II.D.7 Ultra-Thin Proton Conducting Membranes for H_2 Stream Purification with Protective Getter Coatings

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Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Synthesize ultra-thin dense ceramic membranes on microporous supports.
- Incorporate sulfur getter technology into microporous support layer to address impurities in the feedstock.
- Demonstrate the ability of these ultra-thin membranes to separate H_2 at a high flux rate, meeting the DOE 2010 target of 250 scfh/ft^2.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(K) Durability
(L) Impurities
(M) Membrane Defects
(N) Hydrogen Selectivity
(O) Operating Temperature
(P) Flux
(R) Cost

Technical Targets

As this project was initiated in May 2007, the following represents the targets we plan to achieve.

The thrust of this project is the investigation of the efficiency of thin dense ceramic membranes to separate H_2 at elevated temperatures via proton conduction. Insights gained from these studies will be applied toward the design and synthesis of hydrogen separation modules to meet the following DOE 2010 hydrogen separation targets:

- Flux: 250 scfh/ft^2
  - Deposition of an ultra-thin film will enhance the flux rate per square foot by minimizing the path length for protons to be conducted through the dense oxide.
- Hydrogen quality: 99.99% of total (dry) gas
  - The conduction mechanism of separation ensures high purity H_2 as only hydrogen is conducted through the membrane.
- Operating capability: 400 psi
  - The use of a microporous support structure will enhance the ability of the membrane to withstand significant pressure drops.
- Durability: 26,280 hours between membrane replacement
  - Dense ceramics are resistant to steam. The development of a "getter support" on the feed side of the stream addresses other impurities, such as sulfur, and will support a lengthened membrane lifetime.

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Approach

Our approach to meeting the parameters for hydrogen separation membranes focuses on optimizing the H_2 flux through the membrane while also removing feedstock impurities. This project will address the separation of high-purity H_2 (>99%) from various feed streams using supported thin proton conducting ceramic membranes, such as $BaCeO_3$ and $LaBO_3$ [1,2]. These dense oxide membranes exhibit 100% selectivity, resulting in extremely high-purity H_2. As thinner membranes have higher fluxes, over the course of this investigation, we will systematically synthesize and test membranes with a range of thicknesses. The effective pore size of the support material affects the minimum thickness of the membrane; i.e. support materials with smaller pore sizes can support thinner membranes.

Sulfur impurities that are typical of many feedstocks will be addressed through the deposition of a getter material, such as ZnO, onto the support structure. Both the getter and the proton conducting materials will be deposited using atomic layer deposition (ALD) thin film methodology, which is capable of producing layers on the Angstrom scale.

Accomplishments

- Successfully deposited 450 Å conformal ZnO coating on mesoporous alumina support using ALD. Powder X-ray diffraction confirmed presence of ZnO phase.
- Small loss in support surface area after deposition of ZnO (from 1.6 m^2/g to 1.2 m^2/g) was noted using Brunauer-Emmett-Teller analysis, indicating that the porosity of the support is intact.
- After surveying current proton conducting ceramics, we have decided to pursue $BaTiO_3$ and $BaCeO_3$ [3,4]. The proton conduction in these materials is high, and the chemistry is amenable to ALD film synthesis. Development and testing of ALD deposition parameters are underway.
- $BaCeO_3$ ceramic was synthesized by solid state methods. The powder diffraction scan, shown in Figure 1, identifies the product as orthorhombic $BaCeO_3$ [5].

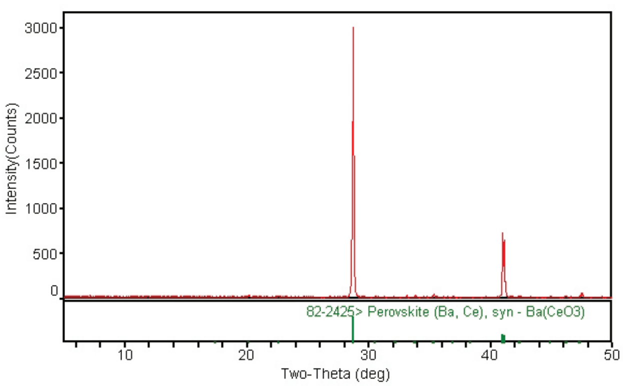

FIGURE 1. Powder X-ray Diffraction Scan of Synthesized $BaCeO_3$ (Reference peak positions from PDF # 82-2425 are shown below the scan in green.)

Planned activities for remainder of FY 2007

- Perform scanning electron microscopy to confirm the ZnO coating is conformal.
- Design and build permeation unit.
- Perform permeation measurements to confirm that acceptable levels of porosity of the support remain after ZnO coating is deposited.
- Synthesize bulk $BaTiO_3$ via solid state techniques.
- Test the H_2 permeation of both $BaTiO_3$ and $BaCeO_3$ in bulk form.
- Test sulfur impurity uptake and regenerability of ZnO getter coating.
- Deposit proton conducting oxide ($BaTiO_3$ or $BaCeO_3$) on alumina support.

References

1. Shimura, T.; Fujimoto, S.; Iwahara, H. Solid State Ionics 143 (2001) 117.

2. Alberti, G.; Casciola, M. Solid State Ionics 145 (2001) 3.

3. Kreuer, K. D.; Schonherr, E.; Maier, J. Solid State Ionics, 70/71 (1994) 278.

4. Kreuer, K. D. J. Solid State Ionics, 125 (1999) 285.

5. Powder Diffraction File reference number 82-2425.