ABSTRACT

A series of doped ceria-based electrolytes were synthesized by the glycine-nitrate method; producing powders of 2-3 μm in particle size. Sintering profiles were determined for all doped ceria compositions. Conductivity measurements were determined in air and open-circuit potential measurements in H₂-H₂O/air for doped ceria pellets from 400 to 800°C. Preliminary results show that calcium, bismuth and lithium doping lowers the sintering temperature of ceria. At 700°C, a maximum open-circuit-potential of 0.84 V was observed for the composition Ce₀.₈Y₀.₁₈C₀.₀₂O₁.₉; this composition also exhibits the lowest grain boundary resistance for the doped samples. The highest total conductivity of 1.7x10⁻² S/cm⁻¹ was observed for the composition Ce₀.₈Y₀.₁₇₈C₈₀.₀₂Li₀.₀₀₂O₁.₈.

INTRODUCTION

Due to their high ionic conductivity, ceria-based electrolytes have been studied by a number of groups as alternatives to yttria-stabilized zirconia electrolytes for solid oxide fuel cells (1,2). Previous studies on cerium oxide show that rare earth oxide doped ceria exhibits higher ionic conductivity than undoped ceria and doped zirconia (3,4) making them interesting for low and intermediate temperature SOFC applications. Previously, our group reported almost 300 mW/cm² for an anode supported, thin-film ceria cell in H₂-H₂O/air operating at 600°C, and observed greater than 400 mW/cm² at 650°C (5). Unfortunately, in a fuel cell environment, ceria exhibits significant electronic conductivity with increasing temperature and expands upon reduction leading to cracking of the electrolyte (6). If the electronic conductivity and expansion of ceria under reducing conditions could be minimized, ceria based electrolytes would offer significant performance improvement relative to zirconia electrolytes. The aim of this work is to study the effect of dopant composition on the sintering behavior, total conductivity, and reliability of ceria-based electrolytes.

EXPERIMENTAL

Powder Preparation

Ce₀.₉Y₀.₁O₁.₉₅, Ce₀.₈₇₈₉₃₂Li₀.₀₂O₁.₉, Ce₀.₈₆₃₇₃₂Li₀.₀₂O₁.₉, Ce₀.₈₅₄₁₃₂O₁.₉, Ce₀.₈₄₅₂₂₂₀₁.₉, Ce₀.₈₃₆₃₃₂O₁.₉, and Ce₀.₈₂₇₄₄₂O₁.₉ powders were prepared by the glycine-nitrate method.
process. A 0.5 glycine/metal mole ratio was used for the combustion. After combustion, each powder was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Beckman Coulter LS Particle Size Analyzer techniques. The powders were calcined at 1000°C for 1 or 4 hours, followed by a second step of characterization. Then the calcined powder was attritor milled with 2% fish oil in isopropanol alcohol solvent for one hour. The colloidal solution was dried under a heat lamp. Once dried, the powder was ground and sieved down to 150 μm. One half gram of the sieved powder was pressed using a 0.5” die at a pressure of 1800 lbs and used for the Dilatometry to study the shrinkage. Approximately three grams of each powder composition was pressed into a disk using a 1” die at a pressure of 7400 lbs. The samples were sintered in air at 5°C/min up to the pre-selected (1200 – 1500°C) temperature for four hours.

Electrochemical Testing

Open-circuit-potential (OCP) and conductivity measurements were performed using a Solartron Analytical 1260 Impedance/Gain-phase Analyzer coupled with a 1286 Potentiostat instrument in the frequency range of 2.6MHz - 0.1Hz with amplitude of 50 mV. The conductivity tests were done on 0.5 inch diameter pellets in air. A 5 μm layer of Au was sputtered on both sides of the pellets, then Au paste was applied and fired at 900°C for 1 hour. The OCP measurements were performed on 1 inch diameter disks. Pt paste was applied on both sides of the disk and fired at 850°C for 30 minutes. Humidified (2% H2) hydrogen was used as fuel and the measurements were taken in the temperature range between 400 to 800°C.

RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of four different compositions of doped ceria powders after attritor milled; the ceria samples exhibited a cubic fluorite structure. Particle size analysis of the combusted and attritor milled powder was found to be ~3 μm and 0.5 μm, respectively.

Sintering studies were done to establish the minimum processing temperature for anode supported thin-film ceria based SOFCs, and to determine the processing temperature for ceria as a buffer layer to prevent reaction with YSZ electrolytes in cathode supported thin-film cells based on zirconia electrolytes. Figure 2 shows the sintering profiles for the electrolytes under study. It was found that calcium, bismuth, and lithium doping lower the sintering temperature of ceria (the high sintering temperature for Li doped Ce0.8Y0.175Ca0.0201.9 might be caused by the cesium additive).

Figure 3 shows the open-circuit-potential data for five doped ceria electrolyte cells. At 700°C it can be seen that the maximum open-circuit-potential is 0.84 V for the composition Ce0.8Y0.175Ca0.02O1.9, while the lithium doped composition, Ce0.8Li0.2O1.9, shows an OCP close to zero. The low OCP for the Li doped ceria is due in part to electronic conductivity as can be seen in the impedance spectra, and may be due in part to through-porosity in the electrolyte (SEM of the electrolyte cross-section indicated that the Ce0.8Li0.2O1.9 thick pellet was not completely dense). The difference in OCP in figure 3 for several samples during heating and cooling is due to the cracking (6) of ceria-based
electrolytes exposed to a large pO2 gradient and temperatures higher than 700°C (750°C and 800°C).

The impedance spectra for a number of doped ceria pellets samples in air at 700°C are shown in figure 4. It was found that the composition Ce0.8Y0.178Ca0.02O1.9 had the lowest total resistivity (ρt), followed by the composition Ce0.8Y0.18Ca0.02O1.9. The lowest bulk resistivity (ρb) was observed for Ce0.9Y0.1O1.95 while the highest bulk resistance was measured for Ce0.8Li0.2O1.9 (impedance spectrum not included). It was also found that Ca doping of yttria-doped ceria lowers the grain boundary resistance (Rgb) significantly in agreement with the literature (9). Table I summarizes the Rb, Rgb, and Rt values of the five doped ceria samples at 700°C; total resistivity as a function of temperature has been plotted in figure 5. The same trends in resistivity were seen at 650°C and 600°C; Ce0.8Y0.178Ca0.02O1.9 electrolyte had the lowest total resistivity.

Total conductivity for the various electrolytes in air is shown in figure 6. The maximum total conductivity at 700°C was 1.7x10^{-2} S cm^{-1} for the composition Ce0.8Y0.178Ca0.02O1.9 followed by the composition Ce0.8Y0.18Ca0.02O1.9 with a total conductivity of 1.4x10^{-2} S cm^{-1}. The composition Ce0.9Y0.1O1.95 had the lowest total conductivity of 0.64 x10^{-2} S cm^{-1}.

The microstructure of both the Ce0.8Y0.18Ca0.02O1.9 and Ce0.8Li0.2O1.9 electrolytes are shown in figure 7. As can be seen from fig. 4, the Ce0.8Y0.18Ca0.02O1.9 electrolyte appears to be very dense which may explain the low measured value for grain boundary resistance (fig. 4). On the other hand, the microstructure of the Ce0.8Li0.2O1.9 sample (fig. 7b) shows clear evidence of liquid phase sintering, in agreement with the lowering of the sintering temperature (fig. 2). The AC impedance of the Ce0.8Li0.2O1.9 sample was very resistive (off-scale in fig. 4), yet the open circuit potential was close to zero volts, indicating significant electronic conductivity. The effect of pO2 on the AC impedance of Ce0.8Li0.2O1.9 at 400°C can be seen in figure 8 (2 samples of different thickness). The impedance of Ce0.8Li0.2O1.9 in air shows two arcs, the low frequency arc corresponding to the grain boundary resistance, and the high frequency arc corresponding to bulk resistance. In H2-H2O/air, the magnitude of both arcs decreases dramatically, indicating significant electronic conductivity. Consequently, Ce0.8Li0.2O1.9 might be interesting as a permeation membrane for synthesis gas production due to its behavior as a mixed ionic-electronic conduction (MIEC).

CONCLUSIONS

The motivation of this study was to investigate a series of doped ceria electrolytes in oxidizing and reducing conditions in order to identify those compositions with maximum ionic and minimum electronic conductivity for fuel cell applications. All selected dopants decreased both the bulk and total resistance of Ce0.8Y0.1O1.9 electrolytes. In particular, the best results were obtained for the Ca doped composition Ce0.8Y0.18Ca0.02O1.9. Although the Ca doped ceria electrolyte still exhibited a depressed open circuit potential, this may be a useful barrier layer in zirconia based fuel cells where it is desirable to prevent reaction of the YSZ electrolyte with high performance cathodes at the firing temperature. It was also found that lithium doping of Ce0.8Y0.2O1.9 electrolytes greatly increased the electronic conductivity of the electrolyte, leading to a
potentially interesting MIEC. The testing of a variety of doped ceria electrolytes, including fuel cell testing, is in progress.

ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy through the National Energy Technology Laboratory under Contract No. DE-AC03-76SF00098.

REFERENCES

1. H. Inaba, H. Tagawa, *Solid State Ionics*, 83, 1 (1996).
2. N. Q. Minh, *J. Am. Ceram. Soc.*, 76, 563 (1993).
3. G. B. Balazs, R. S. Glass, *Solid State Ionics*, 76, 155 (1995).
4. N. Kim, B.-H. Kim and D. Lee, *J. Power Sources*, 90, 139 (2000).
5. C. P. Jacobson, S. J. Visco, and L. C. De Jonghe, in *Third International Symposium on Ionic and Mixed Conducting Ceramics*, Edited by: Ramanarayanan, T. A.; Worrell, W. L.; Tuller, H. L.; Khandkar, A. C.; Mogensen, M.; Gopel, W., PV 97-24, p.726-735 (1997).
6. K. Honegger, R. Krushwitz, M. Keller, and G. M. Christie, in *SOFC VI*, M. Dokiya, and S. C. Singhal, Editors, PV 99-19, p. 1019, The Electrochemical Society Proceedings Series, Pennington, NJ, (1999).
7. T. Mori and H. Yamamura, *J. Am. Ceram. Soc.*, 79, 3309 (1996).
8. S. Dikmen, P. Shunk, and M. Greenblant, *Solid State Ionics*, 112, 299 (1998).
9. C. Moure, D. Gutierrez, J. Tartaj, F. Capel, and P. Duran, *Solid State Ionics*, 141-142, 381 (2001).

| Table I. Bulk, grain boundary and total resistance at 700°C. |
|---|---|---|---|---|
| Material | $R_{B}$, $\Omega$ | $R_{gb}$, $\Omega$ | $R_{t}$, $\Omega$ | Thickness, mm |
| Ce$_{0.8}$Y$_{0.2}$O$_{1.9}$ | 21.39 | 19.48 | 40.88 | 3.58 |
| Ce$_{0.8}$Y$_{0.178}$Ce$_{0.02}$Li$_{0.002}$O$_{1.8}$ | 15.91 | 11.07 | 26.98 | 3.2 |
| Ce$_{0.9}$Y$_{0.1}$O$_{1.95}$ | 10.96 | 31.57 | 42.53 | 2.49 |
| Ce$_{0.8}$Y$_{0.18}$Ca$_{0.02}$O$_{1.9}$ | 14.06 | 6.56 | 20.62 | 2.51 |
| Ce$_{0.8}$Li$_{0.2}$O$_{1.9}$ | 552.77 | 95.92 | 648.69 | 2.51 |

256

Electrochemical Society Proceedings Volume 2003-07
Figure 1. XRD patterns of the ceria powder prepared by the glycine-nitrate method, calcined and attritor milled.

Figure 2. Shrinkage versus temperature profile.
Figure 3. Open-Circuit-potential of five different doped ceria as function of temperature.

Figure 4. AC impedance spectra of doped ceria in air at 700°C.
Figure 5. Total resistivity as function of temperature.

Figure 6. Total conductivity as function of temperature.
Figure 7. SEM microstructure of a fracture sample of (a) Ce$_{0.8}$Y$_{0.18}$Ca$_{0.82}$O$_{1.9}$ and (b) Ce$_{0.8}$Li$_{0.2}$O$_{1.9}$.

Figure 8. AC impedance spectra of Ce$_{0.8}$Li$_{0.2}$O$_{1.9}$ at 400°C (8b is expansion of the sample 2 data shown in 8a). The thickness of sample 1 is 2.512 mm and 0.535 mm for sample 2.