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

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# DISCLAIMER

# 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, new cermet compositions were tested that demonstrated similar performance to previous materials. A 0.5-mm thick membrane achieved a $H_2$ transport rate of 0.2 mL/min/cm$^2$ at 950°C, which corresponded to an ambipolar conductivity of 3 x 10$^{-3}$ S/cm. Although these results were equivalent to those for other cermet compositions, this new composition might be useful if it demonstrates improved chemical or mechanical stability. Ceramic/ceramic composite membranes also were fabricated and tested; however, some reaction did occur between the proton- and electron-conducting phases, which likely compromised conductivity. This sample only achieved a $H_2$ transport rate of ~0.006 mL/min/cm$^2$ and an ambipolar conductivity of ~4 x 10$^{-4}$ S/cm. Chemical stability tests were continued, and candidate ceramic membranes were found to react slightly with carbon monoxide under extreme testing conditions. A cermet compositions did not show any reaction with carbon monoxide, but a thick layer of carbon formed on the membrane surface. The most significant technical accomplishment this quarter was a new high-pressure seal composition. This material maintained a pressure differential across the membrane of ~280 psi at 800°C, and is still in operation.

# 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.

During this quarter, new cermet compositions were tested that demonstrated similar performance to previous materials. A 0.5-mm thick membrane achieved a $H_2$ transport rate of 0.2 mL/min/cm$^2$ at 950°C, which corresponded to an ambipolar conductivity of 3 x 10$^{-3}$ S/cm. Although these results were equivalent to those for other cermet compositions, this new composition might be useful if it demonstrates improved chemical or mechanical stability. Ceramic/ceramic composite membranes also were fabricated and tested; however, some reaction did occur between the proton- and electron-conducting phases, which likely compromised conductivity. This sample only achieved a $H_2$ transport rate of ~0.006 mL/min/cm$^2$ and an ambipolar conductivity of ~4 x 10$^{-4}$ S/cm. Chemical stability tests were continued, and candidate ceramic membranes were found to react slightly with carbon monoxide under extreme testing conditions. A cermet compositions did not show any reaction with carbon monoxide, but a thick layer of carbon formed on the membrane surface. The most significant technical accomplishment this quarter was a new high-pressure seal composition. This material maintained a pressure differential across the membrane of ~280 psi at 800°C, and is still in operation.

# 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 the 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, ANL

### I. **Cermet Membranes** - Eltron, CoorsTek

Cermet compositions with the general formula $AB_{0.8}B^{d}_{0.2}O_{3-\delta}$/44 wt.% metal were fabricated and tested for comparison to compositions presented in earlier reports. Figure 1 summarizes hydrogen transport rates for a 0.52-mm thick membrane under dry and humid conditions as a function of temperature. There was a steady increase in hydrogen permeation with temperature over the test range, with a maximum of 0.2 mL/min/cm$^2$ at 950°C. Figure 2 compares the conductivity

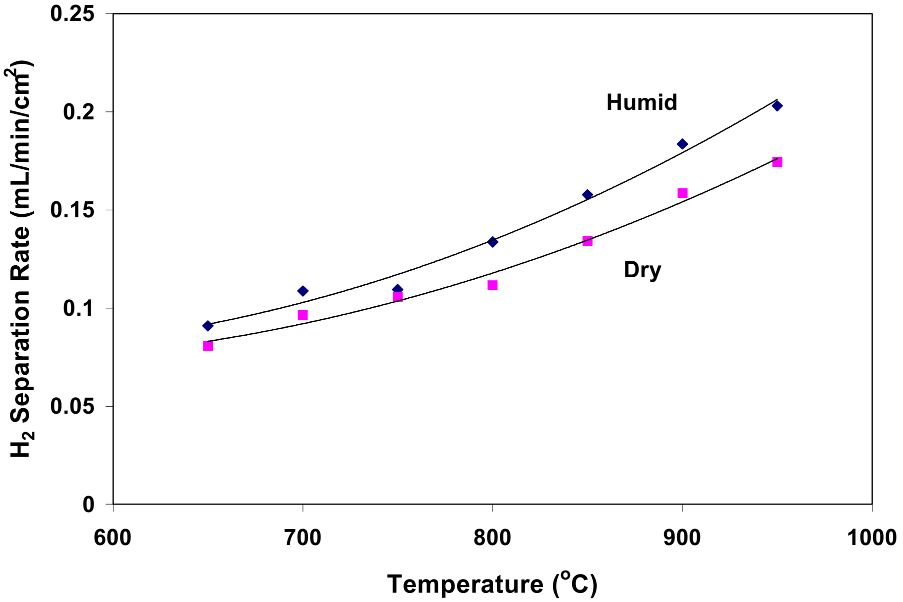


**Figure 1. Plot of hydrogen transport as a function of temperature for a cermet membrane with the general formula $AB_{0.8}B^{d}_{0.2}O_{3-\delta}$/44wt.% metal. The membrane thickness was 0.52 mm. The membrane feed side contained 80/20 vol.% $H_2$/He and Ar was used on the sweep side. Gas flow rates were between 80 and 120 mL/min.**

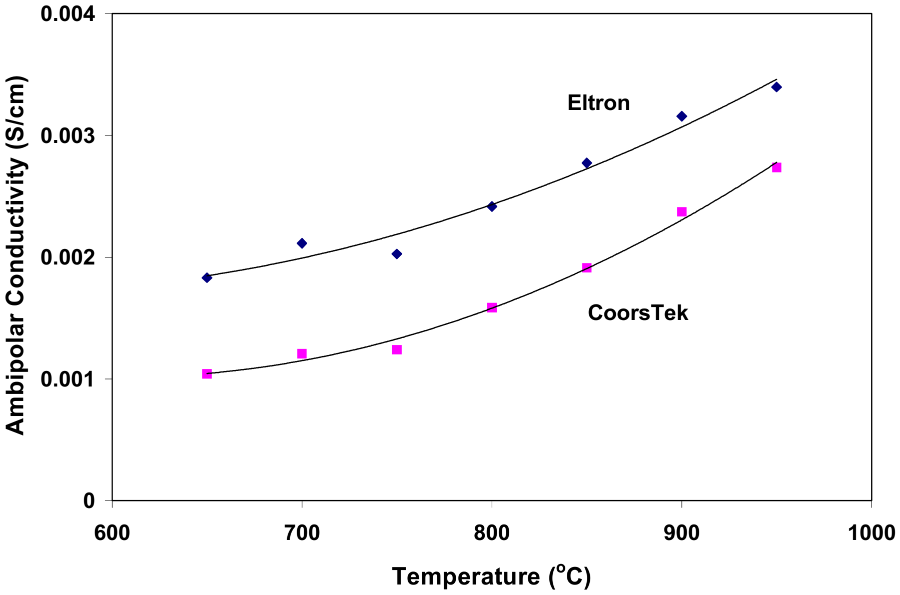


**Figure 2. Plot of ambipolar conductivity as a function of temperature for cermet membrane prepared by Eltron and CoorsTek with the general formula $AB_{0.8}B^{d}_{0.2}O_{3-\delta}$/44 wt.% metal. Ambipolar conductivity was calculated from the hydrogen transport rate. The membrane thickness was 0.52 mm. The membrane feed side contained 80/20 vol.% $H_2$/He and Ar was used on the sweep side. Gas flow rates were between 80 and 120 mL/min.**

of this sample to one with an identical composition prepared by CoorsTek. Both samples showed very similar performance with a maximum ambipolar conductivity of approximately $3 \times 10^{-3}$ S/cm and an activation energy for hydrogen transport near 0.3 eV. These results essentially were equivalent to the best cermets tested to date in this thickness range, and reflect the similar proton conductivity of $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ and $AB_{0.8}B^{d}_{0.2}O_{3-\delta}$. These newer compositions were slightly more expensive, but might be useful if they demonstrate improved chemical or mechanical stability.

## II. Ceramic/Ceramic Composite Membranes - Eltron, CoorsTek

Ceramic/ceramic composites also are under development as possible alternatives to cermets. It is anticipated that these composites might have greater mechanical stability due to similar characteristics between the two phases, and might have greater chemical stability in the presence of sulfur. A preliminary composition represented as $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/CER1 was prepared as described below in Section IV.C.1. Compositions with 60 wt.% $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ and 40 wt.% CER1 were extremely brittle and fractured during preparation for hydrogen transport measurements. However, adjusting the proportions to 75 wt.% $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$ and 25 wt.% CER1 resulted in a much stronger membrane. A 0.94-mm thick membrane with this compositions achieved a hydrogen separation rate of only 0.006 mL/min/cm$^2$, which corresponded to an ambipolar conductivity of $1.7 \times 10^{-4}$ S/cm.

The relatively poor performance likely was due to cross diffusion of constituents from each phase, which compromised proton conductivity. Despite these results, the feasibility of the approach was demonstrated and additional compositions were prepared. Results from those tests will be presented in the next report.

## III. 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 Report 4 (October 30, 2001) and Report 6 (April 30 2002), and analogous materials were described by others.[4,5] As demonstrated in the previous report, these composite materials are capable of much higher $H_2$ transport rates than the other perovskite and cermet analogs developed in this program. Therefore, despite many potential limitations of this category of membranes, some effort will be directed at their development.

During this reporting period, a composite perovskite/$H_2$-permeable metal alloy was tested and the results are shown in Figure 3. Permeation increased from 0.4 to more than 0.5 mL/min/cm$^2$ as the temperature was raised from 650° to 950°C. Although these $H_2$ permeation rates were fairly high, the membrane thickness was only 0.4 mm. For comparison, an analogous 0.4-mm perovskite/$H_2$-permeable metal composite without the metal alloy (*i.e.*, the $H_2$-permeable metal phase was a pure metal) achieved a permeation rate of almost 2 mL/min/cm$^2$ at 950°C. Although the use of a metal alloy might impart desirable mechanical qualities, the compromise in $H_2$ permeation was dramatic.

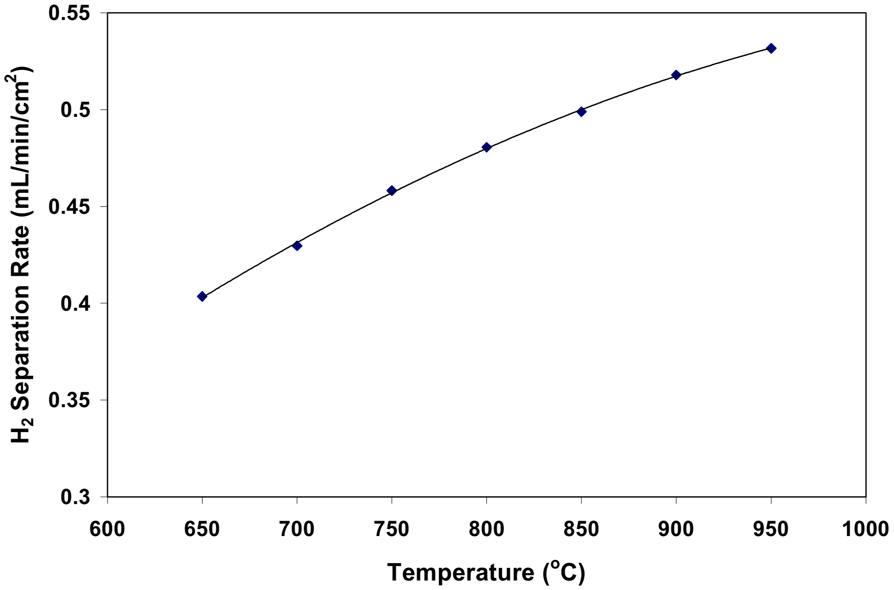


**Figure 3.** **Plot of $H_2$ permeation as a function of temperature for a 0.4-mm thick composite perovskite/metal alloy membrane. The feed gas was humidified 80/20 vol.% $H_2$/He and the sweep gas was Ar. The gas flow rates were between 80 and 120 mL/min.**

## IV. Manufacturing Issues and Relative Economics - CoorsTek, Eltron

The previous report (April 30, 2002) presented a comprehensive overview of progress made by CoorsTek regarding fabrication and manufacturing of materials for hydrogen separation membranes. Results below summarize additional work performed by CoorsTek during this reporting period.

### A. $B^a$-Substituted $ABO_3$

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

*Fabrication*. This composition was evaluated at various calcining temperature conditions to improve the subsequent grinding of the composition for making the corresponding cermet composition. The ceramic formulation was sintered to determine its microstructure. Parts were sintered at 1350°C/2 hrs, 1325°C/2 hrs and at 1300°C/2 hrs. The parts sintered in forming gas at 1300°C/2 hrs yielded a fired density of 5.98 g/cc and the parts sintered in air at 1300°C/2 hrs yielded a fired density of 6.26 g/cc. This difference in density might reflect some lack of stability of the $B^a$-modified perovskite processed in forming gas.

*Microstructure*. The samples fired in forming gas displayed the same layered, laminated structure as the cermet based on this material. The samples fired in air did not exhibit the layered, laminated structure but did show a small amount of a second phase and some porosity.

*Stability*. The samples fired in forming gas hyrolyzed rapidly and disintegrated on polishing. It appears that firing $B^a$-doped parts in hydrogen is not a good process.

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

Further development of this formulation and the other $B^a$-based formulations was put on hold since $B^a$ does not appear to stay in the perovskite phase. The performance results for these compositions were only fair and did not reproduce well. The layered laminated phase was present in parts fired in forming gas.

### B. $B^b$-Substituted $ABO_3$

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

*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 on samples fired at 1150°C/4hrs revealed the presence of the primary $ABO_3$ 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/4hrs 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 appears that the $B^b$ addition is not substituting in the perovskite structure but rather is segregating as an unidentified

BO-$B^bO$ phase. A sample fabricated by Eltron that was sintered at 1190°C/2 hrs showed the same XRD pattern with two small peaks at 31°2θ. It was confirmed by EDS that the darker phase contains $B^b$ and the lighter phase does not. This effect is desirable since the darker $B^b$-containing second phase is likely to be electronically conducting resulting in a ceramic/ceramic composite.

### C. $B^c$-substituted $ABO_3$

#### 1. Ceramic/Ceramic: $AB_{0.8}B^c_{0.2}O_{3-\delta}$/CER1

*Fabrication*. Two paths are being pursued in parallel to develop this material. CoorsTek is fabricating the individual perovskite proton-conducting and electron-conducting (CER1) phases separately, then sintering them together. Eltron is fabricating the two-phase material using a single formulation, followed by sintering. Initial attempts to prepare this material resulted in undesirable reaction with the setter powder. An alternative setter powder was identified and preliminary batches of this composition were prepared.

A composition containing 60% $AB_{0.8}B^c_{0.2}O_{3-\delta}$ and 40% CER1 was formulated and sintered at 1375°C/4hrs and at 1390°C/4hrs in air. The sintered densities were 5.73 g/cc and 5.77 g/cc, respectively. Parts sintered at 1410°C/4hrs in air yielded slightly higher sintered densities of 5.83 g/cc. SEM/EDS analyses revealed the presence of two phases, but some of the $B^c$ diffused into the CER1 phase. Furthermore, these samples were brittle.

In an attempt to offset loss of proton conductivity from $B^c$ diffusion, a formulation having a 75/25 ratio has been processed. Eltron estimated the maximum ratio to be 80/20 in order to maintain continuity in the electronically conducting phase. Parts sintered at 1410°C/4hrs in air also yielded sintered densities of 5.83 g/cc. SEMs revealed a microstructure similar to the 60/40 samples. XRD analyses showed the presence of an $ABO_3$ phase and an unidentified second phase. EDS analyses indicated that some diffusion of constituent cations. Also, XRD patterns indicated that the CER1 component was a mixture of brownmillerite and perovskite phases. This result was not desired since the differences in the crystal structures might compromise structural stability.

### D. $B^d$-substituted $ABO_3$

#### 1. Ceramic: $AB_{0.8}B^d_{0.2}O_{3-\delta}$

This formulation was calcined at 1250°C/2hrs. XRD analysis confirmed that the material a single-phase perovskite. Parts made from this calcine will be sintered later if necessary, but the higher priority initially is to make the metal cermet for a comparison to the $AB_{0.8}B^c_{0.2}O_{3-\delta}$/metal analogs.

#### 2. Ceramic/Metal: $AB_{0.8}B^d_{0.2}O_{3-\delta}$/44 wt.% Metal

This formulation was sintered at 1380°C/4hrs in forming gas. The parts appeared dense and did not show evidence of setter reaction. Three samples having fired densities of 7.11 g/cc, 7.12 g/cc and 7.12 g/cc, respectively were sent to Eltron for performance measurements and comparison to the $AB_{0.8}B^c_{0.2}O_{3-\delta}$/metal analog (see above). This composition had a tendency to form metal beads at sintering temperature >1400°C in a manner similar to the $AB_{0.8}B^c_{0.2}O_{3-\delta}$/metal cermet. The maximum sintering temperature that could be used to process these parts without forming metal beads was determined to be 1400°C. The microstructure was similar to the $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/metal analog and contained a similar needle-like structure likely indicative of recrystallization. Additionally, a higher-density layer of the same composition as the bulk formed over the part.

## V. **Membrane Stability in Carbon Monoxide** - Eltron

Candidate membrane compositions for these tests had the general compositions $AB_{0.9}B^{a}_{0.1}O_{3-\delta}$, $AB_{0.8}B^{b}_{0.2}O_{3-\delta}$, and $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% metal. Sintered membrane pellet 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 48 hours. Upon completion of the test, the gas flow was switched back to Ar, and the cell was cooled to room temperature. After testing, the $AB_{0.9}B^{a}_{0.1}O_{3-\delta}$ and $AB_{0.8}B^{b}_{0.2}O_{3-\delta}$ membranes showed a slight discoloration, and the $AB_{0.8}B^{b}_{0.2}O_{3-\delta}$ membrane also cracked around the edges. XRD patterns of these two membrane surfaces after CO exposure indicated some $ACO_3$ formation, but the predominant pattern remained the $ABO_3$ perovskite. The $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% metal membrane showed no evidence of carbonate formation; however, a thick layer of graphitic carbon was formed on the surface. This effect likely was due to the metal phase, and should be minimized under less extreme conditions using a humidified gas stream.

## VI. **Mechanical Testing of Candidate Membrane Materials** - ORNL

A work plan and methodology for mechanical testing of representative materials was generated and measurements will begin during the next reporting period. Strength will be measured using biaxial flexure (ball-on-ring or ring-on-ring configurations) since this method will easily accommodate the sintered disk specimens generated in the processing trials. Initially strength will be measured as a function of temperature and stressing rate in an air environment. For the environmental testing, special biaxial load fixtures will be used to measure strength in various environments.

## VII. **Membrane Surface Catalysis** - SCI

In the last report, catalyst deposition onto 0.8-mm thick cermet membranes using several methods was described. For most of the samples, subsequent SEM and EDX analysis indicated poor catalyst dispersion, and catalyst adhesion also was poor. The best catalyst characteristics were achieved for Pt and Pd using non-aqueous precursor solutions, and $H_2$ transport measurements obtained for these samples are shown in Figure 4. As with previous tests, no significant effect of the catalysts was observed. Both the Pt and Pd coated samples achieved similar $H_2$ transport rates, and as also shown in the figure, these results were equivalent to a sample with no catalyst. The lack of catalyst influence on permeation likely was due to the use of thick membrane samples, and the fact that cermets already contain a catalytic metal.

To eliminate these contributions to the catalyst study, several thinner (~0.6 mm) ceramic membranes (no metal phase) were supplied to SCI for coating. Metal precursor solutions were designed to achieve higher catalyst dispersion, and the total catalyst content on the samples was reduced. Membranes were successfully coated with Pt, Pd, Ni, and Cr and the samples had very

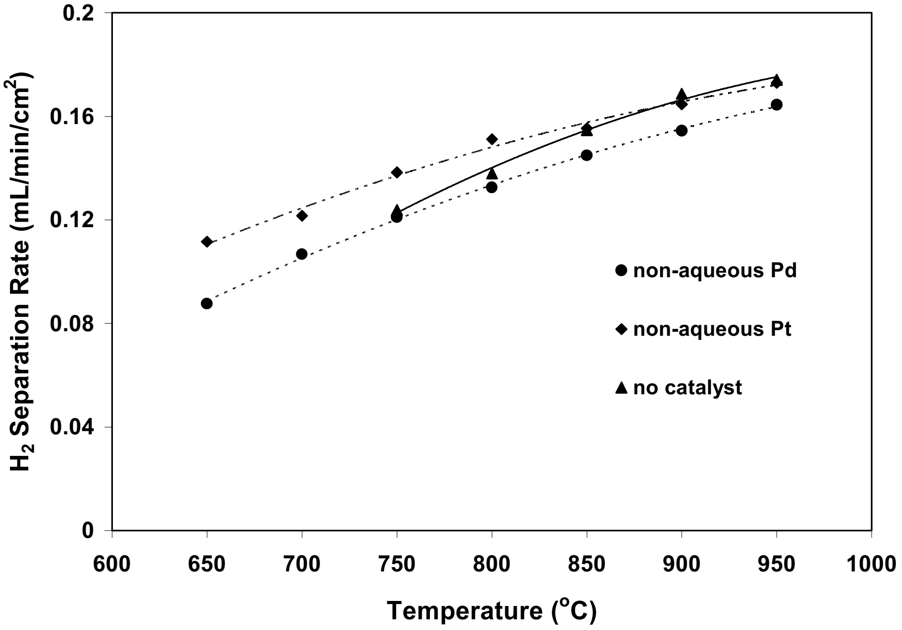


**Figure 4. Plot showing $H_2$ permeation as a function of temperature for perovskite/metal cermet membranes with and without catalyst on the membrane surface. The feed gas was humidified 80/20 vol.% $H_2$/He and the sweep gas was Ar. The gas flow rates were between 80 and 120 mL/min.**

good catalyst adhesion and high dispersion. SEM and $H_2$ transport measurements currently are underway and will be presented in the next report.

## VIII. New Materials Discovery - Eltron, ANL

During this quarter, ANL tested the stability of a range of doped perovskite compositions under 4% $H_2$/bal. $N_2$ at 900°C for 24 hrs. The general formula for these compositions is represented as $AB_{1-x}B_x^aO_{3-\delta}$, where $0.1 \leq x \leq 0.5$. It was determined for this dopant that the phase was only stable under these conditions for $x = 0.1$. These results were consistent with those obtained earlier by Eltron for a related material, and suggest that $B^a$ is not a viable dopant for promoting proton conductivity of the $ABO_3$ phase.

ANL and Eltron reviewed compiled data for a wide range of hydrogen-ion conducting materials and selected a subset for further testing. The focus for this subset of materials will be on proton conductivity rather than $H_2$ permeation. The conductivity is expected to be lower than for other perovskite-based membranes tested to date; however, the chemical stability is expected to be very high. When composited with an appropriate electron-conducting phase, these proton conductors might offer a more rugged alternative.

Additional plans were outlined to test the effect of precursor metal particle sized on cermet membrane characteristics. The objective will be to optimize cermet microstructure so that a minimal quantity of metal is necessary to achieve continuity, and the content of the proton-conducting phase is maximized.

Finally, ANL has had very good success sealing membranes for $H_2$ transport measurements. Therefore, Eltron will send difficult-to-seal membranes to ANL for evaluation

## *Task 3 High Pressure Hydrogen Separation*

**Contributors**: Eltron

### 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 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. The best seal achieved this quarter maintained a pressure differential of 280 psi, which significantly exceeded our previous result of ~ 207 psi. The leak rate for this seal has not been determined exactly, but is less than 400 mL/min. The goal for future high-pressure seal development will be to eliminate the leak at conditions of 250 psi and 800°C.

### 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 continued work 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 were continued.

## *Task 4 Thin-Film Hydrogen Separation Membranes*

**Contributors**: Eltron

Efforts to fabricate thin films were continued using $AB_{0.8}B^{c}_{0.2}O_{3-\delta}$/44 wt.% metal as a model material. Numerous films were prepared using tape casting methods, however, detailed analysis revealed "pin holes" through the film surface prior to firing. The precursor particle dimensions were adjusted, and very dense green films were produced. Currently, these films are being integrated with porous support structures and subsequent evaluation will be presented in the next report.

## *Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit*

Preliminary actions related to prototype device construction were initiated through communication between Eltron and MTI described above in Task 3.

## *Task 6 Membrane-Promoted Conversion of Alkanes to Olefins*

During this quarter, membrane-promoted conversion of alkanes to olefins was measured using propane to propylene as the model reaction. 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.

The membrane used for initial testing was a perovskite/metal cermet with 3.75 wt.%Pt/1.25 wt.%Sn/MgO on the propane feed side and $La_{0.8}Sr_{0.2}CoO_3$ (LSC) on the $H_2$ permeate side. These catalysts previously were shown to result in the highest conversion and selectivity for propane to propylene among a range of compositions under the target operating temperatures.[6] Catalysts were applied to the membrane surfaces using a slurry deposition method. The feed side contained 10/23/66 vol.% propane/He/Ar mixture at a total flow rate of 90 mL/min. The propane source also contained small quantities of methane, ethylene, ethane, iso-butane, and butane. The sweep side contained 120 mL/min Ar.

After passing through the membrane cell, the quantity of propane, iso-butane, and butane were reduced dramatically, and quantities of all the other species increased along with $H_2$ and a very large amount of propylene. Figure 5 shows the ratio of propylene to propane after passing through the cell as the temperature increased. Only a fraction of the $H_2$ formed passed through the membrane, and the maximum permeation rate measured at 800°C was approximately 0.009 mL/min/cm$^2$.

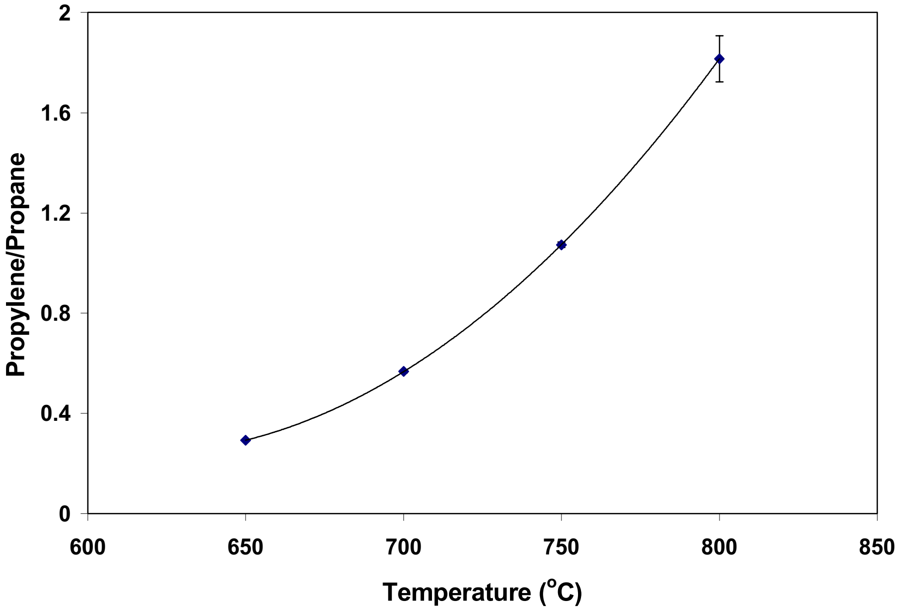


**Figure 5.** **Plot of the propylene to propane ratio as the temperature was increased in a catalytic membrane reactor for alkane dehydrogenation.**

During the next quarter, this experiment will be repeated and the propylene/propane ratio and selectivity will be measured as a function of temperature. $H_2$ permeation rates will be measured using Ar sweep gas, then the sweep will be changed to $O_2$ to promote formation water. This reaction should increase the driving force for $H_2$ transport and result in an increase in the propylene/propane ratio.

## SUMMARY AND CONCLUSIONS

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

- Cermet membranes with an alternative proton conducting phase generated $H_2$ permeation rates equivalent to those developed previously. These newer compositions were slightly more expensive, but might be useful if they demonstrate improved chemical or mechanical stability.
- Preliminary ceramic/ceramic composite membranes were successfully fabricated; however, the $H_2$ permeation was low compared to cermet analogs. The relatively poor performance likely was due to cross diffusion of constituents from each phase, which compromised proton conductivity.
- $H_2$ transport rates for a cermet containing a $H_2$-permeable metal were not improved using an alloy metal phase.
- Candidate ceramic membranes demonstrated a slight reaction with CO under extreme conditions to form carbonates. Cermet membranes did not react with CO, however, a thick layer of graphitic carbon was formed on the surface.
- Relatively thick cermet membranes did not show improved $H_2$ permeation with Pt or Pd surface catalysts.
- New high-pressure seal formulations achieved a pressure differential of 280 psig using a closed-one-end tube configuration. This pressure differential was the highest achieved to date.
- Smaller precursor powder particle sizes dramatically improved the density of green tape cast thin films.
- Alkane dehydrogenation was accomplished in a catalytic membrane reactor, and the ratio of olefin to alkane increased with increasing temperature. A maximum $H_2$ transport rate 0.009 mL/min/$cm^2$ was measured for this configuration at 800°C.

## OBJECTIVES FOR NEXT REPORTING PERIOD

Specific objectives for the next quarter are summarized as follows:

- Continue testing of multi-phase ceramics and cermets.
- Continue refining manufacturing of selected membrane compositions.
- Continue commercial concepting and market and forecast evaluation.

- Perform hydrogen separation analysis on supported thin film membranes.
- Continue catalyst testing.
- Continue membrane stability studies.
- Continue testing catalytic membrane reactors for propane dehydrogenation.
- Continue outlining requirements for prototype and incorporation into a Vision 21 plant.
- Begin mechanical testing of candidate membrane compositions.
- Measure proton conductivity of alternative perovskites with higher anticipated chemical stability.
- Begin optimization of cermet membranes by testing the effect of precursor powder size on membrane characteristics.

## OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

There were no open items or modifications to the work plan during this quarter.

## References

(1) White, J. H.; Schwartz, M.; Sammells, A. F.; Patent No. 5,821,185, Eltron Research, Inc.: USA, 1998.

(2) White, J. H.; Schwartz, M.; Sammells, A. F.; Patent No. 6,037,514, Eltron Research, Inc.: USA, 2000.

(3) White, J. H.; Schwartz, M.; Sammells, A. F.; Patent No. 6,281,403 B1, Eltron Research, Inc.: USA, 2001.

(4) Balachandran, U.; Lee, T. H.; Zhang, G.; Dorris, S. E.; Rothenberger, K. S.; Howard, B. H.; Morreale, B.; Cugini, A. V.; Siriwardane, R. V.; Jr., J. A. P.; Fisher, E. P. In *26th International Technical Conference on Coal Utilization and Fuel Systems*: Clearwater, FL, 2001, pp 751-761.

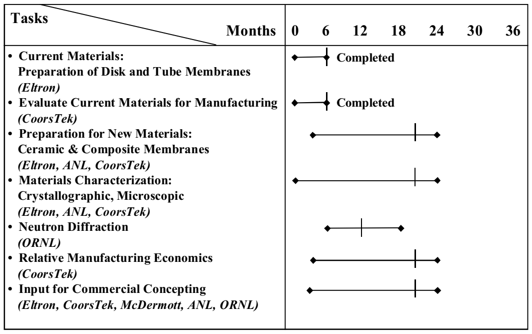
(5) Wachsman, E. D.; Naixiong, J.; Two-Phase Hydrogen Permeation Membrane. Patent No. 6,235,417, USA, 2001.

(6) Roark, S. E.; White, J. H.; Sammells, A. F.; Dane, J.; Keeley, J. "Mixed-Conducting Membranes for the Spontaneous Oxidative Dehydrogenation of Alkanes to Olefins (DOE SBIR Final Report, Contract No. DE-FG0397ER82571)," Eltron Research, Inc., 1999.

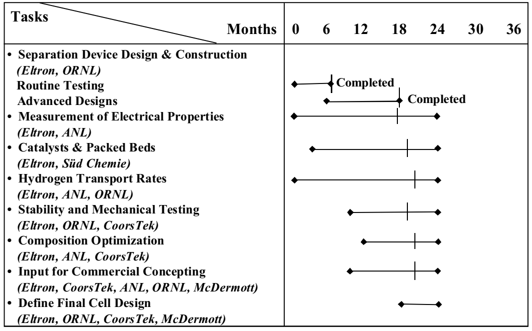
## TIME LINES

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

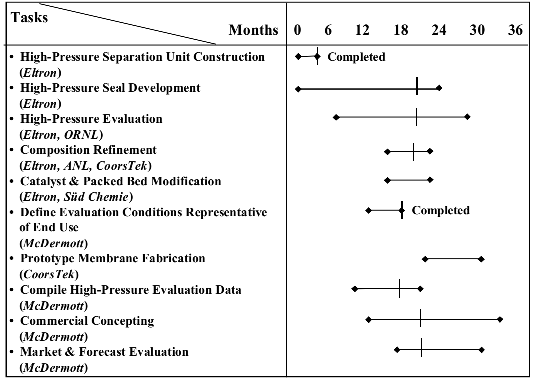
### *Task 1*
### Preparation & Characterization of Membrane Materials



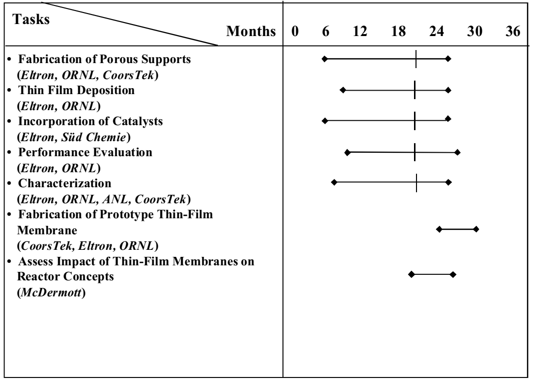
### *Task 2*
### Evaluation of Hydrogen-Transport Membranes



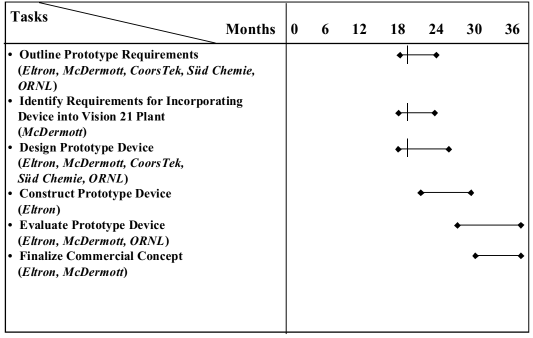
### *Task 3*
### High-Pressure Hydrogen Separation



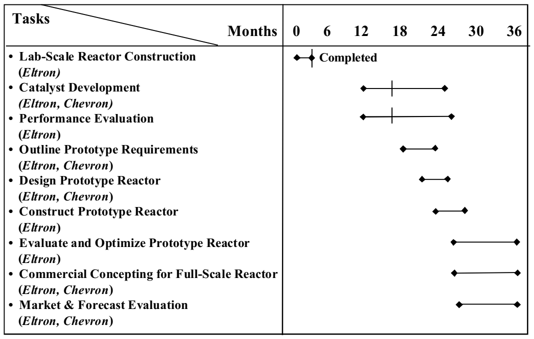
### *Task 4*
### Thin-Film Hydrogen Separation Membranes



### *Task 5*
### Construction & Evaluation of Prototype Hydrogen Separation Unit



### *Task 6*
### Membrane-Promoted Conversion of Alkanes to Olefins



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DE-FC26-00NT40762

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U.S. Department of Energy
9800 S. Cass Avenue
Argonne, IL 60439
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## A. CONTRACTOR ACTION (CONTRACTOR COMPLETES PART A. 1-5)

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

2. Type of Document: ☒ Technical Progress Report ☐ Topical Report ☐ Final Technical Report
☐ Abstract ☐ Technical Paper ☐ Journal Article ☐ Conference Presentation
☐ Other (please specify): ______

3. Date clearance needed: ______

♦4. Patent information.

| Yes | No | |
|---|---|---|
| ☐ | ☒ | Is any patentable subject matter disclosed in the report? |
| ☐ | ☐ | If so, has an invention disclosure been submitted to DOE Patent Counsel?<br>If yes, identify disclosure number or DOE Case Number ______ |
| ☐ | ☒ | Are there any patent-related objections to the release of this report? If so, state the objections. |

______
______

♦5. Signed ______ Date August 2, 2002
(Contractor)

Name & Phone No. Eltron Research Inc. 303-530-0263

Address 4600 Nautilus Court South, Boulder, CO 80301-3241

## B. DOE PATENT COUNSEL ACTION

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(Patent Attorney)

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