stability of a representative layered ceramic/metal alloy membrane at 320°C under a H_2/He mixture on the feed side and Ar sweep gas on the permeate side. The total thickness of the membrane structure was approximately 2 mm, with only 0.13 mm from the metal phase. Over the first 239 hours of operation the average permeation rate (STP) was 11.4 ± 0.5 mL·min^{-1}·cm^{-2} and the average permeability was $6.4 \times 10^{-8} \pm 0.3 \times 10^{-8}$ mol·m·m^{-2}·s^{-1}·Pa$^{-1/2}$. Permeation decreased very slowly at approximately 0.002 mL·min^{-1}·cm^{-2} per hour to an average value of 9.5 ± 0.4 mL·min^{-1}·cm^{-2} over the last 120 hours of operation. Testing will continue on this

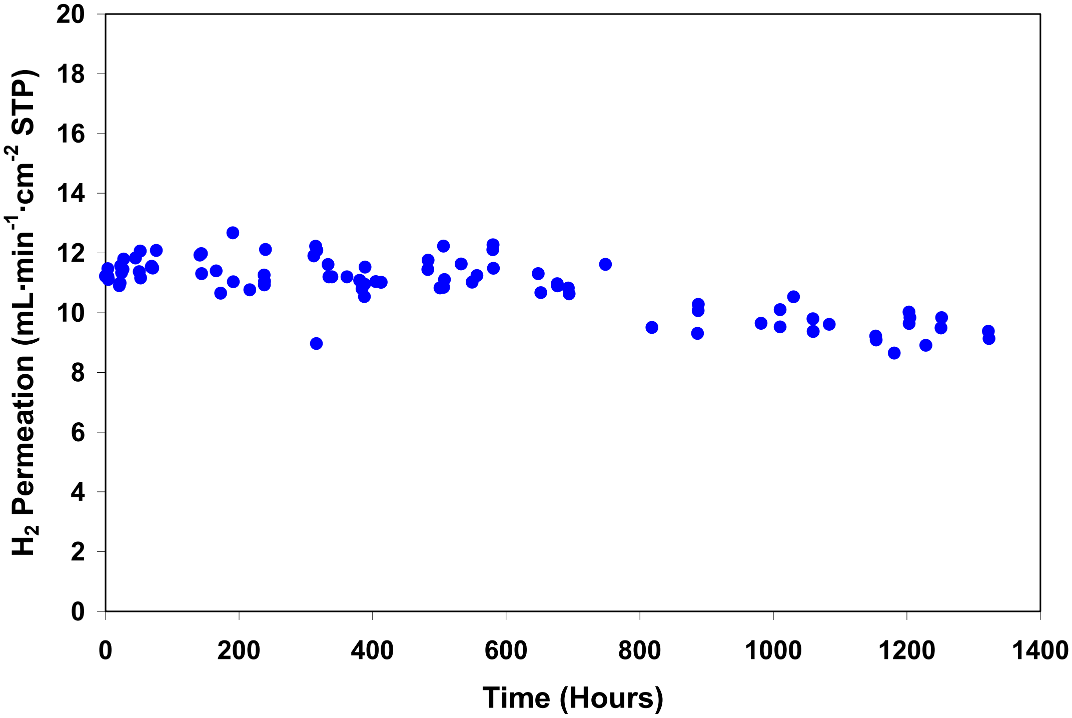


Figure 1. Hydrogen permeation as a function of time for a ceramic/layered metal membrane at 320°C. The feed gas was 200 mL/min 87.5 vol.% H_2 (bal. He) and the sweep gas was 240 mL/min Ar.

sample until permeation is roughly 50% of its original value. At that time, analysis will be performed to identify the mode of performance degradation.

Preliminary stability tests were performed on these materials against CO_2, CO, and high levels of steam. The effect of 20 vol.% CO_2 on H_2 permeation was negligible; however 3 vol.% CO initially reduced permeation by about 50%. After two hours, permeation was partially restored to roughly 75% of its original value. Similarly, addition of 5 to 10 vol.% steam initially dropped permeability nearly to zero, but after 100 hours on stream permeation began to increase and was restored to roughly 50% of its original value.

II. **Cermets Containing Metals with High Hydrogen Permeability** – Eltron

Incorporating the main metal components of the above metal alloy into a ceramic matrix might improve ruggedness and versatility and simplify manufacturing. Figure 2 shows results for cermets with 40 and 60 vol.% of a relatively inexpensive H_2-permeable metal. The ceramic phase had negligible H_2 permeation or proton conductivity, so permeation was exclusively through the metal phase. A thin layer of Pd was deposited onto the membrane surfaces to protect the metal phase and catalyze uptake of H_2 into the membrane.

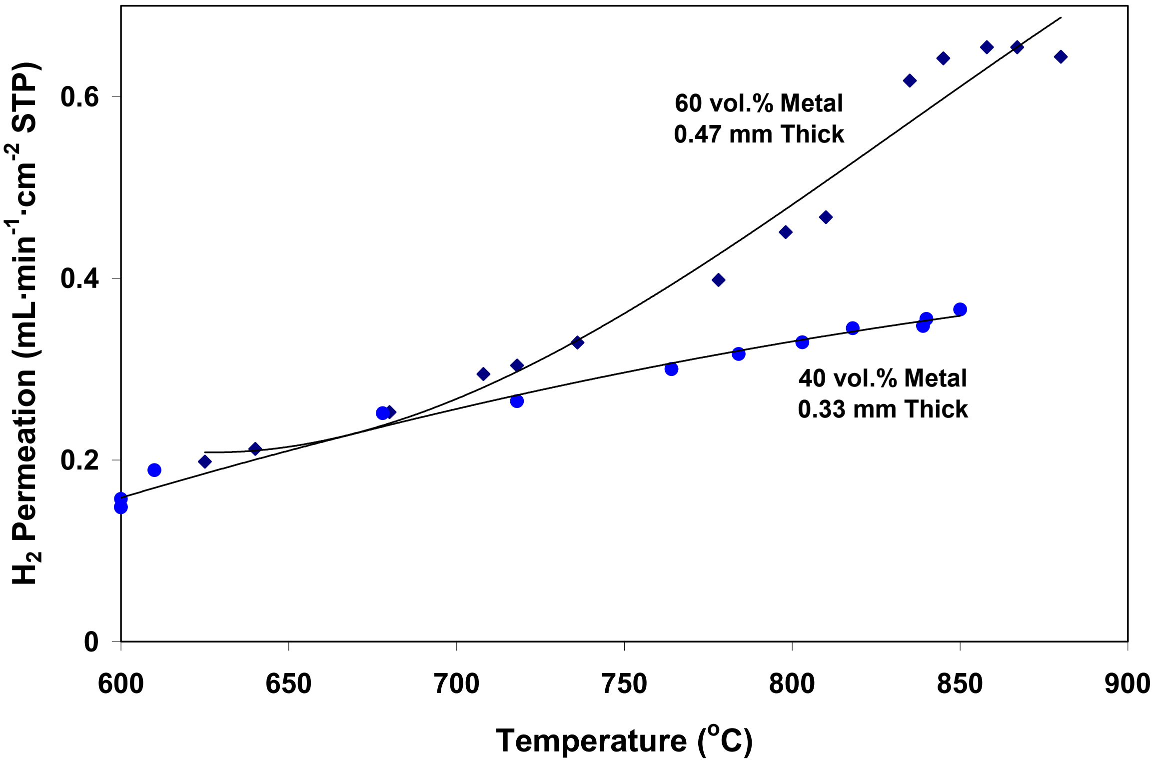


Figure 2. Hydrogen permeation as a function of temperature for cermets containing 60 and 40 vol.% of a hydrogen permeable metal. The bulk material did not contain Pd; however, a 0.5-µm thick film of Pd was coated on each side as a protective catalysts. The feed gas was 75 mL/min 80/20 H_2/He and the sweep gas was 150 mL/min Ar.

Permeation through these membranes was dramatically reduced relative to the above layered ceramic/metal alloy structures, even after accounting for the lower quantity of metal and the increased membrane thickness. Furthermore, permeation was at much higher temperatures than the layered metal analogs. The performance of these membranes was roughly equivalent to mixed proton/electron conducting cermets presented in previous reports.

III. Cermets Containing Metals with Low Hydrogen Permeability – Eltron

Analogs of cermets presented in earlier reports were prepared and tested to determine the effect of the metal phase on permeation. Figure 3 shows permeation as a function of temperature for a 0.45-mm thick membrane designated as $AB_{0.8}B_{0.2}^{c}O_{3-\delta}$/37.5 wt.%MET4. Permeation peaked at approximately 0.17 $mL\cdot min^{-1}\cdot cm^{-2}$ under humid conditions, corresponding to an apparent ambipolar conductivity of 0.003 S/cm. These results were slightly lower than the previous analog ($AB_{0.8}B_{0.2}^{c}O_{3-\delta}$/37.5 wt.%MET1), despite the fact that the membrane was coated with a 0.5 µm Pd film to compensate for the lower anticipated catalytic activity of MET4 relative to MET1. SEM analysis will be performed to determine the similarity of the microstructure for these membranes.

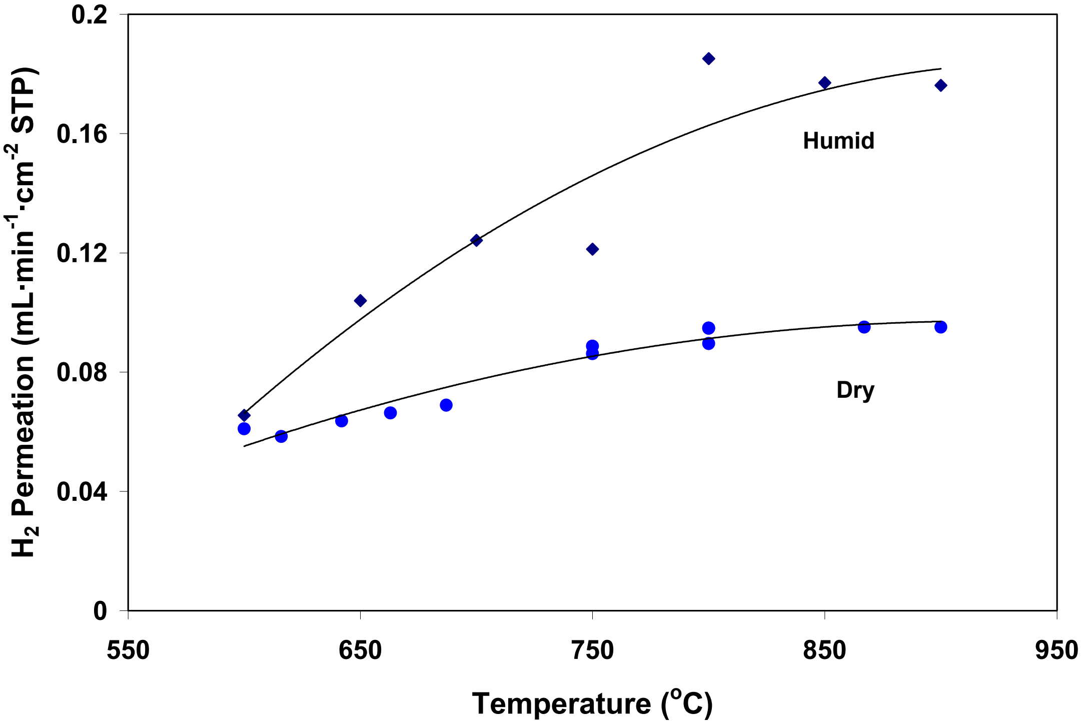


Figure 3. **H_2 permeation as a function of temperature for a 0.45-mm thick cermet designated as $AB_{0.8}B_{0.2}^{c}O_{3-\delta}$/37.5 wt.%MET4. The membrane was coated with 0.5 µm of Pd. The feed gas was 80 mL/min 80 vol.% H_2 (bal. He) and the sweep gas was 150 mL/min Ar.**

IV. **Two-Phase Ceramic/Ceramic Composites** – CoorsTek, Eltron

The ceramic/ceramic composites consist of a proton conducting perovskite phase ($AB_{0.8}B^c_{0.2}O_{3-\delta}$) and an electron conducting transition metal oxide. The greatest potential benefit of this category of membrane is improved resistance against corrosion from feedstream species. Previously it was shown that sintering of certain phase combinations resulted in minimal interdiffusion of phase constituents, yet dramatically increased resistance to corrosion in harsh moisture saturated conditions.

Figure 4 shows H_2 permeation and ambipolar conductivity as a function of temperature for a 1-mm thick membrane. A maximum permeation of about 0.025 $mL \cdot min^{-1} \cdot cm^{-2}$ was obtained, corresponding to an ambipolar conductivity less than 10^{-3} S/cm. These values were 5 to 10 times lower than analogous cermets; however, the content of the electron conducting ceramic phase was fairly low at only 25 wt.%, and it is possible that increasing the content in future formulations might improve permeation.

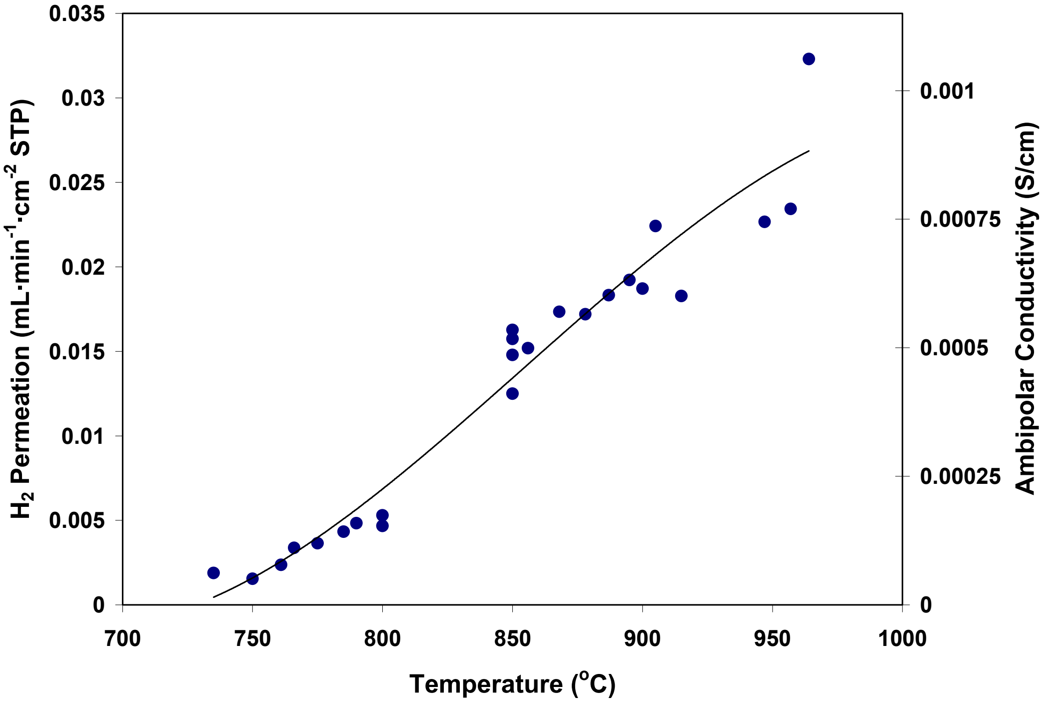


Figure 4. **H_2 permeation and ambipolar conductivity as a function of temperature for a 1-mm thick ceramic/ceramic composite membrane ($AB_{0.8}B_{0.2}^cO_{3-\delta}$/CER2). The feed gas was approximately 80 mL/min of 80 vol.% H_2 (bal. He) and the sweep gas was 150 mL/min Ar.**

V. Membrane Corrosion Resistance – CoorsTek

Corrosion resistance of various proton conducting ceramic compositions was assessed by boiling samples in water for several hours and measuring the sample weight loss. Since this category of membranes is much more stable at operating temperatures (*i.e.*, > 750°C), this simple test represents a worst-case evaluation of resistance to degradation from moisture. Furthermore, hydroxide formation of constituents in these materials loosely parallels carbonate formation, so this test provides a quick and general evaluation of overall membrane stability.

In the previous report it was shown that common proton conducting ceramics lose up to 71% of their mass after only two hours in boiling water. These same ceramics when composited with a metal phase were much more stable, demonstrating only 16% weight loss. However, compositing with 34.4 wt.% of a selected electron-conducting ceramic phase resulted in only 0.06% weight loss after eight hours in boiling water. The H_2 permeation results for this material were presented in section in section III above, and performance was significantly lower than the cermet analog. Accordingly, three-phase ceramic/ceramic/metal samples were prepared where the electron-conducting ceramic phase is used only to impart stability to the proton-conducting phase. These samples indicated very low interdiffusion of phase constituents, and also showed only 0.06% weight loss after eight hours in boiling water. Performance of these analogs for H_2 permeation will be evaluated during the next reporting period.

VI. Dependence of Microstructure on Properties of H_2-Permeable Cermets – ANL

Cermet samples with the same composition (proton-conducting ceramic and 40 vol.% metal) were prepared with different microstructure by varying the particle size of the starting materials. The SEM images in Figure 5 show the largest phase grain sizes after sintering for the sample prepared using precursors with particles sizes between 2.2 and 3.0 μm (left). Additionally, this sample contained isolated pores, and did not sinter well. In contrast, the sample prepared using 0.08- to 0.18-μm precursor particles (right) sintered well, had no open pores, and much smaller grain sizes.

Hydrogen permeation for the large-grain sample increased from about 0.05 to 0.09 $mL \cdot min^{-1} \cdot cm^{-2}$ as the temperature was raised from 600 to 900°C. Permeation measurements for the small-grain sample are underway at ANL and will be presented in the next report.

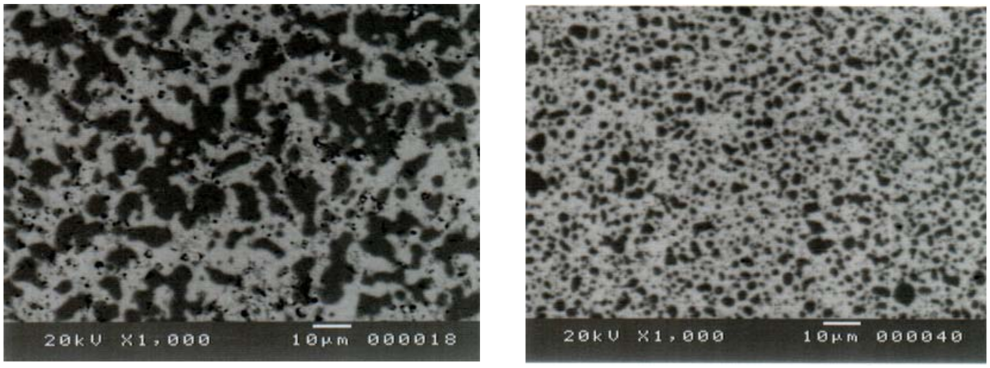


Figure 5. SEM images of cermets (40 vol.% metal phase) prepared with micron (left) and submicron (right) precursor particles.

VII. Membrane Surface Catalysis – SCI

Work this quarter at Süd-Chemie concentrated on conducting pulsed reduction experiments at high temperature since many of the membrane compositions under development operate near 800°C. Usually, temperature programmed reduction experiments are carried out by increasing temperature while the catalyst is exposed to 5%H_2 in Ar at a set rate, and measuring the change in thermal conductivity of the resultant off gas. This sort of experiment is not possible if trying to study the behavior of the material at higher temperatures.

An experimental procedure was devised so that the membrane material would be kept under an inert atmosphere (Ar) and heated to 800°C. When at temperature, 1mL of 5% H_2 in Ar was pulsed over the powder. This process was repeated 30 times and the resulting signal change was monitored relative to an empty tube.

Three different powder samples were subjected to the pulse experiment and the results are shown in Figure 6. Results from the empty tube (null run) yielded an integrated peak area of approximately 9,000. The first sample was a proton conducting perovskite represented as $AB_{0.8}B_{0.2}^{c}O_{3-\delta}$ (Sample A). For the first 8 pulses, this material adsorbed hydrogen in decreasing quantities. After the sixth pulse the material began to adsorb increasing quantities of H_2. From the ninth pulse to the 22nd pulse, all hydrogen pulsed was adsorbed by the material yielding virtually no peak. Then from the 22nd pulse on, H_2 adsorption decreased. The trend indicates that further pulses will most probably result in decreasing adsorption until the peak area approaches that of a null tube (hydrogen saturation of the material).

The experiment was repeated with the same material impregnated with 0.25% Pd (Sample B). The trends were identical but the amplitude of the initial "non-adsorption" was greater than that of the unimpregnated material. The experiment was conducted a third time on a newer batch of $AB_{0.8}B_{0.2}^{c}O_{3-\delta}$ (Sample C). The results mirrored those of the original sample except that the increase in adsorption occurred at pulse seven.

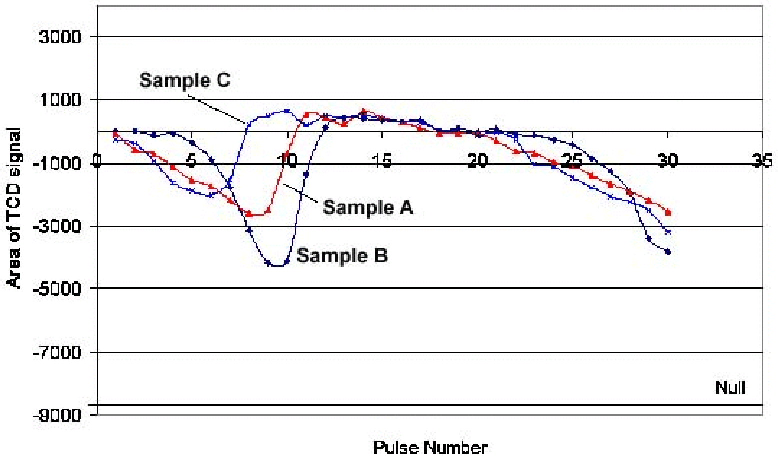


Figure 6. **Pulsed H_2 adsorption results at 800°C for two batches of powdered $AB_{0.8}B_{0.2}^{c}O_{3-\delta}$ (Samples A and C) and Sample A with 25% Pd.**

Although the mechanism for the H_2 adsorption dependence on pulse is unclear, both samples without Pd absorbed significant quantities of H_2 at 800°C and addition of Pd increased high-temperature H_2 adsorption.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

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. To date, differential pressures greater than 250 psi were achieved with selected compositions. Additional compositions were tested during this quarter; however, no improvement relative to previous results were obtained.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: Eltron, CoorsTek

A series of thin film membranes on porous supports were prepared at Eltron and sent to CoorsTek to test conditions for binder burn out and sintering. The sintered structures appeared flat, homogeneous, and defect-free. However, after storage in air for several days, cracks formed across the membrane surface. It is possible that cracking was caused by uptake of moisture from air at room temperature, and this occurrence might be responsible for the lack of adequate seals during previous attempts to evaluate thin films for H_2 permeation. A second series of "green" samples were prepared for sintering at CoorsTek. These samples will be stored in a desiccator after sintering in an attempt to overcome this problem.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: CoorsTek, Eltron

Thin-walled cermet tubes will be used with the high-pressures seals developed in Task 3 to produce a demonstration-scale separation unit for proton-conducting ceramics. During this quarter, thin-walled cermet tube membranes were sintered using different configurations to optimize tube roundness. A preferred configuration was identified that resulted in 0.5-mm thick tubes that were only 0.10 to 0.15 mm out of round. For comparison, using a conventional sintering configuration resulted in tubes that were typically about 0.8 mm out of round.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

The experiments described in the previous report were repeated using a Pt-coated 0.13-mm thick metal-based membrane instead of a cermet. The feed gas was humidified 80 mL/min of 10% propane (bal. Ar) and 15 mL/min He. The sweep gas was 80 mL/min air and 40 mL/min Ar. The maximum temperature tested was only 550°C, and as a result the maximum propane conversion and propene yield were only about 8% and 3%, respectively (compared to 18% and 4% at 650°). However, despite the lower extent of dehydrogenation, hydrogen permeation through the membrane was about the same at 0.01 mL/min/cm^2. Also, very little coke formation was apparent on the membrane surface, likely due to addition of humidity in the feedstream.

SUMMARY AND CONCLUSIONS

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

- Layered composites containing metals with high H_2 permeability demonstrated good long-term stability. Permeation at 320°C decreased by 17% from 11.4 to 9.5 mL·min^{-1}·cm^{-2} (STP) during 1300 hours of continuous operation.

- These membranes were not affected by high levels of CO_2; however, 3 vol.% CO reduced permeation to 75% of its original value. Similarly, addition of 5 to 10 vol.% steam dropped permeability to roughly 50% of its original value.

- Cermets incorporating 40 to 60 vol.% of the same H_2-permeable metals as the layered structures had much lower permeation, showing a maximum of only 0.65 mL·min^{-1}·cm^{-2} (STP) at 800°C.

- New mixed proton/electron conducting cermets achieved a maximum permeation of approximately 0.17 mL·min^{-1}·cm^{-2}, corresponding to an apparent ambipolar conductivity of 0.003 S/cm. These results were slightly lower than previous analogs.

- Replacing the metal phase with an electron-conducting ceramic reduced permeation to 0.025 mL·min^{-1}·cm^{-2} and ambipolar conductivity to below 0.001 S/cm. However, these ceramic/ceramic composites demonstrated very high corrosion resistance under extreme conditions.

- Cermets prepared with smaller grain precursor powders sintered better and were more dense than the large grain analogs.

- A selected proton-conducting ceramic demonstrated significant H_2 uptake at high temperature (800°C), and uptake was dramatically increased by incorporation of Pd.

- Uptake of moisture from air was identified as a potential cause of defects in thin film membranes.

- A sintering configuration for tube membranes was identified that enabled fabrication of very round samples with a wall thickness of only 0.5 mm.

- Layered metal membranes demonstrated H_2 permeation during alkane dehydrogenation equivalent to cermets, but at a temperature 100°C lower.

OBJECTIVES FOR NEXT REPORTING PERIOD

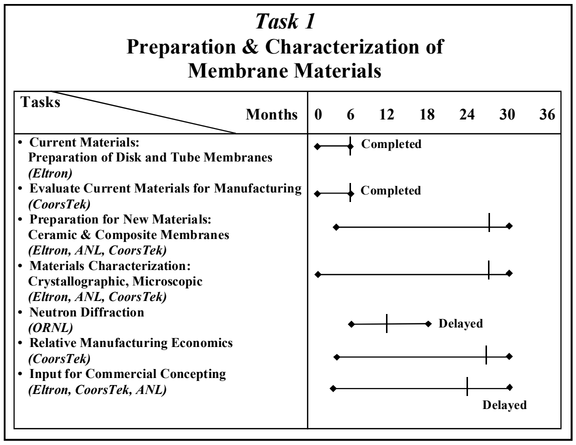
Eltron will focus on screening a variety of layered metal alloy membranes due to the very high flux, intermediate operating temperature, long-term permeation stability, apparent chemical resistance for selected species, and economics. High-pressure testing also will be continued. CoorsTek will continue development of ceramic/ceramic composites, and CoorsTek and ANL will continue development of cermets. Süd Chemie will continue TPR measurements on potential catalysts.

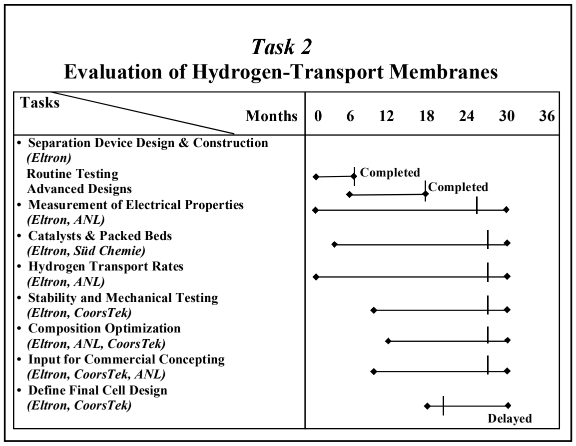
OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

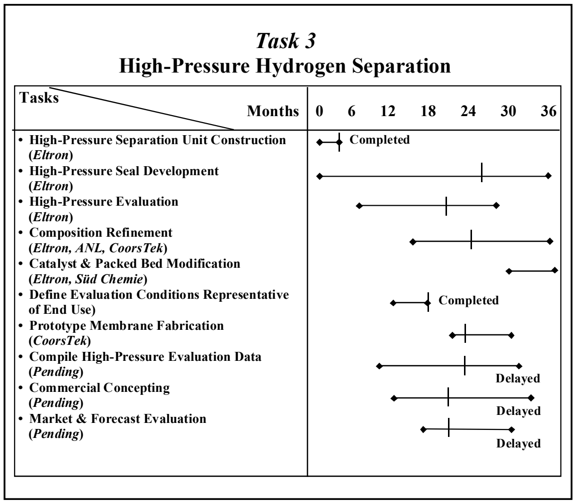
Several tasks shown in the following Time Line have been delayed pending replacement of MTI in this consortium.

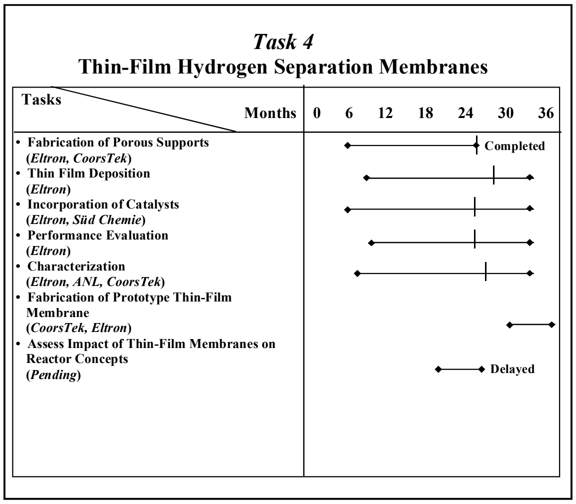
TIME LINES

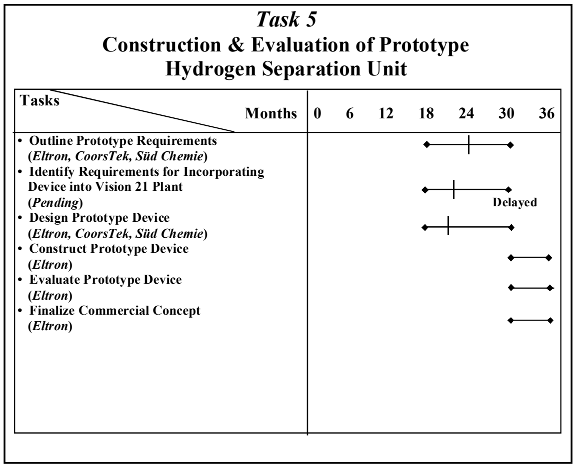
The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

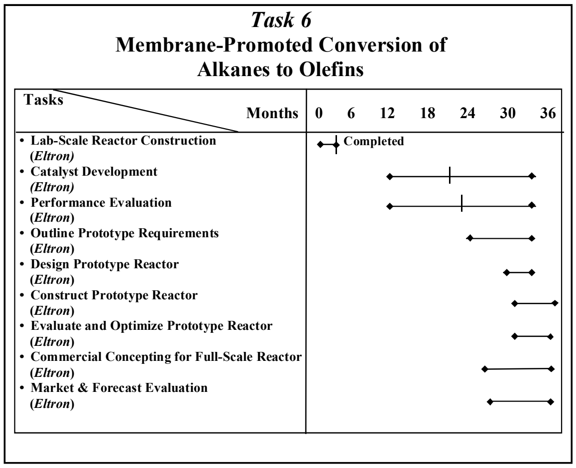












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