PATTERNED SERIES-CONNECTED SOFC

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ABSTRACT

Integrated solid oxide fuel cells (ISOFC) are small, thin-electrolyte cells connected in series on a porous insulating support. Statistically designed experiments have shown that supports made from partially stabilized zirconia using 15 wt% filler have a good combination of porosity and flexural strength. Conductivity measurements of thin-layer Ni-YSZ anode material show excellent conductivity. Similar tests on La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$ (LSCF)-based cathode materials show that applying layers of pure LSCF over the base of LSCF-Ce$_{0.9}$Gd$_{0.1}$O$_2$ greatly improves conductivity. An initial 4-cell ISOFC stack was shown to have a power density of ~ 60 mW/cm$^2$ at 700°C, which can be improved in the future by using a more conductive cathode. A simple electrical model is used to explain the experimentally observed stack performance.

INTRODUCTION

High power densities been reported by many groups for single planar anode-supported SOFCs. However, stacking, sealing, and interconnecting of planar SOFCs remain as major challenges. Typically, stack performance is considerably worse than single-cell performance. New cell/stack geometries that can alleviate these difficulties are thus desirable.

This paper describes the design and fabrication of a new type of patterned series-connected SOFC. As illustrated in Figure 1, a cross sectional schematic view of several cells, this stacking configuration is similar to the well known “banded tubular” design (1, 2, 3) and a similar planar version (4). However, the current design has some unique features. First, the electrolytes are thin (~ 10 μm), such that the cells can potentially achieve high power densities at relatively low temperatures, like typical anode-supported SOFCs. The low operating temperature is important for the usual reasons (5), and also because it reduces the shunting of the cell current by slightly-conducting supports such as fully or partially stabilized zirconia. Second, the cell widths are ~ 1 mm, versus ≥ 1 cm in prior work. This allows one to achieve...
relatively high voltages in small devices, important for portable device applications of SOFCs. It also minimizes resistance losses across the electrodes, even when they are relatively thin. However, this cell width is still large enough that conventional low-cost processing techniques such as screen printing can be used for fabrication. We term the current design "Integrated Solid Oxide Fuel Cell" (ISOFC).

The ISOFC design has a number of advantages compared to planar SOFC stacks:

1. The interconnect is in intimate contact with the electrodes yielding reduced resistance losses compared to interconnect-electrode pressure contacts (6).

2. Since there is no need to make pressure contacts over large areas, the manufacturing flatness requirements are substantially less than for planar stacks.

3. Interconnect conductivity requirements are reduced compared to planar stacks, even though the small interconnect area (= 10% of the cell area) results in a high current density, because the interconnect is much thinner.

4. Since the support does not have an electrical function, it can be chosen to maximize mechanical strength and/or minimize cost.

5. Since the current is collected at the ends of the series-connected cells, rather than flowing through separate PEN’s and interconnects, the ISOFC design is ideally suited for a closed-end flattened tube geometry that simplifies sealing while providing high volumetric power density and allowing use of planar processing methods such as screen printing.

In this paper, we describe basic design considerations of the ISOFC and discuss experimental results obtained to date. The development of the support material, which focused on achieving the necessary substrate porosity and mechanical strength, is described. The deposition of the anode, electrolyte, interconnect, and cathode layers, along with their electrical and microstructural characterization, are described. Early results on ISOFC stack performance are discussed, and compared with a simple electrical model of ISOFC operation.

SUPPORT MATERIAL

The support requirements are:

- high electrical resistivity, to minimize shunting currents
- sufficient porosity for fuel transport to the anode
- good mechanical strength
- chemical compatibility with fuel environment as well as the anode and electrolyte
- a good coefficient of thermal expansion (CTE) match with the YSZ electrolyte (CTE = 10.5x10^-6 K^-1) and other cell components

Partially stabilized zirconia (PSZ) was chosen for the initial development phase. In addition to excellent CTE match with YSZ, its lower yttria content relative to YSZ...
lowers the material cost and results in a lower ionic conductivity. Furthermore, PSZ undergoes transformation toughening, which makes it more mechanically robust than YSZ.

In order to investigate the factors that most affect substrate porosity and strength, an experiment was designed using the computer program EDO (7), which uses the D-Optimal method to pick the trials that will give the most information based on the parameters in the experiment. The factors and levels used in the study are listed in Table 1. The multiple regression software tool MC (8) was used to formulate models for porosity and flexural strength in terms of the factors studied.

Table 1. Factors and levels examined in the substrate porosity study.

| Factor                  | Level 1                                      | Level 2                                      | Level 3                                      |
|-------------------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|
| Material                | PSZ with 20 wt% Al₂O₃ (PSZ-A, Tosoh TZ-3Y20A) | Yttria Stabilized Zirconia (YSZ, 8 mol% Y₂O₃, Tosoh TZ-8YS) | Partially Stabilized Zirconia (PSZ, 3 mol% Y₂O₃, Tosoh TZ-3YS) |
| Calcining Time (hr)     | 2                                            | 3                                            | 4                                            |
| Calcining Temperature (Celsius) | 900                                          | 1000                                         | 1100                                         |
| Filler (starch) amount (wt%) | 5                                             | 10                                           | 15                                           |

Zirconia powders (Tosoh) were first calcined at various temperatures and times. They were then mixed with various amounts of starch pore former and uniaxially pressed into pellets (1 inch diameter, 2 g each) at a die pressure of ~ 175 MPa. The pellets were fired first at 400°C for 2 hours with a ramp rate of 5°C per minute to burn out the starch. The temperature was then increased at 10°C per minute to 1200°C and held for 6 hours. Finally, they were sintered at 1400°C for 6 hours to simulate the high temperature conditions that would be used in electrolyte sintering.

We studied the dependence of biaxial flexural strength and porosity on material, calcining conditions, and filler content. Porosity was determined by the Archimedes method, using water as the fluid, while biaxial flexural strength was determined using the Ball-on-Ring method (9). From the results fitted by a calculated flexural strength model, it was evident that PSZ had higher strength than YSZ and PSZ-A. Higher filler content resulted in lower strength due to increased porosity. Calcining time and temperature had relatively little effect on porosity and strength. Linear shrinkages were ~ 20% in all cases. A reasonable condition was found to be a filler content of 15 wt% in PSZ calcined for 2 hours at 1000°C, which yielded at strength of ~ 130 MPa, and a porosity of 30%. It was subsequently found that the calcining step could be eliminated without significantly changing the properties, and many of the results described below were done with supports made without calcining.

ACTIVE LAYER FABRICATION

Screen printing was chosen for fabrication of ISOFC active layers because it is a simple, inexpensive, widely-used method that can produce patterns with the required lateral...
Screen printing inks were made by mixing powders with a vehicle (Heraeus V-737), which consists mainly of ethyl cellulose and terpineol. After printing, the layers were dried at 150°C for 30 minutes. Prints were generally made using an AMI-Presco model 465 screen printer. The order of deposition was anode, electrolyte, interconnect, and cathode. Anode inks were prepared from NiO (J. T. Baker) and YSZ (Tosoh) powders mixed in a 70:30 weight ratio, translating to ~55 vol% Ni in the reduced state. Electrolyte inks were made with YSZ powder (Tosoh). Interconnects were made using either commercial Ag ink (Shanghai Research Institute of Synthetic Resins) or an ink prepared from La_{0.6}Sr_{0.4}Fe_{0.8}O_3 (LSCF, Praxair) and Ce_{0.9}Gd_{0.1}O_2 (GDC, NexTech) in a 1:1 weight ratio, sintered at 900-950°C for 3 hours after screen printing, or La_{0.8}Sr_{0.2}MnO_3 (LSM, Praxair) and YSZ in a 1:1 weight ratio, sintered at 1200°C for one hour.

Initial work with screen printed electrolytes did not yield the required density so a different method, centrifugal casting (12), was employed to deposit the electrolyte layers. In this technique, the support/anode was partially sintered at 1200°C for 6 hours to provide some strength and adhesive tape was placed on the surface to provide a patterned layer. The substrate and a slurry, formed by dispersing YSZ particles in ethanol, were then placed in a vessel and spun in a centrifuge, leaving a compacted YSZ powder layer on the substrate. A dense electrolyte layer was obtained after co-sintering the support-anode-electrolyte structures in air at 1400°C for 6 hours. It was also found difficult to achieve fully dense LSCC interconnect layers, due to the well-known difficulty of sintering chromite interconnects (6). Thus, Ag, applied after the high-temperature sintering step, was used in place of LSCC in many of the results shown below.

**ELECTRODE PROPERTIES**

The ISOFC design requires that electrodes have sufficiently low sheet resistance $R_s$ to transport current across each cell without significant loss. This is discussed in detail in the section on electrical modeling, but an estimate of the required $R_s$ can be obtained as follows. Assuming a 0.6 $\Omega$ cm$^2$ cell resistance (electrolyte ohmic loss and electrode polarization resistances) and 0.2 cm$^2$ cell area (2 mm wide, 10 mm long), the cell resistance is 3$\Omega$. Assuming that the electrode ohmic loss should contribute <10% of the total resistance, its resistance should be 0.3 $\Omega$; i.e., $R_s = 1.5 \Omega$/square.

Resistance measurements were carried out on screen-printed single Ni-YSZ layers, and on various combinations of LSCF-GDC and LSCF printed layers. Anode sheet resistances, presented in Figure 2, were 0.2 - 0.25 $\Omega$/square from 500°C-800°C, well below the desired value of 1.5 $\Omega$/square. Thus, single Ni-YSZ printed layers easily met the sheet resistance requirements. Given a thickness of ~10 pm, the Ni-YSZ conductivity was ~600
S/cm, in fairly good agreement with literature values (6).

Figure 3 summarizes cathode resistance measurements. LSCF-GDC has a quite high $R_s$ of $\approx 1000$ $\Omega$/square at $800^\circ$C, because of the high content of low-conductivity GDC. While the composite layer is desirable because of its good electrochemical performance (13), it is only needed in the layer in contact with the electrolyte. Thus, multiple prints were made consisting of an initial LSCF-GDC layer followed by one or more layers of pure LSCF. Note that each printed layer was $\approx 10$ $\mu$m thick. As shown in Fig. 3, adding one layer of LSCF significantly reduced $R_s$ to $\approx 25$ $\Omega$/square at $800^\circ$C. Two and three layers of pure LSCF further reduced $R_s$ to $\approx 8$ and 5 $\Omega$/square at $800^\circ$C, respectively. Thus, three or more layers of LSCF will be required to approach the desired sheet resistance of 1.5 $\Omega$/square.

**ISOFC RESULTS**

Figure 4 shows a cross-sectional SEM image of an ISOFC screen printed on a porous PSZ substrate. The fired layer thicknesses are about $10$ $\mu$m and the cathode and anode are visibly porous. The YSZ electrolyte appears to be fairly dense. Furthermore, the substrate shows an open pore network, which is necessary for gas transport to the anode. No catastrophic failures, e.g. layer peeling or cracking, were observed, but there was typically slight curvature after high-temperature sintering. This indicates that the shrinkages of the substrate and the layers were reasonably well matched, but not perfect. Thus, this initial trial of ISOFC processing using screen printing and co-sintering showed that each component had the desired structure. However, attempts to test such cells invariably failed to yield voltages; this was due to porosity in the electrolyte and interconnect layers.

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As described above, some cells were prepared using an alternate electrolyte fabrication method, centrifugal casting, and using Ag as an alternate interconnect material. Four-cell ISOFc tests on these devices are shown in Fig. 5. Voltage versus current and power were measured with air as the oxidant and humidified hydrogen as the fuel, using a standard cell test configuration.

The stack open circuit voltage was \( \approx 3.2 \text{ V} \), lower than the expected value of 4.4 V (1.1 V per cell). The low voltage may result from gas leakage across imperfect electrolyte and interconnect layers, or gas seals. In addition, the use of Ag ink for sealing on the opposite side of the PSZ support may have exacerbated leakage currents in the PSZ support. This is discussed further in the following section. Stack current and power increase with increasing temperature, as expected for SOFCs. The maximum power density was \( \approx 60 \text{ mW/cm}^2 \) at 700°C. This power density is substantially less than expected for anode-supported cells with these materials, \( \approx 400 \text{ mW/cm}^2 \) (12). This was due in part to the low voltage, but was primarily due to the use of a single LSCF-GDC cathode layer in this stack; as described above, this yielded a high sheet resistance. The use of multi-layer cathodes such as those described above will most likely improve power output. Overall, these results demonstrate the ISOFc concept, and much better performance is expected as processing and materials are improved.

**ELECTRICAL MODELING**

A simple model has been formulated to explain ISOFc electrical characteristics and to provide a tool for optimizing stack geometry. The main factors considered are the cell characteristics, shunting of current by the support, and the resistance losses due to current transport across the electrodes.

A calculation was carried out to determine the current distribution between the anode and cathode as current flows through the cell, as illustrated in Figure 6. Equations were written to express the change in voltage and current along incremental length elements in the electrodes. Integration of the differential equations was carried out in Matlab by a simple iterative technique with the boundary conditions \( I_{\text{cathode}}(x = 0) = 0 \) and \( I_{\text{anode}}(x = x_{\text{final}}) = 0 \).
The stack resistance was calculated using area specific resistance values obtained from single cell tests using the same materials and process steps as used to make the stacks; however, a gold current collection grid was used on the cathode to eliminate any collection losses. The values used are given in Table 2. The anode sheet resistance was kept constant at 0.3 $\Omega$/square (see Fig. 2). The data in Figure 3 was used for the LSCF-GDC cathode sheet resistance. Table 2 shows that the stack resistance per cell calculated in this way agreed fairly well with the resistances measured from Fig. 5. That is, the model successfully explains the low power density observed as being due to the cathode ohmic loss.

Table 2. Comparison of calculated and measured 4-cell stack resistances.

| Temperature (C) | Measured single cell resistance ($\Omega$cm$^2$) | Predicted stack resistance per cell ($\Omega$cm$^2$) | Measured stack resistance per cell (from Fig. 5) ($\Omega$cm$^2$) |
|-----------------|-----------------------------------------------|---------------------------------------------------|-------------------------------------------------|
| 600             | 4.88                                          | 26.15                                             | 35.2                                            |
| 650             | 3.45                                          | 16.61                                             | 18.5                                            |
| 700             | 2.72                                          | 9.77                                              | 9.9                                             |
| 750             | 2.04                                          | 6.41                                              | not measured                                    |
| 800             | 1.79                                          | 5.67                                              | not measured                                    |

We have also estimated whether the low stack voltage can be explained by the ionic conductivity of the PSZ support. The measured conductivities $\sigma_s$ of the PSZ support were $6 \times 10^{-4}$ S/cm at 600°C, $2 \times 10^{-3}$ S/cm at 700°C, and $5 \times 10^{-3}$ S/cm at 800°C, in reasonable agreement with published values (14). For a given open circuit voltage $V_{oc}$, the decrease in voltage $\Delta V$ due to shunting can be approximated, assuming a uniform lateral field across the support, as:

Figure 6. Illustration of the current flow in an individual cell of the ISOFC stack.
\[
\Delta V = V_{\text{OC}} \sigma_S R_S t / w^2
\]  

where \( R_S \) is the area-specific resistance of the individual cells, \( t \) is the thickness of the support, and \( w \) is the width of an individual cell (see Fig. 1). The effect of current shunting increases with increasing support conductivity, support width, and cell resistance. Decreasing the width of the cells also increases \( \Delta V \). For the data in Fig. 5 at 700°C, \( R_S = 10 \, \Omega \text{cm}^2 \), \( t = 0.1 \, \text{cm} \), and \( w = 0.2 \, \text{cm} \), while \( V_{\text{OC}} \) should be 1.1 V for the test conditions, such that \( \Delta V = 0.05 \, \text{V} \). That is, even for these relatively high resistance cells and small cell widths, the shunting effect was quite small. For higher power density cells, the shunting effect will be negligible.

In the present stack tests, Ag ink was used to seal the back side of the PSZ pellet to the fuel-gas feed tube. This highly conducting layer allows a shorter current leakage path: directly through the 1-mm-thick PSZ support between the ends of the four-cell array and the Ag seal. The current path length is thus decreased by a factor of 5-10, and hence the leakage current and \( \Delta V \) are increased by a factor of 5-10. This presumably explains the low \( V_{\text{OC}} \) in Fig. 5.

**CONCLUSIONS**

Initial development of integrated SOFCs has been conducted including substrate optimization, electrical evaluation of the electrodes, overall microstructural evaluation, and stack testing. Initial stack tests showed relatively low maximum power density. A simple electrical model yielded stack resistances that agreed well with the experimental resistances, based on the relatively high resistance of the LSCF-GDC cathode. Thus, increased power densities can be achieved by adding multiple LSCF layers to the LSCF-GDC cathode layer.

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