



## LSM-GDC Composite Cathodes Derived from a Sol-Gel Process

### Effect of Microstructure on Interfacial Polarization Resistance

Changrong Xia, Yuelan Zhang, and Meilin Liu<sup>\*,z</sup>

School of Materials Science and Engineering, Center for Innovative Fuel Cell and Battery Technologies, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

Electrodes consisting of strontium-doped lanthanum manganite (LSM) and gadolinium-doped ceria (GDC) were developed with a modified sol-gel process for honeycomb solid oxide fuel cells based on stabilized zirconia electrolytes. The sol-gel derived cathodes show much lower interfacial polarization resistances than those prepared by slurry coating or spray deposition. The interfacial polarization resistances were 0.65 and 0.16  $\Omega \text{ cm}^2$  at 650 and 750°C, respectively, as determined using impedance spectroscopy. The high performance is attributed to the small grain size, high porosity, and large specific surface area of the cathode, demonstrating the dramatic effect of microstructure on electrode performance.

© 2003 The Electrochemical Society. [DOI: 10.1149/1.1621830] All rights reserved.

Manuscript submitted May 3, 2003; revised manuscript received July 7, 2003. Available electronically October 15, 2003.

Cost reduction is a major challenge facing current solid oxide fuel cell (SOFC) technologies. To dramatically reduce the cost of materials, the operating temperature must be reduced; to reduce the cost of fabrication, new design and fabrication processes must be developed. Recently, we developed a unique process for fabrication of honeycomb fuel cells with built-in interconnection and gas manifolding.<sup>1</sup> However, one difficulty in achieving high performance is how to fabricate efficient electrodes on extruded honeycomb cells where the fabrication methods are essentially limited to solution/slurry coating techniques.

Strontium-doped lanthanum manganite (LSM) is a classical cathode for SOFCs due to its chemical and thermal compatibilities with stabilized zirconia. Composite electrodes consisting of LSM and the electrolyte materials such as yttria-stabilized zirconia (YSZ) and gadolinia-doped ceria (GDC) are proven to have better performance than electrodes consisting of LSM alone, due to possible mixed conductions and the presence of an active triple-phase boundary (TPB) between LSM, electrolyte, and gas phase in the bulk of the electrode.<sup>2,3</sup> Furthermore, the performance of an LSM cathode is sensitive to processing, which determines the microstructure and the adhesion of the electrode to the electrolyte, and thus determines the length of the TPB. The TPBs are believed to be the most active sites for oxygen reduction in the electrode.<sup>4,5</sup>

Various methods have been used for the fabrication of LSM cathodes, including slurry coating, flame spraying, tape calendaring, casting, and printing.<sup>1</sup> LSM and LSM-based composite films have also been fabricated by electroless deposition,<sup>6</sup> electrochemical deposition,<sup>7</sup> vacuum evaporation,<sup>8</sup> metallorganic chemical vapor deposition,<sup>9</sup> metallorganic decomposition,<sup>10</sup> vacuum plasma spraying,<sup>11</sup> and screen printing.<sup>12</sup> However, little work has been aimed at developing a composite film of LSM-YSZ or LSM-GDC on honeycomb SOFCs. In this article, we report our finding on LSM-GDC composite films prepared using a sol-gel process as cathodes for SOFCs with honeycomb structures. The electrodes show much smaller interfacial polarization resistances than those prepared by other methods such as slurry coating<sup>3,13</sup> or spray deposition.<sup>14</sup>

#### Experimental

Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> (GDC) sol was prepared from (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> and Gd(NO<sub>3</sub>)<sub>3</sub>. The nitrates were added dropwise into ammonia solution (pH > 11) to form hydroxide precipitates (pale yellow), which were then peptized with nitric acid (to pH 3.5) at 85°C to form a clear GDC sol. (La<sub>0.85</sub>Sr<sub>0.15</sub>)<sub>0.9</sub>MnO<sub>3±δ</sub> (LSM) powder was prepared using a glycine-nitrate process with precursors of

La(NO<sub>3</sub>)<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, and glycine.<sup>13</sup> The powder was fired at 800°C for 4 h to form the perovskite structure as confirmed by X-ray diffraction (PW 1800). The fired powder was subsequently dispersed into the GDC sol with a ball mill to form a slurry-like sol, in which the weight ratio of GDC to LSM was 1:1. The sol was subsequently coated on the inner channels of YSZ (8 mol % yttria-stabilized zirconia) honeycombs, which were fabricated by extrusion and sintering at 1350°C in air for 12 h.<sup>1</sup> The coated layer was dried at room temperature and fired at 600°C for 2 h with a heating and cooling rate of 1 and 5°C per min, respectively. The coating-drying-firing procedure was repeated 10 times before impedance measurements. The microstructures of the cells were revealed using a scanning electron microscope (SEM, Hitachi S800). A layer of the electrode materials, deposited on a dense alumina substrate using the identical processing procedures, was then used for transmission electron microscopy (TEM), X-ray diffraction (XRD), and isothermal nitrogen adsorption-desorption [Brunauer-Emmett-Teller (BET)] measurements.

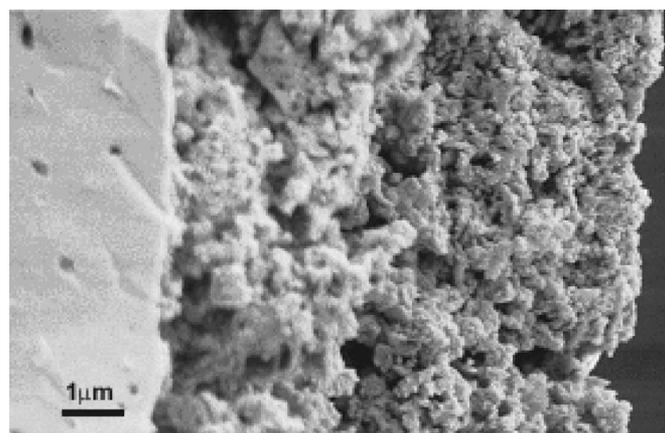
Electrochemical impedance measurements were performed on symmetrical cells, LSM-GDC/GDC/LSM-GDC, in air with the LSM-GDC composite electrodes being finally fired at 800°C for 4 h or without further firing (*in situ* testing) using a Solartron 1255 HF frequency-response analyzer in combination with a Solartron 1286 electrochemical interface. Silver wires were attached to the electrodes with a silver paste, and a thermocouple was positioned close to the sample to provide an accurate measurement of the sample temperature, usually increasing from 500 to 750°C in 50°C intervals. Impedance spectra were obtained in the frequency range from 10 mHz to 1 MHz with an applied ac voltage amplitude of 10 mV. All impedance measurements were taken 30 min after the desired temperature was reached under open-circuit conditions.

#### Results and Discussion

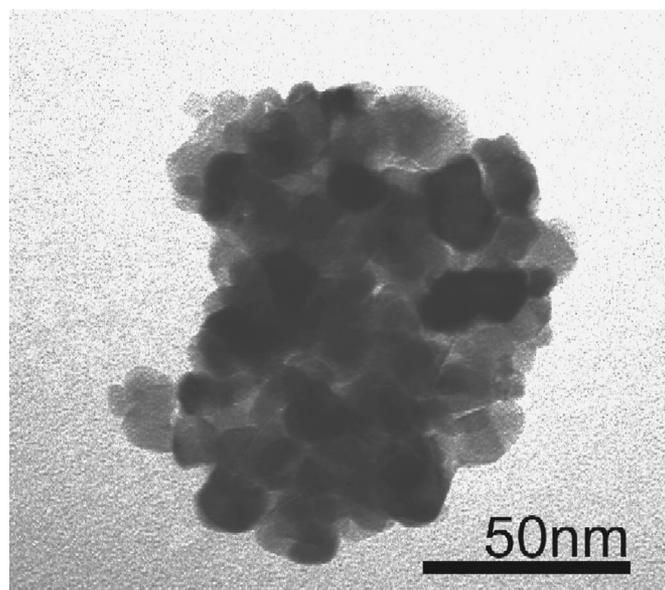
Figure 1a shows a typical cross-sectional view (SEM image) of an LSM-GDC cathode (about 10  $\mu\text{m}$  thick) fired at 800°C, which appears to be well adhered to the electrolyte. The LSM and GDC grains appear to bond together and there is a high level of interconnected porosity. The average grain size (estimated from SEM micrographs) appears to be about 100 nm. However, the BET measurement indicates that the specific area of the cathode fired at 800°C is about 8.6 m<sup>2</sup>/g, implying an average grain size of about 50 nm. TEM observation (Fig. 1b) shows that these grains consist of much smaller particles, with dimension of about 10 nm. Shown in Fig. 2 are the XRD patterns of the composite powder prepared by the sol-gel process, GDC by the sol-gel process, and LSM by a glycine-nitrate process, suggesting that no chemical reaction between GDC and LSM has been developed during the sol-gel process or the sub-

\* Electrochemical Society Active Member.

<sup>z</sup> E-mail: meilin.liu@mse.gatech.edu



(a)

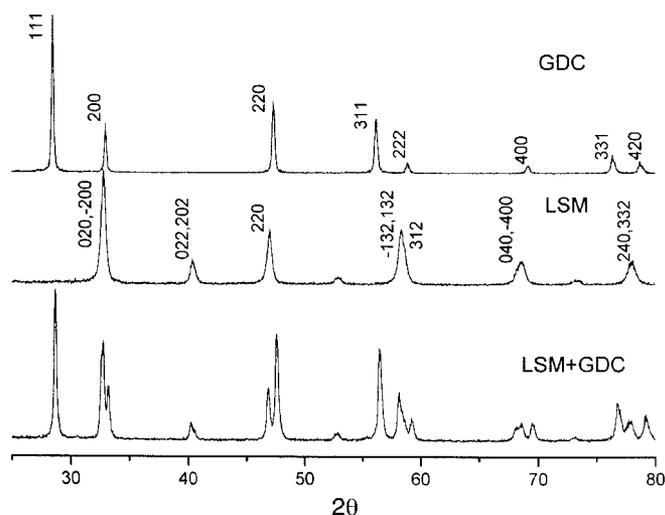


(b)

**Figure 1.** (a) A cross-sectional view (SEM) of a GDC-LSM composite cathode fired at 800°C for 4 h and (b) a TEM view of the composite cathode.

sequent firing of the composite at 1000°C for 4 h. High stability is thus expected for the sol-gel derived cathodes that are processed below 800°C.

Shown in Fig. 3 is a typical impedance spectrum for a symmetric cell, LSM-GDC/YSZ/LSM-GDC, as measured at 700°C in air. The spectrum consists of an arc at low frequencies (0.01-10 Hz) and an arc at high frequencies (10-10,000 Hz). The spectra obtained at different temperatures are similar, each consisting of two well-separated arcs. While any attempt to deduce an oxygen reduction mechanism or even to separate the contributions from mass transfer and charge transfer requires other independent measurements, it is straightforward to determine the total interfacial polarization resistances of the symmetrical cell ( $2R_p$  as marked on Fig. 3) directly from this impedance spectrum.<sup>13</sup> To obtain the actual polarization resistance in  $\Omega \text{ cm}^2$ , however, the total interfacial polarization resistances should be corrected for electrode area and divided by two.<sup>15,16</sup> This is because the total interfacial impedance of a symmetrical cell corresponds to that for two identical electrode-electrolyte interfaces of the cell. Further, the interfacial processes occurring in the symmetrical cell under the conditions for imped-



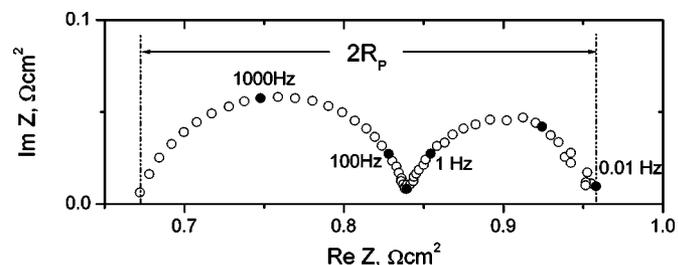
**Figure 2.** XRD pattern of a composite GDC-LSM powder prepared with a sol-gel process and fired at 1000°C for 2 h (the XRD patterns of LSM and GDC fabricated with a glycine-nitrate process and a sol-gel method, respectively, are also shown for comparison).

ance measurements are identical to those occurring at the cathode-electrolyte interface of an SOFC such as

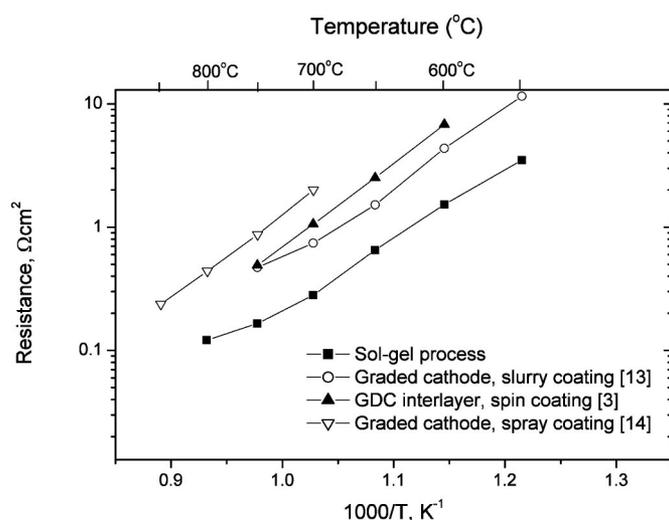
air, LSM-GDC/GDC/Ni-GDC, hydrogen

under impedance measurement at open-circuit conditions. Because the purpose of this study is to characterize the effect of microstructure (or active surface area) on interfacial polarization resistance of the same electrode material, the polarization behavior of the electrodes under different dc voltages were not studied. The interfacial impedance responses under open-circuit conditions represent the equilibrium properties of the interface and, thus, are related to the exchange current densities or catalytic properties of the interface. We believe that the interfacial polarization resistance is the most critical parameter for this study while the cathodic and anodic transfer number should be less sensitive to change in microstructure.

Shown in Fig. 4 is the temperature dependence of interfacial polarization resistances measured under open-circuit conditions for the sol-gel derived cathodes with microstructures shown in Fig. 1a. The interfacial resistances of the composite cathodes (GDC-LSM<sup>3</sup>), and recently developed functionally graded cathodes<sup>13,14</sup> consisting of GDC and LSM are also shown in Fig. 4 for comparison. It is clear that the sol-gel derived cathode displayed much better electrochemical performance than the other cathodes, although they all have the same chemical composition. For example, at 700°C, the interfacial resistance of a sol-gel derived cathode is only 0.28  $\Omega \text{ cm}^2$ , compared to 4.3  $\Omega \text{ cm}^2$  of a graded cathode,<sup>13</sup> and 6.8  $\Omega \text{ cm}^2$  of a



**Figure 3.** A typical impedance spectrum for a symmetric cell, GDC-LSM/YSZ/GDC-LSM, as measured at 700°C in air. The polarization resistance of the electrode (LSM-GDC) and the electrolyte (YSZ) interface,  $R_p$ , was determined directly from this impedance spectrum.



**Figure 4.** Interfacial polarization resistances of LSM-GDC electrodes (on a YSZ electrolyte) prepared by different processes: a sol-gel process as reported in this work, a slurry coating,<sup>13</sup> a spin coating,<sup>3</sup> and a spray coating<sup>14</sup> process.

slurry-coated GDC-LSM composite.<sup>3</sup> The interfacial polarization resistances depend critically on electrode microstructure; high porosity, small grains, and large specific surface area result in low interfacial resistances. The average grain size of the sol-gel derived cathode is about 0.05  $\mu\text{m}$ , smaller than that of glycine-nitrate derived cathode (0.1-0.2  $\mu\text{m}$ ),<sup>13</sup> and much smaller than that of the commercially available particles (2-3  $\mu\text{m}$ ) as used for the composite cathode<sup>3</sup> and graded cathode.<sup>14</sup> The interfacial resistances are sensitive to the firing temperatures as well. When firing temperature of the electrode is too high, the interfacial resistances increase with the firing temperature due to oversintering of electrodes, leading to loss of porosity, surface area, and active triple-phase boundaries. When the firing temperature is too low, the bonding between the electrode and electrolyte is too poor, resulting in high interfacial resistances. For the commercially available and glycine-nitrate derived LSM-GDC powders, the lowest sintering temperatures are 1125 and 1050°C,<sup>13,14</sup> respectively. Generally, it is believed that films fabricated by a sol-gel process have strong bonding with the substrate even when the firing temperature is relatively low. A cell with cathode sintered *in situ* at 600°C behaves in a similar manner as a function of temperature as the cell with cathode fired at 800°C. For example, the interfacial resistance of an *in situ* fired electrode is 3.3  $\Omega\text{ cm}^2$  at 550°C (compared to 3.5  $\Omega\text{ cm}^2$ ), and 0.11  $\Omega\text{ cm}^2$  at 800°C (compared to 0.12  $\Omega\text{ cm}^2$ ). This implies that adequate bond-

ing has been formed between the electrolyte and electrode at a temperature as low as 600°C. This is especially important to SOFCs that are operated at low temperatures.

### Conclusions

Highly porous cathodes consisting of LSM and GDC with low interfacial polarization resistances have been successfully fabricated by a sol-gel process, which has the advantage of developing strong bonding between the electrode and electrolyte at low temperatures and achieving desirable microstructures for fuel cell electrodes: small grains, high porosity, large surface area, and long triple-phase boundaries.

### Acknowledgment

The authors gratefully acknowledge Kevin Hurysz, J. K. Lee, and Joe Cochran for fabrication of the YSZ honeycomb samples. The authors also gratefully acknowledge the support of this research by DoE-NETL SECA Core Technology Program (grant no. DE-FC26-02NT41572) and the DARPA/DSO Palm Power program directed by Dr. Browning and funded through ARMY/ARO grant DAAD19-01-1-0649 monitored by Dr. Richard Paur.

*Georgia Institute of Technology assisted in meeting the publication costs of this article.*

### References

1. C. Xia, B. Rauch, J. Cochran, J. Lee, and M. Liu, in *Proceedings of the Symposium on Fuel Cells: Bridging Processing and Performance*, The First International Conference on Materials Processing for Properties and Performance, Singapore, Aug 1-3, 2002.
2. T. Tsai and S. A. Barnett, *Solid State Ionics*, **93**, 207 (1997).
3. E. P. Murry and S. A. Barnett, *Solid State Ionics*, **143**, 265 (2001).
4. F. van Heuveln, H. J. M. Bouwmeester, and F. P. F. van Berkel, *J. Electrochem. Soc.*, **144**, 126 (1997).
5. M. J. Jorgensen, S. Primdahl, C. Bagger, and M. Mogensen, *Solid State Ionics*, **139**, 1 (2001).
6. T. Sasaki, Y. Matsumoto, J. Homb, and Nagata, *J. Solid State Chem.*, **105**, 255 (1993).
7. Y. Matsumoto, T. Sasaki, and J. Hombo, *J. Electrochem. Soc.*, **138**, 1259 (1991).
8. H. Michibata, H. Tenmei, T. Namikawa, and Y. Yamazaki, in *Proceedings of the First International Symposium on Solid Oxide Fuel Cells*, S. C. Singhal, Editor, PV 89-11, p. 188, The Electrochemical Society Proceedings Series, Pennington, NJ (1989).
9. L. Meda, C. Bacaltchuk, H. Garmestani, and K. H. Dahmen, *J. Mater. Sci.: Mater. Electron.*, **12**(3), 143 (2001).
10. K. Hayashi, M. Hosokawa, T. Yoshida, Y. Ohya, Y. Takahashi, O. Yamamoto, and H. Minoura, *Mater. Sci. Forum*, **49**(3), 239 (1997).
11. K. Barthel, S. Rambert, and S. Siegmann, *J. Thermal Spray Technol.*, **9**(3), 343 (2000).
12. R. N. Basu, S. K. Pratihar, M. Saha, and H. S. Maiti, *Mater. Lett.*, **32**(4), 217 (1997).
13. C. R. Xia, W. Rauch, W. Wellborn, and M. L. Liu, *Electrochem. Solid-State Lett.*, **5**, A217 (2002).
14. N. T. Hart, N. P. Brandon, M. J. Day, and N. Lapena-Rey, *J. Power Sources*, **106**, 42 (2002).
15. E. Perry Murray, M. J. Sever, and S. A. Barnett, *Solid State Ionics*, **148**, 27 (2002).
16. C. R. Xia, Y. L. Zhang, and M. L. Liu, *Appl. Phys. Lett.*, **82**, 901 (2003).