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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, mixed proton/electron conductivity and hydrogen transport was measured as a function of metal phase content for a range of ceramic/metal (cermet) compositions. It was found that optimum performance occurred at 44 wt.% metal content for all compositions tested. Although each cermet appeared to have a continuous metal phase, it is believed that hydrogen transport increased with increasing metal content partially due to beneficial surface catalyst characteristics resulting from the metal phase. Beyond 44 wt.% there was a reduction in hydrogen transport most likely due to dilution of the proton conducting ceramic phase. Hydrogen separation rates for 1-mm thick cermet membranes were in excess of 0.1 mL/min/cm<sup>2</sup>, which corresponded to ambipolar conductivities between 1 x 10<sup>-3</sup> and 8 x 10<sup>-3</sup> S/cm. Similar results were obtained for multi-phase ceramic membranes comprised of a proton-conducting perovskite and electron conducting metal oxide. These multi-phase ceramic membranes showed only a slight improvement in hydrogen transport upon addition of a metal phase. The highest hydrogen separation rates observed this quarter were for a cermet membrane containing a hydrogen transport metal. A 1-mm thick membrane of this material achieved a hydrogen separation rate of 0.3 mL/min/cm<sup>2</sup> at only 700°C, which increased to 0.6 mL/min/cm<sup>2</sup> at 950°C.

## 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 (Patent No. US5821185) with a demonstrated ability for rapid proton 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).

During this quarter, new ceramic/metal (cermet) compositions were tested and compared to multi-phase ceramic membranes. It was concluded that both metals and metal oxides could be added to proton conducting perovskite-based ceramics to achieve comparable hydrogen separation rates and ambipolar conductivities. Moreover, substantial improvements in hydrogen separation rates were achieved by using a metal with high hydrogen permeability in the cermet composition. The membranes used for these tests were 1-mm in thickness, which substantially limited hydrogen separation. However, an improved shrinkage match between thin film membranes and porous supports was achieved during this quarter, and it is anticipated that this development will enable testing of much thinner membranes during the next quarter.

## 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

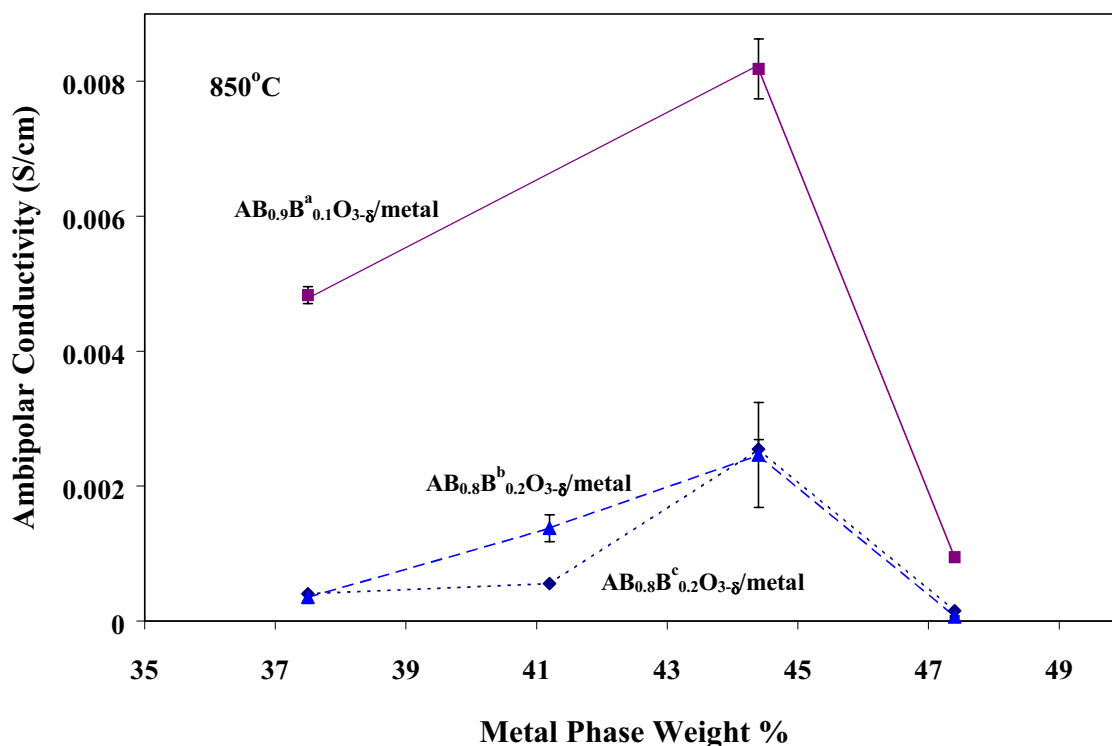
### Tasks 1 & 2      *Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes*

**Contributors:** Eltron, CoorsTek, MTI, SCI, ORNL

#### **a.      Ceramic-Metal (Cermet) Composite Membranes - Eltron, CoorsTek**

During this quarter, the majority of work at Eltron focused on development of cermet membranes. Previously, it was shown for perovskite-based ceramics that ambipolar conductivity and corresponding H<sub>2</sub> transport of the ceramic phase could be increased by doping with selected transition metals. Moreover, there appeared to be a trend of increasing conductivity when moving from left to right across the periodic table within a row of transition metal dopants. Based on those results, new cermet compositions were prepared and tested using three different transition-metal-doped ceramic phases, designated as AB<sub>0.9</sub>B<sup>a</sup><sub>0.1</sub>O<sub>3-δ</sub>, AB<sub>0.8</sub>B<sup>b</sup><sub>0.2</sub>O<sub>3-δ</sub>, and AB<sub>0.8</sub>B<sup>c</sup><sub>0.2</sub>O<sub>3-δ</sub>, each combined with the same metal phase. Ceramic phases AB<sub>0.9</sub>B<sup>a</sup><sub>0.1</sub>O<sub>3-δ</sub> and AB<sub>0.8</sub>B<sup>b</sup><sub>0.2</sub>O<sub>3-δ</sub> were mixed proton and electron conductors, whereas ceramic phase AB<sub>0.8</sub>B<sup>c</sup><sub>0.2</sub>O<sub>3-δ</sub> primarily was a proton conductor. The cermets were prepared with varying ceramic/metal ratios from powders with particle sizes between 0.4 and 1.5 μm. The powders were mixed by ball milling for 1 hr, then pressed into pellets at 15 to 17 kpsi for 2 min. The pellets were sintered between 1100° and 1425°C for 4 hrs under 5% H<sub>2</sub> (bal. Ar), then sanded to the desired thickness and polished. The metal phase of these cermets is not a hydrogen transport material, however, it does have catalytic activity for dissociation of hydrogen. Thus, no catalyst was applied to the cermet samples for these studies.

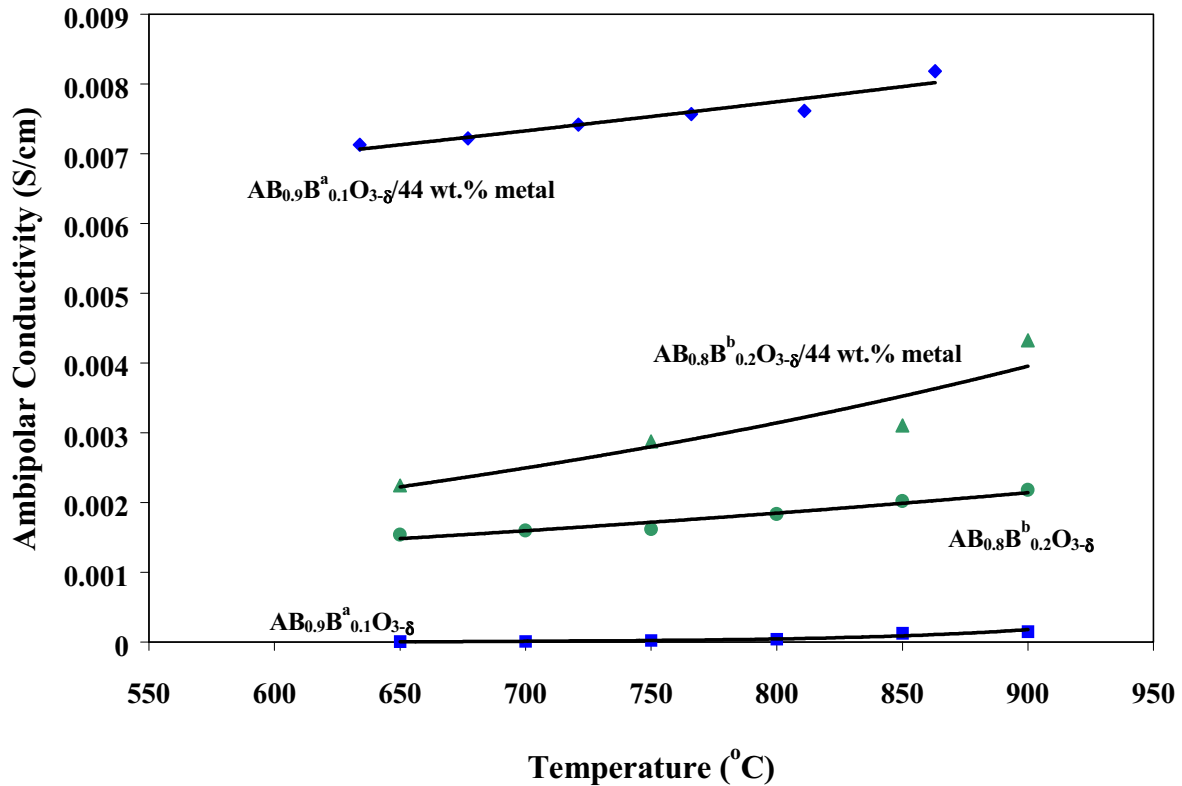
The thicknesses of the membranes tested were between 0.5 and 1.2 mm, which enabled hydrogen transport rates between ~0.01 and 0.3 mL/min/cm<sup>2</sup>. However, since membranes of a range of thicknesses were used for testing, and inevitably the hydrogen concentration on opposite sides of the membranes varied, the data below is presented in terms of conductivity to normalize for these variables. Figure 1 shows a plot of ambipolar conductivity as a function of the metal phase weight percent for each of the ceramic phases tested. Ohmmeter measurements across the thickness of the membrane samples indicated a resistance between 0.1 to 0.3Ω. Considering the very small contact area between the membrane surface and ohmmeter probes, this resistance range corresponded to very high electron conductivity, and indicated that the metal phase content was within the percolation range for each metal volume tested. Similar conclusion were derived from studies of BaCe<sub>0.8</sub>Y<sub>2</sub>O<sub>3</sub>/Ni (Siriwardane *et al.*, Appl. Surf. Sci. v. 167, p. 34, 2000) and Bi<sub>1.5</sub>Er<sub>0.5</sub>O<sub>3</sub>/Ag cermets (Elshof *et al.*, J. Electrochem. Soc., v. 144, p. 4361, 1997). Therefore, the difference in ambipolar conductivity between the three curves in Figure 1 was the result of differences in the proton conductivity of the ceramic phases. The maximum conductivity for each curve was observed at a metal content of 44.4 wt.%, which corresponded to between 34 and 36 vol.% metal phase, and approximately 80 mol% metal phase. Since there was adequate metal phase for electrical continuity in each sample tested, the maximum in the curves at 44.4 wt.% likely was not the result of an optimum bulk electron conductivity. Instead, it is probable that the higher percentage of metal phase resulted in improved hydrogen exchange catalysis at the membrane surface, as also was observed by Siriwardane *et al.* (Appl. Surf. Sci. v. 167, p. 34, 2000). Specifically, as the bulk metal concentration increases, the



**Figure 1.** Plot comparing ambipolar conductivity of three cermet compositions as a function of metal phase weight percent. The ceramic phases designated as  $AB_{0.9}B_{0.1}O_{3.8}$  and  $AB_{0.8}B_{0.2}O_{3.8}$  were mixed proton and electron conductors, whereas, the ceramic phase  $AB_{0.8}B_{0.2}O_{3.8}$  was primarily a proton conductor. The concentration of hydrogen on the feed side was 80 vol.% (bal. He), and Ar was used on the permeate side. The flow rates were 120 mL/min.

membrane surface roughness increases due to formation metal nodules that facilitate dissociative adsorption of hydrogen on the feed side, and desorption of hydrogen on the permeate side. However, at the highest metal phase wt.% tested, the ambipolar conductivity fell sharply. There are two possible explanations for this result. First, when the quantity of metal at the surface is very high, metal annealing at elevated temperatures actually can smoothen surface features and reduce surface area, which can reduce catalytic activity. Second, at the highest metal phase content, continuity of the proton conducting phase could be lost.

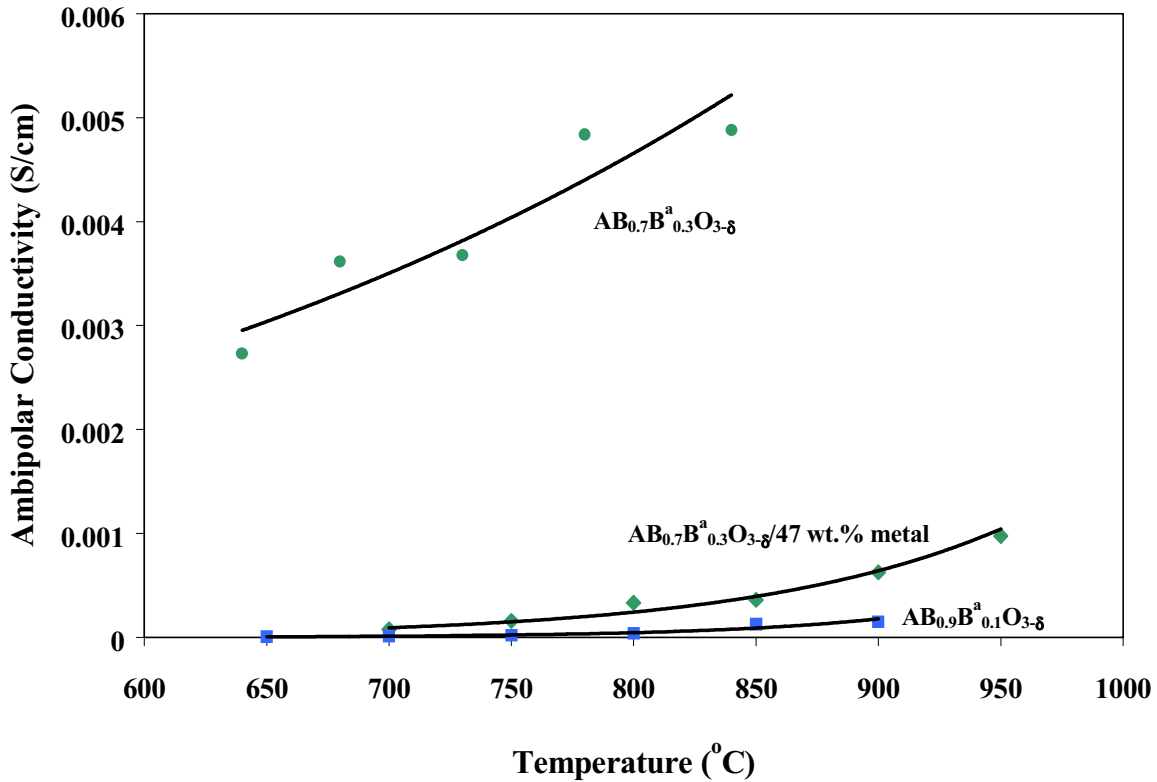
The results in Figure 1 indicated that the ceramic phase  $AB_{0.9}B_{0.1}O_{3.8}$  had significantly higher proton conductivity than the other two phases tested. However, as shown in the lower two curves of Figure 2, the *ambipolar* conductivity of  $AB_{0.9}B_{0.1}O_{3.8}$  was actually lower than for  $AB_{0.8}B_{0.2}O_{3.8}$  over the entire temperature range tested. Thus, it is likely that the higher ambipolar conductivity of  $AB_{0.8}B_{0.2}O_{3.8}$  was the result of higher electron conductivity. Based on this explanation, it was reasonable that the  $AB_{0.8}B_{0.2}O_{3.8}/metal$  cermet demonstrated only slightly higher ambipolar conductivity than the corresponding ceramic phase alone. However, a very significant increase in



**Figure 2.** Plot comparing ambipolar conductivity as a function of temperature for  $AB_{0.9}B^a_{0.1}O_{3-\delta}$  and  $AB_{0.8}B^b_{0.2}O_{3-\delta}$  mixed proton and electron conducting ceramics, and their respective cermet analogs. The concentration of hydrogen on the feed side was 80 vol.% (bal. He), and Ar was used on the permeate side. The flow rates were 120 mL/min.

ambipolar conductivity was observed for the  $AB_{0.9}B^a_{0.1}O_{3-\delta}$ /metal cermet (top curve) because of higher proton conductivity in  $AB_{0.9}B^a_{0.1}O_{3-\delta}$ .

The data in Figure 3 demonstrates that a similar improvement in ambipolar conductivity can be achieved by increasing the quantity of transition metal dopant, rather than adding a metal second phase. Specifically, ambipolar conductivity increased almost by a factor of 40 when the dopant  $B^a$  was increased from a fraction of 0.1 to 0.3. SEM images and energy dispersive X-ray (EDX) measurements of  $AB_{0.7}B^a_{0.3}O_{3-\delta}$  demonstrated a distinct elongated rod-like phase consisting primarily of the  $B^a$  dopant embedded in a matrix containing mainly the A and B cations. XRD patterns of  $AB_{0.9}B^a_{0.1}O_{3-\delta}$  indicated a primary pseudo-cubic  $ABO_3$  phase, with a second pseudo-cubic phase consistent with  $AB^aO_3$ . As shown in the middle curve of Figure 3, adding a metal phase to this two-phase ceramic actually decreased conductivity. This result likely was due to a dilution of the proton conducting by an excessive quantity of electron conducting phase(s).



**Figure 3.** Plot comparing ambipolar conductivity as a function of temperature for dense hydrogen transport membranes. The concentration of hydrogen on the feed side was 80 vol.% (bal. He), and Ar was used on the permeate side. The flow rates were 120 mL/min.

Conductivity and activation energies for samples shown in the previous three figures are summarized in Table 1. Adding the metal phase to  $AB_{0.9}B^a_{0.1}O_{3-\delta}$  significantly increased conductivity and there was a factor of 10 drop in activation energy. Similar results were observed comparing when the dopant concentration of  $AB_{0.9}B^a_{0.1}O_{3-\delta}$  ( $x = 0.1$ ) was increased to  $AB_{0.7}B^a_{0.3}O_{3-\delta}$  ( $x = 0.3$ ). The same trend in conductivity and activation energy was observed for  $AB_{0.8}B^b_{0.2}O_{3-\delta}$  upon addition of the metal phase, however, the differences were small.

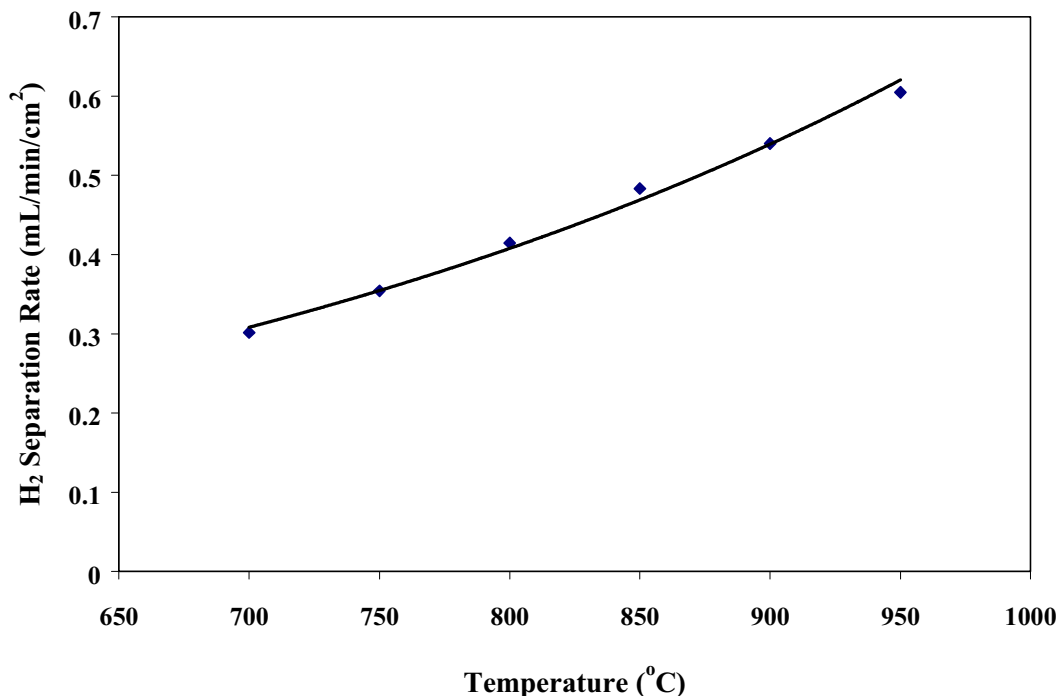


**Table 1.**  
**Comparison of Ambipolar Conductivity and Activation Energies for H<sub>2</sub>**  
**Transport Through Several Cermet and Ceramic Membranes.**

Ceramic Phase	Wt.% Metal Phase	Ambipolar Conductivity (S/cm) at 850°C	Ea (eV)	lnA
AB <sub>0.9</sub> B <sup>a</sup> <sub>0.1</sub> O <sub>3-δ</sub>	44	8.19 x 10 <sup>-3</sup>	0.14	3.6
AB <sub>0.9</sub> B <sup>a</sup> <sub>0.1</sub> O <sub>3-δ</sub>	0	1.5 x 10 <sup>-4</sup>	1.4	11
AB <sub>0.7</sub> B <sup>a</sup> <sub>0.3</sub> O <sub>3-δ</sub>	47	3.6 x 10 <sup>-4</sup>	1.1	11
AB <sub>0.7</sub> B <sup>a</sup> <sub>0.3</sub> O <sub>3-δ</sub>	0	4.9 x 10 <sup>-3</sup>	0.34	5.3
AB <sub>0.8</sub> B <sup>b</sup> <sub>0.2</sub> O <sub>3-δ</sub>	44	3.11 x 10 <sup>-3</sup>	0.30	4.5
AB <sub>0.8</sub> B <sup>b</sup> <sub>0.2</sub> O <sub>3-δ</sub>	0	2.02 x 10 <sup>-3</sup>	0.22	3.1
AB <sub>0.8</sub> B <sup>c</sup> <sub>0.2</sub> O <sub>3-δ</sub>	44	2.55 x 10 <sup>-3</sup>	0.20	3.2

**b. Cermets Containing a Hydrogen Transport Metal - Eltron**

Although the metal phase used in the above samples has some hydrogen solubility and mobility, it is not considered a “hydrogen permeable metal.” As an alternative to the above cermets, additional materials were prepared and tested with the general composition ABO<sub>3</sub>/x%M where M represent a metal with high hydrogen permeability. Similar membranes are under development by Balachandran *et al.* at Argonne National Laboratory (Balachandran *et al.* Proceedings of the 26<sup>th</sup> International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, 2000, p. 751). Figure 4 shows preliminary results for a ABO<sub>3</sub>/57 wt.% metal cermet. In this case, the hydrogen transport mechanism is not necessarily ionic/electronic, so the data is presented in terms of transport rate rather than conductivity. For a 1-mm thick membrane, the transport rate increased from 0.3 mL/min/cm<sup>2</sup> at 700°C to 0.6 mL/min/cm<sup>2</sup> at 950°C. These rates were approximately two to ten times as high as the best results for the analogs described above. Furthermore, the data was obtained with dry hydrogen, and results obtained by Balachandran *et al.* suggest even higher transport rates can be expected with humidified hydrogen. Accordingly, derivatives of this composition will be pursued in the next quarter. However, it is expected that this category of materials will not be as resistant to feedstream poisons, and specially designed catalysts will be needed to maintain stability.



**Figure 4.** Plot showing hydrogen separation rate as a function of temperature for a cermet membrane containing a hydrogen-permeable metal. The membrane was ~1 mm thick, and the hydrogen was dry. The inlet hydrogen concentration was ~80 vol.% (bal. He), and argon was used as the sweep gas. Flow rates were 120 mL/min.

### c. Effect of Catalyst on Hydrogen Transport Rates - Eltron, SCI

To date, membranes have been tested with and without catalytic metals, and during the previous quarter, SCI produced catalyst coatings of Ni, Pd, and Pt on membrane samples provided by Eltron. The precursor compounds chosen were platinum (II) acetyl acetonate (Ac-Ac), palladium (II) acetyl acetonate (Ac-Ac), and nickel (II) ethyl hexanoate. The Pt and Pd compounds were dissolved in tetra-hydrofuran and the Ni compound was dissolved in n-hexane. A high concentration of the Ni catalyst precursor was achieved (~5 wt.%), and thus a sufficient quantity of Ni was applied using a pipette directly to the membrane surface. The disk was dried at 60°C, and then calcined at 500°C. The solubility of Pt and Pd Ac-Ac was very low (<1 wt.% Pt or Pd), and high loadings on the membrane surface was difficult with these precursors. As an alternative approach, slurries of the Pt and Pd Ac-Ac were prepared in acetone and applied to the membranes using a pipette. This procedure produced a thin, uniform, and controllable coating after drying and calcination at 750°C.

Membrane samples containing a catalyst consistently showed higher hydrogen flux than those without. However, no significant difference was observed as a function of catalyst compositions. As predicted in earlier reports, the reason for this observation likely is that the membranes tested so

far have been thick enough (~0.5 to 1 mm) that hydrogen flux likely is mostly limited by transport through the membrane, rather than by surface kinetics. Although the presence of a catalyst did improve transport, the effect of catalyst composition on transport likely will not be apparent until membrane thicknesses are reduced below about 0.1 mm.

**d. Neutron Diffraction Studies - Eltron, ORNL**

During this quarter, neutron diffraction experiments were refined to gain insight into the process for hydrogen transport in model perovskite compounds. The experiments will be performed in collaboration with Oak Ridge National Laboratory either at their facility in Oak Ridge, TN, or at another acceptable facility. Currently, the facility at Oak Ridge is undergoing scheduled maintenance and upgrading, and is not expected to be fully functional until the Spring of 2002. However, the contact at Oak Ridge (Dr. Andrew Payzant) will determine if there is another facility that could be used at an earlier date.

The general experiments to be performed are summarized as follows:

*Experiment 1:* Room-temperature diffraction studies will be performed on the model compound to determine structural distortions from the ideal cubic perovskite lattice. This experiment also will enable determination of oxygen vacancy concentration and ordering.

*Experiment 2:* Diffraction measurements will be performed at high temperature (up to 800°C) to determine the crystal structure at the anticipated operating temperature. Additionally, this experiment will provide information regarding the nature of oxygen vacancies. For example, if oxygen vacancies are ordered at room temperature, it will be useful to know if they maintain order as the temperature is raised.

*Experiment 3:* A powder sample of the model ceramic compound will be conditioned by heating in moist air between 100° and 200°C. Neutron diffraction data will be collected on this preconditioned sample to evaluate the extent of water uptake, location of hydrogen and/or protons in the structure, and degree of vacancy and proton ordering.

*Experiment 4:* A sample from the previous experiment will be heated to operating temperature in a moist atmosphere to promote proton mobility and disordering. Neutron diffraction measurements will be obtained and examined for evidence of proton conduction and conduction pathways. Particular emphasis will be placed on determining whether the major migrating species are protons or hydroxyions. Similar disordering of oxygen and hydrogen will suggest that hydroxyions are the dominant mobile charge carrying species.

*Experiment 5:* The previous two experiments will be repeated, except that dry hydrogen will be used rather than moisture to precondition the sample. The extent of hydrogen uptake will be compared to the previous experiments, and low-temperature diffraction measurements will provide information about hydrogen ordering without filling of oxygen vacancies.

*Experiment 6:* Diffraction measurements of the sample from the previous experiment will be performed at operating temperature and the data will be compared to that obtained in Experiment 4 to identify differences in the conduction pathway as a function of the oxygen vacancy concentration.

**e. Manufacturing Issues and Relative Economics - CoorsTek, Eltron**

Manufacturing and economic aspects of the materials being developed during this program are being addressed by CoorsTek. CoorsTek's specific goal is to develop cost effective manufacturing processes for the proposed membranes, and define material properties required for efficient manufacture and operation of this technology, as well as the final membrane design. As summary of the work completed to date by CoorsTek through collaboration with Eltron is provided below.

CoorsTek initiated cost effective manufacturing development using  $\text{BaCeO}_3$  as a representative perovskite-based hydrogen separation material. The process for fabricating  $\text{BaCeO}_3$  was transferred from Eltron to CoorsTek and optimized at CoorsTek to yield maximum fired density. This fired density was  $5.93 \text{ gm/cm}^3$  and the material was determined to be single phase  $\text{BaCeO}_3$ . In powder form for the purpose of checking powder true specific gravity, the density was observed to decrease in flowing He indicating that a gas species desorbs from the  $\text{BaCeO}_3$  over time. This change in density was not observed on fired parts. However, additional tests are being run to determine the nature of this species and to determine if this will affect the properties of the fired parts. Mobility measurements performed at Eltron are used to confirm that equivalent performance was achieved. CoorsTek will fabricate additional batches of this formulation to verify reproducibility of the process.

The second family of materials transferred from Eltron to CoorsTek was a transition metal-substituted perovskite. Two formulations were transferred to CoorsTek, generalized in this text as  $\text{AB}_{0.7}\text{B}^{\text{a}}_{0.3}\text{O}_{3-\delta}$  and  $\text{AB}_{0.2}\text{B}^{\text{a}}_{0.8}\text{O}_{3-\delta}$ . It became evident during processing that the  $\text{AB}_{0.2}\text{B}^{\text{a}}_{0.8}\text{O}_{3-\delta}$  formulation resulted in multiple complex phases with no  $\text{ABO}_3$  phase present, so further development of this formulation was discontinued as directed by Eltron. High densities were obtained with the  $\text{AB}_{0.7}\text{B}^{\text{a}}_{0.3}\text{O}_{3-\delta}$  formulation. Initial x-ray diffraction measurements indicated that this material sinters with two phases present, a  $\text{B}^{\text{a}}$ -rich phase having an elongated grain structure and a  $\text{B}^{\text{a}}$ -deficient phase, as the continuous matrix phase. Further elemental analysis of  $\text{B}^{\text{a}}$ , A and B cation distribution within the complex microstructure is being pursued. This offers the interesting possibility that the mobility of this material can be altered significantly by varying the relative volume percent of the two phases if one phase, in fact, exhibits higher ionic conduction. This composition in calcined or sintered powder form also exhibited the decrease in density with time, similar to the phenomenon exhibited by  $\text{BaCeO}_3$  indicating that a gas species is desorbing. Additional tests are being run to determine the nature of this species. Mobility measurements from Eltron will be used to confirm that equivalent performance was achieved. CoorsTek will then fabricate additional batches of this formulation to verify reproducibility of this process.

Eltron selected two cermet formulations for transfer to CoorsTek - a  $\text{AB}_{0.7}\text{B}^{\text{a}}_{0.3}\text{O}_{3-\delta}/44 \text{ wt.}\%$  metal formulation and a  $\text{AB}_{0.8}\text{B}^{\text{c}}_{0.2}\text{O}_{3-\delta}/44 \text{ wt.}\%$  metal formulation. Processing has been initiated on the  $\text{B}^{\text{c}}$ -modified formulation first to be followed by the  $\text{B}^{\text{a}}$ -modified formulation.

Several tests have been set up for characterization of the materials as well as for in-process quality control. X-ray diffraction (XRD) specifications have been set up for the calcined process step and the fired process step. A He pycnometer has been set up for determining fired density. It is also used to estimate the true specific gravity of processed powders, since compositional theoretical density is difficult to calculate for complex multi-phase microstructures. Archimedes method based on suspended weight for measuring volume is also being used to calculate density on sintered samples, as an alternative to the He pycnometer method. Mobility tests will be carried out by Eltron.

In an effort to develop processes for these formulations that conform to typical ceramic manufacturing processing methods for high volume cost effective processing, aqueous processing was evaluated. Eltron has developed all of its formulations based on a non-aqueous process, utilizing isopropanol for batch milling and acetone for binder addition. Typical conventional processing of ceramic materials is carried out using aqueous based systems prior to spray drying of powders for part fabrication. Although it is usually more cost effective to use aqueous processing, non-aqueous systems are also used in cases where that is not possible. Tape casting of ceramic substrates is an example of a high volume manufacturing process that is based on non-aqueous processing. In the first series of tests using an aqueous system for the BaCeO<sub>3</sub> formulation, it was determined that the calcined powders could not be dispersed effectively for milling in water. The suspensions flocculated even when using dispersants. When the formulation was milled without dispersants, it exhibited a pH greater than 13. Milling at low solids content was pursued and traditional polyglycol binders were added; however, processed powders would not compact very well and sintered poorly with many defects such as cracks. Also XRD patterns of the calcined powders milled in water showed the presence of additional phases including BaCO<sub>3</sub>, Ba(OH)<sub>2</sub>·H<sub>2</sub>O and Ba(OH)<sub>2</sub>·3H<sub>2</sub>O, which explain the poor powder processing and sintering characteristics. At this point, it appears that an alcohol based process, currently being used for a lab-scale process, will need to be developed for larger-scale applications. Eltron has indicated that modifying BaCeO<sub>3</sub>-based compositions is possible to improve hydrolytic stability, which may be pursued at a later time. Other cost reducing practices such as isostatic pressing and low cost raw materials will be evaluated later. Environmental aspects of the process also will be considered from a manufacturing perspective.

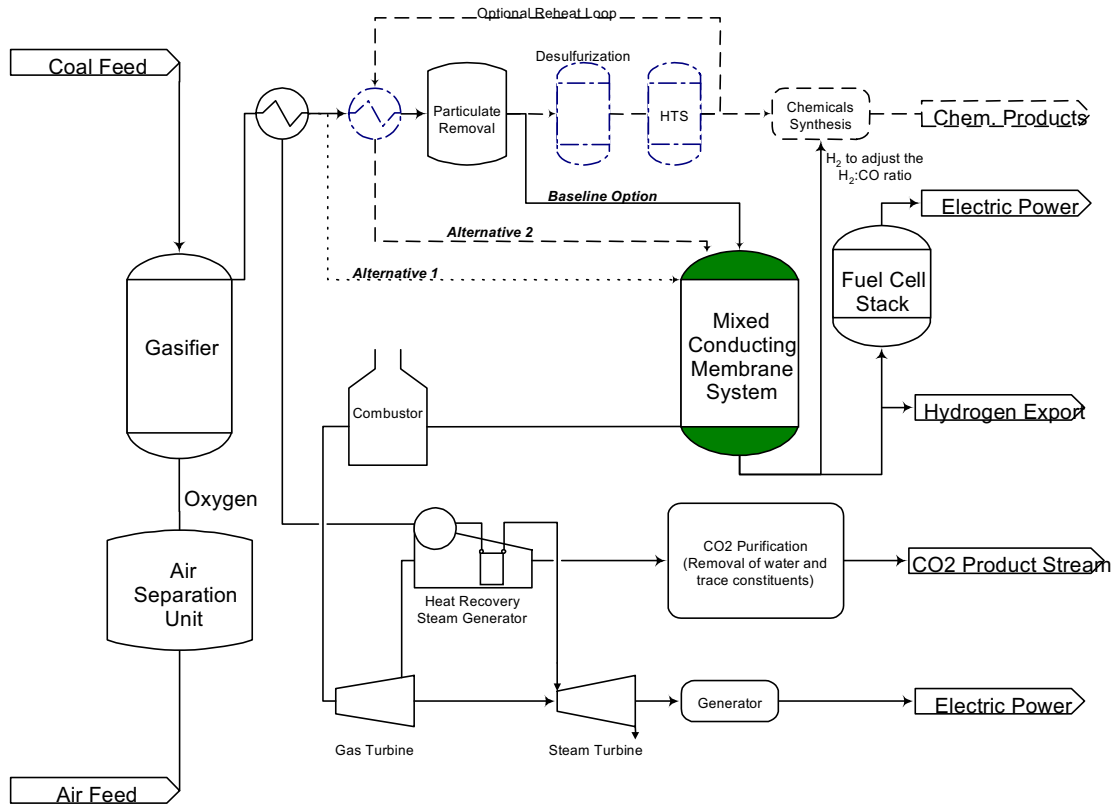
#### **f. Commercial Concepting - MTI**

MTI has focused on gathering and compiling background information needed to define hydrogen separation process conditions and to provide a starting point for assessing the economics for addition of a hydrogen separation system to a Vision 21 Plant. The results to date are summarized below.

**Potential Process Layouts.** Figure 5 is a Process Flow Diagram (PFD) showing integration of the hydrogen separation membrane into the coal gasification system of a Vision 21 power plant. There are different options for location of a hydrogen separator within the plant. Figure 5 shows three of these options that are identified as the baseline option, alternative 1, and alternative 2. For all options as shown on this schematic the system begins with a coal gasification unit. The gasifier is assumed to be oxygen fired for these discussions. In all cases a final step in the system utilizes a portion of the syngas to produce power using a combination of gas and steam turbines. Typically gas pressures are around 10 atmospheres when a portion of the power is being produced using a gas turbine, but operation at pressures two to three times as high are also possible. The intermediate process stages and integration of the hydrogen separation system are the focus of the discussions that follow.

The final layout for the process will depend on the tolerance of the hydrogen separation membrane to sulfur, particulate matter, and trace constituents in the syngas. In addition, application specific factors and economics will impact the process layout and membrane requirements.

**Baseline Option.** The baseline option shows the syngas flow from the outlet of the particulate collector entering the inlet of the separation system. This option assumes that particulate removal is required, but the membrane is sulfur tolerant to some extent. Calcium based sulfur removal can



**Figure 5. Process flow diagram of potential Vision 21 power plant layout, including alternatives for hydrogen separation unit placement.**

be performed in many of the gasifiers in order to collect around 80 to 90 percent of the sulfur upstream of the particulate collector, but significant levels of sulfur can still be expected (Smith, Peter V., Kellogg Brown & Root, Power Systems Development Facility, Telephone Conversation, Wilsonville, Alabama, March 28, 2001).

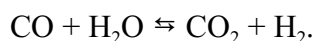
Gasifiers typically collect more ash in the furnace than combustion systems do, but the ratio of fly ash to bottom ash varies with the gasifier design. Additional particulate removal is typically achieved by use of cyclone particle collectors. Cyclones can be designed to remove the bulk of the particulate at temperatures that are usually below 1700°F (927°C) to minimize particulate agglomeration. Technologies for completing the particulate removal at high temperature are under development with a major focus on ceramic candle filters. The target is for operation of these filters at temperatures as high as 1600°F (871°C). Therefore, depending on the direction and results of coal gasification development efforts, the baseline option may provide particulate free syngas at about 1600°F with sulfur at several hundred ppm levels.

Alternative 1. The first alternative shown in the PFD allows higher temperature gas to be fed to the membrane system. The syngas feed to the membrane could be taken from the gas cooler which could be reduced in duty to provide the desired inlet temperature. Not shown would be the likely requirement to reduce the temperature of the syngas leaving the membrane vessel using a second stage of syngas cooling followed by final particulate removal to meet the gas turbine specifications. This alternative assumes that some particulate matter could be tolerated by the

membrane. While the goal is to operate candle filters as high as 1600°F (871°C), much of the early testing has been performed at lower temperatures around 1000 to 1400°F (538 to 760°C) (Wagner, Richard A., McDermott Technology, Inc., Telephone Conversation, Lynchburg, Virginia, April 10, 2001). If lower temperature particulate removal were to become the commercial standard, the feed would have to be taken upstream of the candle filters in order to get higher temperature syngas without reheat. The majority of the particulate is removed in the gasifier and cyclones, but a significant amount of fines would still be present.

Alternative 2. This layout assumes that very little sulfur can be tolerated and a separate desulfurization system is required. If one of the low temperature desulfurization systems is needed, an optional reheat loop could be used to bring the synthesis gas back to the temperatures required for the hydrogen separation system. Some high temperature sulfur removal systems are being developed and may provide a means of avoiding or minimizing the reheat loop even if sulfur is an issue.

In several DOE references IGCC schematics are shown that incorporate hydrogen separation downstream of a shift reactor. The purpose of the shift reactor is to increase the H<sub>2</sub> to CO ratio in the product gas through the water-gas shift reaction,



This would not be as desirable for a mixed conducting membrane system since the temperatures following a shift reactor are relatively low. High temperature shift catalyst can typically operate at temperatures between 320°C to 500°C. The lower end of the temperature range is usually targeted because H<sub>2</sub> conversion is higher at lower temperatures and catalyst life decreases because of sintering at high temperatures. The high temperature shift reactor was included in Figure 5 as an option since if low temperature sulfur removal were required, the gas purity and temperature would be in the range required for the shift reactor which would optimize the hydrogen production of the system. The economics and therefore the decision on the need for a high temperature shift reactor could be expected to vary with application.

If chemicals or liquid fuels are to be synthesized then it is more likely that a shift reactor would be utilized in order to provide higher H<sub>2</sub> to CO ratios in the syngas. However, the shift reactor could potentially be eliminated with the addition of a hydrogen separation membrane. A portion of the hydrogen could be sent to the syngas stream that feeds the chemical plant in order to increase the H<sub>2</sub> to CO ratio in the absence of a high temperature shift reactor. If the membrane could tolerate higher levels of sulfur this would improve the overall economics by allowing elimination of the sulfur polishing system. The remaining hydrogen could either be used locally for power generation in a fuel cell or exported as a high purity source of hydrogen.

**Potential Contaminants.** Typically in coal gasification the primary products are H<sub>2</sub> and CO comprising roughly 70% of the syngas at actual amounts and a ratio that varies with the coal and the gasifier conditions. The balance is usually highest in water vapor and CO<sub>2</sub> with methane present in amounts that again depend upon the gasifier conditions. The syngas produced in coal-gasification can also be expected to contain varied amounts of a large number of minor constituents. The project team will have to identify the level of tolerance the hydrogen separation system has to each of these constituents in order to define process conditions for the reactor and any changes required for the process flow diagram. The two most obvious syngas components that could be of potential concern are particulate matter and sulfur. As mentioned above, typical gasification plants provide particulate

removal and some level of sulfur control. The issue becomes how well the hydrogen separation system fits within these typical control schemes and any concerns related to the trace constituents that are typically present.

The particulate control systems for gasifiers are already being pushed toward operation as high in temperature as is feasible in order to maximize the overall process efficiency. There are many different technologies for >99.99% removal of particulate matter from flue gases. The one that seems to get the most attention for coal gasification is high temperature and pressure candle filter systems. These systems are targeting removal at temperatures up to about 850°C. Therefore, with these targets in mind it is reasonable to assume that particulate free syngas will be available to the membrane reactor at temperatures as high as 850°C without any additional processing. However, as mentioned above, most of the testing has been performed at lower temperatures to allow removal of the alkali and to reduce the severity of conditions seen by the particulate control equipment.

The next step is to determine if expected sulfur concentrations pose any concerns for the hydrogen separation system. The sulfur from the gasifier is primarily in the form of H<sub>2</sub>S, with some COS and trace amounts of CS<sub>2</sub>, thiophenes, and mercaptans (Understanding Coal Gasification, Alice Kristiansen, IEA Coal Research, March 1996). Calcium based sorbents can be used to remove 80 to 90% of the H<sub>2</sub>S upstream of the particulate removal. The final sulfur concentration depends in large part on the coal being utilized and the performance of gasifier sulfur removal, but the syngas could be expected to contain a few hundred PPM of H<sub>2</sub>S. Input is needed from testing to determine what sulfur levels are acceptable for the membrane.

If sulfur reduction to levels around 10's of PPM or lower are required, similar to the requirements of shift catalysts, then a final sulfur removal system will be required. Most of these are liquid absorbers that also remove CO<sub>2</sub> (Berkowitz, N., An Introduction to Coal Technology, Academic Press, Inc., New York, 1979). These systems typically operate at low temperatures in order to increase the H<sub>2</sub>S solubility. For applications where polishing only small amounts of sulfur is required, a zinc oxide bed is a possibility, and they typically operate at around 400°C to optimize the capture of organic sulfur compounds and the bed capacity. If any of these systems were required, a reheat system would be needed upstream of the hydrogen separator. However, high efficiency hot desulfurization is in the early stages of commercialization, and may prove to be a match for implementing the hydrogen separation system in a Vision 21 power plant. Again the sulfur removal requirements, if any, need to be determined through evaluation of the hydrogen transport membranes.

Coal can vary greatly in the amount and composition of mineral matter. Selected coals presented in "Steam" contain between 5 and 69% ash on a dry basis (Steam, It's Generation and Use, 40<sup>th</sup> ed., Babcock & Wilcox, a McDermott Company, Stultz, S.C., and Kitto, J.B., 1992). The major components that are analyzed for in ash analyses are provided in Table 2 along with the ranges of values shown for ten U.S. coals.

These values are reported as oxides and can be present in numerous forms in the utility system. Also, the reducing conditions in the gasifier and the downstream processes can impact the fate of these ash constituents. In addition to the presence of these components in the coal ash, furnace refractory is typically high in silica and alumina. As with the ash components, depending on the conditions and the temperature and efficiency of downstream particulate control, various forms of these species can potentially reach the hydrogen separation reactor.



**Table 2.**  
**Reported Ash Analysis Results for Ten U.S. Coals.**

<b>Species (as oxide)</b>	<b>Low Value (for ten U.S. coals)</b>	<b>High Value (for ten U.S. coals)</b>
SiO <sub>2</sub>	23.32	66.85
Al <sub>2</sub> O <sub>3</sub>	10.0	34.0
Fe <sub>2</sub> O <sub>3</sub>	1.18	19.0
TiO <sub>2</sub>	0.4	1.57
CaO	0.6	22.0
MgO	0.3	5.0
Na <sub>2</sub> O	0.39	7.41
K <sub>2</sub> O	0.27	2.65
P <sub>2</sub> O <sub>5</sub>	Unmeasured	0.99
SO <sub>3</sub>	0.99	20.85

The alkali components of the coal can promote corrosion and act as fluxing agents at high temperatures. Removal of alkali is performed upstream of the gas turbine to eliminate these concerns. This is typically performed by absorbing the alkali components (especially sodium) at temperatures below 1400°F (760°C) and lower. Alkali species can be expected to be present in the gas fed to the separation membrane in concentrations that will vary with the coal, the syngas temperature, and upstream processing.

In addition to the major components found in coal ash there are numerous trace elements. Many of these have been evaluated in more detail lately in light of questions over the potential environmental impact of these trace elements from coal fired power plants. Trace elements evaluated by MTI included antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium (Madden, D.A., Holmes, M. J., AECDP Data Library, McDermott Technology, Inc., <http://www.mtiresearch.com/aecdp.html>, 1998). Concentrations of these species are typically very low in coal. For one selected coal analyzed by MTI, all of these species were at concentrations less than 20 ppm in the coal. In addition, flue gas measurements showed that over 95% of flue gas concentrations were captured with the particulate for all of these constituents except for arsenic, selenium, and mercury. Removals in the particulate control devices was above 80% for arsenic, greater than 50% for selenium, and can be as low as single digit percentages of capture for mercury. These results are from a composite sample of an eastern bituminous coal and could be expected to vary greatly as a result of the coal and operating conditions of the firing system and of the particulate control device. Additional information can be gathered for any of these components that are determined to pose specific concerns for operation of the separation membrane.

Also present in higher concentrations are several acid gases. The most commonly measured of these are hydrogen chloride and hydrogen fluoride. The concentrations of chlorides and fluorides were measured for the same coal as described above in reference to trace elements. The results indicated a chloride concentration slightly above 1000 ppm and a fluoride concentration of about

35 ppm. These components also vary widely with the coal. Western coals are typically much lower in chloride and eastern coals can be either higher or lower in chloride than the coal selected. The fate of all of these components will depend on both the gasifier operation and the coal composition. Compared to a combustion system a gasifier will typically capture more of the inorganics within the firing system, but if particulate control is performed at higher flue gas temperatures less of the species with higher volatilities may be removed.

The next step is to identify the process limitations of the hydrogen separation system. After the temperature, pressure, and syngas composition requirements are identified, the PFD can be revisited and revised to accommodate the needs of the system. Any changes to the overall process will then be the inputs required to begin to evaluate the economic feasibility of incorporating hydrogen transport membranes into a Vision 21 power plant.

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

**Contributors:** Eltron

Operation of dense ceramic hydrogen separation membranes at high temperatures and pressures requires a chemically resistant seal with similar mechanical and expansion characteristics as the membrane material. During this quarter, seal compositions testing was continued and complemented with coefficient of thermal expansion measurements. Seal formation was achieved by ramping the cell assembly up to 1000°C and holding for a period of time. The assembly then was cooled to 800°C for seal testing. Seals tested during this quarter did not exceed results in the previous quarter, which enable a pressure of 100 psig to be maintained.

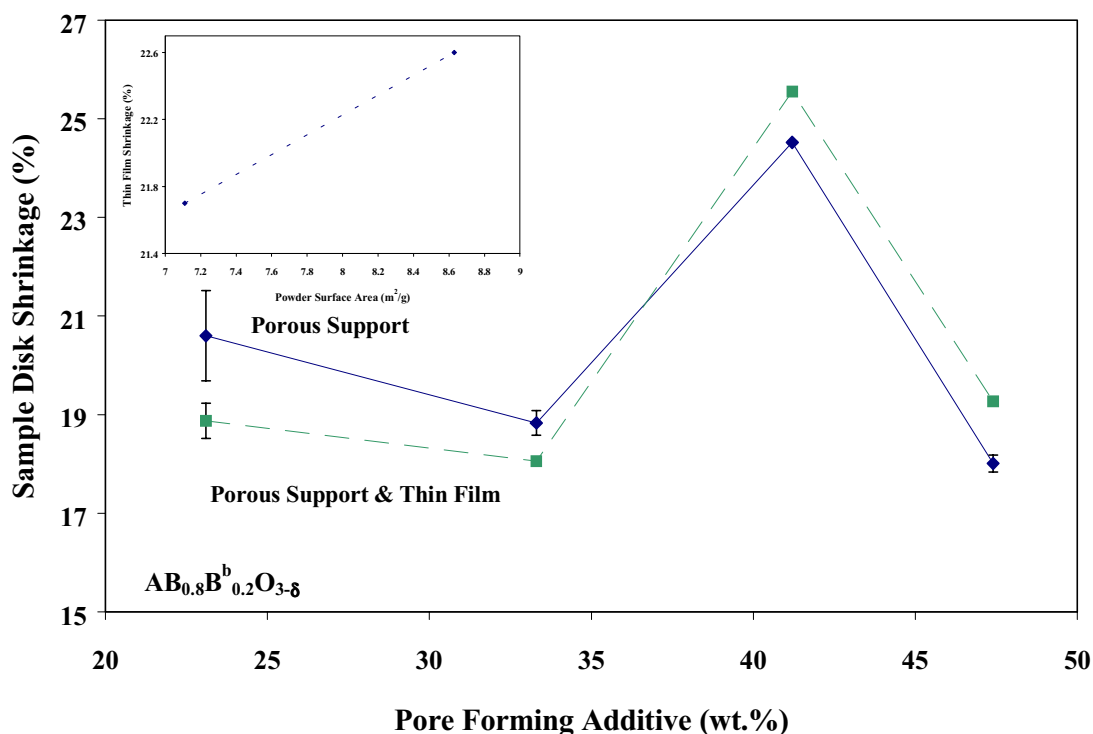
### **Task 4**     *Thin-Film Hydrogen Separation Membranes*

**Contributors:** Eltron

During the last quarter, it was determined that smooth, homogeneous, crack-free thin films could be deposited onto porous supports using both spin coating and tape casting techniques. However, despite the fact that the support and thin film were of the same composition, the extent of shrinkage of the thin film during sintering was much higher than the support, which caused delamination and cracking. During this quarter, efforts were directed at improving the shrinkage match between the support and thin film.

The shrinkage of the thin film can be controlled by varying the surface area of the powder prior to sintering, whereas shrinkage of the support is controlled primarily by the degree of porosity or the content or pore forming additive included in the powder prior to sintering. Figure 6 shows the variation in disk shrinkage for a porous support and a porous support with a thin film. The composition of the support and thin film is represented as  $AB_{0.8}B^b_{0.2}O_{3-\delta}$ , consistent with the data presented earlier. There was very little difference between the samples, and both had a clear maximum in shrinkage at a pore formation additive content of 41.2 wt.%. The inset in the figure shows the shrinkage of the thin film without the support as a function of the surface area of the powder prior to sintering. Based on the shrinkage data in Figure 6, appropriate combinations of porous supports and thin film precursors prepared, and supported thin film samples were fabricated without cracks or delamination. These samples currently are being evaluated for hydrogen transport,

and the results will be presented in the next report.



**Figure 6.** Plot showing the percent shrinkage versus wt.% of pore formation additive included in the porous support powder prior to sintering. The inset shows shrinkage of the thin film alone (without the support) as a function of powder surface area prior to sintering.

#### **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

In the previous report, the time line for several of the actions in Task 6 were moved out to enable more thorough characterization and evaluation of potential membranes for this application. During this quarter, modifications to one on the membrane screening reactors was performed for preliminary dehydrogenation catalyst testing. Also, a gas chromatograph was set up for analysis of propane dehydrogenation, and appropriate chemicals and gases for this task were acquired. During the next quarter, dehydrogenation catalysts to be applied to hydrogen separation membranes will be screened for propane dehydrogenation.

## SUMMARY AND CONCLUSIONS

Conclusions based on the work performed during this quarter, and other relevant actions are summarized as follows:

- Electron conductivity can be introduced into primarily proton conducting materials using transition metal dopants, metal oxides, or a pure metal phase.
- Highest hydrogen transport and mixed proton/electron conductivity is achieved with multi-phase membranes.
- For cermets, continuity of the metal phase was observed for all samples between 38 and 48 wt.% metal. However a maximum in hydrogen transport and conductivity was achieved at a metal phase content of 44 wt.%.
- Multi-phase ceramics and cermets demonstrated conductivities between  $1 \times 10^{-3}$  and  $8 \times 10^{-3}$  S/cm, corresponding to hydrogen separation rates in excess of  $0.1 \text{ mL/min/cm}^2$ .
- The difference in conductivity observed for the three cermet compositions tested was attributed to proton conductivity of the ceramic phase.
- Ceramic materials with high relative electron conductivity exhibited only minor improvements in ambipolar conductivity upon adding a metal phase.
- A cermet containing a hydrogen transport metal had a hydrogen transport rate two to ten times higher than cermets without hydrogen transport metals. A 1-mm thick membrane of this material achieved  $0.3$  to  $0.6 \text{ mL/min/cm}^2$  hydrogen transport between  $700$  and  $950^\circ\text{C}$ .
- Catalyst deposited onto membrane feed and permeate surfaces increased hydrogen separation rates. However, no significant difference in hydrogen separation rate was observed as a function of catalyst composition.
- Several key issues regarding practical and economical manufacturing of perovskite-based and cermet hydrogen separation membranes have been identified and improved.
- Analysis of potential Vision 21 plant configurations has identified important aspects for integration and application of the proposed technology.
- Progress was made in eliminating the shrinkage mismatch between thin film membranes and porous supports.

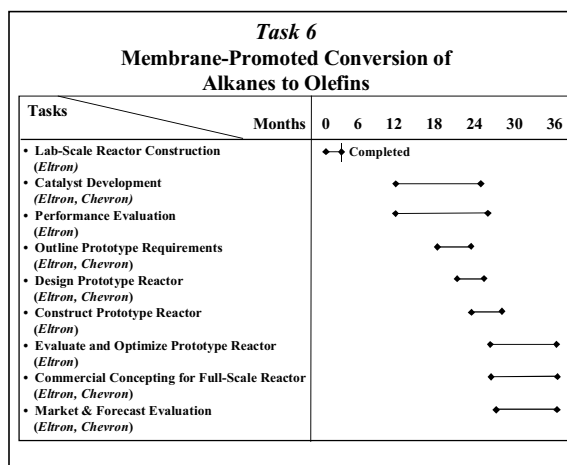
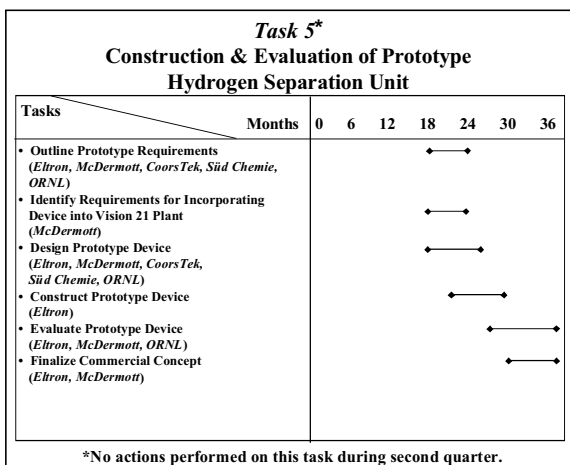
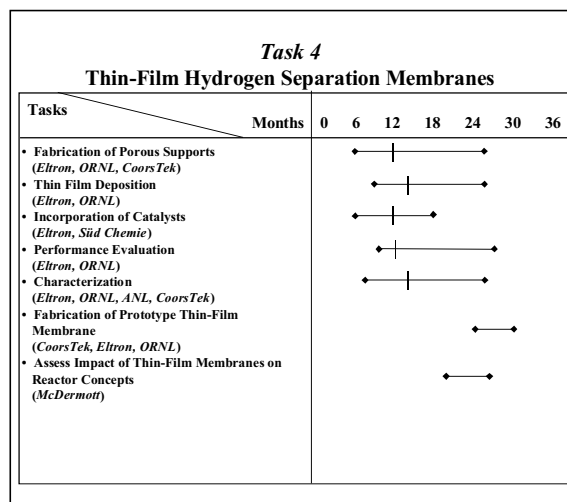
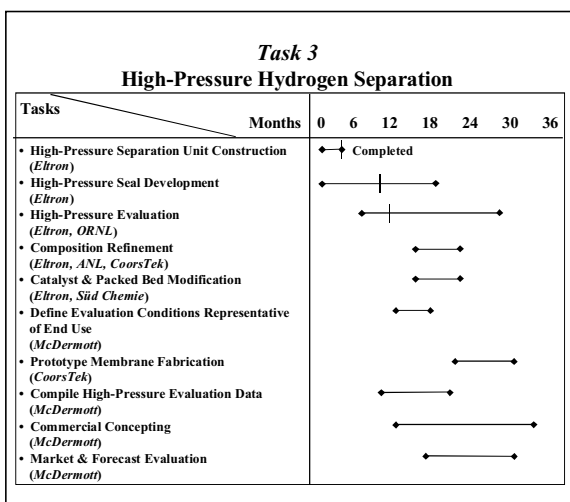
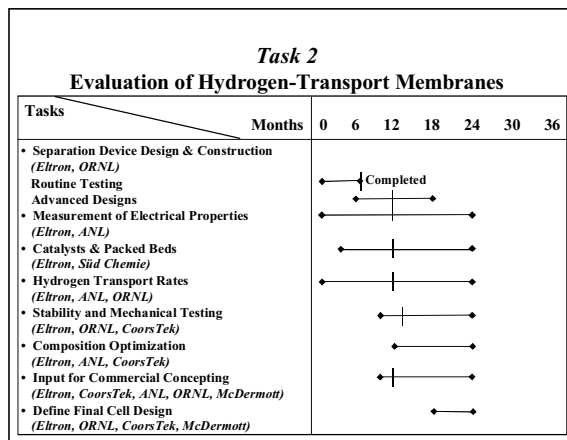
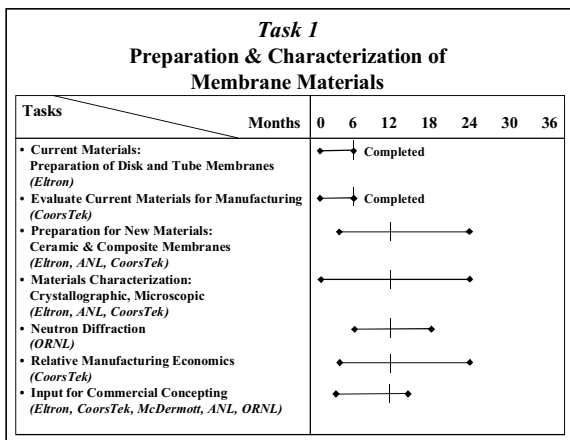
## OBJECTIVES FOR NEXT REPORTING PERIOD

Specific objectives for the next quarter are summarized as follows:

- Continue testing of multi-phase ceramics and cermets, including cermets containing hydrogen transport metals.
- Perform hydrogen separation analysis on supported thin film membranes.
- Perform catalyst testing on membranes sanded down to  $0.5 \text{ mm}$  in thickness.
- Initiate membrane stability studies.
- Begin screening catalysts for propane dehydrogenation.

# TIME LINES

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



# REQUEST FOR PATENT CLEARANCE FOR RELEASE OF CONTRACTED RESEARCH DOCUMENTS

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Mark P. Dvorscak  
U.S. Department of Energy  
9800 S. Cass Avenue  
Argonne, IL 60439  
FAX: (630) 252-2779

## 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?

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 October 31, 2001  
(Contractor)

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

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

## B. DOE PATENT COUNSEL ACTION

Patent clearance for release of the above-identified document is granted.

Other: \_\_\_\_\_

Signed \_\_\_\_\_ Date \_\_\_\_\_  
(Patent Attorney)

◆ Must be completed by the contractor.