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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1. INTRODUCTION

This report describes the work performed during the latest reporting period. During the previous reporting period, work was performed in all the areas of the program. Specifically, additional pyrochlore compositions were synthesized. Second, thin-film membranes that had previously been fabricated by thermal spray were tested. Finally, heat and mass balances were added to the process flow diagrams. A model for membrane performance was also included in the process flow diagrams in order to optimize the process.

During this reporting period, work continued in all the above areas. Specifically, additional novel proton conducting materials have been fabricated and tested with some problems noted with high porosity. Additional thin-film membranes have also been fabricated and tested. Again, leakage has been found to be a problem. Finally, the plant design work is progressing with a slight shift in emphasis to account for the Department of Energy’s “FutureGen” program. These results will now be discussed.

2. EXPERIMENTAL

2.1 Task 2 - Membrane Materials Development and Evaluation

2.1.1 Experimental Apparatus

The only change made to the experimental apparatus was in using helium for leak detection rather than nitrogen. Since helium and hydrogen are closer in size and molecular weight than hydrogen and nitrogen, the use of helium will give a more accurate picture of leaks occurring in the system. This change also precipitated switching the carrier gas on the gas chromatograph from helium to argon so the helium could be detected.

2.1.2 Preparation of Pyrochlore Membrane Materials and Cermet Membranes

During the previous reporting period, ITN continued with the fabrication of both pyrochlore powders and cermet membranes from these powders. During this reporting period, additional compositions of proton conducting pyrochlore powders were fabricated. Cermet membranes comprised of nickel and these proton conducting powders in an approximate 1:1 weight ratio were also fabricated. No major changes to powder and membrane fabrication procedures were made during this reporting period.

Implementation was begun on an additional experiment related to membrane fabrication. Specifically, we began the development of a x-ray fluorescence (XRF) technique for determining the composition of the ceramic powders. ITN has in-house XRF equipment for determining elemental compositions. During this reporting period, we began to develop the procedures for using this technique to determine the elemental composition of our ceramic powders. This will permit us to ensure that the compositions of the powders are what we expect. This is particularly important for the powders prepared by the Pechini method due to the uncertainty in the starting materials and potential changes in composition during the precursor decomposition and powder fabrication steps.

2.1.3 Membrane Sealing Techniques

No major changes were made to the sealing techniques during this reporting period. All three options – brazing, gold rings and Pyrex paste – are being pursued simultaneously. The latter two are more consistent than the former with leakage rates of 10-20% which is considered acceptable at this stage of the program. The flux rates of the membranes are high enough so that any leakage can be reliably subtracted from the overall measured hydrogen flux. Additionally, the switch to helium for leak detection as described above also increases the reliability of the flux measurements.

3. RESULTS AND DISCUSSION

3.1 Task 1 - Test Plan and Project Management

Regular teleconference calls were held between ITN and INEEL and ITN and Nexant and Praxair in order to direct work in this program. A teleconference call was also held between TIN, Nexant, Praxair and DOE representatives to gain DOE insight into plant process design. In addition, the Principal Investigator presented results of this work at the 14^{th} Annual Meeting of the North American Membrane Society. Finally, an Invention Disclosure on the composition of the proton conducting materials was submitted by ITN. ITN will decide shortly on whether to pursue a patent.

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 continued on fabricating novel pyrochlore materials and membranes from these materials. During this reporting period, screening of these new compositions was begun and additional compositions fabricated.

The strategy that is directing the development of new materials compositions is to vary the stoichiometry and oxygen defect concentration within the basic pyrochlore structure, $A_2B_2O_7$. For example, by changing the A and B cations, the basicity, and therefore the propensity to incorporate protons into the lattice, can be changed. This change can be made independently of the oxygen stoichiometry. The latter parameter can also be changed independently by incorporating dopants into the lattice. This also can increase the concentration of interstitial protons in the lattice which will in turn increase the proton conductivity. However, it needs to be noted that changing the A and B cations, as well as introducing dopants, will also change structural parameters of the material. This may have a negative effect on the conductivity. Of course, it is possible that changes to the structural parameters can also have a positive effect. This will need to be determined experimentally.

During the current reporting period, several additional novel compositions have been prepared following the above strategy. Proton conductivities as high as 0.02 S/cm at 900 ^{o}C have been obtained. We have not yet screened enough compositions to determine which are the most important parameters in obtaining high proton conductivity but additional compositions are being prepared and will allow us to pinpoint these parameters.

We are also measuring the proton conductivities in wet atmospheres, in addition to dry atmospheres, in order to gain information as to the conduction process in these materials. Since protons can be introduced into the lattice through two different mechanisms, one dry and one involving humidity, this is an important measurement. To date, we have not collected enough data to be able to determine which mechanism is dominant but these measurements will continue.

One problem that has arisen recently is in consistently obtaining dense cermet membranes of the various compositions. This problem does not seem to be a function of the specific ceramic phase composition. All work to date has been performed by dry-pressing the cermet powder with binders and subsequently sintering close to the nickel melting point, 1420-1460 ^{o}C, under a forming gas atmosphere. In an attempt to obtain higher densities, we have begun to evaluate potential sintering aids for the cermet membranes. The issues involved are both getting the ceramic to densify at lower temperatures as well as creating a better interface for stronger bonding between the metallic and ceramic components of the cermet membranes. The goal is to obtain higher densities and lower porosities in the cermet membranes without losing the high conductivity. Currently, several potential sintering aids have been identified. Results from these experiments will be obtained in the upcoming reporting period.

3.3 Task 3 - Thin-Film Device Fabrication

During the previous reporting period, the initial results on thermally-sprayed cermet membranes were described. One problem that had been found with these membranes was high leak rates. During this reporting period, work focused on reducing the leak rate while still maintaining high hydrogen flux rates.

One change that was made to the thin-film membrane fabrication procedures was the use of a more powerful spray gun. This allows for denser films and results in decreased porosity. Another change that is being made is to return to the grit-blasting procedure for enhancing adhesion between the film and porous substrate. However, as discussed in a previous report, the grit-blasting procedure closed some of the porosity of the substrate surface. Therefore, we are currently investigating using substrates with higher porosities, 0.5-10 µm, rather than the current 0.2 µm porosity. The strategy is that the surface of the larger porosity substrate is inherently rougher than the finer porosity substrate and therefore grit-blasting may not be necessary. Additionally, if it is still necessary to grit-blast the surface, the surface of the higher porosity substrate will be less likely to be closed off. Initial experiments fabricating thin-film membranes on stainless steel porous substrates with porosities as high as 10 µm have been performed and the membranes did not show leakage at room temperature. New substrates with higher porosities are currently being fabricated and will be used for thin-film membrane deposition when they are received in the next few weeks. We are also examining the role of grit-blasting to determine if it is necessary for obtaining leak-tight membranes.

3.4 Task 4 - Engineering

In the previous reporting periods, Nexant, with input from Praxair and ITN, had developed and refined several potential process flow diagrams for the Vision 21 plant. Work continued in this area by incorporating heat and mass balances into the process scenarios. One shift in emphasis has been made in that the design scenarios will follow closely the Department of Energy's "FutureGen" program specifications. Specifically, the plant design will be based on a 275 MW single-train gasifier which produces approximately one million tons of carbon dioxide. The goal will be to sequester 90% of this carbon dioxide. The split between hydrogen production and power in these plants will be allowed to vary. The plant will also use an advanced hydrogen-fired turbine. These specifications will be incorporated into the plant designs currently being performed.

4. CONCLUSIONS

Work on this program is continuing in all areas. At ITN, work continued on fabricating and evaluating novel pyrochlore proton conducting materials. Additional proton conducting compositions are being fabricated and tested to identify pyrochlore phases with higher proton conductivities. Cermet membranes from these powders have also been fabricated and are currently being tested. One problem that has arisen has been high porosity in the membranes resulting in high leakage rates. We are currently investigating sintering aids as a method for improving the density of the dry-pressed membranes.

In the area of thin-film fabrication, leakage through the membranes has been identified as a major issue. We are currently examining different porosity substrates, deposition parameters with the new spray gun and the effect of pretreatment on membrane quality in order to develop the procedures required for obtaining leak-free, thin-film membranes.

Finally, the design component of the program is continuing with a slight shift in emphasis. The plants will now consider the specifications of a "FutureGen" plant in putting together the overall plant design. At this stage, the process flow diagrams have been completed and initial economic models are being developed.