

## II.B.3 Pyrochlore/Perovskite Proton Transport Membranes

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### Objectives

- To develop a thermodynamically stable, high-temperature, high-flux proton transport membrane (PTM) 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:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance
- C. Feedstock and Water Issues
- E. Control and Safety
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- AB. Hydrogen Separation and Purification

### Approach

- Atomistic computer simulations are being developed to identify and evaluate potential new proton-conducting ceramic systems.
- High-purity materials are being rapidly synthesized for testing using a modified combustion synthesis process.
- Structure and properties (particularly hydrogen flux) characterization is being carried out over a broad range of temperatures (300-800°C).
- Long-term stability testing is taking place in simulated hydrogen environments containing CO, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S.

### Accomplishments

- Potential proton transport materials have been identified in the pyrochlore, brownmillerite, and fluorite families.
- Computer simulation with empirical potential models has been completed for several pyrochlore, perovskite, and brownmillerite end members, with solid solution models and calculation of defect chemistry now in development.

- Crystal structure and phase identification studies have been completed for over 100 samples prepared to date using x-ray and neutron diffraction.
- High-temperature conductivity measurements in air have been completed for over 40 samples to date – hydrogen testing is in progress.
- High-temperature structure and stability testing by x-ray diffraction has been completed 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.

### **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.

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### **Introduction**

High-temperature ion transport membranes 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 this project is to exploit recent developments at ORNL on novel mixed-phase ion transport materials and develop a practical high-temperature proton 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 reformat or syngas streams. The main objective of this project is to develop thermodynamically stable, high-temperature, high-proton-flux ion transport membranes using a computational combinatorial chemistry approach.

### **Approach**

An integrated approach to materials development combining atomistic modeling (incorporating structure and property prediction) of PTM 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.

Empirical potential models simulate the oxide systems  $(A_1A_2)(B_1B_2)O_x$ , where  $(A_1A_2)$  are larger cations, such as a lanthanides or alkali earths, and  $(B_1B_2)$  are smaller cations, such as transition metals. The cation valences are essential for the creation of anion vacancies in fast ion oxygen conductors, but the impact of these vacancies on protonic conductivity is still not well understood. The crystal

structure is modeled by calculating the forces produced by specified interatomic potentials. The simulation uses a combination of several different models to reproduce the structure and properties of the physical material. The Born model is used to model interatomic potentials by separating them into long-range Coulombic interactions and short-range pair potentials. Ionic polarization is reproduced using the Dick-Overhauser core-shell model; this model has been demonstrated to reliably reproduce dielectric and elastic properties of ionic oxides. Defect chemistry is modeled using the two-region Mott-Littleton approach. For simulation of proton incorporation and migration, the O-H interactions are modeled using a Morse potential model. The Morse potential model uses the results of ab-initio calculations to appropriately modify the empirical potential model. While not as rigorous a simulation as ab-initio calculations based on first principles, the empirical potential model is valuable because of its economy of processor time. Empirical potential models can be performed faster and on less powerful systems than those required for ab-initio calculations. Empirical potential models can be used to simulate larger systems consisting of more atoms, or to simulate a greater number of systems.

Before application to unknown systems, the potential models must be refined using the known characteristics of a few well-studied parent phases. After the potential models are refined, they can then be used to simulate other related phases. The computer simulations are then applied to identify the compositional regions with the highest proton mobility for further study, a procedure termed "computational combinatorial analysis." Rapid processing methods are used to synthesize these compositions for analysis of conductivity, stability, and crystal structure properties. Ultimately, the most promising compositions are selected for detailed studies of proton conduction mechanisms, stability, and defect chemistries.

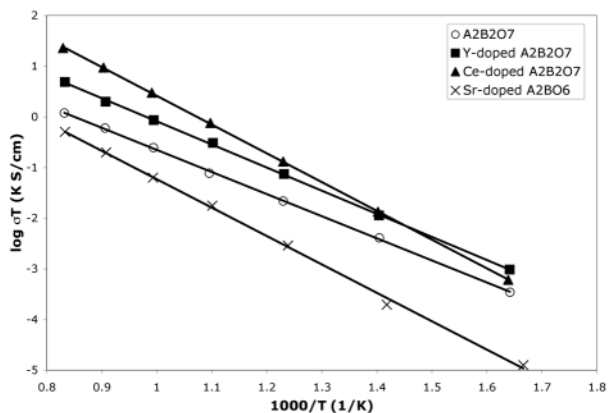
## **Results**

Empirical potential models were used to successfully model doped pyrochlore phases based on  $\text{La}_2\text{Zr}_2\text{O}_7$  using a slight modification of published pair-potential models. Substitutional doping of  $\text{La}_2\text{Zr}_2\text{O}_7$  was then examined under the following

constraints: (1) the pyrochlore crystal structure has two cation sites – the A site and the B site, and two oxygen sites – the 8b site and the 48f site; (2) Y, Ga, Sc, In, and Sm dopants were placed on the A site, the B site, or both in varying concentrations; and (3) charge-compensating oxygen vacancies were placed on one of the oxygen sites. Calculated lattice energies were evaluated to determine the most stable (i.e., energetically favorable) condition. Lattice parameters and calculated properties (bulk modulus, piezoelectric constant, static and high-frequency dielectric constants) were used to evaluate the physical validity of the simulation.

For Y-doping, A-site doping was more energetically favorable since it did not require charge-compensating vacancies, whereas for B-site doping, compensating vacancies were predicted on the 8b oxygen site. The less energetically favorable B-site doping was the objective since the resulting formation of defects might enhance proton conductivity. Analysis of synthesized Y-doped  $\text{La}_2\text{Zr}_2\text{O}_7$  revealed that Y could be substituted onto the B site at levels less than 0.10 mole fraction in a formulated composition,  $\text{La}(\text{Zr}_{1-x}\text{Y}_x)\text{O}_{3.5-x/2}$ . The simulation of mass-balanced systems was used to investigate the stabilizing mechanism, with mixed success. Simulation indicated that B-site substitution of Y for Zr was more energetically favorable than forming a binary system  $\text{La}_2\text{Zr}_2\text{O}_7 + \text{Y}_2\text{O}_3$  or  $\text{La}_2\text{O}_3 + \text{Y}_2\text{O}_3 + \text{ZrO}_2$ . However, the formation of  $\text{La}_{1-x}\text{Y}_x\text{ZrO}_{3.5} + (x/2)\text{La}_2\text{O}_3$  was more energetically favorable than other scenarios. This was contradictory to observed results of the synthesized materials and may indicate a weakness in the models.

Of the other dopants, Ga was indicated as the most likely to dissolve into the A- or B-site in  $\text{La}_2\text{Zr}_2\text{O}_7$ , and Sc and In were both more energetically favorable than Y. However, doping by Sm was energetically unfavorable on all cation sites. For all dopants, A-site substitution was preferred over B-site. In this regard, Ga had the smallest energy differential, and Y had the greatest energy differential, between A- and B-site occupancy. For all dopants, the charge-compensating oxygen vacancies were most favored to form on the 8b site for Zr substitution.



**Figure 1.** In-situ dc conductivity measurements identify trends for doped  $A_2B_2O_7$  compositions to better understand the structure-property relationships. Such measurements were used to discriminate between the  $A_2BO_6$  and  $A_2B_2O_9$  systems and revealed the  $A_2B_2O_9$  system as the most promising for further development.

Examples of high-temperature conductivity data on synthesized samples are shown in Figure 1. The Y-doped  $La_2Zr_2O_7$  pyrochlore showed an increase in conductivity when Zr was replaced with Y at levels  $x=0.04$  and  $0.08$ . Greater levels of B-site doping were not possible because Y began to replace La on the A site rather than Zr on the B site. Neutron pair distribution function analysis of the Y-doped  $La_2Zr_2O_7$  pyrochlores, currently in progress, reveals localized regions of structural distortion within the pyrochlore structure. The greatest conductivity was observed for  $La(Zr_{0.25}Ce_{0.75})O_{3.5-d}$  and  $(La_{0.5}Sr_{0.5})(Zr_{0.5}Ce_{0.5})O_{3.25}$ .  $La(Zr_{0.25}Ce_{0.75})O_{3.5-d}$  formed a defect fluorite structure not previously described in the literature. While doped  $La_2Zr_2O_7$  yielded promising results in the pyrochlore-

perovskite binary system, the pyrochlore-fluorite binary system may hold a greater potential for an effective proton conductor.

## 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 fluorites.

## FY 2004 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. S.A. Speakman, E.A. Payzant, and T.R. Armstrong, "Using Structure-Property Relationships to Select Among Candidate Systems for High-Temperature Proton Conductor Development," 2004 Denver X-ray Conference, 2-6 August 2004, Steamboat Springs, CO.
3. E.A. Payzant, S.A. Speakman, R.D. Carneim, T.R. Armstrong, and T.E. Proffen, "Studies on Long-range and Short-range Ordering in Y-doped  $La_2Zr_2O_7$ ," 2<sup>nd</sup> American Conference on Neutron Scattering, 2-6 June 2004, College Park, MD.