THE EFFECT OF POLARIZATION ON LSM-YSZ COMPOSITE CATHODES

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ABSTRACT

The impact of previous polarization history on the performance of (La\textsubscript{0.8}Sr\textsubscript{0.2})MnO\textsubscript{3}-8YSZ (LSM-YSZ) electrodes for SOFC has been studied. Polarization of these electrodes at 973 K leads to a dramatic reduction in area specific resistance (ASR) which is only reversible over periods of several hours. By studying electrodes with different surface areas, the effect has been attributed to increased porosity in the LSM phase. It is suggested that reduction of the LSM phase, accompanied by the formation of pores, is the mechanism responsible for the changes in ASR observed upon polarization.

INTRODUCTION

Sr-doped LaMnO\textsubscript{3} (LSM)-yttria-stabilized zirconia (YSZ) composite electrodes are commonly used as the cathodes of solid oxide fuel cells. In this system, the LSM provides electronic conductivity whereas the YSZ provides oxygen anion conductivity and a strong bond to the YSZ electrolyte. Although such composite electrodes are widely used it is difficult to find consistent measurements of the performance of such electrodes in the literature (1). Estimates of cathode ASR values from 27 (2) to 2.49 Ω.cm\textsuperscript{2} (3) have been reported. Although variation in preparation technique and electrode microstructure may explain some of these differences, the uncertainty in reported data is significant for such a technologically important material.

Furthermore these large values of ASR, cannot be reconciled with the performance of actual SOFC utilizing such composite cathodes. High performance SOFC can exhibit maximum power densities as high as 1.08 W/cm\textsuperscript{3} with total cell ASR as low as 0.28 Ω.cm\textsuperscript{2} (4). A common explanation of these differences is the non-linearity of the cells V-I characteristics. Most measurements of cathode ASR are made under open circuit conditions using symmetric cell configurations and are difficult to relate to measurements on cells made under load.

In order to elucidate the fundamental factors governing SOFC cathode performance it is necessary to first reconcile these differences. In this work we have examined the impact of both electrode polarization and measurement technique on the measured ASR of composite LSM-YSZ cathodes. Both anode supported SOFC and symmetric cathode-
cathode configurations were used to characterize the electrode performance. Furthermore, using a novel manufacturing technique developed at the University of Pennsylvania, the effect of LSM sintering temperature was also studied. The performance of the electrode was then related to the surface area of the LSM phase.

**EXPERIMENTAL**

Anode supported SOFC with Cu-CeO$_2$-YSZ or Pt-CeO$_2$-C-YSZ anodes, YSZ electrolyte and LSM-YSZ cathodes were prepared as described elsewhere (5). Briefly, the procedure involves tape-casting of a bilayered YSZ green tape where one layer contains graphite and poly-methyl methacrylate pore formers. The second layer is free of pore formers. Sintering at 1823 K results in a dense, 60 μm thick, YSZ electrolyte supported on a 600 μm thick porous YSZ substrate. The cathode was prepared by ball-milling a 50/50 wt% mixture of (La$_{0.8}$Sr$_{0.2}$)MnO$_3$ (Praxair Surface Technologies) and 8-YSZ (Tosoh, TZ-8Y) for 24 hr with zirconia media in an acetone solution. After drying, a glycerine-based slurry of the LSM-YSZ and a graphite pore former (Alfa Aesar, 325 mesh) was painted onto the electrolyte surface. The cathode was calcined for 2 hours at 1523 K. After application of the cathode, the anodes were prepared by impregnation of the porous YSZ substrate with aqueous solutions of the appropriate nitrate salts. The active cell area was 0.33 cm$^2$. Electrical contact was made using a loop of Ag wire and paste on the cathode and a loop of Au wire and paste on the anode. The cells were sealed onto alumina tubes, using an alumina-based sealant (Aremco, 552-VFG), and then heated to 973 K with the anode exposed to flowing H$_2$ and the cathode held in air. Finally, to form conductive carbon phases in the anode, the Cu-CeO$_2$-YSZ and C-Pd-CeO$_2$-YSZ anodes were exposed to n-butane at 973 K for 1 h and 6 h respectively (6). In an important distinction, the Cu-CeO$_2$-YSZ cell was heated to 973 K under open circuit conditions, whereas the C-Pd-CeO$_2$-YSZ cell was heated under short circuit.

For the symmetric cell tests, YSZ green tapes with and without pore formers were cast separately. Discs of these green tapes were then cut and pressed together. The discs with pore formers were placed centrally on either side of a larger disc without pore formers. Upon sintering this created a dense YSZ electrolyte supporting two, symmetric, porous YSZ layers. The porous layers were then impregnated with a solution of La, Sr and Mn nitrates, in the ratio 0.8:0.2:1, to a total of 40 wt% LSM. Multiple impregnation steps were required, with intermediate calcinations at 723 K, to reach 40 wt%. This loading level is sufficient to form a well-connected LSM phase with acceptable electronic conductivity (7). The samples were then calcined at higher temperature for 2 hours in air. Three samples were prepared in the same way, varying only in final calcination temperature (1123, 1323 and 1523 K). XRD analysis showed the formation of the LSM phase at all calcination temperatures; however, small peaks associated with La$_2$Zr$_2$O$_7$ were observed for the highest calcination temperature. Electrical contact was made with Ag wire and paste for the SOFC tests.

**RESULTS AND DISCUSSION**

The majority of cathode ASR values reported in the literature are measured on symmetric cells, where the application of current through the cell forces one of the electrodes to run
in reverse. One explanation for the discrepancy between these measurements and the performance of SOFC is that the LSM-YSZ cathode is not reversible. That is, the electrode behaves differently under anodic and cathodic polarization. To test this hypothesis, V-I characteristics and impedance spectra were measured for the SOFC with Pt-CeO₂-C-YSZ anode running both ‘forwards’ (i.e. cathodic polarization on the cathode, anodic polarization on the anode) and ‘backwards’ with the current reversed. The V-I characteristics of the cell were linear from open to short-circuit conditions in the forward mode and up to the maximum, -50 mA/cm², tested under reverse operation. Corresponding to this constant V-I slope, the impedance spectra were found invariant with current density, Figure 1. The constant ohmic resistance of approximately 0.5 Ω.cm², in agreement with the electrolyte and lead wire resistance, has been subtracted. The impedance spectra are dominated by two arcs with peak frequencies of 2 kHz and 40 Hz, previously attributed to the cell cathode and anode respectively (8,9). The constant nature of the impedance spectra demonstrates the reversibility of the LSM-YSZ electrodes under our operating conditions.

Figure 1. Impedance spectra for an anode-supported cell with LSM-YSZ cathode, 60μm YSZ electrolyte and CeO₂-Pd-C-YSZ anode in 3% humidified H₂ at 973 K. Impedance curves were measured at 50 (.), 12.5 (○), OCV (△), -12.5 (○) and -50 (●) mA/cm².

Further measurements of ASR for symmetric LSM-YSZ cells and those with Pt counter electrodes, in our laboratory and others, have revealed large changes in ASR upon polarization (10,11). The primary difference between these measurements and those on the SOFC presented above was that the SOFC cathode had been subject to significant polarization for several hours before the measurements were made.

The impedance spectra of an anode supported SOFC with LSM-YSZ composite cathode and CeO₂-Cu-YSZ anode held at open circuit during heating were measured at open circuit as a function of applied load, Figure 2. After heating to 973 K, the measured total...
cell ASR was 3 Ω.cm². The spectrum is dominated by a large arc with a peak frequency of 0.8 Hz spanning 2.6 Ω.cm² and a smaller arc, 0.2 Ω.cm², with 2 kHz peak frequency. Upon application of currents of 60, 150 and then 850 mA/cm² (short circuit) for ten minutes, the 2 kHz arc was found constant where the lower frequency arc showed a strong dependence on applied current in terms of both span and peak frequency. The impedance spectrum is in good agreement with that previously reported (8) where the higher frequency arc, 2 kHz, is attributed to the cathode and the low frequency arc, 4Hz, to the anode. The effect of polarization was found to be reversible but only with very long time constants, requiring the cell to be left under open circuit conditions for over 12 hours at 973 K to reproduce the original unpolarized state. This polarization effect is observed for symmetric LSM-YSZ electrode, LSM-YSZ|YSZ|Pt and SOFC configurations clearly indicating that the changes occurring with polarization are attributable to the LMS-YSZ cathode.

Figure 2. Two probe impedance spectra for a cell with LSM-YSZ cathode and CeO₂-Cu-YSZ anode at 973K in 3% humidified H₂. All of the spectra were measured at OCV immediately after current flow. Each current density was applied for 10 minutes in the following order: ♦- after heating at OCV, ◇- 60 mA/cm², ●- 150 mA/cm², ○ - short circuit (850 mA/cm²).

A number of explanations for the apparent change in electrode performance with polarization have been put forward in the literature. These theories include the reduction of the Mn in the surface and/or bulk of the LSM under polarization (12). It is proposed that this leads to an extension of the TPB, increasing the area for reaction. Certainly the short times observed for changes during polarization fit with this model, however, the extremely long times required to recover to the original state are more difficult to correlate. Another possible explanation is the removal of secondary Sr-0 and MnO₂-like phases from the LSM surface (11,13). In contrast to the LSM reduction theory, the formation or disappearance of such phases would likely require several hours. A third possibility is a morphological change in the cathode structure (14) resulting in an increased area for reaction and to a corresponding reduction in the electrode ASR. This theory was tested by preparing electrodes with different LSM surface areas.
Using a recently developed technique for the preparation of perovskite-YSZ composites developed at the University of Pennsylvania (7), it was possible to fabricate LSM-YSZ electrodes where the LSM phase is formed in situ at temperatures as low as 1123 K. This allows the formation of an LSM phase with relatively high surface area. Table 1 shows the surface area of LSM-YSZ composites as a function of calcinations temperature (denoted in K by the value in parentheses in the electrode label). The surface area is maximized for the lowest calcination temperature. Table 1 also gives the electrode ASR measured in air on symmetric electrode cells before and after polarization. As may be expected from considerations of the area available for incorporation of oxygen, the most porous, highest surface area electrode, LSM(1123)-YSZ, shows the lowest ASR.

Table 1. Surface area and area specific resistance of composite electrodes on symmetric cells at 973 K before and after polarization with a current of 250 mA/cm² for 10 minutes. The ASRs were determined at open circuit and were multiplied by 0.5 to account for both electrodes.

| Composite Electrode | Surface Area (m²/g) | ASR before polarization, Ω.cm² | ASR after polarization, Ω.cm² |
|---------------------|---------------------|-------------------------------|-------------------------------|
| Porous YSZ         | 0.77±0.02           | -                             | -                             |
| LSM(1123)-YSZ       | 2.53                | 0.48                          | 0.48                          |
| LSM(1323)-YSZ       | 0.66±0.03           | 4.6                           | 2.6                           |
| LSM(1523)-YSZ       | 0.38±0.03           | 6.4                           | 3.8                           |
| LSM(1523)-YSZ after reduction | 0.78±0.03 | 1.5                           | 2.4                           |

Perhaps more significantly, this high porosity electrode shows no change in ASR upon polarization. Electrodes fired at higher temperatures, 1323 K and 1523 K, showed lower porosity with large changes in ASR upon polarization. These results support the theory of increasing porosity upon polarization. For highly porous LSM phases, the introduction of additional porosity has no impact on the electrode performance. For dense LSM phases, small increases in surface area can have a dramatic impact upon performance. It is proposed that these pores may be formed due to the reduction of the LSM phase under polarization.

To test this hypothesis an LSM-YSZ electrode was reduced under hydrogen atmosphere. The surface area was found to increase significantly from 0.38 to 0.78 m²/g. In conjunction with this, the ASR of the sample after exposure to air for 2 hours was 1.5 Ω.cm² compared to 6.4 Ω.cm² for the unreduced sample. After initial polarization the ASR increased to 2.4 Ω.cm², most likely due to oxidation of the highly reduced LSM phase undergoing limited oxidation. Upon further exposure to air under open circuit conditions, the ASR slowly increased to 4.5 Ω.cm² after 100 hours. Subsequent polarization produced a reduction in ASR similar to that previously discussed. These results strongly suggest that the changes observed in electrode ASR can be correlated to changes in electrode porosity resulting from reduction of the LSM phase.
CONCLUSIONS

It was demonstrated that polarization of LSM-YSZ electrodes causes a reduction in area specific resistance. The discrepancies between literature values of LSM-YSZ ASR measured on symmetric cells and SOFC is attributable to the inherent polarization of the electrode on a working SOFC; not the irreversibility of the cathode material. The effect of polarization is similar to that of reduction of the LSM phase and is not present for electrodes with high LSM-phase porosity. It is suggested that polarization causes reduction of the LSM phase, leading to increased porosity.

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REFERENCES

1. M. J. Jørgensen, M. Mogensen, *J. Electrochem. Soc.*, 148, A433 (2001).
2. M. Juhl, S. Primdahl, C. Manon, M. Mogensen, *J. Power Sources*, 61, 173 (1996).
3. E. P. Murray, S. A. Barnett, *Solid State Ionics*, 143, 265 (2001).
4. J-W. Kim, A. V. Virkar, K-Z. Fung, K. Mehta, S. C. Singhal, *J. Electrochem. Soc.*, 146, 69 (1999).
5. R. J. Gorte, S. Park, J. M. Vohs and C. Wang, *Adv. Mat.*, 12, 1465 (2000).
6. S. McIntosh, J. M. Vohs and R. J. Gorte, *J. Electrochem. Soc.*, 150, A470 (2003).
7. H. He, Y. Huang, J. Regal, M. Boaro, J. M. Vohs, and R. J. Gorte, *J. Am. Ceram. Soc.*, 87, 331 (2004).
8. S. McIntosh, J. M. Vohs and R. J. Gorte, *J. Electrochem. Soc.*, 150, A1305 (2003).
9. S. McIntosh, J. M. Vohs and R. J. Gorte, *Electrochem. Solid-State Lett.*, 6, A240 (2003).
10. S. McIntosh, S.B. Adler, J. M. Vohs and R. J. Gorte, *Electrochem. Solid-State Lett.*, 7, A111 (2004).
11. S. P. Jiang, J. G. Love, J. P. Zhang, M. Hoang, Y. Ramprakash, A. E. Hughes, S. P. S. Badwal, *Solid State Ionics*, 121, 1 (1999).
12. X. J. Chen, S. H. Chan, K. A. Khor, *Solid State Ionics*, 164, 17 (2003)
13. S. P. Jiang, J. G. Love, *Solid State Ionics*, 138, 183 (2001).
14. S. P. Jiang, J. G. Love, *Solid State Ionics*, 158, 45 (2003).