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# Low-Temperature Solid-Oxide Fuel Cells Utilizing Thin Bilayer Electrolytes

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ABSTRACT

Solid-oxide fuel cells (SOFCs) with electrolytes that provide high open-circuit voltage (OCV) and low ohmic loss down to 550°C are described. The electrolytes were bilayers consisting of a 4 to 8 μm thick Y-doped ceria (YDC) layer with a 1 to 1.5 μm thick Y-doped zirconia (YSZ) layer on the fuel side. The cathode/supports were $La_{0.85}Sr_{0.15}MnO_3$-YSZ. The anodes consisted of thin YDC and Ni-YSZ layers. The YDC/YSZ electrolyte SOFCs yielded 85 to 98% of the theoretical OCV, compared with ≈50% for YDC electrolyte SOFCs. The cathode overpotential, which was a main factor limiting SOFC power density, was lower for YDC/YSZ than YSZ electrolytes. The maximum power density at 600°C, 210 mW/cm², is higher than for previously reported SOFCs.

## Introduction

Lowering SOFC operating temperatures $T_c$ below ≈1000°C is of interest for allowing the use of higher performance, lower cost materials for the stack and balance-of-plant, reducing stack thermal-insulation requirements, and increasing cell life because of reduced thermal degradation and thermal cycling stress.[1] Recent advances have led to SOFCs yielding high power densities at $T_c$ down to 700°C.[1-4] Achieving $T_c$ values from ≈450 to 650°C would be particularly useful for two main reasons. First, low cost ferritic stainless steels, that retain significant strength in this temperature range, could be used for stack components, such as interconnects and gas manifolds. Second, there are indications that direct oxidation of methane without carbon deposition is possible at ≤650°C,[5] eliminating the need for fuel reforming. However, there are significant barriers to low-temperature (450 to 650°C) SOFCs: electrolyte ohmic resistance and electrode overpotentials.

In most medium temperature (700 to 800°C) SOFCs, an ≈10μm thick YSZ electrolyte is employed to minimize ohmic loss.[1-4] However, the YSZ area-specific resistance for a 10 μm thickness becomes appreciable at 600°C, ≈0.5 Ω cm², and is very large at 500°C, ≈2 Ω cm². While significantly thinner YSZ electrolytes would allow lower $T_c$, the long-term stability and reliability of very thin electrolytes remains an issue. Thus, oxide materials with higher conductivity $\sigma$ should be considered. However, they typically have some property that precludes their use in SOFCs; doped $BaCeO_3$ appears to exhibit mixed conductivity,[6] while doped $Bi_2O_3$ is reduced by typical fuel gases and Sc-doped $ZrO_2$ undergoes a structural transformation at ≈600°C.[7] A relatively new candidate, (La,Sr)(Ga,Mg)O (LSGM), appears promising.[8] Much of the work on alternate electrolytes has focused on ceria.[9-16] Representative $\sigma$ values for Sm, Gd, or Y-doped ceria[11] are ≈3 times that for YSZ, such that ohmic losses with ≈10 μm thick ceria electrolytes would extend the range of SOFC operation to well below 600°C. The electronic conductivity and volume change observed on reduction of ceria are serious problems. For example, an anode-supported SOFC with a 5 to 10 μm thick Gd-doped ceria (GDC) electrolyte provided an OCV value <70% of theoretical, along with a low maximum power density of ≈70 W/cm², at 600°C.[9] While the electrolytic domain increases with decreasing $T_c$, the electronic conductivity of GDC is negligible only for $T_c \leq 450$°C.[12] Other dopants, *e.g.*, Sm [11] or Gd-Pr double doping,[9,13] may slightly increase the electrolytic domain compared to Gd, but not enough for typical SOFC fuel gases at $T_c > 450$°C. One method for obtaining high OCV with ceria electrolytes is to add a YSZ layer to block the electronic current.[14,15]

SOFC overpotentials typically increase rapidly for $T_c$ decreased below 700°C,[2] limiting power densities. The electrolyte material chosen should help minimize overpotentials. Oxygen surface exchange coefficients are higher for ceria than any other electrolyte materials for which data are available, suggesting that it would provide optimal cathode performance.[16] Y-doped ceria (YDC) interfacial layers have been shown to decrease anode overpotentials.[17]

In this article, we describe results on SOFCs with bilayer yttria-doped ceria (YDC)/YSZ electrolytes that provide low electrolyte ohmic loss, decrease overpotentials, and overcome the problems associated with reduction of ceria. The maximum power density of 210 mW/cm² at 600°C compares favorably with the highest value that has been reported for a SOFC at this temperature, ≈140 mW/cm².[9]

## Experimental

The cells were deposited on $La_{0.85}Sr_{0.15}MnO_3$-YSZ support/cathodes that were prepared using ceramic processes.[2] $(Y_2O_3)_{0.15}(CeO_2)_{0.85}$(YDC) and $(Y_2O_3)_{0.1}(ZrO_2)_{0.9}$ (YSZ) were reactively sputter deposited at ≈5 μm/h from Y-Ce and Y-Zr composite targets, respectively, in Ar-$O_2$ mixtures (1 to 1.2 Pa Ar, ≈0.013 Pa $O_2$). The substrate temperature was ≈400°C, and a negative substrate bias $V_s$ was used throughout electrolyte deposition. Previous studies of YSZ deposition showed that $V_s$ = 75 V produced high-density films.[18] However, larger $V_s$ values led to delamination of the electrolyte from the cathode due to compressive film stress. Two types of electrolytes were prepared. One was an 8 μm thick YDC layer followed by a 1 μm thick YSZ layer (8YDC/1YSZ) deposited with $V_s$ = 75 V. The other was a 4 μm thick YDC layer followed by a 1.5 μm thick YSZ layer (4YDC/1.5YSZ) deposited with $V_s$ = 60 V. $V_s$ = 30 to 60 V was used during YDC deposition. Annealing was carried out at 600°C for 4 h after the YDC layer deposition, and at 750°C for 4 h after the YSZ deposition. The highest temperature used in this study was 750°C, such that any interdiffusion between YDC and YSZ, which could lead to reduced ionic conductivity and electronic conduction,[19] was minimized. The anodes consisted of 0.2 μm thick porous YDC layers, deposited first to enhance anode performance, and 2 μm thick porous Ni-YSZ layers.[17] The cell test apparatus was similar to that described previously.[18] Cell tests were made in air and $H_2$-Ar fuel mixtures that had been passed through a 20°C water bubbler.

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## Results and Discussion

A cell with an 8 μm thick YDC electrolyte, and no YSZ layer, was first tested to provide a standard. OCVs were always well below theoretical values. For example, the OCV at 600°C in air and a fuel composition of 3% $H_2$, 3% $H_2O$ (balance Ar), was <0.6 V, well below the theoretical value of 1.010 V. The maximum power density was <50 mW/cm$^2$ at 600°C, largely due to the low potential.

Adding a YSZ electrolyte layer increased the OCV to ≥85% of theoretical values in all cell tests. Voltage *vs.* current density plots are shown in Fig. 1a for two cells tested at 600°C in 10% $H_2$. For a cell with an 8YDC/1YSZ electrolyte, the OCV was 1.007 V, compared with a theoretical value of 1.021 V. The maximum power density was 155 mW/cm$^2$. The cell with a 4YDC/1.5YSZ electrolyte showed a lower OCV, but a higher maximum power density of 210 mW/cm$^2$. For comparison, an SOFC with an 8 μm thick YSZ electrolyte but the same electrodes yielded the same OCV as the 8YDC/1YSZ cell (see Fig. 1a), but the cell resistance was higher, and the maximum power density lower, 110 mW/cm$^2$.

Results of impedance spectroscopy measurements made during the cell tests are shown in Fig. 1b. Note that these measurements were at a current density of ≈100 mA/cm$^2$, not at the open-circuit condition, because the impedance spectrometer loaded the cell. The high-frequency real-axis intercepts give the total ohmic losses, including the electrolyte and an ≈0.1 Ω cm$^2$ resistance due primarily to connecting wires. The bilayer electrolytes showed two to three times lower ohmic losses than the YSZ electrolyte. While this contributed to the better cell performance, the electrode arcs were the larger part of the total cell resistances at 600°C. The size of electrode arc was smaller for the bilayer electrolytes. Since the electrodes were the same for all the cells, the primary change was replacing the cathode-YSZ interface with a cathode-YDC interface. A lower cathode overpotential with the YDC electrolyte is consistent with the ≈ ten times higher oxygen surface exchange coefficients measured for YDC compared with YSZ.[16] The 4YDC/1.5YSZ electrolyte SOFC exhibited a smaller electrode arc than the 8YDC/1YSZ electrolyte SOFC; this is not understood at present.

Figure 2 shows the *J-V* dependence for the 8YDC/1YSZ cell tested in 10% $H_2$ from 500 to 600°C. OCVs increased slightly with decreasing $T_c$, as expected. Current densities increased rapidly with increasing $T_c$. The OCV and maximum power densities, listed

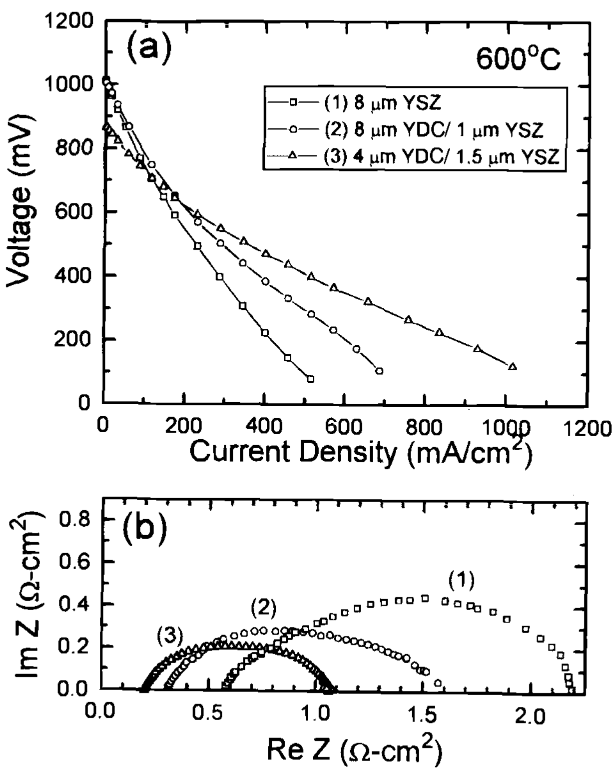


**Fig. 1. The current-voltage curves (a) and impedance spectra (b) of cells with three different electrolytes, tested at 600°C with 10% $H_2$ + 3% $H_2O$ + balance Ar and air.**

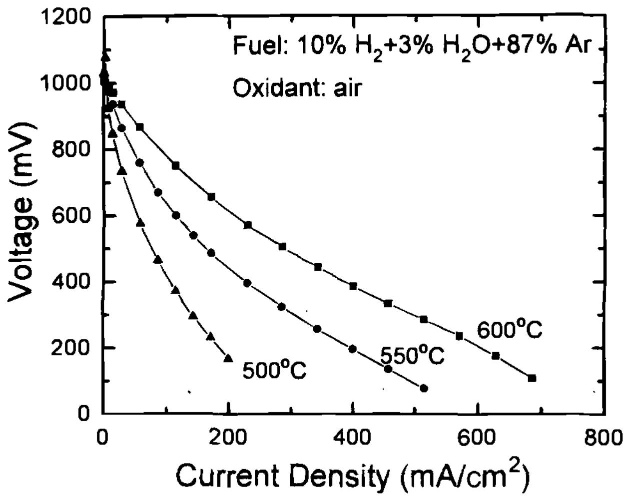


**Fig. 2. Current-voltage curves from a YDC (8 μm)/YSZ (1 μm) bilayer electrolyte cell tested between 500 and 600°C in 10% $H_2$ + 3% $H_2O$ + balance Ar and air.**

in Table I for 10% and 97% $H_2$, generally increased with increasing $H_2$ partial pressure. OCVs were >96% of theoretical values, except for ≥600°C, where the OCV and power density were lower. This indicates that electronic conduction became important under the most reducing conditions and at higher temperatures where the YDC electrolytic domain is smallest.

Similar OCV results have been obtained previously for thin YSZ layers on thick ceria electrolytes. Eguchi *et al.*[14] increased the OCV at 800°C from ≈0.8 to 1.1 V by depositing a 2 μm thick YSZ layer on the fuel side of ≈650 μm thick Sm-doped ceria electrolyte. Mehta *et al.*[15] showed an OCV increase with a fuel-side or air-side YSZ layer. In these results, the YSZ layers apparently blocked the electronic current. In the present electrolytes, the YSZ layers were a much larger fraction of the total electrolyte thickness, 11 or 27%, such that a significant fraction of the oxygen partial pressure gradient is across the YSZ layer. The potential at the YDC/YSZ interface at the OCV condition was estimated assuming no electronic conduction, and accounting for the different electrolyte thicknesses and conductivities. The $p_{O_2}$ at the interface was then calculated using this value in the Nernst equation, an air side $p_{O_2}$ of 0.21 atm, and a fuel-side $p_{O_2}$ of $5.3 \times 10^{-25}$ at 600°C (for 10% $H_2$). The calculated interface $p_{O_2}$ is $\approx 10^{-18}$ atm for the 8YDC/1YSZ electrolyte and $\approx 10^{-12}$ atm for the 4YDC/1.5YSZ electrolyte. As the electrolytic domain boundary for YDC is $\approx 10^{-18}$ atm at 600°C,[10] the bilayer electrolytes should eliminate electronic conduction in the YDC at open-circuit condition, in addition to blocking electronic current. These calculations show a second reason for the fuel-side YSZ layer; the YDC is isolated from highly reducing conditions, minimizing any volume changes associated with oxidation-reduction.[20]

Neither type of YDC/YSZ electrolyte provided the theoretical OCV under the most reducing conditions. Previous results on thick GDC electrolytes have shown that the YSZ coating structure is important in determining the OCV.[15] SEM fracture cross-sectional images of the present YDC/YSZ electrolytes showed a dense columnar structure, similar to images of sputtered YSZ electrolytes,[2] with no distinguishing features at the YDC/YSZ interface. The structure was similar before and after cell testing. However, some nodular defects that originated from substrate surface imperfections were observed. There was sufficient porosity at the nodules to allow fuel-gas penetration to the YDC, and hence electronic conductivity that reduced the OCV. The above arguments

**Table I. OCV and maximum power density of a YDC (8 μm)/YSZ (1 μm) bilayer electrolyte cell tested between 500 and 600°C in 10% $H_2$ and 97% $H_2$.**

| OCV/max power density | 10% $H_2$ | 97% $H_2$ |
|---|---|---|
| 500°C | 1033 mV/43 mW | 1089 mV/55 mW |
| 550°C | 1021 mV/90 mW | 1068 mV/110 mW |
| 600°C | 1007 mV/155 mW | 959 mV/96 mW |

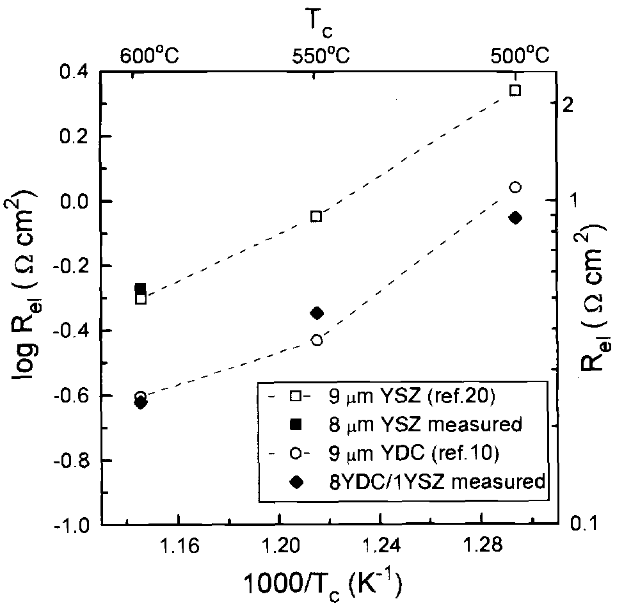


**Fig. 3. The measured electrolyte area-specific resistance $R_{el}$ of 8 μm thick YSZ and YDC (8 μm)/YSZ (1 μm) bilayer electrolytes. Shown for comparison are values predicted from conductivity data for 9 μm thick single-layer YDC and YSZ electrolytes.**

suggest that the present results can be improved by optimizing the substrate surface, deposition conditions, and electrolyte layer thicknesses.

Impedance spectra for the SOFC shown in Fig. 2 were similar to those shown in Fig. 1b, with the ohmic loss contributing 20 to 25% of the total cell resistance between 500 and 600°C. Figure 3 shows the electrolyte area-specific resistance $R_{el}$, obtained from impedance spectra by subtracting ≈0.1 Ω cm² due to other ohmic contributions, plotted *vs.* $1/T_c$. Also shown are $R_{el}$ values calculated assuming 9 μm thick YDC and YSZ electrolytes based on reported conductivity data.[10,21] The measured $R_{el}$ for the 8YDC/1YSZ electrolyte is near that for YDC, as expected. The $R_{el}$ for the 4YDC/1.5YSZ electrolyte gave a similar result, despite the smaller total thickness, because of the thicker YSZ layer. The bilayer electrolytes yield resistances that are ≈ two times lower than YSZ electrolytes and provide the same resistance at a 50 to 75°C lower $T_c$ value.

## Summary

The thin YDC/YSZ bilayer provides both near theoretical OCV values and electrolyte area-specific resistances of 0.25 Ω cm² at 600°C and 0.45 Ω cm² at 550°C. Replacing YSZ with YDC/YSZ decreased the cathode overpotential and, combined with the decreased electrolyte ohmic loss, led to higher low-$T_c$ power densities than previously reported. With electrolyte losses reduced to low levels, power densities can be increased substantially by developing electrodes with improved low-temperature performance.

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