IMPROVED PERFORMANCE IN 
(La,Sr)MnO₃ AND (La,Sr)(Co,Fe)O₃ CATHODES 
BY THE ADDITION OF A Gd-DOPED CERIA SECOND PHASE

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ABSTRACT

L₀.₈S₀.₂MnO₃ - Ce₀.₈Gd₀.₂O₂₋ₓ (LSM-GDC) and L₀.₆S₀.₄C₀.₂Fe₀.₈O₃ 
- Ce₀.₈Gd₀.₂O₂₋ₓ (LSCF-GDC) composite cathodes were studied for 
potential applications in low-temperature solid oxide fuel cells. These 
composite electrodes are analogous to the widely used LSM-YSZ 
cathodes, but have potential advantages as GDC has higher ionic 
conductivity than YSZ and is non-reactive with the perovskites. For the 
LSM-GDC cathodes, the GDC concentration ranged from 0-60 wt%. 
LSM-GDC, as well as LSM-GDC/GDC bi-layer electrodes, were spin-
coated onto YSZ substrates. Impedance spectroscopy and current-voltage 
measurements were performed from 500-750°C. The smallest low-current 
interfacial resistance, Rᵢ = 0.34 Ω cm² at 750°C, occurred for the bi-layer 
sample containing 50 wt% GDC in the LSM-GDC layer. The LSCF-GDC 
cathodes, also spin-coated onto YSZ, were a 50-50 wt% mixture. 
Impedance measurements for LSCF-GDC resulted in extremely low Rᵢ 
values, e.g. ~0.01 Ωcm² at 750°C and 0.33 Ωcm² at 600°C.

INTRODUCTION

The primary factor limiting the power density in low-temperature (500-800°C) solid 
oxide fuel cells (SOFCs) is the cathode overpotential. For example, a prior study of thin-
electrolyte SOFCs showed that the low-current cathode interfacial resistance Rᵢ was 70-
85% of the total cell resistance from 550-800°C (1). While the interfacial resistance 
decreased considerably at larger current densities, the cathode still played a major role in 
limiting cell performance. Improved cathode materials are thus important for increasing 
cell power densities and/or allowing further decreases in operating temperature. One 
commonly used means for improving electrode performance is to add an ionically-
conducting second phase, typically yttria-stabilized zirconia (YSZ), to the electronically-
conducting electrode material, typically (La,Sr)MnO₃ (LSM) (2-4).

The improved performance of composite cathodes can be understood based on a high 
density of triple phase boundaries (TPB). This, combined with a contiguous ionically-
conducting phase, allows electrochemical reactions to occur within the electrode, at 
distances up to tens of μm from the electrode/electrolyte interface (5). Approximate
calculations have shown that this increase in the effective length of TPB leads to a decrease in the polarization resistance, with a value given by Kenjo. et. al. as

$$R_p = \sqrt{r \rho k \coth \frac{t^2 \rho}{k}}$$  \[1\]

where $t$ is the electrode thickness and $\rho$ is the ionic resistivity of the ionically conducting phase (6). The effective interfacial resistance is given by

$$k = \frac{k' r}{2}$$  \[2\]

were $k'$ is an intrinsic interfacial resistance and $r$ is the pore radius. Note that two key materials parameter dependencies appear in eq. 1. First, increasing the conductivity of the ionically-conducting phase improves the performance by allowing ions produced within the electrode to more readily reach the electrolyte. Second, the interfacial resistance $k'$ associated with interfaces between the ionically and electronically conducting phases is important. Similar studies by Tanner et. al. (5) agree with Kenjo et. al. in that $R_p$ decreases with increasing $t$. However, calculations by Tanner et. al. provide a more detailed interpretation of the effective electrode thickness as the porosity and geometric factors for a composite electrode are entered into the polarization resistance equation.

In this paper, we describe results on alternative two-phase cathode compositions: LSM-GDC and LSCF-GDC. ($\La\text{Sr})(\text{Co,Fe})_3$ (LSCF) was chosen because of successful low-temperature SOFC tests results (7) and impedance spectroscopy data for LSCF on Y-stabilized ZrO$_2$ and doped CeO$_2$ electrolys, showing lower interfacial resistances than conventional LSM electrodes. This has been attributed to the mixed conductivity of LSCF, the rapid surface exchange kinetics, and the high oxygen vacancy concentration. GDC was chosen as an alternative to YSZ for a few reasons. First, its $\approx$ 3 times higher conductivity should improve electrode performance based on eq. 1. Second, the interfacial resistance of LSM/ceria interfaces appears to be substantially lower than LSM/YSZ interfaces, which should reduce the $k'$ term in eq. 1. Third, there are no known reactions between doped ceria and LSM; in contrast, LSM and YSZ can react to form the resistive phases La$_2$Zr$_2$O$_7$ and/or SrZrO$_3$ during high-temperature sintering, which could compromise electrode performance.

**EXPERIMENTAL**

The electrodes were made from slurries consisting of fine agglomerate La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$Co$_0.2$Fe$_{0.8}$O$_3$, and Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ powders (Praxair Specialty Ceramics, Inc.) with particle sizes of 3.0, 0.7, and 2.3\(\mu\)m, respectively. Each slurry contained the desired powder composition, along with 3wt% polyvinyl buteral-76 binder, and 25% sodium free corn oil. Methyl ethyl ketone was used as the solvent. The LSM-GDC slurries had GDC contents of 0-60 weight percent. The LSCF-GDC slurry was a 50-50 weight percent mixture. The slurries were ballmilled for approximately 24 hours, and then spin-coated onto either side of single-crystal YSZ substrates that were $\approx$1.2 mm thick. The surfaces of the YSZ electrolytes were roughened with silicon carbide paper (grit #240) in order to improve adhesion between the spin-coated electrode film and substrate. The symmetric
Electrode samples were fired at 400°C for 2 hours allowing the binder to burn off, and then sintered. The LSM-GDC samples were sintered at 1150°C for 4 hours. LSCF and LSCF-GDC samples were sintered at 900°C. The total thickness of the electrode films was 20 ±1μm.

LSM-GDC/GDC bi-layer samples were prepared in order to determine the performance of the cathodes on ceria electrolytes. A pure GDC layer was first spin-coated onto the YSZ substrate, followed by the desired electrode slurry. The samples were co-fired at 1150°C for 4 hours. The thickness of the GDC and electrode layers were approximately 2.5μm and 20μm, respectively. Since there is negligible impedance for oxygen ion transport across the ceria/YSZ interface (8), the impedance results should be the same as for LSM-GDC on a GDC electrolyte.

The phase purity of the cathodes were examined using X-ray powder diffraction (XRD) using Cu-Kα radiation. Scanning electron microscopy (SEM) was used to observe the morphology of the electrodes.

Complex impedance measurements were carried out using a Schlumberger 1260 analyzer. The counter and working electrodes were identical since the same spin-coating was applied on either side of the substrate. The frequency range was 0.1 to 5x10³Hz with a signal amplitude of 60mV. Measurements were taken as a function of oxygen partial pressure (1x10⁻³ - 1atm) and temperature (600 - 750°C). The non-linear least squares fitting program EQUIVCRT (9) was used to fit the impedance data and obtain equivalent circuits. In cases where two arcs overlapped, EQUIVCRT was used to determine the resistance values associated with each of the arcs. A Keithley 220 Programmable Current Source, as well as a Keithley 196 System DMM were used to collect current-voltage measurements for an LSM-GDC symmetric electrode spin-coated onto a thin (=0.5mm thick) YSZ substrate.

RESULTS

Figure 1 shows SEM images of typical LSM-GDC (a) and LSCF-GDC (b) electrodes prepared using the above procedures. Also shown are LSM-YSZ (c) and LSCF (d) electrodes, whose properties will be compared with the GDC-based electrodes below. The images showed good porosity with good necking of particles in all electrodes. The structures appeared similar for the LSM-based electrodes, with particle and pore sizes of ~400 nm. The LSCF-based electrodes had much smaller feature sizes, 100 - 200 nm, a result of the smaller starting powder size. No resistive phases (e.g. La₂Zr₂O₇ or SrZrO₃) could be detected in any of the cathodes on YSZ electrolytes using x-ray diffraction.

LSM-GDC Cathodes

Figure 2 shows Nyquist impedance plots measured in air that are representative of the LSM-GDC cathodes with ≥40wt% GDC. Good fits to the data in Fig. 2 using EQUIVCRT were obtained using the equivalent circuit LR₀(RQ)(RₑW), by resolving the arc into two overlapping arcs. (RQ) and (RₑW) represent the high and low frequency arcs, respectively. Q represents a constant-phase element and W a Warburg impedance. The low frequency arc appeared to be the same as the arc for LSM, as it occurred over
the same frequency domain. The second, high frequency arc was absent for <30 wt% GDC samples.

The temperature dependence of the low frequency arc is given in Table 1 for each of the LSM-GDC cathodes. The activation energy values decrease from ≈ 1.36 eV for LSM-GDC30 to ≈ 1.20 eV for LSM-GDC60. Overall, varying the GDC content over a wide range had relatively little effect on the frequency range and temperature dependence of the low-frequency arc. Calculated values for the activation energy associated with the high frequency arc for cathodes with ≥40 wt% GDC are also listed in Table 1. As seen for the low-frequency arc, the activation energy decreased with increasing GDC content.

Figure 3 summarizes the results for electrodes of various compositions tested in air, showing the low-current interfacial resistance $R_i$ (i.e. the difference between the real-axis intercepts of the electrode arcs). $R_i$ decreased with increasing temperature, as expected. For a given temperature, $R_i$ decreased with increasing GDC content up to 650°C, before increasing rapidly for a further increase in GDC content.

The LSM-GDC electrodes on GDC electrolytes had lower $R_i$ than on YSZ, as shown in Table 2. For a pure LSM cathode, the GDC layer decreased $R_i$ from 3.50 to 1.13 Ω cm$^2$ at 750°C in air. This result illustrates that the kinetics of electrochemical reactions are faster on GDC electrolyte surfaces than YSZ surfaces, in agreement with prior SOFC test results (1). For LSM-GDC50 cathode, the GDC layer decreased $R_i$ from 0.49 to 0.34 Ω cm$^2$ at 750°C in air. This decrease presumably results from replacing LSM-YSZ TPBs with LSM-GDC TPBs at the cathode/electrolyte interface. The effect is small because the TPBs already present within the LSM-GDC cathode dominate the electrode performance.

Figure 3 shows the temperature dependence of $R_i$ for LSM-GDC on YSZ electrolytes. LSM-GDC cathodes yielded $R_i$ values a factor of ≈ 7 lower than LSM, and a factor of ≈ 2 lower than LSM-YSZ electrodes prepared using identical conditions and with similar structures. Based on eq. 1, this could be attributed to the higher ionic conductivity, $\sigma$, of GDC. The LSM-GDC cathodes were tested from 600°C, where $\sigma_{\text{GDC}}$ = 2.8 x 10$^{-2}$ S/cm, to 750°C, where $\sigma_{\text{GDC}}$ = 6.3 x 10$^{-2}$ S/cm (10). For comparison, $\sigma_{\text{YSZ}}$ = 3.1 x 10$^{-3}$ S/cm at 600°C and ≈1.8 x 10$^{-2}$ S/cm at 750°C. Using these numbers in eq. 1, assuming that all other factors did not change, shows that the increased ionic conductivity results in a factor of 2 change in $R_i$. On the other hand, the improvement may also be attributable, at least in part, to the improved electrochemical properties of LSM/GDC interfaces compared to LSM/YSZ.

Current-voltage measurements for a LSM-GDCC50 electrode (~0.36 cm$^2$ in area) are illustrated in figure 4 for T = 650°C and 750°C. Note that this figure represents only the electrode contribution, as the ohmic resistance associated with the YSZ electrolyte has been subtracted. The low-current resistance values from these curves, 24Ω at 650°C and 4.7Ω at 750°C, agreed well with the low-current interfacial resistance values measured by impedance spectroscopy. As expected, the electrode resistance decreased as the current increased. For example, for a 0.5 V drop across the cathode at 650°C, the electrode resistance dropped to 45% of that observed at zero current.

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Figure 5 shows impedance spectra for typical LSCF-GDC and LSCF cathodes. For LSCF, two depressed arcs were observed. The low frequency arc was dominant at lower temperatures (<700°C), which typically indicates that the primary rate-limiting mechanisms are diffusion related. At higher temperatures, the high frequency arc became more pronounced, suggesting that charge transfer limited the electrode reaction.

The LSCF-GDC electrodes yielded much smaller arcs than pure LSCF. The arcs also differed in shape and occurred over different frequency regimes than LSCF, suggesting that different mechanisms may be involved. In addition, for LSCF-GDC the high frequency arc vanished at 700°C, and a lower frequency arc developed. The considerable overlap between the high and low frequency arcs prevented the acquisition of accurate fits using EQUIVCRT.

The difference in size of the LSCF and LSCF-GDC electrode arcs is listed in Table 2. The values for the LSCF-GDC electrode were a factor of ~10 lower than those for the LSCF cathode. The activation energies indicated in Fig. 6, ~0.16eV, were very similar for LSCF and LSCF-GDC. Other studies concerning LSCF report an activation energy of about 0.1 eV over a temperature range of 100-500°C (11).

The difference in cathode performance for LSCF and LSCF-GDC may be linked to the electrochemical reaction zone of each electrode. Penetration depth studies by Adler et al. (12) indicate that for mixed conducting oxides with an average particle size of 1μm, the electrode reaction zone extends ≤10μm from the electrolyte. Electrodes composed of submicron particles tend to have an even narrower reaction zone. The present LSCF cathodes were ≈ 20μm thick. Thus, it is possible that more than half of the LSCF electrode was electrochemically inert. The addition of 50 wt% GDC, with a factor of 10 times higher ionic conductivity (10, 13), would presumably extend the reaction zone further into the electrode. It is also possible that electrochemical reaction rates are large at LSCF-GDC triple-phase boundaries, and the high density of boundaries present in the mixed cathode contributed to the enhanced performance. Finally, it should be noted that a small amount of zirconate phase, too small to detect by x-ray but enough to affect performance, may have been present at the LSCF/YSZ interface. If this was the case, the GDC/YSZ contacts at the LSCF-GDC/YSZ interface would provide an easy path for ionic transport that by-passes the LSCF/YSZ interfaces, thereby reducing Rf.

Comparisons of the performance of different composition electrodes are often difficult because processing induced differences in structure may dominate chemically induced differences. In the present case, we believe the comparisons between LSCF and LSCF-GDC are valid since identical processing conditions were used and SEM images of the electrodes showed nearly identical structures. Comparisons of the LSCF-based electrode results with the LSM-based electrode results in Fig. 4 must be made with care, since the LSCF particle sizes were smaller. This probably explained, in part, order of magnitude decrease in Rf for LSCF-GDC vs. LSM-GDC. However, the lower Rf was also presumably due to the mixed conductivity of the LSCF, which has previously been shown to provide lower Rf than LSM.
CONCLUSIONS

Overall, the LSCF-GDC electrodes provided the best performance of those studied. The addition of 50 wt% GDC to LSCF cathodes on YSZ electrolytes produced a factor of \( \approx 10 \) reduction in the low-current interfacial resistance, e.g. \( R_i \approx 0.01 \ \Omega \text{cm}^2 \) at 750°C and 0.33 \( \Omega \text{cm}^2 \) at 600°C. Note that these are low-current values, and the resistance probably decreases with increasing current density. Combined with a low ohmic resistance thin electrolyte and a low-resistance anode, this would allow high SOFC power densities at 600°C or lower.

A few mechanisms may explain the enhanced electrode performance produced by the GDC addition. However, it seems likely that the high ionic conductivity of GDC played a key role by expanding the electrochemical reaction zone further from the electrode/electrolyte interface. Though the rate limiting mechanisms were not determined in this study, the difference in appearance of the impedance arcs for LSCF and LSCF-GDC suggest that different mechanisms limit the electrode kinetics of each cathode.

Improved cathode performance may be possible by determining the appropriate thickness for the LSM-GDC and LSCF-GDC cathodes. The cathodes presented in this study were arbitrarily chosen to be 20μm thick. Previously studied LSM-YSZ cathodes were suggested to have an optimum thickness at about 40μm (12). Since the conductivity of GDC exceeds that of YSZ, the optimum thickness may be even higher.

For practical applications, these cathodes would be best suited for use in cells with ceria-based electrolytes, because of the good thermal expansion coefficient match of GDC and LSCF. The thermal expansion mismatch with YSZ electrolytes is larger; indeed, in our initial attempts to make thin-YSZ electrolyte cells with LSM-GDC cathodes, electrolyte cracking has been observed in some cases.

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Table 1

| Cathode wt% GDC | Ea(R) eV | Ea(R_ei) eV |
|----------------|---------|-----------|
| 0              | ---     | 1.61      |
| 30             | ---     | 1.36      |
| 40             | 0.65    | 1.23      |
| 45             | 0.82    | 1.22      |
| 50             | 0.92    | 1.26      |
| 55             | 0.99    | 1.31      |
| 60             | 1.11    | 1.36      |

**Table 1.** List of the activation energy values, Ea(R) and Ea(R_ei) corresponding to the low-frequency and high-frequency arcs, respectively for each of the LSM-GDC cathodes.

Table 2

| Sample            | 600°C | 650°C | 700°C | 750°C |
|-------------------|-------|-------|-------|-------|
| LSM-GDC50/GDC     | 4.44  | 1.74  | 0.75  | 0.34  |
| LSM-GDC50         | 6.81  | 2.51  | 1.06  | 0.49  |
| LSM-YSZ50         | 11.37 | 4.92  | 2.49  | 1.31  |
| LSM/GDC           | 16.32 | 6.38  | 2.67  | 1.13  |
| LSM               | 51.03 | 20.58 | 7.82  | 3.50  |

**Table 2.** Summary of the interfacial resistance in units of Ω cm² for the different types of electrodes studied. The data was collected in air.
Figure 1. SEM cross-sectional images of typical a) LSM-GDC, b) LSCF-GDC, c) LSM-YSZ and d) LSCF cathodes.
Figure 2. Nyquist impedance plots measured in air for LSM-GDC50 at 700°C.

Figure 3. Interfacial resistance shown for various temperatures according to GDC concentration.
Figure 4. Current-voltage measurements for LSM-GDC50 electrode. The YSZ electrolyte contribution has been excluded.

Figure 5. Impedance spectra measured in air for LSCF-GDC and LSCF at 750°C.

Figure 6. Activation energies for LSCF and LSCF-GDC.