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DISCLAIMER

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) 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 presents hydrogen permeation data during long term tests and tests at high pressure in addition to progress with cermet, ceramic/ceramic, and thin film membranes.

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), and Argonne National Laboratory (ANL).

Layered composite membranes containing inexpensive metals with high H_2 permeability demonstrated good long-term stability. High permeation has been maintained near 8 $mL \cdot min^{-1} \cdot cm^{-2}$ at 320°C and ambient pressure for over 154 days. Moreover, analogous membranes demonstrated stable permeation rates over 20 $mL \cdot min^{-1} \cdot cm^{-2}$ at a differential pressure of 250 psi. Improvements were made in the fabrication process for cermets containing these metals and dense, strong membranes with only the desired phases were prepared. A relatively thick membrane sample achieved a permeation rate of 3.6 $mL \cdot min^{-1} \cdot cm^{-2}$ at only 320°C, corresponding to a very high permeability of 1.9×10^{-7} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$. This permeability was roughly an order of magnitude higher than pure Pd. Also described in this report is progress with cermet, ceramic/ceramic, and thin film membranes.

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

Figure 1 shows hydrogen permeation measurements over 154 days for a layered metal/ceramic composite 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 500 hours of operation, permeation remained steady at approximately 11.5 $mL\cdot min^{-1}\cdot cm^{-2}$ with permeability greater than 6 x 10^{-8} $mol\cdot m\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-0.5}$. Between 500 and 1700 hours, there was a slow loss of performance; however, beyond 1700 hours permeation and permeability remained stable at roughly 8 $mL\cdot min^{-1}\cdot cm^{-2}$ and 4 x 10^{-8} $mol\cdot m\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-0.5}$, respectively.

Figure 2 indicates that these composite structures also function very well at high pressure. The data show permeation as a function of H_2 feed concentration at 360°C and a differential pressure of 250 psi. Permeation increased from approximately 9 to 22 $mL\cdot min^{-1}\cdot cm^{-2}$ as the H_2 feed concentration increased from 10 to 40 vol.%. Currently, this membrane has been in operation at 250 psi for over 150 hours, and permeation dependence on temperature is being tested.

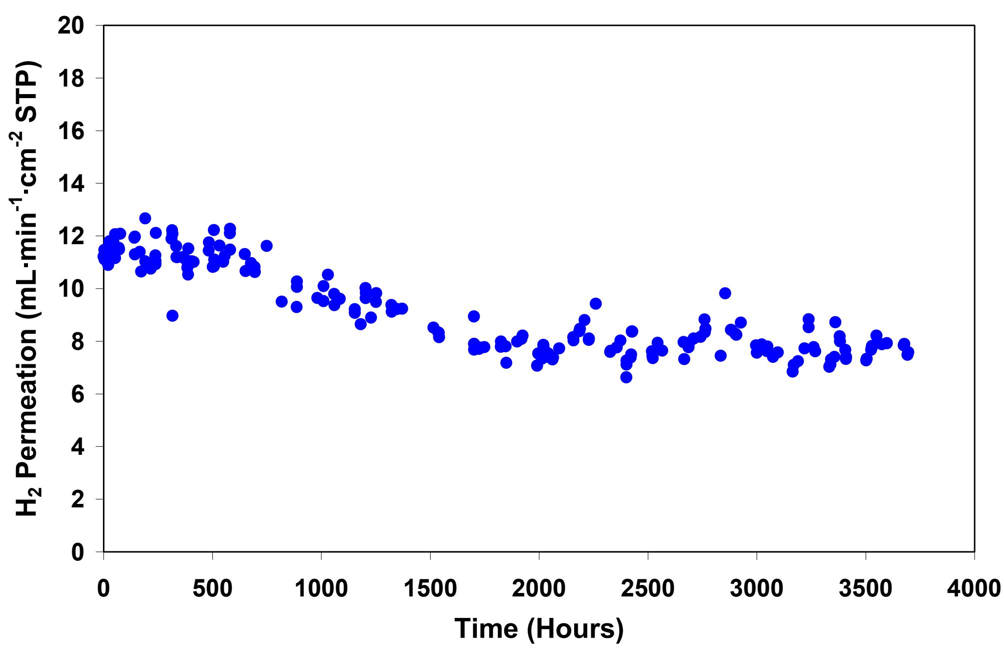


Figure 1. Hydrogen permeation over time at 320°C for a layered metal/ceramic composite membrane. The feed gas was 80 mL/min 80/20 H_2/He, and the sweep gas was 250 mL/min Ar.

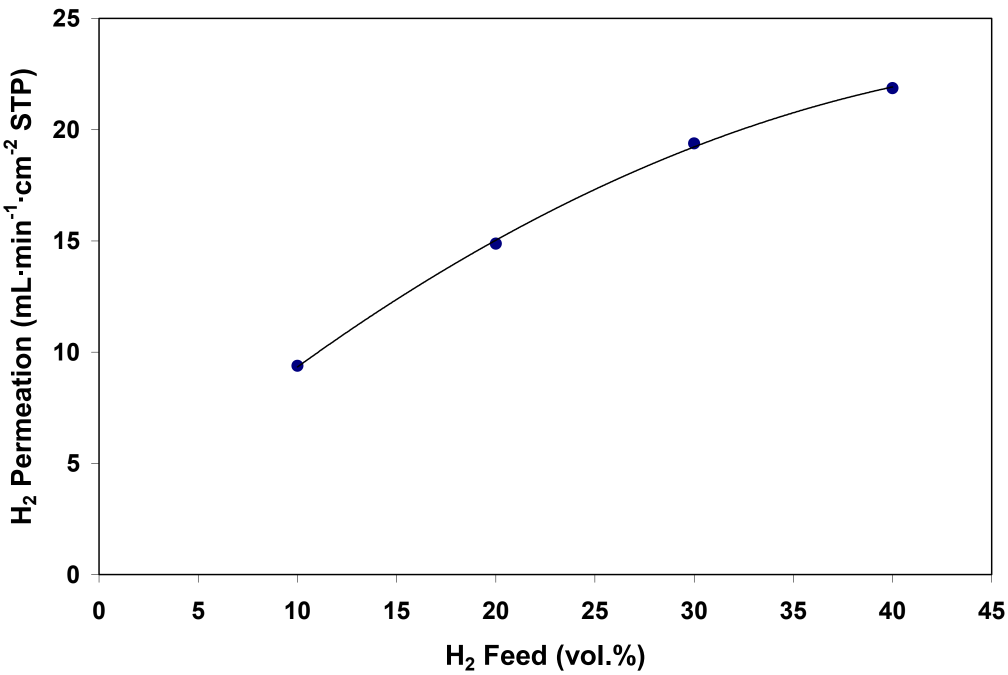


Figure 2. Hydrogen permeation as a function of feed concentration at 360°C and a differential pressure of 250 psi. The membrane was a layered composite.

Three additional samples with different metal phase compositions also were tested at high pressure. These samples demonstrated similar characteristics to those in Figures 1 and 2, although the maximum flux was lower. Additionally, ambient pressure tests were performed on 16 different layered metal membranes and effort is underway to identify compositions capable of high permeation and desirable mechanical properties.

II. Cermets Containing Metals with High Hydrogen Permeability – Eltron

Incorporating the main metal components of the above layered composites into a ceramic matrix might improve ruggedness and versatility and simplify manufacturing. In the previous report, cermet analogs were shown to have much lower permeation and operate at much higher temperatures than the above layered metal structures, even after accounting for the lower quantity of metal and the increased membrane thickness. However, recent results summarized in Figure 3 demonstrated a maximum permeation of 3.6 $mL \cdot min^{-1} \cdot cm^{-2}$ at only 320°C for a cermet containing 60 vol.% of a relatively inexpensive H_2-permeable metal. Moreover, the membrane was relatively thick (0.8 mm), thus this permeation rate translated into a very high permeability of 1.9×10^{-7} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$ — more than an order of magnitude greater than pure Pd. 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.

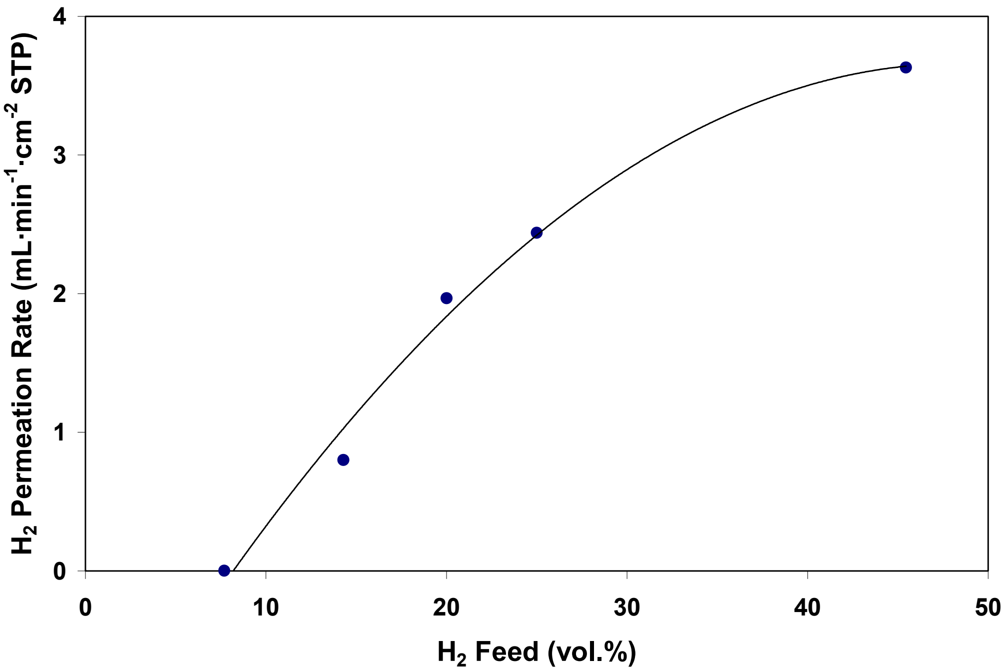


Figure 3. Hydrogen permeation rate as a function of feed concentration for a 0.8-mm thick cermet at 320°C.

III. Two-Phase Ceramic/Ceramic Composites: Performance and Corrosion Resistance – CoorsTek, Eltron

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.

Table 1 summarizes the performance of several compositions tested during this quarter. Included in the table are three compositions that also contained a metal phase. Generally, the performance of these materials with or without the metal phase was only slightly lower than cermet analogs. For samples based on proton-conducting ceramics, humidity in the feedstream typically improves performance. However, when a continuous layer of Pd catalyst was applied, humidity either decreased performance or had no effect. For the ceramic/ceramic samples, CER2 was better than CER1, and performance improved when the CER2 content increased. The samples containing a metal phase all behaved similarly. Performance was not likely improved by Pd since the metal phase had very good catalytic activity for H_2 dissociation.

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. The general conclusions from these tests are that CER2 improved corrosion resistance more than CER1 or a metal phase, and corrosion resistance improved with increasing CER2 content. A sample containing 34.4 wt.% CER2 demonstrated only a 0.03-% weight loss after boiling in water for two hours. The corrosion resistance of the ceramics was higher than the cermets, but the difference became less significant at greater than 25 wt.% CER2.

Based on these results, addition of a stabilizing ceramic phase appears to be a viable approach for improving the performance of H_2 permeable materials using proton-conducting ceramics. If the H_2 permeation rates of these materials prove to be to low for commercial viability, it is possible that derivatives of these materials will have application in H_2 separation technology as protective barrier coatings in layered membranes.

Table 1.
Performance Summary for Multiphase Ceramic Composite Membranes

Sample	Thickness (mm)	Catalyst	Max. Permeation ($mL\cdot min^{-1}\cdot cm^{-2}$)	Max. Conductivity (S/cm)
65%$AB_{0.8}B^c_{0.2}O_{3-\delta}$/35%CER2	0.63	0.5 µm Pd	0.54 at 893°C (humid)	1.12×10^{-2} S/cm
75%$AB_{0.8}B^c_{0.2}O_{3-\delta}$/25%CER2	0.91	0.5 µm Pd	0.028 at 950°C (dry)	8.00×10^{-4} S/cm
75%$AB_{0.8}B^c_{0.2}O_{3-\delta}$/25%CER1	0.21	Pt islands	0.03 at 850°C (humid)	1.69×10^{-4} S/cm
39%$AB_{0.8}B^c_{0.2}O_{3-\delta}$/21%CER2/40%MET1	0.47	0.5 µm Pd	0.094 at 725°C (dry)	1.96×10^{-3} S/cm
51%$AB_{0.8}B^c_{0.2}O_{3-\delta}$/9%CER1/40%MET1	0.67	0.5 µm Pd	0.068 at 800°C (humid)	2×10^{-3} S/cm
51%$AB_{0.8}B^c_{0.2}O_{3-\delta}$/9%CER1/40%MET1	0.46	None	0.065 at 850°C (humid)	1×10^{-3} S/cm
			0.029 at 850°C (dry)	4×10^{-4} S/cm

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

Effort at ANL continued a study of the effect of metal grain size on the hydrogen permeation flux of ANL-1a membranes based on proton-conducting ceramics. ANL-1a membranes that contain metal with a small grain size have had a problem of high electrical resistance. In this quarter, conditions were identified for fabricating small-grain-metal ANL-1a membranes that are conductive. The effect of metal grain size on hydrogen permeation was studied by comparing the permeation rates of a small-metal-grain ANL-1a membrane and a large-grain membrane with similar thickness.

A series of membranes were prepared that contained 40, 42, 44, 46 and 48 vol.% of small-grain-metal powder (0.08 to 0.18 µm). When the metal content was less than 46 vol.%, the membrane was insulating, suggesting that the metal grains were isolated from one another. When the metal content was 46 vol.%, the resistance depended on where the multimeter leads contacted the membrane, with readings varying from several hundred ohms to insulating. This suggests that metal grains were beginning to connect to one another but had not formed a completely continuous three-dimensional network. At 48 vol.%, the membrane was conductive, indicating that a three-dimensional network of metal had been formed. Microstructures of these samples were determined from back-scattered images (BEI). Compared with microstructures for membranes with 40, 42, and 44 vol.% metal, the metal grains were more irregularly shaped and had a broader size distribution when the metal content was 46 and 48 vol.%. The larger grain size and the irregular shape of the metal grains are both favorable to forming a continuous metal network, which is consistent with the conductivity results. These observations suggest that discontinuity of metal phase probably caused the small-grain-metal ANL-1a membrane to be insulating.

The sintering atmosphere can also affect the continuity of the metal phase, so the sintering atmosphere was changed to 200 ppm H_2 while keeping other conditions the same. All membranes sintered in this way were conductive. Starting at 40 vol.% metal, the shape of metal grains became more irregular and the metal grain size showed a broader distribution. Both could contribute to the formation of a continuous metal phase.

Figure 4 shows the hydrogen permeation of two ANL-1a membranes versus temperature, one made with small-grain metal and the other with large-grain metal. Both membranes contained 40 vol.% metal. The membrane with small-grain metal was sintered in 200 ppm H_2, that with large-grain metal was sintered in 4% H2. The feed gas for permeation measurements was wet 4% H_2/balance He, i.e., dry 4% H_2/balance He was bubbled through water at room temperature to give ~3% H_2O. For comparison, the flux of the large-grain-metal membrane was normalized to 0.2 mm thick, the thickness of the membrane with small-grain metal. The flux of the small-grain membrane increased from 0.09 to 0.11 cm^3(STP)/cm^2-min as temperature increased from 600-900°C, while the flux of large-grain membrane increased from 0.14 to 0.17 cm^3(STP)/cm^2-min. These permeation results were counterintuitive. Decreasing the grain size increases the triple-phase-boundary at the membrane surface and hence decreases the surface resistance. This effect is expected to increase the flux of the membrane if the membrane is thin, or if the membrane is thick, have no effect on the flux. These results show that the small-grain-metal membrane gave lower flux, as seen in Figure 4. This result was not expected and will be further investigated.

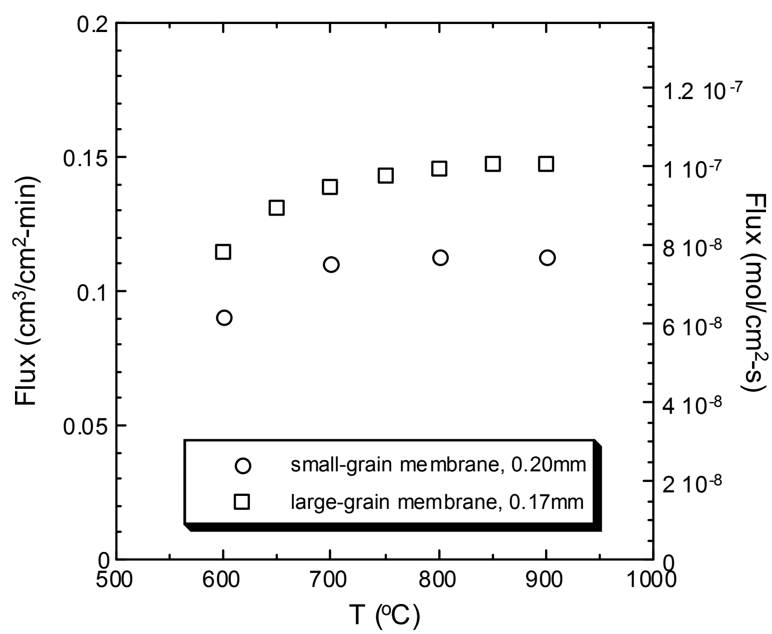


Figure 4. Hydrogen permeation of ANL-1a membranes vs. temperature with a feed gas of wet 4% H2 /He (containing ~3% H2O). Flux of large-grain membrane was normalized to 0.2-mm-thick for comparison. The actual thickness was 0.17mm.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

During this quarter, high-pressure seals were achieved using very flat samples and a compression flange assembly with annealed copper seal rings. This assembly is only good for planar membranes; however, as described above and shown earlier in Figure 2, stable permeation in excess of 20 $mL \cdot min^{-1} \cdot cm^{-2}$ was achieved at a differential pressure of 250 psi with zero leak rate. Depending on the ceramic content of the sample, careful attention must be directed to the torque on the connector bolts of the compression flange. Attaining perfect high pressure seals with this assembly now is routine and four different compositions were tested during this quarter.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: Eltron, CoorsTek

Effort was continued to produce tape cast laminate membranes using mixed proton/electron conducting membrane compositions. Four sets of thin film membranes on porous supports were prepared at Eltron and sent to CoorsTek to test conditions for binder burn out and sintering. A variety of defects were observed in the membranes that likely were due to problems associated with uncontrollable variables in the cast tape rather than the curing cycle.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: Eltron

In addition to the thin-walled cermet tubes described in the previous report, a stacked planar configuration also will be pursued for selected membrane compositions, *i.e.* layered composite membranes. During this quarter, designs were drafted and suppliers were identified to construct a small multi-membrane assembly with a total membrane surface are of 20 cm^2. If this configuration proves scalable, then the total membrane area can be increased in 10 cm^2 increments while maintaining a very small demonstration-scale unit.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

To increase propane to propene conversion and take greater advantage of the hydrogen separation membrane, catalyst beads were prepared and will be used to fill the dehydrogenation cell. It is expected that the higher conversion and H_2 concentration on the feed side will amplify the effect of the membrane relative to previous experiments.

SUMMARY AND CONCLUSIONS

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

- Layered composite membranes containing inexpensive metals with high H_2 permeability demonstrated good long-term stability. High permeation has been maintained near 8 $mL \cdot min^{-1} \cdot cm^{-2}$ at 320°C and ambient pressure for over 154 days. Moreover, analogous membranes demonstrated stable permeation rates over 20 $mL \cdot min^{-1} \cdot cm^{-2}$ at a differential pressure of 250 psi.

- Improvements were made in the fabrication process for cermets containing the above metals and dense, strong membranes with only the desired phases were prepared. A relatively thick membrane sample achieved a permeation rate of 3.6 $mL \cdot min^{-1} \cdot cm^{-2}$ at only 320°C, corresponding to a very high permeability of 1.9×10^{-7} $mol \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-0.5}$.

- Addition of a stabilizing ceramic phase appears to be a viable approach for improving the performance of H_2 permeable materials based on proton-conducting ceramics.

- For cermets based on proton-conducting ceramics, it was determined that when the metal grain size was small, a higher metal content was necessary to achieve continuity. Additionally, despite an assumed decrease in surface resistance for H_2 transport with small-metal-grain samples, H_2 transport was higher for samples with larger metal grain size.

- High pressure seals easily were attained using a compression flange with annealed copper seal rings. Although this assembly only is good for planar membranes, a stacked configuration will allow high total membrane surface area.

OBJECTIVES FOR NEXT REPORTING PERIOD

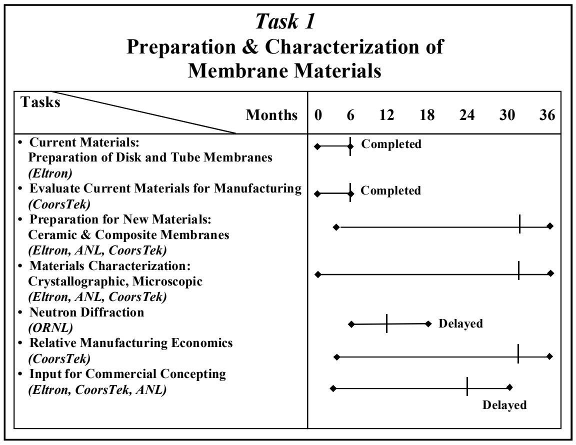
Eltron will continue screening a variety of layered metal alloy membranes due to the very high flux, intermediate operating temperature, long-term permeation stability, high-pressure tolerance, apparent chemical resistance for selected species, and economics. CoorsTek will focus on development of thin film membranes, and ANL will continue testing the relationship between microstructure and H_2 permeation of cermets.

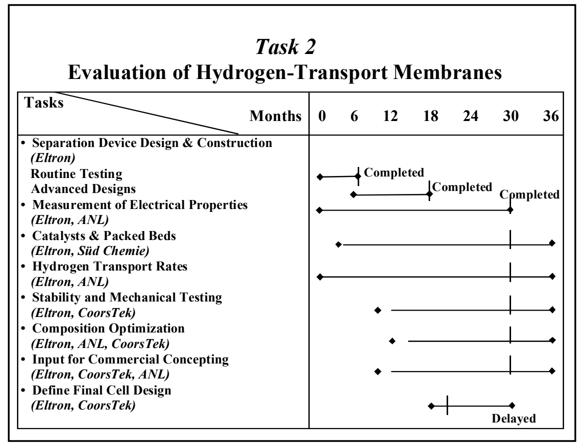
OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

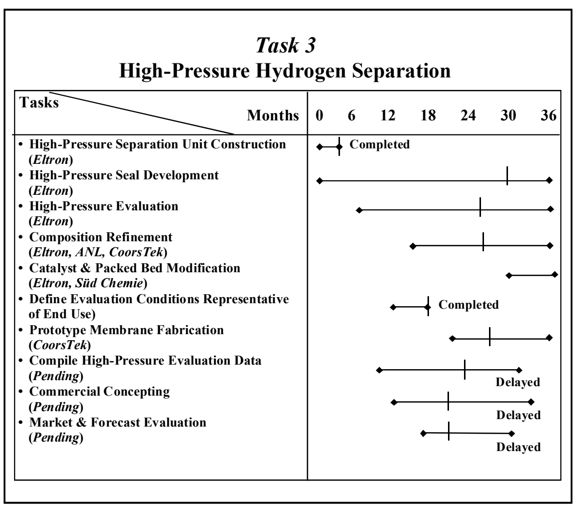
Several tasks shown in the following Time Line have been delayed pending replacement of MTI in this consortium.

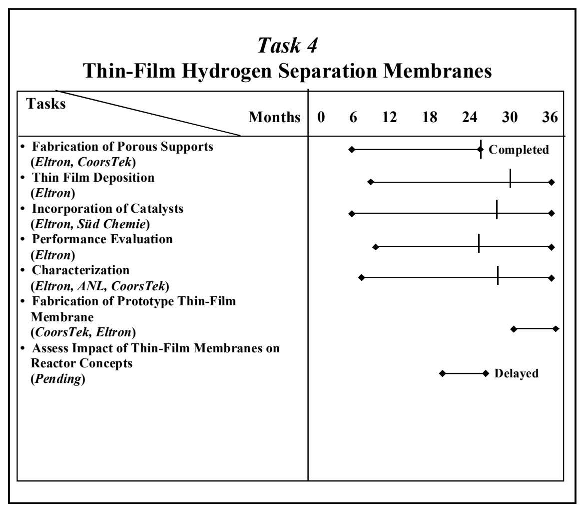
TIME LINES

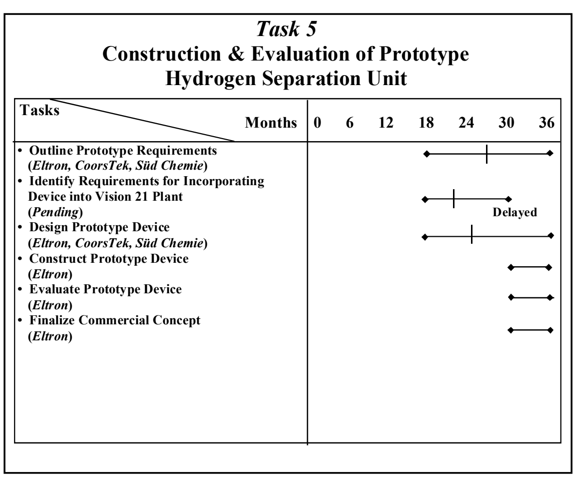
The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

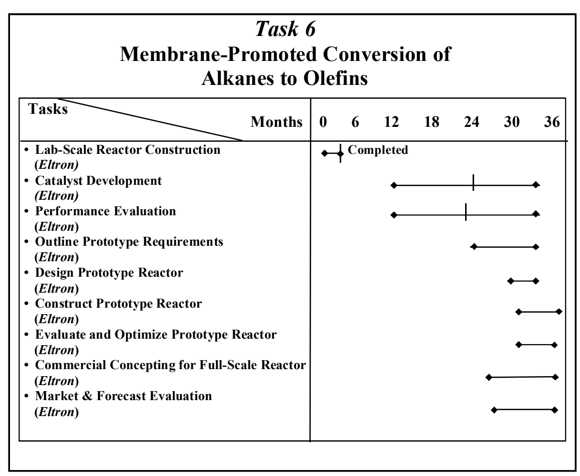












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