

V.1 Proton Conducting Solid Oxide Fuel Cell

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Objectives

- Identification of dopant type and concentration in a perovskite host to achieve high proton conductivity and high protonic transference number under solid oxide fuel cell (SOFC) operating conditions.
- Selection of dopant type and concentration in a perovskite host to provide resistance to reactivity towards CO_2 and H_2O .
- Evaluation of electrode materials using symmetric cells and full cells in button cell configuration.
- Test button cells using selected perovskite compositions.

Approach

- Select an appropriate B-site dopant in a perovskite matrix by evaluating protonic conductivity and transference number in SOFC relevant atmospheres.
- Investigate stability of compositions in syngas.
- Select a composition and evaluate in button cell tests.

Accomplishments

- Dopant type was identified to achieve a high protonic conductivity of 3×10^{-3} S/cm.
- Selected compositions were found to be less prone to formation of BaCO_3 in the presence of CO_2 .
- High ionic transference number was demonstrated as indicated by open circuit voltage in button cells.
- A proton transference number of 0.7 was estimated at 800°C .
- Potential for high efficiency operation using a proton conductor-based SOFC relative to oxygen conductor-based SOFC was shown.

Future Directions

- Optimization of electrode compositions and electrode application techniques to improve cell performance.
- Evaluation of performance in button cell and stack tests using syngas fuel.

Introduction

One of the prime attractions of fuel cells is the possibility of realizing higher energy conversion efficiencies than are possible with thermal cycle systems. The basis of this difference is that thermal cycle system efficiencies are bounded by Carnot cycle thermodynamics, whereas fuel cell efficiencies are determined by chemical equilibrium thermodynamics and non-equilibrium force-flux relationships that govern charge, mass, momentum and energy transport. Materials have been developed which function as high temperature solid electrolytes in fuel cell applications. Two of the most widely considered materials are yttria doped ZrO_2 (YSZ) which transports oxygen ions and gadolinium doped BaCeO_3 which transports protons [1].

The thermodynamic difference between proton and oxygen ion cells is manifest in reversible potential variation with reactant utilization as a function of product water location. Excess air flow, used to remove the heat generated by cell operation, results in a lower water concentration in the cathode stream of a proton cell than in the anode stream of an O^{2-} cell.

Reversible potential variation with fuel utilization is shown for both proton and oxygen ion cells in Figure 1. The proton cell has a substantially higher reversible

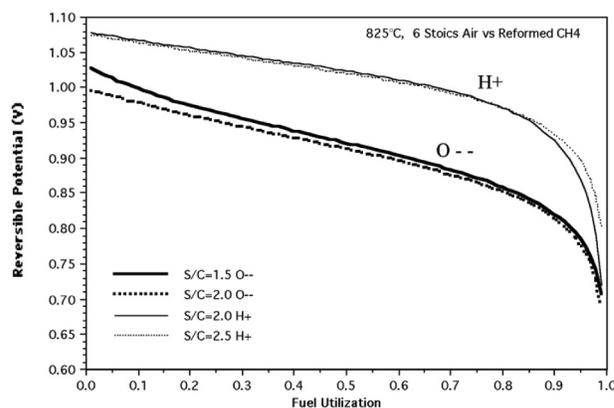


FIGURE 1. Comparison of Reversible Cell Potential

potential across the full range of fuel utilization. An interesting observation is that steam ratios greater than stoichiometric ($S/C=2$) increase the high utilization potential of a proton cell while oxygen ion cell potentials are uniformly higher with sub-stoichiometric steam ratios. This is due to the use of carbon monoxide via the shift reaction. The oxygen ion cell generates water in the anode stream so inlet compositions can be water deficit (high potential) and still have sufficient water to drive the shift reaction as utilization increases. The proton cell, on the other hand, must have sufficient or even excess water at the inlet to drive the shift reaction at high utilizations. However, water in the anode stream does not directly enter in the calculation of proton cell potentials and thus has little effect on the potential until higher utilizations where shift produced hydrogen is important. Thus, high temperature proton conductors have a thermodynamic advantage over oxygen ion conductors.

Comparable electrolyte ionic conductivities are required to take practical advantage of the thermodynamic benefit. Applications driven by maximizing efficiency at the expense of power density would favor proton cells. Thus, the opportunity for very high efficiency operation is one of the primary motivating factors for investigating proton conducting solid oxide fuel cells (P-SOFC). However, to date the research work on P-SOFCs has lagged far behind the well-known YSZ-based oxygen conducting solid oxide fuel cells (O-SOFC). The challenges that have been encountered in P-SOFC systems are discussed below.

Proton Conductivity

As mentioned earlier, the differences in electrolyte ionic conductivity may be greater than differences in the driving force and must be included in any comparison of an operating cell at a fixed current density. In general, the protonic conductivity of commonly known perovskite materials, such as doped SrCeO_3 and BaCeO_3 , are considerably lower than the oxygen ion conductivity of YSZ. The proton conductivity ranges from 5×10^{-3} to 2×10^{-2} S/cm at 800°C [1-5]. While the high end of this range is comparable to the oxygen conductivity of 8-YSZ, the perovskite materials also possess some level of oxygen ion conductivity and electronic conductivity at various temperatures. Thus, the protonic transference number varies as a function of temperature. While the doped BaCeO_3 composition functions as an effective electrolyte, an increase in hydrogen conductivity is preferable to fully exploit the benefit of high efficiency with high power density.

Stability

One of the biggest technical challenges lies in maintaining the chemical stability of the perovskite in

the presence of CO_2 and moisture; both are present in a typical hydrocarbon fuel. Numerous studies have confirmed the instability of the perovskite compositions.

It has been shown [1] that partial replacement of the B-site dopant with Zr completely eliminates this reaction. A similar improvement in stability in moist conditions was also reported with Zr substitution [1]. However, the stability improvement is at the expense of protonic conductivity. The proton conductivity was found to decrease monotonically with increasing Zr content [1, 2, 3].

Thus, what is required for successful development of a P-SOFC is an electrolyte material that has high proton conductivity to achieve a low area specific resistance, high protonic transference number relative to oxygen transference number to realize high efficiency, and stability in CO_2 and H_2O without compromising protonic conductivity for cell operation using practical hydrocarbon fuels.

Approach

Perovskite compositions that are known to exhibit protonic conductivity were evaluated for dopant study. The B-site dopants, typically rare earth metals, have been shown to increase the proton conductivity of perovskites such as BaCeO_3 . Several dopants and dopant levels were screened to identify compositions that have high conductivity and stability. Selected compositions were evaluated in button cell tests.

Results

A variety of B-site dopants were evaluated for their effect in total ionic conductivity and proton transference number. Protonic conductivities as high as 0.015 S/cm at 700°C and 0.02 to 0.03 S/cm at 800°C were measured. In addition, the estimated protonic transference number ranged from 0.6 to 0.7 at 800°C , while the total ionic transference number was around 0.9.

BaCeO_3 -type perovskite materials are known to be difficult to achieve good sintered density. A small amount of a sintering aid was added to achieve a sintered density in excess of 98%. The addition of the sintering aid did not affect the ionic conduction properties of the material. Micrographs of sintered BaCeO_3 are shown in Figure 2. As can be seen, the addition of the sintering aid improves densification to achieve the needed density for an electrolyte.

Selected compositions, baseline and modified perovskites, were also exposed to syngas at 800°C . Comparison of powder X-ray diffraction patterns showed a significant reduction in the BaCeO_3 for certain modified compositions relative to the baseline material as shown in Figure 3.

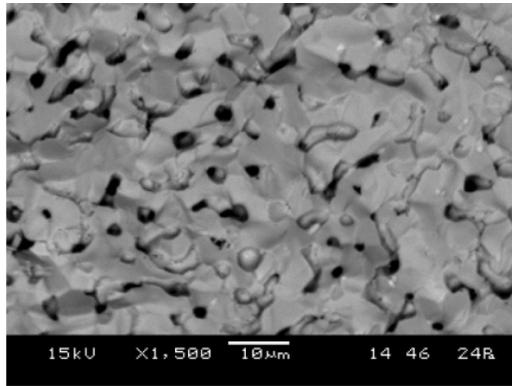
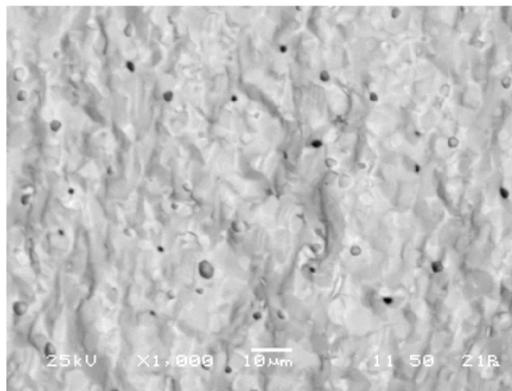
Sintered BaCO₃Sintered BaCeO₃ with a sintering aid

FIGURE 2. Comparison of Sintered Density With and Without the Addition of a Sintering Aid

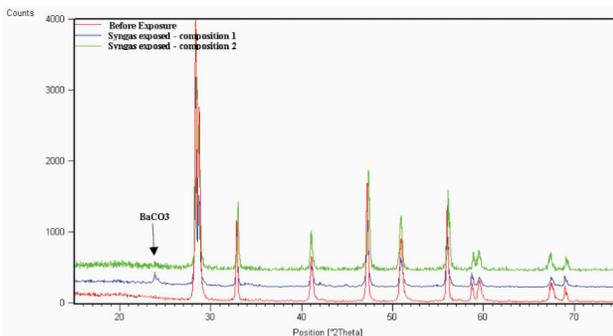


FIGURE 3. Powder X-ray Diffraction Patterns of 800°C Syngas Exposed Baseline and Modified Compositions

Button cell tests with 500 µm thick doped BaCeO₃ pellets were conducted. The cell performance was somewhat low. Post-test examination showed poor anode bonding to the electrolyte. However, comparison of proton and oxygen conducting electrolyte fuel gas potential as a function of cell current density, as measured by independent reference electrodes, showed the high efficiency potential for the proton SOFCs. This is shown in Figure 4.

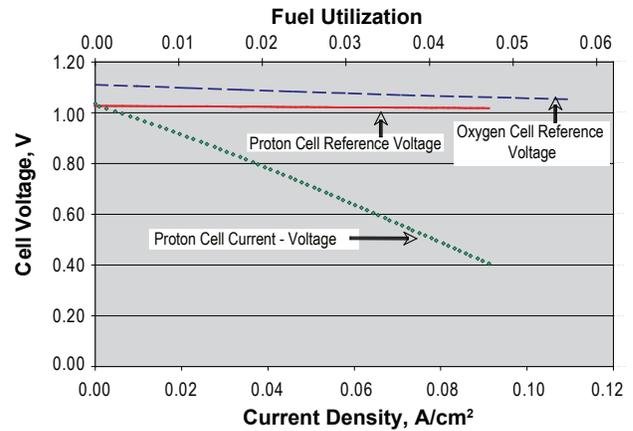


FIGURE 4. Comparison between Proton SOFC and Oxygen SOFC: Fuel Potential as a Function of Fuel Utilization

Comparison of the reference voltage trace provides several interesting points.

- First, at open circuit the proton open circuit voltage (OCV) is lower than that of oxygen OCV. This again is a confirmation of pure ionic conduction of zirconia electrolyte providing near theoretical Nernst potential. The lower OCV of the proton cell is indication of the ionic transference number, t_{ion} , being less than one, in this case about 0.96.
- As a function of utilization however, the driving potential of the oxygen cell drops more steeply than the proton cell again confirming the benefit of the proton cell in maintaining higher driving force.
- Because of t_{ion} being less than 1, the true benefit of the proton cell does not manifest until the cell reaches much higher utilization. The driving potential in this case will cross over at about 10 to 15% fuel utilization. It is theoretically possible to achieve very high utilization at a higher operating voltage with a proton cell.
- Finally, while high efficiency operation is clearly possible with the proton cell, the cell resistance must be lowered by a factor of 10 to fully realize the benefits of the proton cell in terms of cost/kW as well as specific weight and volume. Improvements to electrode compositions and electrode application technique as well as the use of thin electrolytes are expected to provide the necessary performance improvement.

Conclusions and Future Directions

The project results reconfirm the high efficiency potential for proton conductor-based SOFCs. By proper B-site doping very high proton conductivity, comparable to that of the oxygen ion conductivity of yttria-doped zirconia can be achieved to enable high performance cell operation. The inherent oxygen and electron

conductivities in the BaCeO₃-type of material limit the efficiency benefit to some extent depending on the operating conditions. When the cell is operated at high utilization, significantly higher electrochemical efficiency can be realized compared to an oxygen ion conductor-based SOFC. Electrode improvements and process development for fabrication of thin supported electrolyte cells need to be the research focus for realizing the full capability of proton SOFC systems.

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