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## V.4 A Thin Film, Anode-Supported Solid Oxide Fuel Cell Based on High Temperature Proton Conducting Membrane for Operation at 400 to 700°C

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water vapor at the cathode. One advantage of SOFCs based on a proton conducting membrane over an oxygen ion conducting membrane is that with hydrogen as the fuel, there is no fuel dilution, allowing for operation at high fuel utilization, and thus at high overall system efficiency. SOFCs based on high temperature proton conducting membranes also offer important advantages over low-temperature proton exchange membrane fuel cells (PEMFCs), namely: (i) Higher operating temperature allows for the use of non-noble metal catalysts, thus lowering cost; (ii) The catalysts are not poisoned by CO due to high operating temperatures; and, (iii) Highly efficient thermal integration with fuel processors and other balance-of-plant components is possible unlike lower temperature PEM.

In this project, we demonstrated fully fabricated anode-supported HTPC cells which exhibited good performance. We also demonstrated that the fabricated cells can be subjected to repeated thermal cycles without a significant loss of performance, a key requirement for virtually any application. Further, we have demonstrated that Ni+YSZ as the anode support is ideally suited for many solid electrolytes, including HTPC. All these indicate that HTPC-SOFCs can be operated stably at very high fuel utilization, thus allowing for attaining high system efficiency, and further reduce green house gas emission per kWh produced.

### Objectives

- Fabricate high-temperature proton conductor (HTPC), anode-supported solid oxide fuel cell (SOFC) button cells and measure performance on hydrogen/air up to a maximum of 700°C.
- Demonstrate successful thermal cycling of cells.

### Accomplishments

- Fabricated anode-supported thin film HTPC cells using various electrolyte materials including BCY ( $\text{BaCe}_{1-y}\text{Y}_y\text{O}_{3-\delta}$ ), SCYb ( $\text{SrCe}_{1-y}\text{Yb}_y\text{O}_{3-\delta}$ ), and KBZY (K-doped and Y-doped  $\text{BaZrO}_3$ ).
- Demonstrated satisfactory performance on anode-supported thin film HTPC-SOFCs at 650~700°C with a maximum power density of ~0.5 W/cm<sup>2</sup>.
- Demonstrated excellent stability upon repeated thermal cycling, showing no degradation after 3~4 thermal cycles.
- Fabricated large-area cells of HTPC electrolyte on Ni+YSZ anode support successfully for both planar (4"×4" active area) and tubular designs.

### Approach

The best known materials for application in HTPC-SOFCs are B-site doped  $\text{BaCeO}_3$  and  $\text{SrCeO}_3$ . These materials exhibit high proton conductivity, with values reported as high as  $\sim 10^{-2}$  S/cm at 700°C. However, the stability of the materials must be demonstrated, especially for application in SOFCs, because these materials are known to exhibit sensitivity to  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at relatively low temperatures (below 600°C), but are known to be stable at higher temperatures. The reactivity with  $\text{CO}_2$  is not a major consideration in fuel cells, since the possible interaction will be limited only on the surface of electrolyte, and does not affect stability. The reactivity with  $\text{H}_2\text{O}$  is an issue for stability, since water vapor dissolves into the lattice, which is required for conduction. There is no reactivity of  $\text{BaCeO}_3$  and  $\text{SrCeO}_3$  at the SOFC operating temperature (above 600°C), but there is the potential for reaction at lower temperatures, for example if the SOFC is idling in humid atmospheres at low temperatures. The following approach was used to achieve and demonstrate stability of HTPC-SOFCs: (i) Fabrication of anode-supported thin film HTPC-SOFCs; (ii) Optimization of materials

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### Introduction

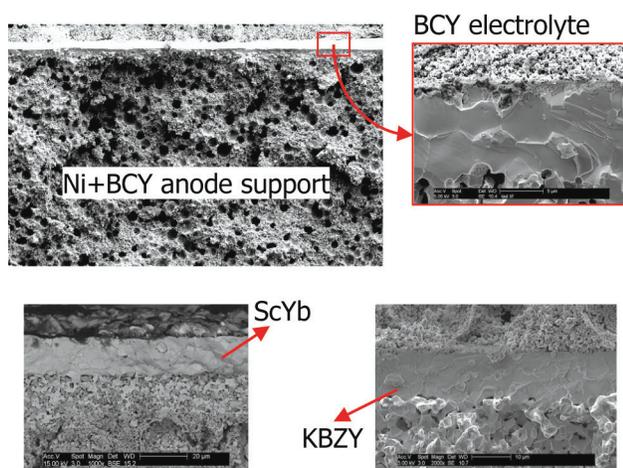
SOFCs typically employ oxygen-ion-conducting membranes as a solid electrolyte. Alternatively, HTPC solid oxide membranes (analogous to the low temperature polymer electrolyte membrane fuel cells) can be used wherein protons transport from the anode through the electrolyte membrane to the cathode, where they react with oxygen molecules and electrons to form

and microstructure for high performance; and (iii) Operation under conditions such that the SOFC is not exposed to too high a humidity at low temperatures, especially not to liquid water. Prior work has shown that HTPC materials remain stable in water vapor even at low temperatures, and are only affected by liquid water [1]. In this project, HTPC-SOFCs were subjected to several thermal cycles.

## Results

Anode-supported thin film HTPC-SOFCs were successfully fabricated. Button cells were fabricated in several steps to have four or five distinct layers: (i) porous anode support; (ii) porous anode interlayer; (iii) dense thin film electrolyte; (iv) porous cathode interlayer; and/or (v) porous cathode current collector. The cathode area was approximately 2 cm<sup>2</sup>, which was used as the basis for the current density calculation. Three different HTPC materials were used: Y-doped BaCeO<sub>3</sub> (BCY), Yb-doped SrCeO<sub>3</sub> (SCYb), and K-doped and Y-doped BaZrO<sub>3</sub> (KBZY). Micrographs showing the cross-section of those cells are given in Figure 1. Note that the HTPC electrolytes are fully dense and the electrolyte thickness is in the range of 8 to 15 μm. Both the anode and cathode exhibit fine porous microstructures.

Work done to date has shown that BaZrO<sub>3</sub> or BCN18 (Ba<sub>3</sub>Ca<sub>1.18</sub>Nb<sub>1.82</sub>O<sub>9-d</sub>) are generally more stable in water vapor and liquid water compared to BCY and SCYb. Their stability has been demonstrated by heat-treating them in an autoclave at temperatures as high as 500°C and water vapor pressures as high as 180 bars [2]. In addition, it has been demonstrated that BaZrO<sub>3</sub> and BCN18 can be boiled in water without any reaction.

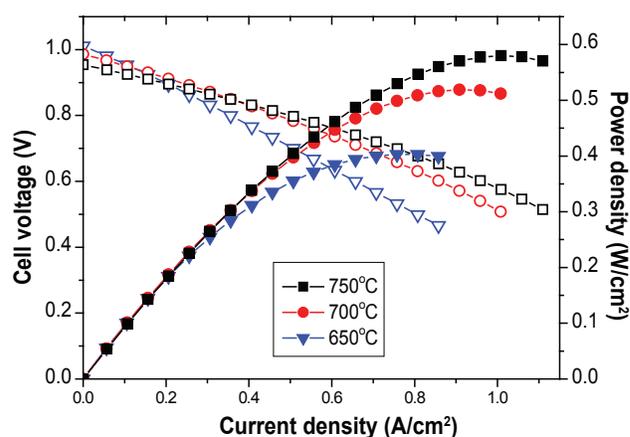


**FIGURE 1.** Micrographs of typical anode-supported thin film HTPC-SOFCs, using three different electrolytes (BCY, SCYb, and KBZY). Anode-support materials were Ni+HTPC, and cathode materials were LSCM, LSM, LSC, or Ag.

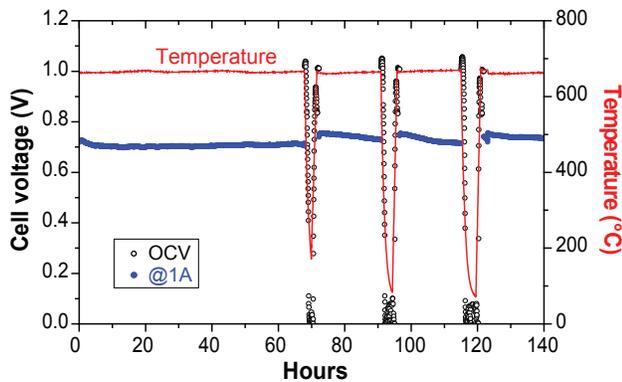
Proton conductivities of these materials are, however, lower than BaCeO<sub>3</sub> and SrCeO<sub>3</sub>-based materials, due to their lower basicity (the affinity towards water vapor). Doping on the A-site of BaZrO<sub>3</sub> with an alkali ion is expected to increase affinity for water vapor by increasing basicity. The reason for doping on the A-site is because of the comparable size of monovalent alkali ions (Na, K, etc.) to those of divalent alkaline earth ions (Ba, Sr, etc.). For this reason, the fabrication of KBZY cells was tried using fine powders made in-house, and cells were successfully fabricated as shown in Figure 1.

Of all the perovskite type materials investigated to date, rare earth ion-doped BaCeO<sub>3</sub> exhibits the highest proton conductivity, followed by rare earth ion-doped BaThO<sub>3</sub> and SrCeO<sub>3</sub>. For this reason, much work has been conducted on BaCeO<sub>3</sub> and SrCeO<sub>3</sub>. For the same reason, thin film anode-supported HTPC-SOFC button cells with Y-doped BaCeO<sub>3</sub> (BCY) and Yb-doped SrCeO<sub>3</sub> (SCYb) were tested over the temperature range 600~800°C using hydrogen or syngas as the fuel. In these cells, the electrolyte was BCY or SCYb, and the anode support was Ni+BCY or Ni+SCYb. Figure 2 shows the current-voltage and power density curves for a typical BCY cell with LSC as the cathode material. The performance is satisfactory, showing ~0.45 W/cm<sup>2</sup> at 0.7 V (700°C). For HTPC-based cells, this is an excellent result, especially with non-optimized anode.

Even though BaCeO<sub>3</sub> or SrCeO<sub>3</sub> are thermodynamically unstable at low temperatures (below 600°C) [3,4], work conducted in the present work showed that the cells fabricated using these materials can be operated stably under repeated thermal cycles. In the solid state, both BaCeO<sub>3</sub> and SrCeO<sub>3</sub> are kinetically stable over a wide temperature range. This is due to slow solid-state diffusion at low temperatures. At room



**FIGURE 2.** I-V curves of a BCY cell with LSC cathode tested between 650 and 750°C using hydrogen as the fuel (without humidification) and air in the cathode. Anode-support = Ni+BCY, anode interlayer = Ni+BCY, electrolyte = BCY, cathode interlayer = BCY+LSC, cathode = LSC.

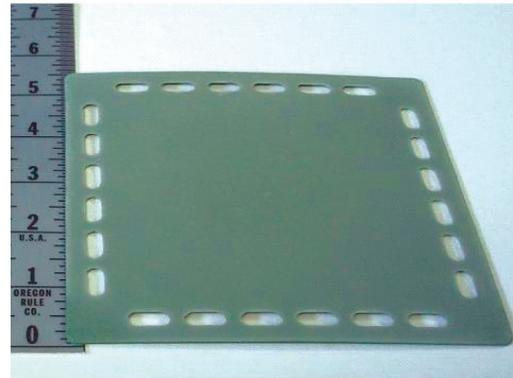


**FIGURE 3.** The test results of thermal cycling with a BCY-electrolyte cell. The discharge current was 1.0 A ( $0.5 \text{ A/cm}^2$ ) at  $650^\circ\text{C}$ . Open circuit voltages are also shown in the plot (open circle). Both the anode and cathode gases were not humidified externally. Anode-support = Ni+BCY, anode interlayer = Ni+BCY, electrolyte = BCY, cathode interlayer = BCY+LSC, cathode = LSC.

temperature, both  $\text{BaCeO}_3$  and  $\text{SrCeO}_3$  maintain their stability indefinitely. At higher temperatures (above  $800^\circ\text{C}$ ), the materials are thermodynamically stable. It is anticipated that an SOFC stack/system will be subjected to several thermal cycles during the operating life. Thus, it is imperative that stability under the conditions of thermal cycling be evaluated via experiments. For these reasons, many cells were subjected to several thermal cycles under various conditions. The key to the stable thermal cycling of HTPC-SOFCs is to maintain dry gas conditions during thermal cycle. High-temperature operation mode can be either humidified or dry fuel for the anode and either humidified or dry air for the cathode. Cool-down and re-heating mode should be dry fuel for the anode and dry air for the cathode. The objective was to minimize any possibility of BCY and SCYb decomposing. Figure 3 shows the results of thermal cycling of a BCY cell with LSC as the cathode material. The open circuit voltages are larger than 1.0 V as shown in the figure. The performance was excellent ( $\sim 0.35 \text{ W/cm}^2$  at 0.7 V,  $650^\circ\text{C}$ ) and very stable between thermal cycles. This is an important milestone demonstrating the practical viability of HTPC solid oxide fuel cells in terms of both high performance and stability.

For any practical application, it is imperative that SOFC stacks withstand several hundred to even several thousand thermal cycles. This means all possible steps should be taken to make the cells as robust as possible. To this end, a new approach of using the proven Ni+YSZ anode support was developed. Since Ni+YSZ is a proven anode support (and anode) in YSZ-based SOFC, it was reasoned that it should also be a viable support for other electrolytes, including HTPC, as long as the electrolyte and anode are compatible and do not react. In order to explore this possibility, we also fabricated HTPC-based cells with Ni+YSZ anode support.

4" Planar cell



Tubular cells



**FIGURE 4.** Photos of 4"×4" (cathode area) planar cells and tubular cells. Both types of cells have BCY electrolyte on Ni+YSZ support and were sintered at  $1,450^\circ\text{C}$ .

Assuming success, this also opens other options for the cathode. That is, the general approach developed is to use the established anodes and cathodes for SOFCs, but make a suitable choice of the electrolyte, in the present case an HTPC. The feasibility of Ni+YSZ anode-supported, HTPC electrolyte cell was demonstrated from a button cell test using SCYb as electrolyte in our recent experiment. Based on that result, it was recognized that cells of practical size need to be demonstrated. Therefore we fabricated a couple of 4"×4" planar BCY cells on Ni+YSZ anode support as shown in Figure 4. Tubular cells, being another practically important SOFC technology, were also fabricated using Ni+YSZ support tubes and BCY electrolyte layers as shown in Figure 4.

## Conclusions and Future Directions

Thin film anode-supported HTPC-SOFCs were successfully fabricated and their high performance was demonstrated. Stable operation with repeated thermal cycles was demonstrated as well. In the future, larger planar cells (e.g.  $100 \text{ cm}^2$  active area) and tubular cells of up to 10 inches long need to be fabricated. Short stacks

of both planar cells and tubular cells need to be tested and their performance needs to be analyzed. A kW-scale stack demonstration will prove practical applicability.

## References

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