IV.C.2 Novel High-Temperature Ion Transport Membrane Development

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Start Date: October 1, 2004
Projected End Date: September 30, 2008

Objectives

- To develop thermodynamically stable, high-temperature (<500°C), high-proton-flux proton transport membranes (PTMs) using a computational combinatorial chemistry approach.
- To expand the computational model to enable the materials properties to be predicted based on the electronic properties of the elements of the periodic table.

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:

- C. Fuel Processor Capital Costs
- AB. Hydrogen Separation and Purification

Approach

- Atomistic computer simulations are being developed to identify and evaluate potential new proton-conducting ceramic systems.
- Employ rapid high-purity materials synthesis using a modified combustion synthesis process.
- Characterize structure and properties (particularly hydrogen flux).
- Conduct long-term stability testing.

Accomplishments

- Identified potential proton transport materials in the pyrochlore, brownmillerite, and fluorite families.
- Completed computer simulation with empirical potential models for several pyrochlore, perovskite, and brownmillerite end members, with solid solution models and calculation of defect chemistry now in development.
- Completed crystal structure and phase identification studies for over 100 samples prepared to date using x-ray and neutron diffraction.
- Completed high-temperature conductivity measurements in air for over 40 samples to date – hydrogen testing is in progress.
- Completed high-temperature structure and stability testing by x-ray diffraction (XRD) for several systems in reducing atmospheres.

- Produced sintered samples for pyrochlore-perovskite binary systems.
- Produced sintered samples of $A_2B_2O_5$ compositions with 6 different doping schemes in the srebrodolskite and brownmillerite crystal structures.
- Produced sintered samples of $A_2B_2O_9$ compositions with 2 different doping schemes in the monoclinic and cubic crystal structures.
- Produced samples of $Bi_2Al_4O_9$. Demonstrated with in-situ XRD that the system decomposes at temperatures below the sintering temperatures, making the system unsuitable for further development.
- Enhanced capabilities for in-situ conductivity measurements. Added atmospheric control and added the capability for measuring high-conductivity $A_2B_2O_5$ mixed conductors, which exceeded the range of our previous electrometers.
- Identified new proton-conducting ceramic oxide with strong potential to meet program requirements.

Future Directions

- Expand Analytical Interatomic Potential (AIP) computer models to accommodate doped compositions and predictive power for dopant solubility.
- Refine models of hydrogen transport.
- Determine hydrogen flux as a function of temperature and pressure for candidate compositions.
- Characterize long-term stability of candidate materials under service conditions.
- Develop metal-supported asymmetric membranes using Oak Ridge National Laboratory (ORNL) support tubes.

Introduction

High-temperature ion transport membranes (ITMs) are presently limited in availability and performance. Current high-temperature proton conductors either have low conductivities or are highly susceptible to chemical attack by contaminants such as sulfur (H_2S) and CO_2 (e.g., $BaCeO_3$-based materials). The purpose of the proposed research is to exploit recent developments at ORNL on novel mixed phase ion transport materials and develop a practical lower-temperature (<500°C) ion conductor, where high conductivity and stability are the primary requirements. Durability will be addressed by avoiding the use of polyvalent lanthanides and transition metals that bind readily with sulfur—especially under the reducing conditions found in reformate or syngas streams. ORNL has developed new ion transport material by exploiting the phase boundary between binary oxides. The result is a ternary composition that meets the primary requirement for a practical high-temperature proton conductor—high conductivity.

Approach

The main objective of this project is to develop thermodynamically stable, high-temperature (but less than 500°C), high-proton-flux ion transport membranes using a computational combinatorial chemistry approach. An integrated approach to materials development, combining atomistic modeling (incorporating structure and property prediction) of ITM materials, advanced synthesis of promising compositions, detailed crystal structure analysis based on Rietveld refinement of x-ray and neutron scattering data, and conductivity and H_2 flux characterization, will be used to develop ion transport membranes. One of the goals of this project is to expand the computational model under development at ORNL that will allow the materials properties to be predicted based on the electronic properties of the elements of the periodic table. Such a model does not exist and is much needed to guide development, expedite material selection and avoid "Edisonian" research where possible.

Results

No funding was allocated for this project in FY 2005, consequently limiting the effort. At the beginning of FY 2005, a proton-conducting ceramic oxide was identified that appeared to meet the requirements for a hydrogen separation membrane. Ceramic powders were produced using a modified combustion synthesis process ORNL recently developed for these materials. This technique offers several advantages over traditional solid-state synthesis, namely: high-precision compositional control, atomic-scale mixing in the precursor, and rapid production of homogeneous sub-micron powders. Due to the homogeneous nature of the precursor and powders, sample preparation time is significantly reduced. XRD has been used to identify the phase composition of each product.

Hydrogen flux tests have been performed on relatively thick proton-conducting ceramic pellets. However, a practical membrane will require a thin electrolyte (<200 mm self-supported and <2 mm supported on a porous substrate) to maximize the hydrogen flux, and therefore power density of the fuel cell. The reduction of the thickness of the ceramic electrolyte from the 2.5 mm pellet to a 200 mm layer can be expected to increase the overall flux by an order of magnitude.

Conclusions

A new approach to development of proton-conducting ceramics, combining atomistic modeling and structure-properties characterization, is being developed at ORNL. The computational modeling has been validated and refined based on experimental results. Several potential proton-conducting ceramic systems have been investigated to date, including pyrochlores, perovskites, brownmillerites, and fluourites.

Further work will focus on down-selecting to the most promising candidate systems and providing a detailed characterization of structure, properties, and stability, particularly in the service environment (high temperature, reducing atmosphere, etc.).

FY 2005 Publications/Presentations

1. S.A. Speakman, R.D. Carneim, E.A. Payzant, and T.R. Armstrong, “Development of Proton Conductors Using Pyrochlore-Perovskite Phase Boundaries”, *J. Matls. Eng. Perf.* 13, 303-308 (2004)
2. T.R. Armstrong, S.A. Speakman, and E.A. Payzant, “Electrical Properties of Substituted $Ca_2Fe_2O_5$”, International Conference on Nonstoichiometric Compounds, 3-9 April 2005, Kauai, HI.
3. S.A. Speakman, E.A. Payzant, T.R. Armstrong, and R.D. Carneim, “Using Structure-Property Relationships to Select among Candidate Systems for High-Temperature Proton Conductor Development”, 2004 MRS Fall Meeting, 29 November – 2 December 2004, Boston, MA.