

# MATERIALS

## HIGH TEMPERATURE ELECTROLYZER MATERIALS SCIENCE

### PROJECT GOAL

*The goal of the current effort is to:*

Determine the feasibility of using ceramic proton-conducting electrolytes together with compatible electrodes to develop reversible solid oxide fuel cells for low-cost, high efficient power generation and hydrogen production from renewable energy sources.

### STATE-OF-THE-ART

Although the reversible fuel cell concept has been proven, no complete reversible fuel cell materials set has yet been identified with sufficient performance, robustness and cost characteristics to enable commercialization. Several organizations are developing reversible fuel cells of various types, including polymer membrane and solid oxide fuel cells. Notable reversible fuel cell achievements have been demonstrated by Proton Energy using a polymer membrane fuel cell [1] and several investigators have recently studied the use of traditional oxide ion conductor-based solid oxide fuel cell (SOFC) materials. [2,3,4] Significantly, commercial development of reversible SOFC technology has begun with companies such as Ion America of Menlo Park. Also, the U.S. Department of Energy (DOE) has recently awarded contracts to General Electric to investigate reversible SOFC technology. [5]

One of the most significant efforts underway to advance SOFC technology is that taking place under the U.S. DOE sponsored Solid State Energy Conversion Alliance (SECA). The SECA program involves significant support and development efforts amongst the major SOFC developers, national laboratories and universities. The current reversible SOFC effort benefits from the advances made in the SECA program; however, the current research is not directly applicable to this program since SECA program is focused on the advancement of SOFC technology for single mode fuel cell applications.

The current state-of-the-art materials sets, like those used in the efforts mentioned above, are not proving themselves sufficiently to-date as reversible fuel cell technology that is ready for commercialization. In the current effort are determining the feasibility of a significantly different approach that is based upon the use of ceramic proton conductors. Although the electrolyte materials we are using (perovskites) have been studied extensively, no research has yet been applied to develop a complete materials set that is applicable to reversible SOFCs.

### REVERSIBLE SOLID OXIDE FUEL CELLS

The solid oxide fuel cell (SOFC) is an electrochemical device that converts the chemical energy in a fuel directly to the electricity without the mechanical energy losses of traditional heat engines. As a result, SOFC technology has demonstrated performance that ranks as one of the most efficient technologies for power generation. [6,7] The electrochemical reactions that occur in the SOFC can also be reversed from generating electricity to utilizing electricity for water (steam) electrolysis to produce hydrogen. This hydrogen can thereafter be used as either a fuel for the SOFC itself, as a fuel for other devices (e.g., fuel cell vehicles), or as a raw material for other processes (e.g., industrial hydrogenation). The SOFC capable of this dual-mode operation is categorized as a "reversible solid oxide fuel cell." A reversible SOFC is an energy conversion/storage device that could well complement the development of a hydrogen economy based on renewable energy sources, such as solar and wind, since such sources usually require some form of energy storage to meet specific power demands.



The reversible SOFC has the potential advantage of higher energy density compared to batteries (the typical renewable system storage technology), since the stored energy amount is decoupled from the energy conversion device size. A reversible SOFC energy system has been shown superior to reversible proton exchange membrane (PEM) technology since it can achieve higher electrolysis efficiencies (20-30% higher due to high-temperature operation leading to lower electrode polarization and lower theoretical water decomposition voltage), and it has potentially lower cost and higher reliability. [8] The use of a reversible SOFC energy conversion unit may also have capital cost advantages compared to use of a discrete fuel cell and electrolyzer.

Several investigators have recently studied the use of traditional oxide ion conductor-based SOFC materials sets in reversible SOFCs using an yttria-stabilized zirconia (YSZ) electrolyte with Ni-YSZ anode and a strontium-doped lanthanum manganite (LSM) cathode. [9,10,11] These studies have advanced understanding of reversible SOFC technology and provided useful insights into means of optimizing electrode performance, expected degradation rates in fuel cell and electrolysis modes, and manufacturing process impacts on reversible SOFC performance. However, the reversible SOFC using oxide-ion-conducting electrolyte advanced to-date has not been proven robust enough and especially exhibits high rates of degradation in the electrolysis mode.

## APPROACH

The current research effort is a feasibility study of ceramic proton conductor-based reversible SOFCs that may result in a materials set and understanding of operating conditions that can resolve many of the problems associated with oxide ion conductor-based reversible SOFCs. The operating temperature of ceramic proton conductors is lower than oxide ion conductors, leading to lower cost materials of construction and lower degradation rates. When an oxide ion-conducting electrolyte is used, water vapor is formed as the product in the anode compartment during the fuel cell mode of operation, where it accumulates and dilutes the fuel (i.e., H<sub>2</sub>), so that it has to be removed by fuel circulation with additional cost and system complexity. On the other hand, when a proton-conducting electrolyte is used, water is formed at the cathode, where it can be easily swept away by the air flow (Figure 1). In the electrolysis mode of operation, dry and high purity hydrogen can be more directly produced by the proton conductor-based system than the oxide ion conductor-based system, avoiding the needs for additional gas separation systems (Figure 1). However, despite the abovementioned advantages of ceramic proton conductor-based reversible SOFCs, very few research activities have been accomplished with ceramic proton-conducting materials sets to-date. This may be due to lack of fundamental understanding or lack of availability of "good" (i.e., robust and high protonic conductivity) ceramic proton conductors and compatible electrodes that are operable in both fuel cell and electrolysis modes.

## CERAMIC PROTON CONDUCTOR

Within the scope of ceramic proton conductors investigated by researchers worldwide in recent years, there are basically two classes of perovskite-structured materials: (1) simple perovskites,  $ABO_3$  (where A is divalent and B is quadravalent), and (2) complex perovskites,  $A_3B'B''_2O_9$  (where A and B' are divalent, B'' is pentavalent). [12, 13, 14] A prerequisite for introducing protonic conductivity to these perovskite oxides is the presence of oxygen vacancies ( $V_O^{\bullet\bullet}$ ). Oxygen vacancies can be introduced in two ways: (1) for the simple perovskites, by doping with trivalent elements on the B site, such as  $Y^{3+}$ ; or (2) for the complex perovskites, by making a stoichiometric shift of B' and B'' sites (e.g.,

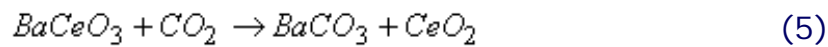
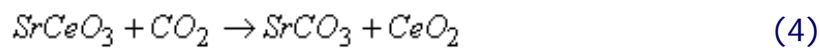
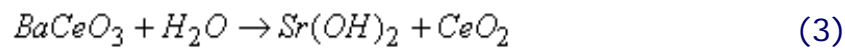
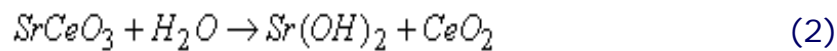
$A_3^{II} B'_{1+x}^{II} B''_{2-x}^V O_{9-\delta}$ ). In complex perovskites, a small stoichiometric shift  $x$  is necessary to reduce the overall ionic charge on the B' and B'' sites that will be compensated for by the creation of oxygen vacancies in the oxide ion lattice.

Heating these perovskite materials with oxygen vacancies in water vapor leads to water absorption, thus replacing oxygen vacancies by protons in the structure, as given by:



where the hydroxyl ion ( $\overset{\bullet}{\text{OH}}\text{O}$ ) denotes the proton embedded in the electron cloud of an oxygen ion. Proton conduction then proceeds by proton hopping between two adjacent oxygen ions (Grotthus mechanism). With protons being mobile, the perovskite oxides therefore display protonic conductivity and lead to potential application as electrolytes for fuel cells if the protonic conductivity is sufficiently high (typically greater than 10 mS/cm at 600°C). Application of these ceramic proton conductors in SOFCs requires that they exhibit adequate protonic conductivity as well as stability in the fuel cell environment. Extensive investigations have been conducted to examine proton conductivities of these perovskite oxides containing various dopants with various doping levels. However, relatively few studies have been reported on the stability of these materials in certain atmospheres ( $\text{H}_2\text{O}/\text{CO}_2$ ), on the materials' partial electronic conductivity, or on the emergence of oxide ion conductivity at higher temperatures ( $> 600^\circ\text{C}$ ).

Although simple doped strontium and barium cerate-based perovskite proton conductors ( $\text{SrCeO}_3$ ,  $\text{BaCeO}_3$ ) have relatively high protonic conductivities, their stability is poor in highly moist or even low level  $\text{CO}_2$ -containing environments, as given by the equations below. [1, 2]



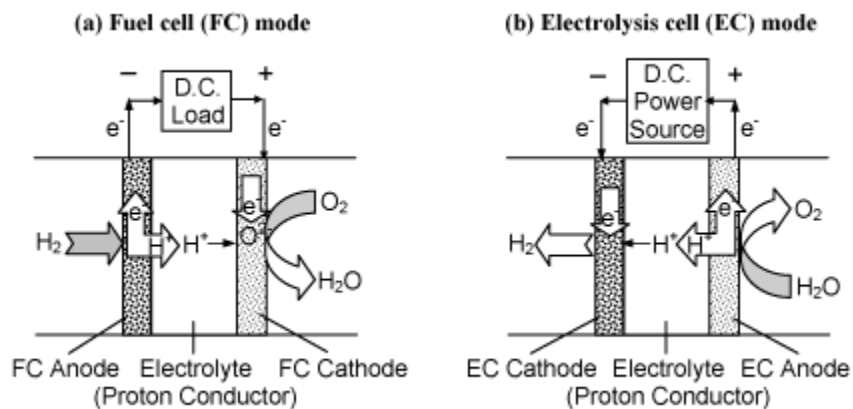
In contrast to cerates, zirconates hardly react with water, and they are stable in  $\text{CO}_2$ -rich environments.[17] Yttrium-doped  $\text{BaZrO}_3$ -based perovskite oxides have been demonstrated to combine high stability with high protonic conductivity that exceeds the conductivity of the best oxide ion conductors at temperatures below 700°C, as shown in Figure 2. [1, 2] Among the complex perovskites, very promising results have been shown for the compound  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-d}$  (BCN18). Both Y-doped  $\text{BaZrO}_3$  and BCN18 have high lattice constants and symmetry that is essential for the high solubility limit and mobility of protons. These ceramic proton conductors have the potential to be operated at lower temperatures (500-700°C) compared with oxide ion conductor-based SOFCs. Although there is interest in studying both simple and complex perovskites, we will limit the scope of the current 1-year study to the simple doped perovskite, Y-doped  $\text{BaZrO}_3$ .

## PROJECT TASKS

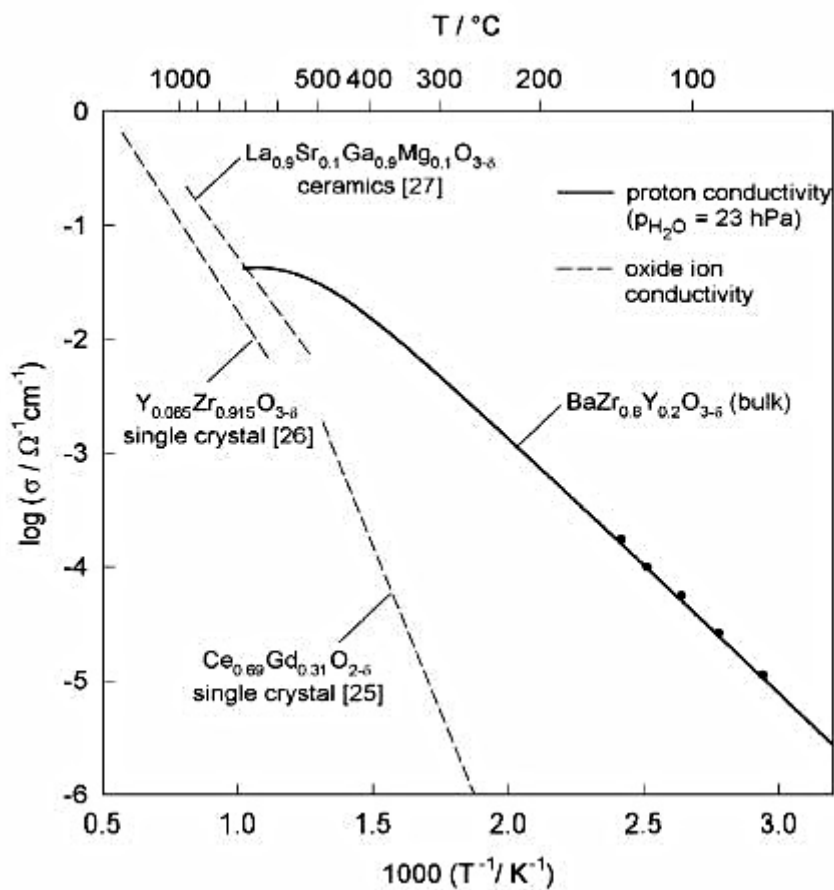
The key research and development tasks of the project are focused on developing intermediate-temperature (500-700°C) ceramic proton conductors with adequate protonic conductivity to meet the commercial target of reversible SOFCs and finding compatible electrodes with optimized functionality for dual-mode operation of reversible SOFCs.

A set of tasks and associated performance objectives has been identified to meet the project goal as follows:

- **Materials Manufacturing:** Investigate and use wet chemical fabrication routes for Y-doped  $\text{BaZrO}_3$  ceramic proton conductors and associated electrode materials in glycine nitrate, sol-gel, and co-precipitation processes;
- **Electrolyte Performance Testing:** Characterize the protonic conductivity of the ceramic proton conductors produced with wet chemical approaches, and determine how to improve the protonic conductivity and sinterability;
- **Electrode and Cell Performance Testing:** Investigate compatible electrodes by constructing 1" button test cells of reversible SOFCs to evaluate electrode performance in dual-mode operation, as well as initial chemical and mechanical stability under operating conditions.



**Figure 1.** Comparison of ceramic proton conductor-based reversible solid oxide fuel cell operating in (a) fuel cell (FC) mode and (b) electrolysis cell (EC) mode



**Figure 2.** Proton conductivity of 20% Y-doped BaZrO<sub>3</sub> (BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub>) at a water partial pressure of 23 kPa compared to oxide ion conductivities of the state-of-the-art oxide ion conductors: LSGM (La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>3-δ</sub>), YSZ (Y<sub>0.085</sub>Zr<sub>0.915</sub>O<sub>2-δ</sub>), and doped CeO<sub>2</sub> (Ce<sub>0.69</sub>Gd<sub>0.31</sub>O<sub>2-δ</sub>).

## PERSONNEL

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## SPONSORS

California Energy Commission Energy Innovative Small Grants (EISG) Program

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