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ABSTRACT

Eltron Research Inc., and team members CoorsTek, McDermott Technology, Inc., Süd Chemie, Argonne National Laboratory, and Oak Ridge 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. This objective is being pursued using dense membranes based in part on Eltron-patented ceramic materials with a demonstrated ability for proton and electron conduction. The technical goals are being addressed by modifying single-phase and composite membrane composition and microstructure to maximize proton and electron conductivity without loss of material stability. 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.

During this quarter, measurements of H_2 permeation as a function of membrane thickness were continued for selected ceramic/metal (cermet) compositions. A 0.16-mm thick cermet membrane enabled H_2 permeation at a rate of 0.84 mL/min/cm^2 at 950°C, which was the highest rate to date for this category of membranes. The increase in H_2 flux with decreasing cermet membrane thickness indicated that the H_2 permeation mechanism remained largely dependent on bulk transport in this thickness range. When the metal phase of this cermet composition was replace with a metal of known high H_2 permeability, H_2 flux increased dramatically. For this category of cermet, a 0.43-mm thick membrane enabled a H_2 permeation rate of 1.8 mL/min/cm^2 at 950°C, and greater than 1 mL/min/cm^2 at only 650°C. Also described in this report are recent results and overall progress regarding manufacturing and surface catalysis issues of candidate materials. Finally, new high-pressure seal formulations achieved a pressure differential of 207 psig, which was more than twice as high as previous results.

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. This objective will be accomplished by employing dense ceramic and composite membranes based in part on Eltron-patented materials[1-3] with a demonstrated ability for rapid hydrogen ion and electron conduction. The primary technical challenge in achieving the goals of this project will be to optimize membrane composition and microstructure 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, McDermott Technology, Inc. (MTI), Süd Chemie, Inc. (SCI), Argonne National Laboratory (ANL), and Oak Ridge National Laboratory (ORNL).

Currently two basic categories of membranes are under development: i) ceramic/metals (cermets) and ii) multi-phase ceramics. The cermets demonstrate several advantages, such as higher H_2 permeation rates, better structural stability, and the fact that the metal phase acts as an excellent catalyst for promoting the surface process. Unfortunately, the metal phase will be particularly susceptible to sulfur poisoning. Early sulfur stability measurements of multi-phase ceramics also demonstrated reactivity with sulfur, but conceivably it will be easier to design ceramics with some sulfur tolerance. By the end of this project it is anticipated that the final membrane compositions will include a cermet designed for maximum H_2 permeation and used only in concert with desulfurization, and a ceramic composite with greater chemical stability (sulfur tolerance, in particular), but lower H_2 permeation.

During this quarter, measurements of H_2 permeation as a function of membrane thickness were continued for selected cermet compositions. A 0.16-mm thick cermet membrane enabled H_2 permeation at a rate of 0.84 mL/min/cm^2 at 950°C, which was the highest rate to date for this category of membranes. The increase in H_2 flux with decreasing cermet membrane thickness indicated that the H_2 permeation mechanism remained largely dependent on bulk transport in this thickness range. When the metal phase of this cermet composition was replace with a metal of known high H_2 permeability, H_2 flux increased dramatically. For this category of cermet, a 0.43-mm thick membrane enabled a H_2 permeation rate of 1.8 mL/min/cm^2 at 950°C, and greater than 1 mL/min/cm^2 at only 650°C. Also described in this report are recent results and overall progress regarding manufacturing and surface catalysis issues of candidate materials. Finally, new high-pressure seal formulations achieved a pressure differential of 207 psig, which was more than twice as high as previous results.

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 conductivity apparatus, (e) construction and operation of ambient-pressure hydrogen separation units, (f) construction and operation of high-pressure hydrogen separation units, (g) hydrogen transport and ambipolar conductivity measurements and calculations, and (h) 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, MTI, SCI, ORNL

I. Cermet Membranes - Eltron, CoorsTek

Measurements of H_2 permeation dependence on membrane thickness were continued during this quarter for cermet membranes with the general composition $AB_{0.8}B^c_{0.2}O_{3-\delta}$/44 wt.% metal. The metal phase for this material had high catalytic activity for promoting H_2 dissociation, but low (negligible) H_2 permeability. Four membranes were prepared with an initial thickness > 3 mm, then sanded down to 1.2, 1.0, 0.80, and 0.16 mm, respectively. Each side was sanded flat, then polished prior to testing. The results are summarized in Figure 1, and clearly show a substantial increase in H_2 permeation with decreasing membrane thickness. The increase in permeation was roughly inversely proportional to the membrane thickness, which suggested that bulk diffusion of H_2 was rate limiting, rather than interfacial reacion kinetics.[4] However, interfacial resistance does become

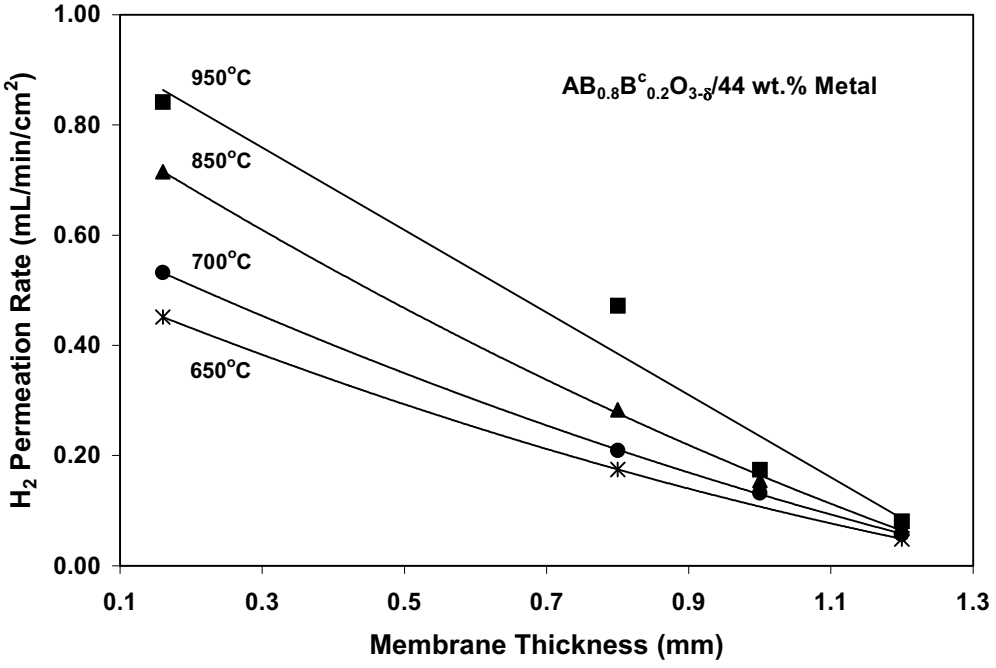

Figure 1. Plot showing H_2 permeation rate as a function of cermet membrane thickness. The inlet gas was 80 vol.% H_2 (bal. He), and the sweep gas was Ar.

significant for thin membranes, and this effect was evident by a slight increase in apparent activation energy for H_2 permeation as membrane thickness decreased.

The thinnest membrane in Figure 1 (0.16 mm) generated the highest H_2 permeation rate to date for this category of materials. Figure 2 shows H_2 permeation as a function of temperature under both dry and humid conditions. At 950°C, a maximum permeation rate of 0.84 mL/min/cm^2 was achieved. Moreover, at only 650°C, permeation was still significant at 0.45 mL/min/cm^2. Permeation was approximately twice as high under humid conditions than dry, which was a slightly larger difference than what is typically observed. Since moisture interacts more favorably with the ceramic surface than dry H_2, this result might reflect the greater contribution of surface kinetics to the rate limiting step of the overall permeation process for thinner membranes. However, in this case it also would be expected that moisture would improve transport more at lower temperatures than higher temperatures, which was not observed.

Figure 3 shows Arrhenius plots of conductivity (apparent, based on H_2 permeation) versus temperature, which indicated an activation energy of 0.23 eV under humid conditions compared to only 0.19 eV under dry conditions. The data fit well to a straight line, which suggested that the permeation mechanism did not change over this temperature range. Ambipolar conductivity for this sample over the temperature range shown in Figures 2 and 3 varied from 1.7 x 10^{-3} S/cm (650°C, dry) to 5.2 x 10^{-3} S/cm (950°C, humid). Since the metal phase of these materials was continuous (*i.e.*, negligible electron resistance), the ambipolar conductivity was roughly equal to the proton conductivity. However, since conductivity was calculated based on H_2 transport, the values incorporate surface polarization and are, therefore, underestimated.

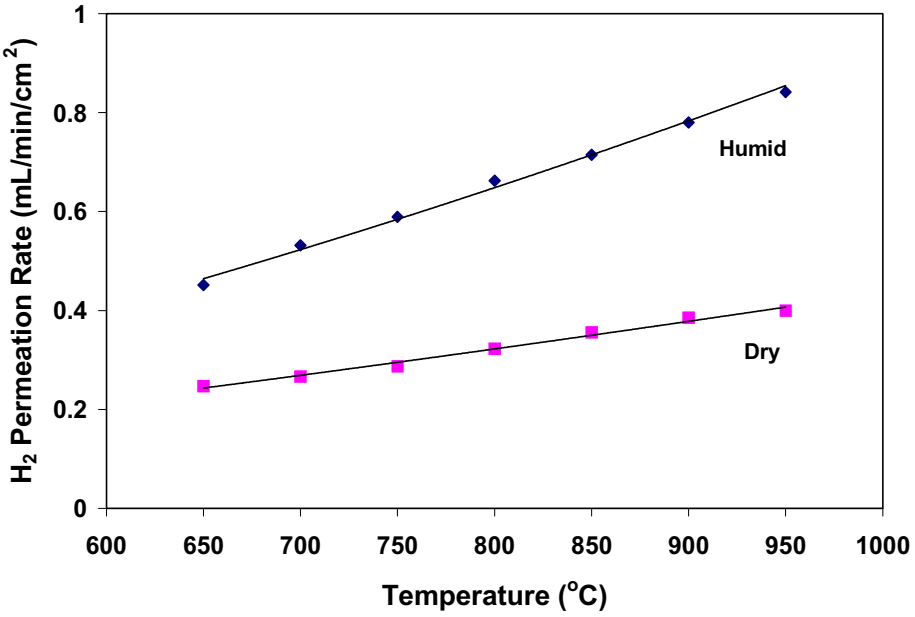

Figure 2. Plot showing H_2 permeation as a function of temperature for a 0.16-mm thick cermet membrane with the general composition $AB_{1-x}B^c_xO_{3-\delta}$/44 wt.% metal. The inlet gas was 80 vol.% H_2 (bal. He) and the sweep gas was Ar.

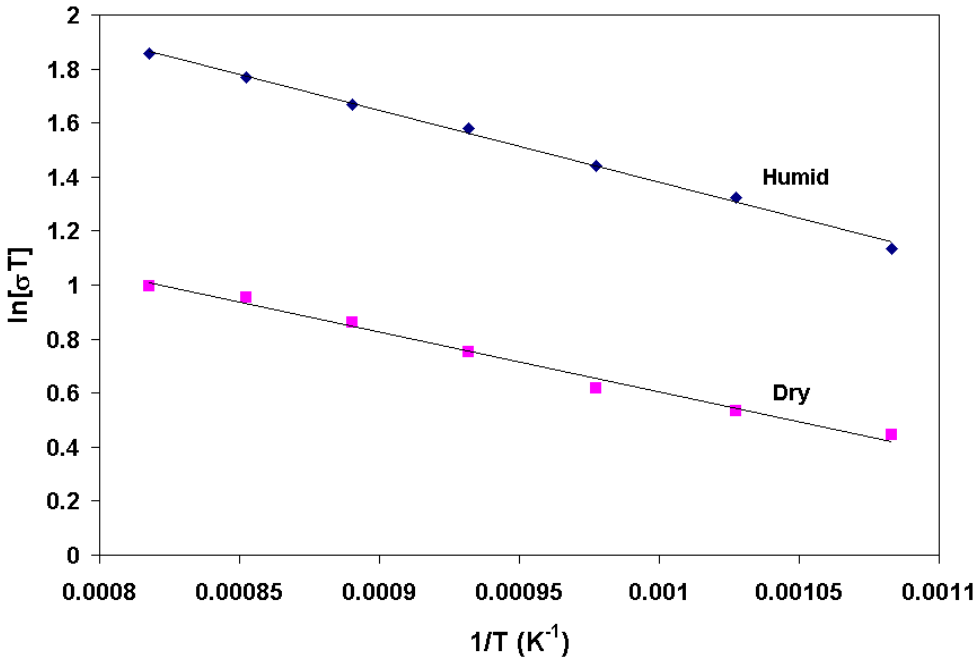

Figure 3. Arrhenius plot showing conductivity (apparent ambipolar) versus temperature for a cermet membrane with the general composition $AB_{1-x}B^{c}_{x}O_{3-\delta}$/44 wt.% metal.

II. Cermets Containing a H_2-Permeable Metal - Eltron

As an alternative to the above cermets, materials also were tested with the general composition $AB_{1-x}B'_xO_{3-\delta}$/40 vol.% metal, where the metal phase has high H_2 permeability. These materials were described briefly in Report 4 (October 30, 2001), and analogous materials were described by others.[5, 6] Figure 4 shows the H_2 permeation rate as a function of temperature for two membranes with different ceramic compositions. Both membranes were approximately 1 mm thick, and the permeation rates observed were several times higher than ceramic membranes without the metal phase. The sample with the ABO_3 ceramic had higher maximum H_2 permeability at 0.60 mL/min/cm^2, however, at lower temperatures permeability was higher using the $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ ceramic. The fact that the ceramic phase influenced permeability suggested that the permeation mechanism was not exclusively associated with the metal phase. Furthermore, the data in Figure 4 also demonstrated that humidity improved permeation, which is a quality associated with the ceramic phase.

Figure 5 shows H_2 permeation rates as a function of temperature for three membrane thicknesses. At 950°C, reducing membrane thickness from 1.1 to 0.43 mm increased permeation from 0.47 to 1.8 mL/min/cm^2, which significantly exceeded the inverse thickness dependence. Furthermore, the 0.43-mm thick membrane enabled H_2 permeation greater than 1 mL/min/cm^2 at only 650°C.

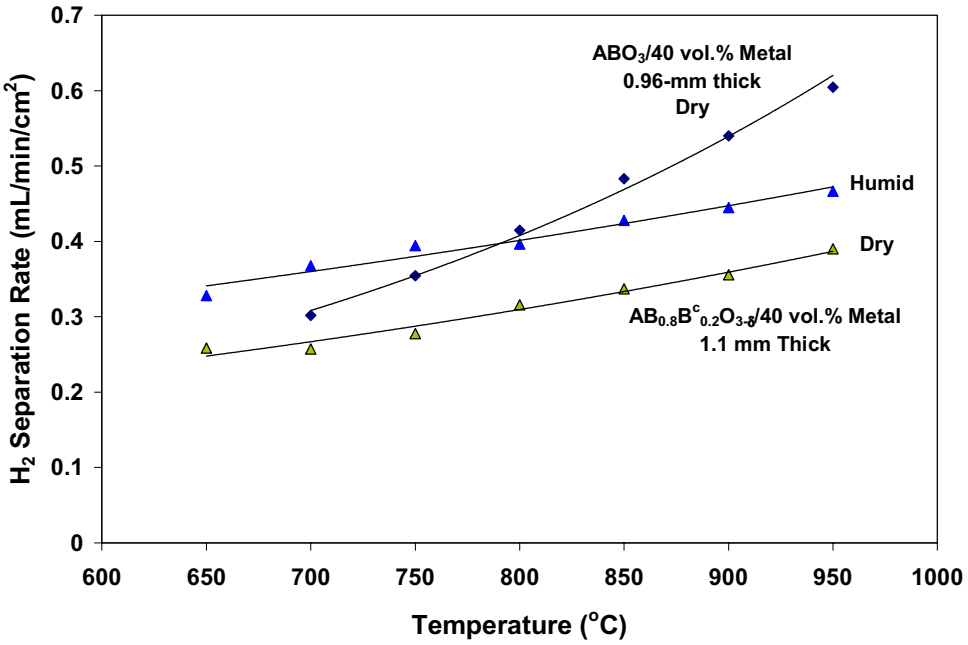

Figure 4. **Plot showing H_2 permeation versus temperature for two cermet membranes containing a H_2-permeable metal. The inlet gas was 80 vol.% H_2 (bal. He) and the sweep gas was Ar.**

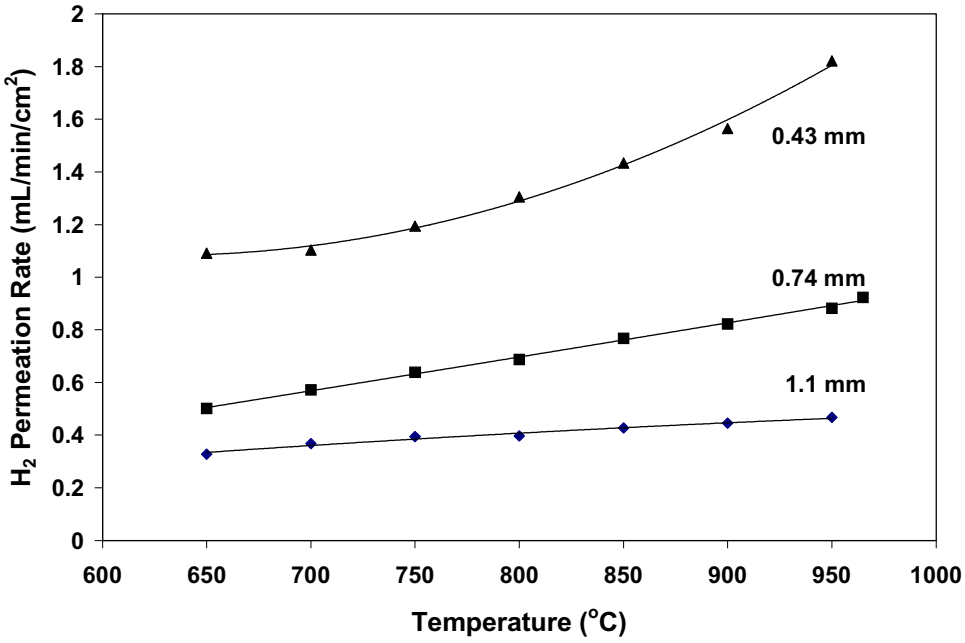

Figure 5. **Permeation data for cermet membranes of different thicknesses containing a metal with high H_2 permeability. The inlet gas was 80 vol.% H_2 (bal. He) and the sweep gas was Ar.**

III. Manufacturing Issues and Relative Economics - CoorsTek, Eltron

The following section details specific membrane manufacturing issues addressed by CoorsTek. This report includes results and conclusions regarding cermet and ceramic compositions that have been the current focus of this project.

A. Results Summary

The status on the development of the candidate cermet and ceramics fabricated by CoorsTek are summarized as follows. Details are provided below.

- Cermet: $AB_{0.7}B^{a}_{0.3}O_{3-\delta}$/44 wt.% Metal

The conductivity and hydrogen permeability performance results on these samples were not as good as the results on the B^{c} -substituted series. Stability of this formulation appears to be a problem with delayed cracking occurring on exposure to ambient conditions.

- Cermet: $AB_{0.9}B^{a}_{0.1}O_{3-\delta}$/44 wt.% Metal

The conductivity and hydrogen permeability results on these samples were in the same range as the previous cermet. Two samples tested did not reproduce well, possibly because the low concentration of B^{a} is difficult to evenly distribute throughout the entire structure. The material also exhibited two vastly different morphologies with one appearing as a layered, laminated structure.

- Cermet: $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% Metal

The performance tests on these samples were the best of all the samples tested to date. The morphology of these samples exhibited a needle-like structure. The sample fired in forming gas at 1415°C exhibited approximately twice the performance of the sample fired in nitroneal at 1425°C.

- Ceramic: $AB_{0.8}B^{b}_{0.2}O_{3-\delta}$

SEM microstructure revealed the presence of a second phase with all the B^{b} distributed within it along with some A. XRD patterns indicated the presence of an unidentified minor phase, which probably reflected the presence of this A-B^{b} phase observed in SEM images.

B. Evaluate Current Baseline Materials for Manufacturing

- ABO_3 — No further activity planned.

The fired density of 6.27 g/cc has been reproduced on several batches made from this formulation. It fulfilled its purpose as a baseline to transfer perovskite processing technology to CoorsTek.

C. Preparation of New Materials: Ceramic and Cermet Composite Membranes

1. B^a-Substituted ABO_3

a. Ceramic: $AB_{0.2}B^a_{0.8}O_{3-\delta}$

Fabrication. The optimum firing condition determined for this formulation was ~1475°C. The density of this formulation was ~ 6.0 g/cc. Eltron made the decision to stop further development work on this formulation due lack of a hydrogen ion conducting phase and chemical instability of secondary phases.

b. Ceramic: $AB_{0.7}B^a_{0.3}O_{3-\delta}$

Fabrication. The optimum firing condition determined for this formulation was ~ 1475°C. The fired density of this formulation was ~ 6.2 g/cc. Fired parts exhibited a ABO_3 phase and at least one additional unidentified phase. Eltron reported good separation and transport properties of this material. Since there are applications that contain significant quantities of S in the feedstream, Eltron recommended that we revisit ceramic materials with better S tolerance than the metal phase of the cermets. Ceramic materials such as this one will be evaluated in parallel with the cermet materials.

c. Cermet: $AB_{0.7}B^a_{0.3}O_{3-\delta}$/44 wt.% Metal

Fabrication. This formulation was sintered in forming gas (3% H_2/ 97% Ar) at 1100°C/4hrs. The fired density was ~7.05 g/cc. Eltron observed cracking on parts made with this formulation when they were fired at higher temperatures.

Microstructure. SEM/EDS analyses revealed a fine grain structure. The metal phase showed solubility in the ceramic phase. An ICP analysis of metal beads showed the presence of major B^a with a trace of A and B.

Stability. Delayed cracking was observed on these samples. This effect were directly attributed to the environmental conditions for sample are storage. Delayed cracking was observed on samples stored under ambient conditions at Eltron and at CoorsTek. Cracking was not observed on samples stored in a desiccator at Eltron and at CoorsTek for several weeks, but after 6 weeks, some cracks were apparent. XRD measurements on the surface of parts before and after cracking exhibited the same metal and ABO_3 phases.

Manufacturing. The process was repeated with 4% H_2 certified forming gas. It yielded good reproducibility with respect to fired density and XRD.

Performance Testing. Conductivity and H_2 permeation tests were conducted on these samples. The results were fair as shown in Table 1.

Table 1.
Summary of Performance Evaluation for Selected Membranes Manufactured by CoorsTek.

Composition	Sintering Conditions	Max. Ambipolar Conductivity (S/cm)	Max. H_2 Permeability* ($mL/min/cm^2$)
$AB_{0.8}B^c_{0.2}O_{3-\delta}$/ 44 wt.% Metal	Forming Gas 1415°C	0.0053	0.13
$AB_{0.8}B^c_{0.2}O_{3-\delta}$/ 44 wt.% Metal	Nitroneal 1425°C	0.0026	0.08
$AB_{0.9}B^a_{0.1}O_{3-\delta}$/ 44 wt.% Metal	Forming Gas 1375°C	0.0013	0.06
$AB_{0.7}B^a_{0.3}O_{3-\delta}$/ 44 wt.% Metal	Forming Gas 1100°C	0.0012	0.04
$AB_{0.7}B^a_{0.3}O_{3-\delta}$/ 44 wt.% Metal	Forming Gas 1100°C	0.0009	0.03
$AB_{0.9}B^a_{0.1}O_{3-\delta}$/ 44 wt.% Metal	Forming Gas 1375°C	0.0006	0.02

*Relatively thick membranes — approximately 1 mm. Test performed at 850° - 950°C.

d. Ceramic: $AB_{0.9}B^a_{0.1}O_{3-\delta}$

Fabrication. This composition was not evaluated in a sintering study, but was evaluated at various calcining temperature conditions to improve the subsequent grinding of the composition for making the cermet composition below.

e. Cermet: $AB_{0.9}B^a_{0.1}O_{3-\delta}$/44 wt.% Metal

Fabrication. These parts were sintered at 1425°C/4hrs. A single metal bead was formed on the top surface of each of the parts. Lower sintering temperatures were tested on this series. At 1400°C/4hrs, the beads were still present. At 1375°C/4hrs, the beads were generally eliminated. These conditions resulted in a fired density of 7.07 gm/cc. Parts, however, will be sintered at temperatures below 1375°C to determine if the layered laminate structure can be eliminated and if the B^a can be stabilized in the perovskite phase and not in the metal phase where it appears to be migrating.

Microstructure. SEM images were conducted on the first batch fired without metal beads. The microstructure was not uniform with the ABO_3 phase distributed as both a normal appearing phase and as a layered, laminated structure with neither phase showing the presence of any B^a in an EDS analysis. XRD analyses indicated that ABO_3 and metal phases were the only phases present. EDS

also showed a minor amount of B^a in the metal phase. Although only one phase was detected, the microstructure was not uniform and could prove to be a problem with respect to reproducibility. Lower firing temperatures will be evaluated in order to eliminate this problem.

Stability. No delayed cracking was observed on samples made with this formulation, however, the effect may occur over longer periods of time.

Manufacturing. If Eltron decides to proceed with this formulation, the working range will need to be determined and reproducibility will need to be established. The working range is the sintering temperature range over which acceptable performance is achieved on the final parts or components. A wide working range is desirable from a manufacturing perspective. Samples fired at the lowest temperature that still yield a uniform microstructure with few voids and no metal beads then should be measured for H_2 permeability to determine the optimum processing conditions.

Performance testing. H_2 permeation tests were conducted on these samples as shown in Table 1. The results are similar to the $AB_{0.7}B^a_{0.3}O_{3-\delta}$/44 wt.% metal cermet composition, and also were not as good as the B^c-substituted series. The two $AB_{0.9}B^a_{0.1}O_{3-\delta}$/44 wt.% metal cermet samples did not reproduce well, possibly because the low concentration of B^a was difficult to disperse evenly throughout the structure.

2. B^c-substituted ABO_3

a. Ceramic: $AB_{0.8}B^c_{0.2}O_{3-\delta}$ — No further activity planned.

Fabrication. Samples were fired in both nitroneal (25% H_2) and forming gas (3% H_2) atmospheres to determine a baseline for comparison to the cermet composites when metal is added to these compositions. Samples fired in dry nitroneal (25% H_2 / 75% N_2) exhibited one major ABO_3 phase with peak shifting and line broadening. Samples fired in forming gas (3% H_2 / 97 % Ar) also exhibited one major ABO_3 phase, however, peak shifting and line broadening were not present.

Manufacturing. A new batch was prepared and the sintered density reproduced well. The fired density of the $AB_{0.8}B^c_{0.2}O_{3-\delta}$ formulation was 6.07 g/cc.

b. Cermet: $AB_{0.8}B^c_{0.2}O_{3-\delta}$/44 wt.% Metal

Fabrication.

Atmosphere. This formulation was sintered in a refractory metal furnace using dry nitroneal gas (25% H_2 / 75% N_2) at 1425°C/4hrs. The fired density of this formulation was in the range 6.90-6.94 g/cc. Parts also were fired at 1425°C/4hrs in certified forming gas. Samples fired in nitroneal revealed two major phases. The first phase was metal. The second phase, as with the ceramic sample, was ABO_3 with some peak shifting and line broadening. Samples fired in forming gas also revealed two major phases. The first phase was metal. Again, as with the ceramic sample, the second phase was ABO_3 with no peak shifting or line broadening. A decision will be made as to which firing atmosphere to use based on the results of H_2 permeation tests on samples fired in both atmospheres. Comparative analyses are underway to study elemental distribution between nitroneal

and forming gas atmosphere firing cycles.

Metal Beads. Several test firings have produced parts with multiple metal beads on the surface in parts fired at 1425°C. Lowering the firing temperature to 1415°C/4 hrs eliminated severe metal bead formation. The microstructure near the metal beads was determined to be more porous than the microstructure when metal beads were not present. The metal leaves voids when it forms beads at the surface and leaves some residual metal present in the structure.

Whiskers. In the part fired in forming gas, fresh fractured surfaces revealed a very unusual phenomenon, the presence of whiskers. EDS of the whiskers revealed that they contained A, B, B^c, and O, but no metal. Attempts to reproduce whisker formation were unsuccessful. However, SEM images revealed, needle-like grains. An EDS analysis revealed that the needle-like grains contained the same constituents as the whiskers, except the metal. The needle-like structure might be formed by recrystallization of the ceramic phase.

Microstructure. The microstructure of parts fired at 1425°C/4 hrs in certified forming gas exhibited discontinuous grain growth and beads of metal. The microstructure of parts fired at 1415°C/4 hrs were more uniform and finer grained, however, an elongated structure that appeared to look like remnants of whiskers (needle-like grains) appeared present in all the microstructures. This effect will be investigated further. SEM images show that the ceramic phase contains a small amount of metal. However, the metal is clearly diffusing into the ceramic and very little or no ceramic elements diffused into the metal.

Manufacturing. The process was repeated on new batches fired at 1425°C/4 hrs and at lower temperatures. XRD and SEM data reproduced well. Parts fired at 1415°C/4 hrs and at 1410°C/4 hrs in certified forming gas addressed the metal bead formation problem favorably in providing a working range of the formulation. Even lower firing temperatures will be tested to determine the working range that yields a uniform microstructure. New samples fired in forming gas at 1415°C/4 hrs representing a change in firing temperature to eliminate the metal beads were sent to Eltron to measure H_2 permeation.

Performance Testing. These results were significantly better than the performance measurements for $AB_{0.7}B^a_{0.3}O_{3-\delta}$/44 wt.% metal. The sample sintered in forming gas at 1415°C yielded properties that were approximately twice as good as the sample sintered in nitroneal at 1425°C. The two variables need to be isolated in order to determine if the atmosphere or sintering temperature had the most significant effect.

3. B^b-substituted ABO_3

a. Ceramic: $AB_{0.8}B^b_{0.2}O_{3-\delta}$

Fabrication. The initial formulation was prepared with by calcining at 1250°C/4 hrs. This condition resulted in hard agglomerates. Calcining at 1200°C/4 hrs resulted in the same very hard agglomerates still being formed indicating that some melting occurred. Test sintering cycles conducted at 1120°C/4 hrs and 1100°C/4 hrs in air resulted in porous parts. Tests carried out at

1150°C/4 hrs and 1175°C/4 hrs appeared to have solved the porosity problem. These samples were sent to Eltron.

Microstructure. Powders calcined at 1250°C/4 hrs consisted of the primary ABO_3 phase and some unidentified secondary peaks. The peaks appeared at 31° 2θ. Eltron identified a $AB^bO_{2.6}$ phase at 26° 2θ, which was observed in one of the samples. So, it is possible that the peak at 31° 2θ is indicative of a different AB^bO_x phase. SEM images of samples fired at 1150°C/4 hrs revealed the presence of the primary BaCeO3 phase and most, but not all of the secondary peaks observed in the calcined powders. Parts sintered at 1175°C/4 hrs exhibited the same phases as the parts sintered at 1150°C/4 hrs. On the 1150°C/4 hrs sintered composition, EDS showed the lighter phase to contain A, B with no B^b. The darker phase revealed A, B^b and no B. On the 1175°C/4 hrs parts, EDS showed similar phases to that observed in the 1150°C/4 hrs samples. It appeared that the B^b addition was not substituting in the perovskite structure, but rather segregated as an unidentified AO-B^bO phase. Eltron plans to test this two-phase structure with the idea that the AB^bO_x structure is electronically conducting and will improve the properties. Eltron will review their latest test results, then make recommendations as to whether to proceed with further development of B^b-containing ceramics and/or cermets. Eltron reported a problem in sealing these samples in their test apparatus and indicated they may request CoorsTek's assistance on some of these sealing problems.

b. Cermet: $AB_{0.8}B^b_{0.2}O_{3-\delta}$/44 wt.% Metal

This cermet composition has been discussed with Eltron, but has not been prepared yet. Eltron will provide direction regarding current interest in this composition. The low required sintering temperature for this composition and the formation of the B^b-containing minor phase are difficulties that need to be overcome in addressing the formulation of a cermet.

4. Other Substitutions

Other substitutions were discussed. Eltron indicated that they investigated a range of transition metal substitutions and obtained mediocre performance. An outline for future compositions and strategies was generated, and preliminary results are needed to define the next focus materials.

IV. Membrane Stability in Reactive Gases - Eltron, ORNL

A. Sulfur and Carbon Monoxide - Eltron

As described in the previous report, permeation tests performed over a range of temperatures for up to several weeks at a time have indicated that most of the current membranes materials are stable in H_2 and can tolerate very reductive conditions. These same tests also indicated that these materials are stable in moisture under operating conditions. Other potentially reactive gases present in Vision 21 energy plants include, CO, CO_2, and H_2S, and the concentrations of these species will depend on the location within the processor (*i.e.,* before or after catalyst units or moisture condensers). Using coal gasification as a model process, typical values for these gases (volume percent) after sulfur removal are roughly 46% H_2, 47% CO, 6% CO_2, 0.02% H_2S, and 0.34% H_2O.

However, prior to desulfurization, H_2S can be as high as ~0.9%, or 9,000 ppmv. As described in the fourth quarterly report, information compiled by MTI indicated that membrane sulfur tolerance is the primary factor that will determine where the H_2 separation unit will be placed within the energy plant. However, regardless of the separation unit positioning, the membrane material also will be exposed to large concentrations of CO. Accordingly, testing has been continued to assess the effect of both S and CO on membrane characteristics.

Candidate membrane compositions for these tests had the general compositions $AB_{0.7}B^{a}_{0.3}O_{3-\delta}$, $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% metal, and $AB_{0.8}B^{b}_{0.2}O_{3-\delta}$. Membrane samples were placed in a cell and heated to 950°C under flowing Ar. Once this test temperature was reached, the Ar flow was replaced with UHP CO (99.999%) for 96 hours. Upon completion of the test, the gas flow was switched back to Ar, and the cell was cooled to room temperature. XRD patterns of the membrane surfaces before and after CO exposure showed no signs of carbonate formation. However, residual sulfides present in the test system from the previous H_2S stability measurements were sufficient to react strongly with the membrane materials. The predominant XRD patterns after testing were from the A-site sulfides. Also, $AB_{0.7}B^{a}_{0.3}O_{3-\delta}$ reacted very strongly with S to produce an A-B^{a}-S sulfide. Surprisingly, no evidence of a sulfide from the metal phase of the cermet was observed. Although these ceramic-based materials presumably have higher tolerance to S relative to Pd-based technologies, S poisoning remains a difficult technical challenge.

B. Carbon Dioxide - ORNL

Hydrogen separation membranes in Vision 21 energy plants will be continuously exposed to several vol.% CO_2 under normal operating conditions. It is well known that perovskite materials can react with CO_2, thus it is important to identify the conditions where this reactivity becomes problematic, and determine if stability can be improved by relatively minor adjustments in membrane composition.

A range of perovskite ceramic powders with the general composition $A_xB_{0.8}B'_{0.2}O_{3-\delta}$, $0.90 \leq x \leq 1.0$ were prepared to test the dependence of A-site deficiency on perovskite stability in CO_2. The powders were placed in a high-temperature XRD instrument, sealed, and raised to 1200°C in air or helium. XRD patterns confirmed a single-phase perovskite structure for the powders, then the gas flow was switched to 1 atm CO_2. XRD patterns then were obtained every 5 minutes after lowering the temperature in 50°C increments. Peaks associated with the A-site carbonate, *i.e.*, ACO_3, were observed for $AB_{0.8}B'_{0.2}O_{3-\delta}$ (no A-site deficiency) once the temperature was lowered to approximately 1120°C. However, the A-site deficient compositions resisted carbonate formation until ≤ 1060°C. This measurable difference, though modest, indicated that a A-site deficiency could be accommodated and improved the stability of the phase. The stability of $A_{0.98}B_{0.8}B'_{0.2}O_{3-\delta}$ against CO_2 was further improved by selectively doping the B-site. This modified composition remained a single-phase perovskite at temperatures ≥ 900°C.

The above stability tests were performed under a "worst-case-scenario": high surface area powder was subjected to pure, flowing CO_2. In actual application, the material is a dense body subjected to conditions with a much lower partial pressure of CO_2. Further stability studies will be done under more representative conditions, including behavior in moisture-containing gas.

V. Hydrogen-Ion Conducting Ceramic Synthesis - ORNL

Combustion synthesis (CS) was tested for preparation of the A-site deficient perovskite, $A_{0.98}B_{0.8}B'_{0.2}O_{3-\delta}$, describe above. This methods is attractive for its ability to produce high-purity nanocrystalline powders with excellent compositional homogeneity and low energy input requirements. These studies indicated that several variations within the synthesis routes can be used depending on the processing or product requirements. A conventional CS method was the most straightforward and forgiving synthesis procedure. However, the resulting powders had very low density and were, therefore, more difficult to store and process than other options. With slightly more effort, an alternative CS method was tested, which generated much more workable powders. Ultimately, an unconventional CS method generated the best sample homogeneity and more complete combustion. This preferred procedure was considerably more time consuming and complicated that the conventional procedures, however, several options to alleviate these limitations currently are being pursued.

VI. Membrane Surface Catalysis - SCI

As membrane thickness decreases, surface catalysis becomes increasingly important for maximizing H_2 permeation rates. In the previous report, several catalysts were tested on 0.8-mm thick cermet membranes, but these catalysts did not improve H_2 permeation rates. It was proposed that the metal in the cermet alone provided an optimal catalyst intimately connected with the ceramic lattice, and additional catalyst likely blocked sites for hydrogen ion uptake.

To further test catalysts on cermet membranes, SCI used a variety of methods and precursors to apply transition metal and noble metal catalysts, as summarized in Table 2. SEM images of the

Table 2.
Summary of Catalyst Metals Applied to Cermet Membranes by Süd Chemie.

Catalyst Metal	Membrane Wt. Before Catalyst Addition (g)	Membrane Wt. After Catalyst Addition (g)	Catalyst Precursor	Catalyst Loading (wt.%)
Co	0.5567	0.5625	Aqueous	1.03%
Ni	0.6127	0.6268	Aqueous	2.25%
Ni	0.7554	0.7745	Aqueous	2.47%
Pt	0.6563	0.6640	Non-aqueous	1.16%
Pt	0.5839	0.5946	Aqueous	1.80%
Pd	0.6763	0.6799	Non-aqueous	0.53%
Pd	0.5585	0.5636	Aqueous	0.90%

membrane surfaces after catalyst application generally indicated that it was difficult to achieve good catalyst dispersion and adhesion on these samples. This result likely was due to the nonporous, high-density nature of these membranes. Observations from the SEM images are as follows:

- For Pd, the aqueous precursor resulted in poor dispersion and clusters of sintered metal about 20 μm in size.
- Both Pt disks yielded very high dispersion, but the sample from the non-aqueous precursor resulted in less sintering on the surface than the aqueous precursor.
- The samples impregnated with Ni showed very large Ni crystallites on the surface (40 μm) and appears to have sintered.

These samples currently are being tested for H_2 permeation, and results will be reported at the end of the next quarter.

VII. New Materials Discovery - Eltron, ANL

During this quarter, ANL compiled data for a wide range of hydrogen-ion conducting materials for potential use as membrane materials. Based on this data, materials with desirable properties have been selected for testing as potential components in composite H_2 separation membranes. The electrical properties of these candidate materials will be more thoroughly evaluated during the next quarter.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron, MTI

I. High-Pressure Seals - 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 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 testing. The best seal evaluated this quarter maintained a pressure differential of 207 psig, which significantly exceeded our previous results of ~ 100 psig.

II. Commercial Concept Development - MTI

Possible scenarios for insertion of a full-scale H_2 separation unit into a Vision 21 energy plant already were outlined by MTI in Report 4. During this quarter, MTI has begun estimating specific H_2 separation unit characteristics necessary for commercial viability based on a membrane H_2 separation rate of 10 mL/min/cm^2. Additionally, estimation of the general economics associated with the H_2 separation unit have been initiated.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: Eltron

As described in Report 5, fabrication of thin films ≤ 100 μm has been successful, however, attaining adequate seals for H_2 permeation evaluation has been very difficult. For thicker membranes, pressure can be applied to promote seal formation at temperatures above the seal material softening point. However, thin films are comparably fragile, and applied pressure sufficient for seal formation results in membrane cracking. By using an additional porous support piece, a good seal was achieved for a 160-μm thick cermet membrane, and those results were presented in Figure 1 of Section I. Although this membrane was much thicker than the target range, the seal was very good, and the permeation rate of 0.84 mL/min/cm^2 was the highest value to date for a membrane that did not contain an H_2-permeable metal. This sealing method will be applied to membrane ≤ 100 μm thick during the next quarter.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

No actions were performed on this task during this reporting period.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

During this quarter, calibration curves for relevant reactants and products were completed and catalyst for preliminary membrane testing were selected. Propane will be used as the model olefin for this task. Dehydrogenation of propane to propylene in a dense H_2-separation membrane reactor proceeds according to,

feed side: $CH_3CH_2CH_3 \rightleftharpoons CH_2{=}CHCH_3 + H_2$

H_2 permeate side: $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$

net: $CH_3CH_2CH_3 + \frac{1}{2}O_2 \rightleftharpoons CH_3CH{=}CH_2 + H_2O$

Thus, although the net reaction is an oxidative dehydrogenation, the O_2 and propane remain separated by the membrane. Propane dehydrogenation typically is less than 50% selective, and previous testing at Eltron indicated significant quantities of ethylene, ethane, and methane also are produced.[7]

Catalysts to be used for initial membrane testing will be 3.75%Pt/1.25%Sn/MgO and 3.75%Pt/1.25%Sn/SiO_2. These catalysts previously were shown to result in the highest conversion and selectivity for propane to propylene among a range of Pt/Sn compositions under the target operating temperatures.[7] The O_2 reduction catalyst for the H_2 permeate side will be $La_{0.8}Sr_{0.2}CoO_3$ (LSC). Catalysts will be applied to the membrane surfaces using a slurry deposition method.

SUMMARY AND CONCLUSIONS

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

- Permeation of H_2 increased significantly as the membrane thickness decreased for a selected cermet composition. A maximum permeation rate of ~0.84 mL/min/cm^2 was achieved for a 160-μm thick cermet membrane at 950°C.

- Cermet compositions containing a H_2-permeable metal demonstrated the highest H_2 permeation rates. A 0.43-mm thick membrane generated a permeation rate of 1.8 mL/min/cm^2 at 950°C, and greater than 1 mL/min/cm^2 at only 650°C.

- $AB_{0.8}B^c_{0.2}O_{3-\delta}$/44 wt.% metal cermets performed better after sintering in forming gas at 1415°C, than in nitroneal at 1425°C.

- $AB_{0.7}B^a_{0.3}O_{3-\delta}$/44 wt.% metal cermets were not as good as the results on the B^c -substituted series, and the stability of this formulation appears to be a problem with delayed cracking occurring on exposure to ambient conditions.

- $AB_{0.9}B^a_{0.1}O_{3-\delta}$/44 wt.% metal cermets did not reproduce well, possibly because the low concentration of B^a was difficult to evenly distribute throughout the entire structure.

- Sulfur and carbon dioxide react with membrane materials. Stability against carbon dioxide can be improved by modifying the composition.

- Catalyst deposition on membranes resulted in low dispersion due to the low membrane porosity and surface area.

- New high-pressure seal formulations achieved a pressure differential of 207 psig.

OBJECTIVES FOR NEXT REPORTING PERIOD

Specific objectives for the next quarter are summarized as follows:

- Continue testing of multi-phase ceramics and cermets.
- Further refine manufacturing of selected membrane compositions.
- Continue commercial concepting and initiate market and forecast evaluation.
- Perform hydrogen separation analysis on supported thin film membranes.
- Continue catalyst testing.
- Continue membrane stability studies.
- Begin testing catalytic membrane reactors for propane dehydrogenation.
- Begin outlining requirements for prototype and incorporation into a Vision 21 plant (Task 5).

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

Modifications to the work plan and time line are as follows:

Task 1

- Neutron diffraction studies of candidate H_2 separation membranes has been delayed, and are pending completion of repairs and maintenance at the Oak Ridge National Laboratory facility.

- The time line for "Input for Commercial Concepting" has been extended to 24 months to accommodate continued improvement in membrane compositions and performance.

Task 3

- "High-Pressure Seal Development" has been extended to accommodate changes in membrane composition as new materials are identified.

Task 4

- "Incorporation of Catalyst" has been extended to 24 months to parallel membrane fabrication.

Task 6

- The project is slightly behind schedule on "Catalyst Development" and "Performance Evaluation."

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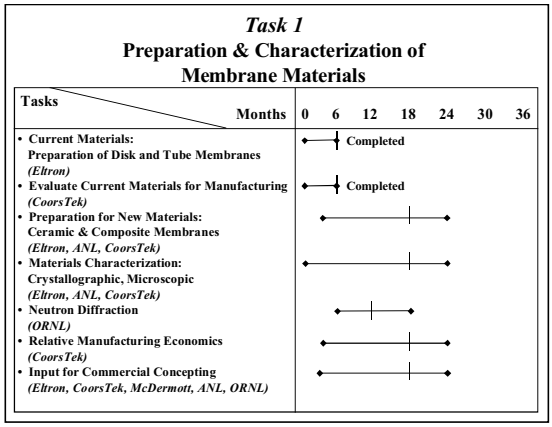
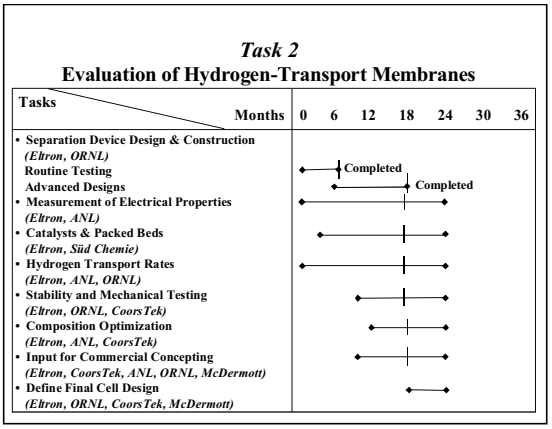
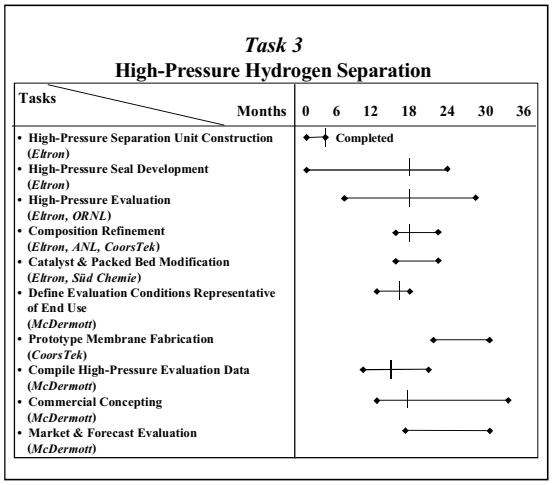
5. Balachandran, U., et al. *Development of Dense Ceramic Membranes for Hydrogen Separation*. in *26th International Technical Conference on Coal Utilization and Fuel Systems*. 2001. Clearwater, FL.
6. Wachsman, E.D. and J. Naixiong, *Two-Phase Hydrogen Permeation Membrane. Patent No. 6,235,417*. 2001, Her Majesty the Queen in right of Canada: USA.
7. Roark, S.E., et al., *Mixed-Conducting Membranes for the Spontaneous Oxidative Dehydrogenation of Alkanes to Olefins (DOE SBIR Final Report, Contract No. DE-FG0397ER82571)*. 1999, Eltron Research, Inc.: Boulder, CO.

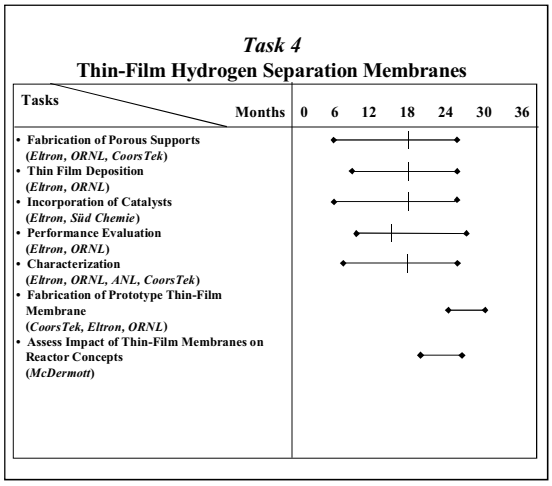
TIME LINES

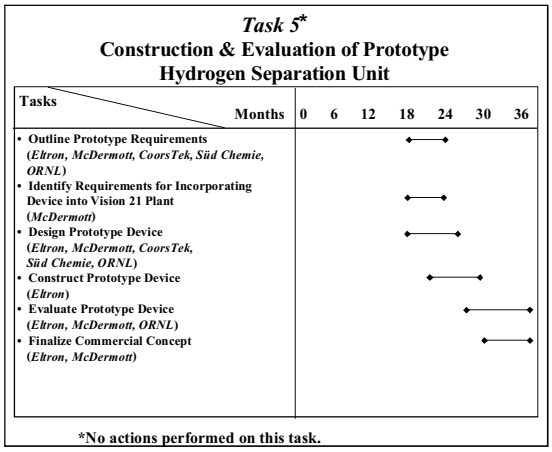
The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

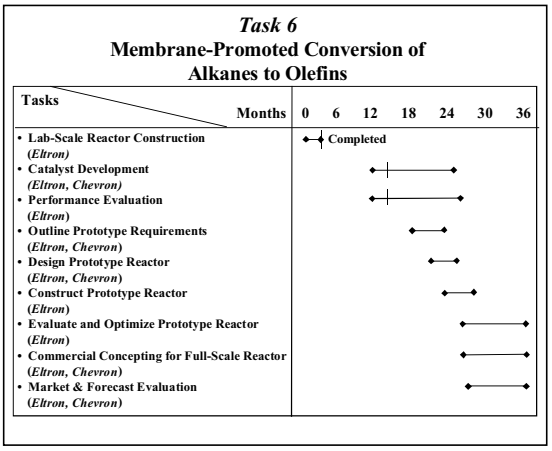












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