MATERIALS AND COMPONENTS FOR SOLID OXIDE FUEL CELL SYSTEMS

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ABSTRACT

Electrolyte supported solid oxide fuel cells are noted for their simple construction and mechanical robustness. The relatively thick (> 150 micron) electrolyte layer provides a robust core to the cell architecture. However, the high ohmic resistance of the same thick electrolyte layer limits cell performance at temperatures < 800°C. Two strategies are suggested to improve electrolyte supported cell performance. The first, the development of scandia-doped zirconia laminates, has demonstrated that high strength, high conductivity electrolytes can be fabricated. The resultant self-supporting membrane can be thinner, and the high ionic conductivity of the laminate further reduces cell resistance. The second strategy, the development of cathode materials designed to offer lower interfacial resistance at 700°C, has demonstrated that a number of ferrite-based cathode materials with low interfacial resistance can be synthesized by co-doping on the A- and B-sites of the perovskite structure.

INTRODUCTION

Planar solid oxide fuel cell development has traditionally been focused on two major architectures, electrolyte supported and anode supported designs. Electrolyte supported designs have been favored for applications where mechanical stability and cell robustness are favored. The relatively thick (< 150 μm) electrolyte layer provides a strong cell component that simplifies manufacturing and improves cell robustness during operation. As such, a number of manufacturers are evaluating this technology in prototype systems. However, the thick electrolyte layer contributes a high ohmic resistance to the resultant cell, which mandates the use of high operating temperatures. This effect is exacerbated in designs that utilize partially-stabilized yttria-doped zirconia electrolytes, selected to further enhance mechanical strength and ruggedness.

To address this shortcoming of the electrolyte supported cell, a great number of developers have evaluated electrode-supported SOFCs, predominantly anode supported cells. The anode supported cell design allows electrolyte layers less than ten microns to be deposited, greatly reducing its contribution to the cell resistance. However, the stresses resulting from thermal expansion mismatch, sintering rate mismatch and anode reduction and subsequent re-oxidation all complicate cell fabrication and take their toll on anode-supported cell stability during operation. These issues are alleviated to an extent
with lower operating temperatures, but improved cathode materials are required for lower temperature operation.

An alternative approach to achieving improved cell performance is to re-evaluate the electrolyte supported cell and through materials selection, enhance cell performance while retaining the advantages of the electrolyte supported design. Two strategies for designing such improved cells include the development of improved electrolyte components and higher performance thick-film cathode materials.

EXPERIMENTAL RESULTS

Laminate Electrolyte Development

One approach to reducing electrolyte resistance is to evaluate alternative electrolyte materials and architectures. Scandia doped zirconia has comparatively higher ionic conductivity than zirconia doped equivalently with yttria (1-3). While the cost of this electrolyte is greater than YSZ, the enhancement of ionic conductivity is considerable. Partially stabilized (6 mol% Sc$_2$O$_3$) zirconia possesses conductivity similar to fully stabilized YSZ (1), while fully stabilized (10 mol% Sc$_2$O$_3$) zirconia has an ionic conductivity value nearly two times greater than fully stabilized YSZ (2).

Figure 1 shows the relative strength of 150 micron thick samples of fully (8 mol% Y$_2$O$_3$) stabilized zirconia, partially (3 mol% Y$_2$O$_3$) stabilized zirconia, fully (10 mol% Sc$_2$O$_3$) stabilized zirconia and partially (6 mol% Sc$_2$O$_3$) stabilized zirconia. The fully stabilized grades of zirconia show lower strength than the partially stabilized materials in both families. However, the fully stabilized Sc-doped zirconia shows promising mechanical properties. Furthermore, while the mechanical properties of Y$_2$O$_3$ and Sc$_2$O$_3$ partially stabilized zirconia is comparable, there is nearly a 5 times difference in conductivity.

![Figure 1. Comparative mechanical strength of Y$_2$O$_3$- and Sc$_2$O$_3$-doped zirconia materials, based on ring-on-ring testing of 12 mm diameter discs of 150 micron nominal thickness.](image-url)
To further evaluate the potential for enhancing the electrolyte mechanical strength and conductivity, a series of laminate composites were prepared. Thin layers (~40 microns fired thickness) are cast, cut, stacked and laminated prior to firing. An example of a sintered four layer laminate microstructure is shown in Figure 2. In this example, the dark center layers are 10 mol% Sc-doped zirconia and the external layers are 6 mol% Sc-doped zirconia. There is no evidence of delamination at either the homogeneous or heterogeneous interfaces. This process for building laminate structures has been demonstrated on parts as large as 10 × 10 cm and as thin as 100 microns.

A number of laminates were produced and tested for mechanical strength using ASTM Standard Test Method C 1499. Table 1 and Figure 3 compares the collected data on the multi-layer electrolyte structure to the conventional substrates of 3 mol% and 8 mol% yttria-stabilized zirconia, as well as 6 mol% and 10 mol% scandia-stabilized zirconia.

**Table 1. Mechanical Strength of Single Composition and Laminate Electrolytes.**

| Description | 3 YSZ | 8 YSZ | 6ScSZ | 10 ScSZ | 3Y8Y3Y | 6Sc10Sc6Sc | 10Sc6Sc10Sc |
|-------------|-------|-------|-------|---------|-------|-----------|------------|
| Average strength (MPa) and 95% confidence interval | 719.9±90.4 | 187.1±44.9 | 670.1±280.2 | 310.0±148.1 | 676.5±121.9 | 909.1±241.3 | 528.8±174.3 |
| Weibull characteristic strength (MPa) | 739.9 | 197 | 733.5 | 343.4 | 706 | 967.1 | 565.1 |
| Weibull modulus | 17 | 9 | 4.74 | 3.97 | 11 | 7.28 | 6.7 |

Mechanical strength data (Figure 3) for laminates produced with interior layers of fully-stabilized scandia-doped zirconia and external layers of layers of partially stabilized scandia doped zirconia show an impressive improvement over a fully stabilized sample of the same geometry, and in preliminary evaluations, higher mechanical strength than either end member composition. When the fully and partially stabilized layers are interchanged, a mechanical strength of the resultant laminate is intermediate to the two end members. This result may indicate that when the interior layer is fully stabilized, the exterior partially stabilized layers are placed in compression, increasing the strength of the laminate. Further evaluation to understand the relative impact of composition and processing on the mechanical strength is underway.
Figure 3. Mechanical strength of laminate composite materials, based on ring-on-ring testing of 12 mm diameter discs of 150 micron nominal thickness.

Electrolyte Supported Cell Development

Based on the mechanical testing results of the scandia-doped laminates, electrolyte supported cells have been fabricated and tested. Using the 6/10/6 mole percent scandia doped zirconia laminates (150 μm thick), NiO/GDC composite anode and lanthanum-strontium manganite (LSM)-Gd-doped ceria composite cathode inks were applied and sintered, resulting in an active area of 28-cm². After firing the anode and cathode layers, fuel cell performance testing was performed. The cell was heated to 850°C between

Figure 4. Current-Voltage performance of 6/10/6 mole percent Sc₂O₃ laminate electrolyte supported cell, at testing onset and after 500 hours. Tests were performed at 200 sccm H₂ + 100 sccm N₂ fuel flow and 1500 sccm air flow at 825°C.
Inconel manifolds, which served to distribute the fuel and air gases over the respective anode and cathode sides. The manifolds also served as current collectors for the test. Current density-voltage and current density-power density curves were generated, at a fuel flow rate of 200 sccm of hydrogen and 100 sccm of nitrogen per minute and an air flow rate of 1500 sccm of air per minute. The resultant current-voltage curve for the cell is shown in Figure 4, under initial test conditions and after 500 hours at 0.8 V. While some slight decrease in performance is observed, Figure 5, a plot of current as a function of time, shows changes in cell performance occurs in the first one hundred hours of testing, after which the cell shows good stability with time.

![Figure 5. Lifetime performance of 6/10/6 mole percent Sc$_2$O$_3$ laminate electrolyte supported cell, at testing onset and after 500 hours. Tests were performed at 200 sccm H$_2$ + 100 sccm N$_2$ fuel flow and 1500 sccm air flow at 825°C, under a constant voltage of 0.8 V.](image)

**Cathode Development**

Using conventional LSM cathodes, the performance of planar cells is limited at temperatures below 800°C. Cathode development efforts have identified a number of lanthanum- and praseodymium ferrite compositions that are of interest for low temperature, high power density operation. (4-6) In a recent study, the generic formulations $(A_{0.60}Sr_{0.40})_{0.995}(Fe_{0.90}B_{0.10})O_3$ were prepared using copper, zinc, nickel and magnesium as dopant species. The baseline formulation was selected for its similarity to the commonly used cobalt-doped LSF composition. X-ray diffraction studies confirmed that phase-pure perovskite materials resulted for all compositions. Using a solid-state processing route, phase-pure powders were produced from oxide and carbonate precursor materials. The resultant powders had a surface area of 6-8 m$^2$/g and submicron particle size distribution. The thermal expansion coefficient, bulk conductivity and sintering behavior of the materials were evaluated, and are listed in Table 2.
Table 2. Physical Properties of Doped Lanthanum- and Praseodymium-Ferrite Materials.

| Composition                          | CTE @ 1000°C (10⁻⁶/°C) | σ (700°C) (S/cm) |
|--------------------------------------|------------------------|------------------|
| (LaₐₓSrₜ₋ₐₓ)o.₉₉₅FeO₃               | 14.08                  | 210.1            |
| (LaₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓNi₀₁)O₃    | 14.86                  | 203.9            |
| (LaₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓZn₀₁)O₃   | 15.58                  | 219.0            |
| (LaₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓCu₀₁)O₃   | 14.16                  | 281.8            |
| (LaₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓMg₀₁)O₃   | 15.87                  | 223.9            |
| (PrₐₓSrₜ₋ₐₓ)o.₉₉₅FeO₃               | 15.772                 | 245.7            |
| (PrₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓNi₀₁)O₃    | 16.81                  | 127.6            |
| (PrₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓZn₀₁)O₃   | 15.27                  | 126.1            |
| (PrₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓCu₀₁)O₃   | 15.42                  | 158.4            |
| (PrₐₓSrₜ₋ₐₓ)o.₉₉₅(Fe₀.₉ₓMg₀₁)O₃   | 14.32                  | 198.6            |

The various doped materials were mixed into a commercial screen printing vehicle using a three roll mill and printed on opposite sides of a Gd-doped ceria disc to produce a symmetric sample. The inks were fired to achieve adherence at 1000°C, and then characterized by electronic impedance spectroscopy. The resultant curves were characterized and an area specific resistance calculated for each electrode material. A summary of the data collected at temperatures between 400-700°C is shown in Figure 6 (lanthanum ferrite compositions) and Figure 7 (praseodymium ferrite compositions). The data show that the magnesium, copper and zinc dopants appear to reduce the resistance at the electrolyte/electrode interface. It also appears that the substitution of Pr for La reduces interfacial resistance for this family of materials.

Figure 6. Impact of B-site dopant on \((\text{La}_{0.66}\text{Sr}_{0.40})_0.995(\text{Fe}_{0.90}\text{B}_{0.10})\text{O}_{3.3}\) area specific resistance as a function of temperature. ASR was measured by electronic impedance analysis on symmetric electrode/GDC/electrode samples.
Figure 7. Impact of B-site dopant on \((Pr_{0.60}Sr_{0.40})_{0.995}(Fe_{0.90}B_{0.10})O_{3.5}\) area specific resistance as a function of temperature. ASR was measured by electronic impedance analysis on symmetric electrode/GDC/electrode samples.

Similar to other perovskite-based electrodes, the doped ferrite materials interact with zirconia at temperatures above 1000°C. The use of ceria-based interlayers has been observed to ameliorate this interaction. In ongoing cell development efforts, the barrier layer and the electrode deposition approaches are being coordinated to improve electrolyte supported cell performance at low temperature.

CONCLUSIONS

In the development of planar fuel cell components, significant opportunities remain to improve the processing and performance of electrolyte supported cells. Additionally, the selection of alternative materials with improved physical properties may also enable new cell designs that cannot be achieved using traditional electrolytes and electrodes. Scandia-based electrolytes offer the ability to significantly enhance electrolyte mechanical strength and maintain cell performance. Further development of thinner electrolyte-supported cells is underway. To complement high performance electrolytes, new cathode materials that provide low interfacial resistance and stable performance are necessary. A family of B-site doped ferrite materials has been identified that provides advantages in this over undoped materials. Initial evaluations have been promising and large-area cell demonstrations are underway.

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