Novel Composite Membranes for Hydrogen Separation in Gasification Processes in Vision 21 Energy Plants

Quarterly Technical Progress Report

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ABSTRACT

ITN Energy Systems, along with its team members, the Idaho National Engineering and Environmental Laboratory, Nexant Consulting, Argonne National Laboratory and Praxair, propose to develop a novel composite membrane structure for hydrogen separation as a key technology module within the future “Vision 21” fossil fuel plants.

The ITN team is taking a novel approach to hydrogen separation membrane technology where fundamental engineering material development is fully integrated into fabrication designs; combining functionally graded materials, monolithic module concept and plasma spray manufacturing techniques.

The technology is based on the use of Ion Conducting Ceramic Membranes (ICCM) for the selective transport of hydrogen. The membranes are comprised of composites consisting of a proton conducting ceramic and a second metallic phase to promote electrical conductivity. Functional grading of the membrane components allows the fabrication of individual membrane layers of different materials, microstructures and functions directly into a monolithic module. Plasma spray techniques, common in industrial manufacturing, are well suited for fabricating ICCM hydrogen separation modules inexpensively, yielding compact membrane modules that are amenable to large scale, continuous manufacturing with low costs.

This program will develop and evaluate composite membranes and catalysts for hydrogen separation. Components of the monolithic modules will be fabricated by plasma spray processing. The engineering and economic characteristics of the proposed ICCM approach, including system integration issues, will also be assessed. This will result in a complete evaluation of the technical and economic feasibility of ICCM hydrogen separation for implementation within the “Vision 21” fossil fuel plant.

The ICCM hydrogen separation technology is targeted for use within the gasification module of the “Vision 21” fossil fuel plant. The high performance and low-cost manufacturing of the proposed technology will benefit the deployment of “Vision 21” fossil fuel plant processes by improving the energy efficiency, flexibility and environmental performance of these plants. Of particular importance is that this technology will also produce a stream of pure carbon dioxide. This allows facile sequestration or other use of this greenhouse gas. These features will benefit the U.S. in allowing for the continued use of domestic fossil fuels in a more energy efficient and environmentally acceptable manner.

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EXECUTIVE SUMMARY

ITN Energy Systems, along with its team members, the Idaho National Engineering and Environmental Laboratory, Nexant Consulting, Argonne National Laboratory and Praxair, propose to develop a novel composite membrane structure for hydrogen separation as a key technology module within the future “Vision 21” fossil fuel plants.

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Specific work performed and accomplishments for this reporting period include:

- Development of a sintering aid that allows for dry-pressed membranes close to 100% of theoretical density;
- Evaluation of alternate metals in the cermet membranes;
- Measurement of the temperature dependence of the membrane conductivity;

- Evaluation of process parameters for the thin-film deposition process;
- Evaluation of thin-film membranes prepared using commercially fabricated ceramic powders;
- Further refinement of the process flow diagrams; and
- Initial work on a model for membrane performance.

1. INTRODUCTION

This report describes the work performed during the latest reporting period. During the previous reporting period, work was performed in all areas of the program. Specifically, additional pyrochlore compositions were synthesized, thin-film membranes that had previously been fabricated by thermal spray were tested and work continued on process design.

During this reporting period, work continued in all the above areas. Specifically, work progressed on the development of sintering aids to obtain membranes with lower porosity. The temperature dependence of the conductivity of the membranes was also measured. In the area of thin-film membrane fabrication, work continued on investigating process parameters with the goal of obtaining thinner membranes than what had been done previously. Finally, in the area of process design, work continued in refining the models previously developed and in adding more detail. Work also began on developing a model for membrane performance.

2. EXPERIMENTAL

2.1 Task 2 - Membrane Materials Development and Evaluation

2.1.1 Experimental Apparatus

No major changes were made to the experimental apparatus during this reporting period.

2.1.2 Preparation of Pyrochlore Membrane Materials and Cermet Membranes

No major changes were made to the powder, membrane fabrication and membrane evaluation procedures during this reporting period.

3. RESULTS AND DISCUSSION

3.1 Task 1 - Test Plan and Project Management

Regular teleconference calls were held between ITN and the Idaho National Engineering and Environmental Laboratory (INEEL). A site visit of DOE personnel to ITN was held in December. This meeting also included representatives of all the program subcontractors. During the previous reporting period, ITN began to prepare a patent application for the materials discovered in this program. This application process is continuing.

3.2 Task 2 - Membrane Materials Development and Evaluation

3.2.1 Preparation and Characterizations of Pyrochlore Materials and Cermet Membranes

During the previous reporting period, work focused on obtaining higher densities through the use of sintering aids and using a nickel boron alloy in place of nickel as the metallic component of the membrane. This work was not successful in that higher density membranes with lower leakage rates were not obtained. During this reporting period, work in this area continued by evaluating additional sintering aids and alternate metals. The temperature dependence of proton conductivity was also measured to evaluate the feasibility of lower temperature operation. These results will now be described.

3.2.1.1 *Evaluation of Sintering Aids*

During the previous reporting period, the use of SiO_2, MgO, BaO, Na_2O and Li_2O as potential sintering agents were examined but were not adequate in obtaining densities sufficient for hydrogen flux measurements. We then evaluated sintering aids prepared from mixtures of these compounds and now obtained membranes with acceptable densities. Specifically, with a sintering aid mixture of 7wt%, a sintered density 100% of theoretical was obtained. This is in contrast to a typical density of 75% of theoretical when no sintering aid is used. Additionally, the porosity of the membranes decreased from 34% to 7% when the sintering aid was used. Figure 1 shows a comparison of membranes fabricated with and without a sintering aid. As can be seen in the figure, the sample with the sintering aid had a much smaller diameter, reflecting greater shrinkage and higher density. Measurements of the hydrogen flux through these dense membranes are currently being performed.

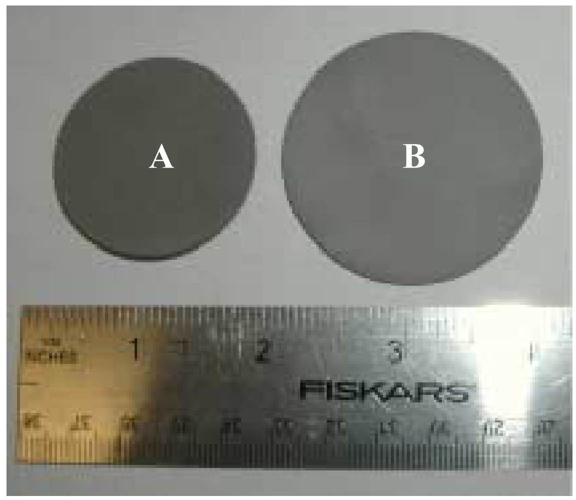

Figure 1. Photograph comparing membranes prepared with (A) and without a sintering aid (B).

The reason that much higher densities were obtained for membranes using the sintering aid mixture as compared to the single component sintering aid is not known. However, it is likely that the combination of Na_2O and/or Li_2O with SiO_2 leads to lower melting phases than what is obtained for the pure components. This then leads to greater sintering, although chemical interactions between the sintering aid components and the ceramic component of the membrane, resulting in a lower sintering temperature, cannot be ruled out.

Experiments are continuing in order to determine the least amount of sintering aid required to obtain acceptable densities so as not to effect the measured proton conductivity of the membrane materials. Additionally, work is continuing in order to modify the ceramic component of the membrane so as to obtain not only higher conductivity, but also lower sintering temperatures. Initial results on a new composition indicate that we can prepare membranes close to 100% of the theoretical density without any sintering aid. These membranes are currently being evaluated for conductivity.

3.2.1.2 *Alternate Metals*

During the previous reporting period, membranes containing a nickel boron (15wt%) alloy in place of the nickel were fabricated and evaluated. The idea behind this was that the boron component of the alloy would enhance the wetting between the alloy and ceramic component, leading to higher density and lower porosity. However, membranes with acceptable density and low porosity were not obtained. Further work was performed during this reporting period using different metal alloys so as to obtain higher densities.

Potential alloys for use in the membranes were identified based on metallic components that oxidize easier than nickel and might therefore enhance the wetting between the metal and ceramic components of the membranes. Specific alloys investigated during this reporting period included Ni/Zr (30wt%), Ni/Al (21wt%) and Ni/Ti(10wt%). Membranes were fabricated in a manner identical to the membranes using pure nickel except that the sintering temperatures were adjusted so that they were 10-30 ^{o}C below the melting point of the specific alloy.

The membrane containing the Ni/Zr alloy shattered upon sintering. This is most likely due to volume changes associated with absorption of hydrogen by the alloy component. Membranes containing the remaining two alloys have not yet given acceptable densities but we are continuing to refine the fabrication procedures. Results from this work will be reported in the upcoming reporting period.

3.2.1.3 Temperature Dependence

One major issue associated with proton conducting cermet membranes is the temperature of operation. Any decrease in the operating temperature will have a beneficial impact on the overall economics of the hydrogen separation process. To this end, we have begun to evaluate the temperature dependence of the hydrogen flux rate through the pyrochlore-based membranes.

Figures 2 and 3 show the results of these experiments. Figure 2 show the dependence of the proton conductivity as a function of temperature for both wet and dry atmospheres. As expected, the conductivity in a wet atmosphere is slightly higher, most likely due to the presence of additional charge carriers. Figure 3 shows a plot of ln(σT) as a function of inverse temperature. A fit of a straight line to this data yields the activation energy for proton conduction (E_a),

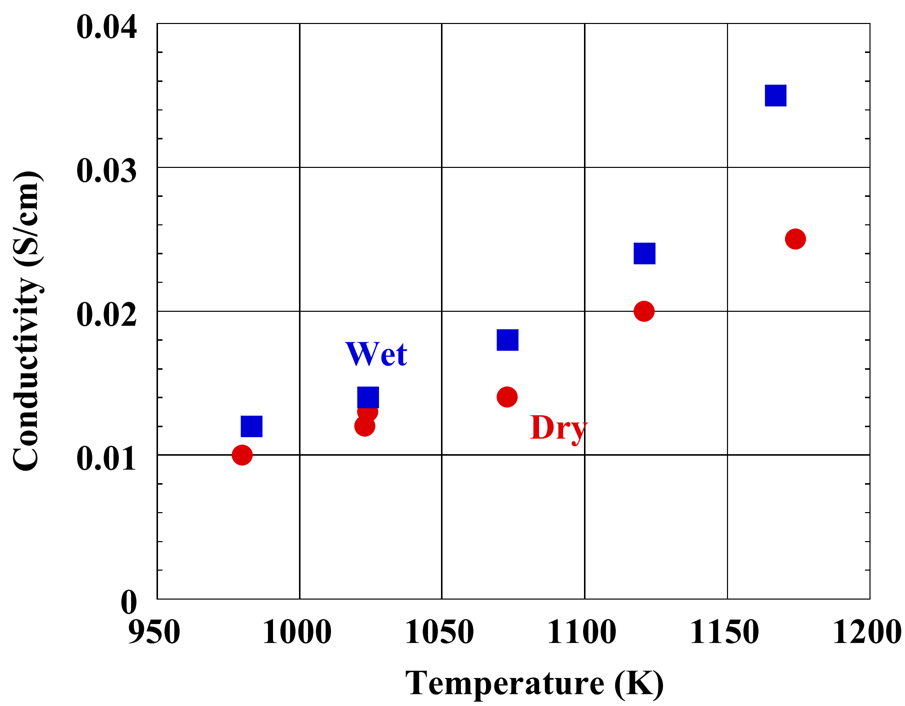

Figure 2. Plot of conductivity vs. temperature for a Ni (40v%)/pyrochlore proton conducting membrane.

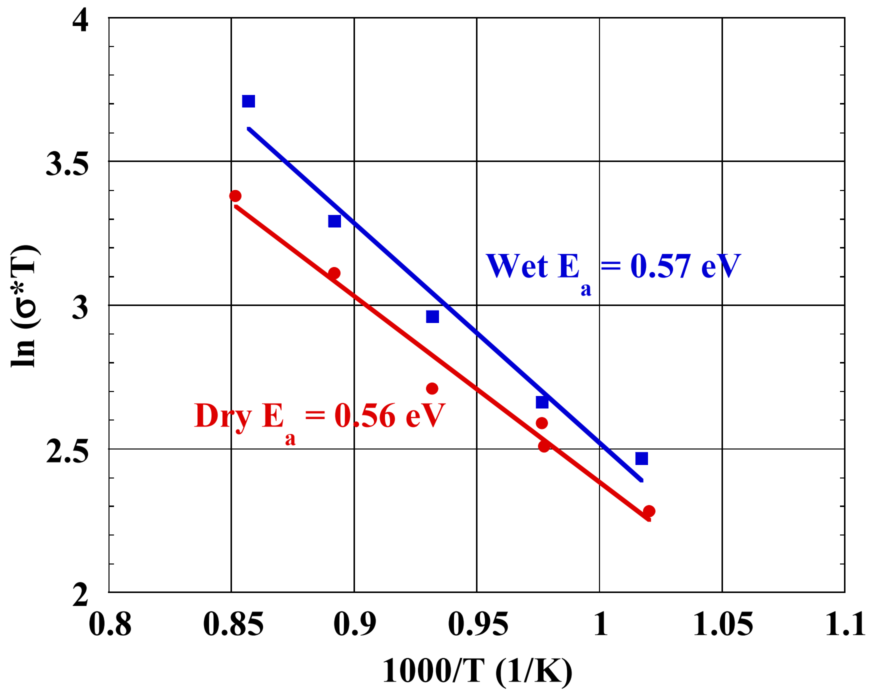

Figure 3. Plot of ln(σT) vs. inverse temperature for a Ni (40v%)/pyrochlore proton conducting membrane.

assuming Arrhenius behavior. Values of 0.56 and 0.57 eV are obtained for dry and wet atmospheres, respectively. The wet and dry activation energies are similar, indicating that no major structural changes or changes in conduction mechanism are occurring upon exposure to the wet atmosphere. The observed activation energies are relatively low and similar to other proton conductors.[1,2] These results indicate that lower temperature operation of the membrane is possible without a great loss in flux rate. As more materials are screened, we will measure their activation energies.

3.3 Task 3 - Thin-Film Device Fabrication

During the previous reporting period, work was performed on fabricating and evaluating thermally-sprayed, thin-film membranes. The membranes prepared exhibited a conductivity of ~0.03 S/cm and were stable towards carbon dioxide and water. Additionally, the samples exhibited leak rates less than 1% and were stable to multiple thermal cycles. During this reporting period, additional membrane samples were generated by varying the deposition parameters. The goal of this work was to determine the reproducibility of the process and develop a strategy for fabricating thinner membranes. An important parameter investigated was the speed of the head as it passed across the substrate surface. This has the effect of producing thinner layers per pass across the substrate. The membrane then would be built up by a greater number of thinner layers. This has resulted in membranes of reduced thickness but still exhibiting very low leak rates.

Another parameter determined to be important was the use of an inert gas shroud during the spray process. This has the effect of keeping the nickel from oxidizing during the spray process.

Nickel oxide present in the membrane will reduce to nickel upon exposure to hydrogen during membrane operation. This in turn causes porosity in the membrane. Elimination of nickel oxide during the fabrication process is then expected to lower porosity and leakage rates.

A third parameter that has been investigated is the ceramic powder. To date, all thermally-sprayed membranes had been prepared using powder fabricated at ITN using conventional ceramic powder processing techniques. Powders of an ITN proprietary pyrochlore composition were prepared commercially by Praxair Surface Technologies (Woodinville, WA). The powders were spray-granulated as part of the preparation procedure. Membranes prepared from these powders exhibited a more uniform microstructure with lower porosity than those prepared from powders fabricated at ITN (Figure 4). The reason for the difference is not clear but may have to do with the better flowability of the commercial powders. This leads to a more homogenous mixture entering the torch. The commercial powders are also more spherical which leads to a more homogeneous melting during the spray process. Independent of the cause, the observation of lower porosity thin films using the commercial powders is an important result in that it indicates that thinner membranes are possible with better powders. It also indicates that the compositions being investigated are amenable to large-scale manufacturing which will be important as we scale up the membrane size.

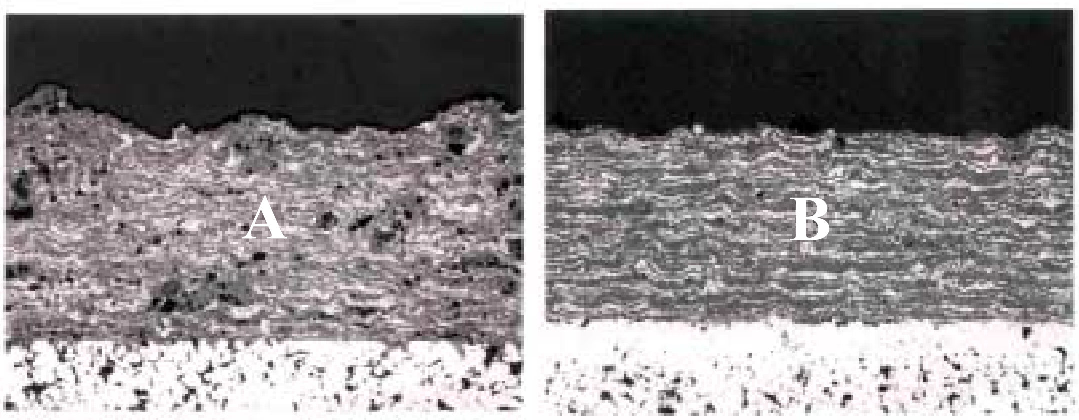

Figure 4. Comparison of microstructures of thermally-sprayed cermet membranes using powder prepared conventionally at ITN (A) and commercial powder (B).

3.4 Task 4 - Engineering

In the previous reporting periods, Nexant, with input from Praxair and ITN, continued in refining the potential process flow diagrams for the Vision 21 plant according to DOE's "FutureGen" program specifications. Specifically, the plant design is based on a 275 MW single-train gasifier which produces approximately one million tons of carbon dioxide and has the goal of sequestering 90% of this carbon dioxide. During this reporting period, work continued on refining and adding detail to these flow diagrams. An additional aspect of the work was putting together a model of the membrane itself. This work will now be described.

The objectives for putting together the membrane model are twofold. The first is to determine which membrane properties and design variables have the most effect on unit cost and membrane performance. The second is to aid in determining development targets for the critical membrane properties. A steady-state, one-dimensional, finite difference model is being used in this work. A schematic illustration of the model is shown in Figure 5.

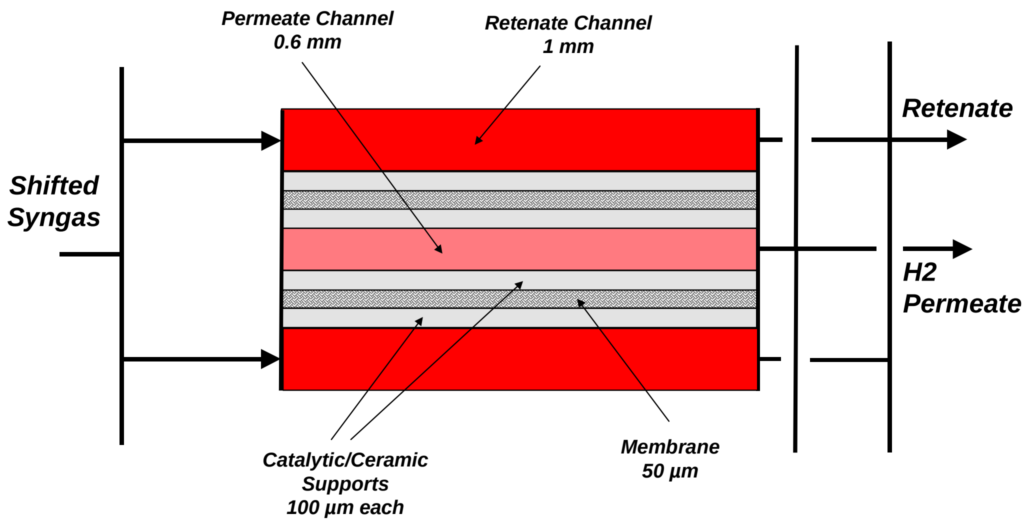

Figure 5. Schematic illustration of the one-dimensional membrane model.

Figure 6 shows a plot of the H_2 partial pressures as a function of the distance along the model membrane. Plots for three different flux dependencies are shown. The plot illustrates the trade-off between H_2 recovery, *i.e.* the retentate partial pressure, and the membrane length. The

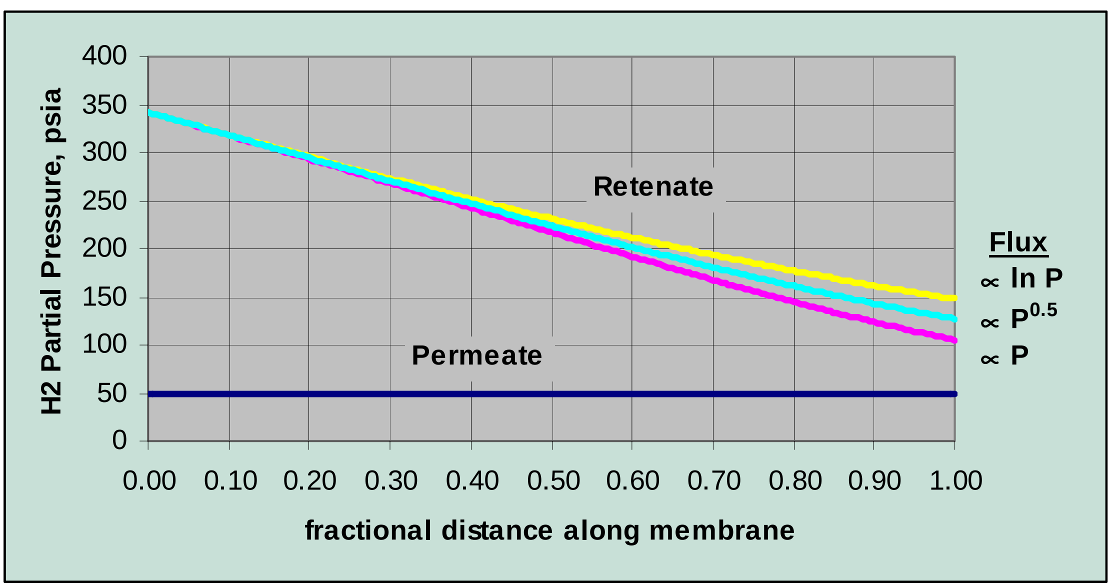

Figure 6. Plot of H_2 partial pressures as a function of the fractional distance along the one-dimensional membrane.

membrane length translates directly into cost. Work will continue on this model by putting in more details such as the water-gas shift reaction and fluid flow. The model will also be refined with input from the experimental work. The data resulting from this model will be fed into the process design work to further refine those models.

4. CONCLUSIONS

Work on this program is continuing in all areas. At ITN, work continued on fabricating and evaluating novel pyrochlore proton conducting materials. The major issue to date has been the difficulty in reproducibly fabricating dense membranes by dry pressing. During this reporting period, we were able to develop a sintering aid that allowed for sintered densities close to 100%. Additionally, changes in membrane composition also resulted in membranes with much higher densities. We are now testing these membranes for hydrogen flux rates.

In the area of thin-film fabrication, work continued in optimizing the deposition process with the goal of obtaining thinner membranes while maintaining very low leak rates. Parameters that were investigated included deposition speed and the use of an inert gas shroud. Commercially-prepared powders were also obtained and use of these powders resulted in membranes with superior microstructure, particularly lower porosity. When combined, these results indicate the feasibility of obtaining thinner membranes through thermal-spray processing. This work will continue into the next reporting period with a focus of obtaining thinner membranes.

Finally, the design component of the program is continuing on the three process flow schemes developed during the previous reporting period that account for the specifications of a "FutureGen" plant. Details are being added to these process schemes. Additionally, a model for the membrane performance was also begun and will be further refined during the next reporting period.

5. REFERENCES

1. N. Bonanos, B. Ellis, K.S. Knight and M.N. Mahmood, Solid State Ionics, 35, 179 (1989).
2. X. Qi and Y.S. Lin, Solid State Ionics, 120, 85 (1999).