V.7 Component Manufacturing and Optimization of Protonic SOFCs

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Objectives

- Demonstrate protonic solid oxide fuel cell (p-SOFC) performance of 125 mW/cm^2 at 600°C, using scalable manufacturing approaches and improved cell electrodes.
- Demonstrate enhanced cell electrode performance through compositional and microstructural tailoring. Demonstrate (cathode + anode) contributions of <0.5 Ω-cm^2 to cell ASR at 600°C.
- Establish tape casting and sintering routes to produce conventional electrolyte supports and electrolyte components at the button cell and 10 x 10 cm cell size. Minimize cell membrane thickness, with a target of ASR of <1.0 Ω-cm^2.
- Produce of Zn-modified BYZ $Ba(Zr_{1-X}Y_X)O_{3-\delta}$ electrolyte powders at the 600 g batch size, using scalable preparation routes, and demonstrate that these powders in tape cast forms can be sintered to densities of more than 95% ρ_{th} at temperatures of less than 1,400°C.

Accomplishments

- Manufactured $Ba(Zr_{0.6}Ce_{0.4})_{0.8}Y_{0.2}O_{2.9}$ with ZnO (BYZC-Zn) doping by a solid state synthesis route.
- Densified $Ba(Zr_{0.6}Ce_{0.4})_{0.8}Y_{0.2}O_{2.9}$ with ZnO doping material to 97% of expected theoretical density at 1,550°C.
- Demonstrated significantly improved conductivity over standard BYZ-Zn powder.

Introduction

Protonic solid oxide fuel cells (p-SOFCs) offer unique characteristics compared to competing technologies. In a p-SOFC, protons diffuse from the anode to the cathode through a thin membrane layer, generating power from the electrochemical reaction. P-SOFCs are characterized by their potential for high fuel utilization without steam diffusion limitation, and their intermediate operating temperatures (450-600°C). P-SOFCs avoid steam formation at the anode (experienced by SOFCs), maintaining high fuel concentration over the anode, allowing high fuel utilization and the high efficiency operation. The cells operate at temperatures that increase the reaction kinetics compared to proton exchange membrane (PEM) fuel cells, but low enough to offer the potential for metal interconnects without corrosion. If operating temperatures can be kept at the lower end of this range (using thin membranes and efficient electrodes) conventional high temperature seals may become practicable, avoiding a design issue of SOFC systems.

To date, p-SOFC development has been hampered by processing difficulties associated with ceramic proton-conductors. In this project, NexTech and Caltech will collaboratively advance the materials science and manufacturing technology for ceramic p-SOFCs. Using materials processing strategies for $Ba(Zr_{0.8}Y_{0.2})O_{2.9}$ identified by Caltech, NexTech will fabricate its thin-membrane electrolyte-supported cells using proprietary designs well suited to the BZY material set. This demonstration will require the transition of demonstrated laboratory processes to commercially viable approaches. Caltech will assist this transition and use the resultant cell platform to optimize p-SOFC electrodes. The successful completion of this program will shift p-SOFC development from electrolyte development to electrode optimization and the large cell demonstration.

Approach

Researchers at Caltech have developed a chemical approach in which a sintering aid is used to enhance grain growth and enable densification at reduced temperatures [1]. From a comprehensive screening of transition metal oxides, it was determined that ZnO enhances sintering without generating deleterious intermediate phases or introducing excessive electronic conductivity.

NexTech has developed cost-effective manufacturing processes for a range of state-of-the-art SOFC cell designs. These efforts have revealed the manufacturing and performance strengths and weaknesses of various cell manufacturing approaches. Based on this experience, NexTech developed target specifications for an optimized solid oxide fuel cell, a planar cell component with a thin (≤50 µm) electrolyte, a 30-50 µm thick anode (to improve fuel oxidation kinetics) and a 30-50 µm thick cathode (to minimize oxygen diffusion limitations). The cell should be mechanically robust and have a dense periphery to simplify sealing.

The cell developed by NexTech offers an excellent demonstration platform for protonic electrolyte and fuel cell research. The principal manufacturing step for the cell platform are tape casting and co-sintering. The processing routes developed at Caltech have been demonstrated with glycine-nitrate produced powders having surface area values (5-8 m^2/g), ideal for tape casting approaches. In this project, NexTech will tailor this process for scaled-up powder production, and validate its utility in tape casting and cell fabrication experiments.

Results

ZnO-doped $Ba(Zr_{0.6}Ce_{0.4})_{0.8}Y_{0.2}O_{2.9}$ (BYZC-Zn) material was synthesized by a solid state route and subsequently cast into thin tapes consisting of ~74 microns in thickness. Laminates of the cast tape were hot pressed into sheets measuring 400 microns thick. The sheets were cut into button cell shapes. The button cells were fabricated into two designs, the standard circular disc with no texture and a thin (~50 micron) membrane design. The button cells were sintered at various temperatures, up to 1,450°C. This allowed for dense, non-porous parts while preventing unwanted surface reaction with the surrounding sacrificial powder. Cells were sent to Caltech for electroding and subsequent performance tests. Measurements resulted in 4 mW/cm^2, which is nominal to the performance seen with BYZ-Zn based substrates.

Figure 1 demonstrates the sintering curve of the BYZC-Zn materials. The densification data on pressed pellets indicates that BYZC-Zn samples can densify as low as 1,250°C. However, upon firing tape casted parts, densification behavior required increased temperatures to 1,450°C most likely due to changes in geometrical design of the part.

In addition, Figure 2 shows results of conductivity values as measured by AC Impedance of the BYZC-Zn pellets sintered at 1,550°C. The results demonstrated a 115% increase in conductivity over BYZ-Zn powders measured at 600°C. Although promising, the conductivity of 5.15 mS/cm is still a below that of equivalent oxygen ion conductor ceramics for the fuel cell industry.

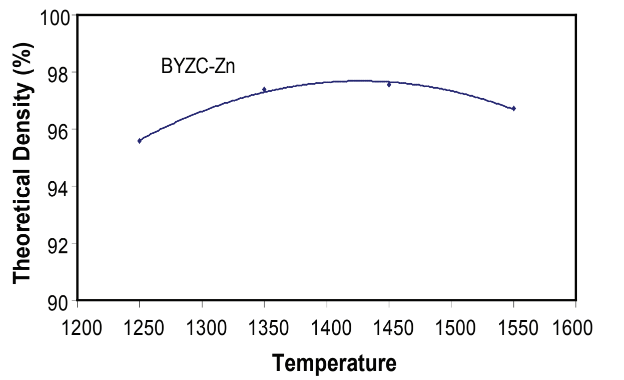

FIGURE 1. Sintering Study for BYZC-Zn Synthesized by Solid State Route

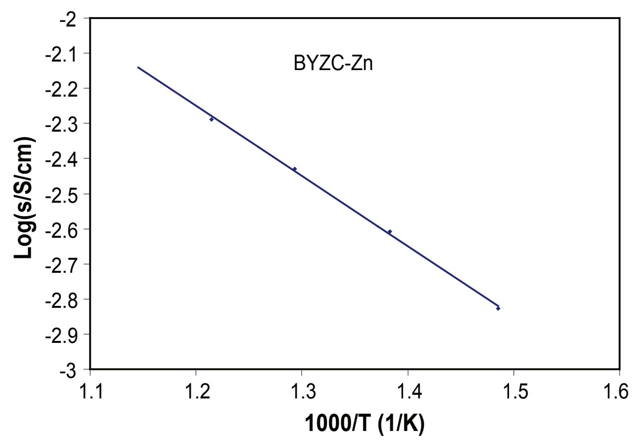

FIGURE 2. Conductivity Measurements for BYZC-Zn Synthesized by Solid State Route

Conclusions and Future Directions

NexTech has been able to demonstrate manufacture of BYZC-Zn doped ceramics that demonstrate 115% more conductivity over BYZ-Zn powders. Button cell size discs have been fabricated by a low cost synthesis route and fired at reasonable sintering temperatures while demonstrating dense parts. The improved conductivity should provide better performance in fuel cell and other electrochemical reactors.

References

1. Babilo, P., and Haile, S.M., *J. Am. Ceram. Soc.*, 88 (9), 2362-2368 (2005).