INTERACTIONS AND COMPATIBILITIES OF LSGM ELECTROLYTE AND LSCM ANODE

Yanhai Du and Nigel M. Sammes
Connecticut Global Fuel Cell Center, University of Connecticut
44 Weaver Road, Storrs, CT 06269-5233, USA

ABSTRACT

Interactions between La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ (LSGM) electrolyte and La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) anode in the cell fabricating temperature range (1100-1500°C) were studied using XRD, SEM and EDS techniques. Powder mixtures and bi-layer samples were fired for 2-72 h at 1400-1500°C. Although there were 15-20% differences in firing shrinkage during fabrication, the thermal expansion coefficients of the LSCM anode closely matched (less than $1 \times 10^{-6}$/°C) with the LSGM electrolyte in the fuel cell operating temperature range. There were no interactions detected from XRD data during fabrication under 1500°C and dwell for 2 h. However, severe reactions were found in samples with dwell time 6 h and over at 1500°C to form low conductive phases. EDS analysis indicated that the reaction/diffusion zones were between 50-150 μm. The overall results suggested that LSCM is a thermomechanically and chemically compatible anode material with LSGM electrolyte at the fuel cell operating temperatures and fuel cell fabrication conditions (under 1500°C and dwell for 2 h and shorter).

INTRODUCTION

With high efficiency and fuel-flexibility, solid oxide fuel cells (SOFCs) are emerging alternative electrochemical energy devices, which, if successfully commercialized, will deliver clean, quiet, and potentially renewable energy for back-up, base-load and primary power. In addition to hydrogen, the SOFCs can be operated from many low-cost hydrocarbon fuels, such as propane, syngas, methane, natural gas and JP-8 through internal reforming [1]. Technical trends in SOFC development and deployment include: (1) reducing operating temperatures by (a) using new electrolyte materials, doped lanthanum gallate, scandia doped zirconia or doped ceria; (b) minimizing electrolyte resistance (using the electrode as a support, thin film electrolyte); (2) increasing cell/stack performance and reliability; (3) lowering costs; and (4) modularity and fuel flexibility.

The strontium- and magnesium-doped lanthanum gallate (LSGM), as one of the few available electrolyte materials, has drawn much attention due to its high ionic conductivity (0.12-0.17 S/cm at 800°C) over a wide range of oxygen partial pressures (1-10$^{-20}$ atm) [2-4]. The conductivity is higher by a factor of over two compared to the existing yttria doped zirconia (YSZ) (0.052 S/cm [6]). The LSGM materials, however require a very high temperature, 1450-1550°C for example, to be fully densified [5]. Three issues associated with these high firing temperatures are: (1) the LSGM electrolyte...
reacting with the currently used nickel-based anode during sintering, forming low conductive compounds, for example LaNiO$_3$[6-9]; (2) Ga depletion [10]; and (3) decreasing anode porosity [11]. Because of these reasons, LSGM based SOFCs are limited, at this time, to the LSGM electrolyte supported configuration, which is usually prepared by densifying the LSGM electrolyte first and then applying the anode and cathode layers afterwards.

Although a thin and dense LSGM layer with the support substrate can be fabricated using various techniques, attempts to fabricate LSGM thin film SOFCs have been without much success. For example, electrostatic spraying could produce a crystallized LSGM layer after annealing at 900°C for 2 h; however the LSGM layer was porous [12]. Joseph et al. [13] successfully obtained a 0.5 μm LSGM layer using pulsed laser ablation on a quartz substrate, however, this must be done under high vacuum and high temperature conditions, and there was no density data from that report. Mathews et al. [14] prepared a dense film of 4 μm on Pt using electrophoretic deposition after five repetitions of deposition and sintering at 1400°C. Majewski et al.’s study [15] concluded that only at temperatures higher than 1400°C could a dense single phase LSGM structure be obtained. One possible approach to use electrode supported LSGM thin electrolyte configuration is to use a plasma spray technique to apply the LSGM layer onto the fired electrode (anode or cathode) support. Feasibility studies [16] showed difficulties in putting down very thin (less than 50 μm) dense LSGM layers, and furthermore, the use of plasma spray is also costly.

On the anode side, attempts to composite LSGM and Co, Ni or Fe have been reported to be unsuitable due to interactions [8]. The focus is then turned to LaCrO$_3$-based materials. LaCrO$_3$-based materials have been mainly used as interconnect materials for SOFCs [17, 18] due to their high electrical conductivity, stability in both fuel and oxidant atmospheres at high temperatures [19] and compatibility with other fuel cell components. Dopants on A- and B-sites, for example with Sr and Mn, respectively, showed significant reduction of the polarization resistance (from 10 to <1 Ωcm$^2$) and increase in electrical conductivity (to 1.5 S/cm in 5% H$_2$ at 900°C) [20, 21]. In addition to good chemical compatibility with the YSZ electrolyte, when using methane as a fuel, the LSCM anode requires only ambient humidification (~3%) to prevent coke formation, compared to about 50% steam requirement for Ni-YSZ anodes for the same purpose (direct oxidation). On the cathode side, a number of mixed electric and ionic conductors were explored for possible use as cathodic materials with the LSGM electrolyte. These included $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) [22, 23], $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) [24], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Ga}_{0.5}\text{Ni}_{0.5}\text{O}_3$ (LSGN) [25], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSFC) [26, 27]. In this study, we proposed a set of all-perovskite materials: $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mn}_{0.2}\text{O}_2$ (LSGM) electrolyte, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) anode and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSFC) cathode. It is our anticipation that the all-perovskite structured and multilayered ceramic materials could increase the electrochemical and thermomechanical compatibilities of the SOFC system and eliminate the interactions between the electrolyte and electrode at the cell operating and fabricating temperatures (800-1500°C).

Interfacial studies between the proposed materials have primarily focused in the cell operating temperature range, and very little information is available in relation to the compatibilities within the cell fabrication (LSGM sintering) temperature range. This
paper reports the first part of our study, the interactions between the LSCM anode and LSGM electrolyte in the cell fabricating temperature range (up to 1500°C).

EXPERIMENTAL

Materials

La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ (LSGM) electrolyte powder (Rhodia E&G) had a surface area of 4.8 m$^2$/g and particle size of D$_{50}$ 8.8 μm. The nickel-free perovskite anode powder with La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) composition was synthesized from the previous work [28] using a solid state reaction and calcined at 1400°C for 4 h. The as-received LSCM powder had a particle size of D$_{50}$ 1.8 μm.

Samples Preparation

To study the compatibility of the LSCM and LSGM, two types of pressed samples were prepared except LSGM and LSCM samples: (1) double layered LSCM on LSGM support and (2) mixed LSGM and LSCM (50:50 wt%). The mixture of LSCM and LSGM powders was ball milled in acetone for 18 h. The bi-layered samples were formed by first semi-pressing LSGM, then adding LSCM powder on top of the semi-pressed LSGM, followed by fully pressing at the required pressure. Pellets (13 mm diameter and 2 mm thickness), as well as bars (6x6x45 mm), were pressed using a hydraulic press (Carver, Inc.) under a pressure of 365 MPa (for pellets) and 175 MPa (for bars) respectively, and followed by firing at various temperatures (1300, 1400, 1450 and 1500°C) and dwell time (2-72 hours). A methyl cellulose binder (5 wt% A4M, The Dow Chemical Company) was used to increase the formability of the calcined LSCM powder. Figure 1 (a) shows some of the fired samples and Figure 1 (b) shows the LSCM anode tubes extruded and fired at 1300°C for 2 h.

Characterization

Thermal expansion coefficients (TECs) of bar shape LSGM and LSCM samples (5x5x25 mm) were measured using a dilatometer (DIL 402 PC, NETZSCH Instruments, Inc.) from room temperature to 900°C. X-ray diffraction (XRD) was conducted on pellet samples using a diffractometer (D5005, Bruker-AXS) with generator settings of 40 mA and 40 kV incident CuK$_\alpha$. Scanning electron microscope (SEM) images were observed using an Amray 1000A and Jeol JSM-5600LV microscopy. Element concentration in the
interface were detected using an energy-dispersive spectrometry (EDS) (Noran System SIX model 200, Thermo Electron Corporation) attached to the Jeol SEM system.

RESULTS AND DISCUSSION

Thermal Properties

As can be seen in Figure 1, the LSCM and LSGM samples have huge differences in terms of firing shrinkages. The bi-layer bar samples (LSCM/LSGM, fired at 1300 and 1400°C) bended to the LSGM side during firing due to the larger shrinkage of LSGM compared to that of LSCM. Figure 2 illustrates the shrinkage differences in detail. LSCM samples had a 10-15% linear shrinkage after sintering at 1450-1500°C while LSGM was 25-28%. Overall, the firing shrinkages of LSGM samples were 15%-20% higher than that of LSCM samples prepared under the same conditions. The large firing shrinkage differences indicate that it may be difficult to cofire the LSGM thin layer coating onto the LSCM support during cell fabrication.

![Figure 2. Firing Shrinkages of LSCM, LSGM, LSCM+LSGM, and LSGM tube samples.](image)

Despite the large firing shrinkage differences, the TECs of the sintered samples (Figure 3), however, show closer match (the TEC differences are less than $1 \times 10^{-6} ^\circ C$) in the fuel cell operating temperature range (600-900°C). For example at 800°C, the average TEC of LSCM is $11.2 \times 10^{-6} ^\circ C$ compared with $12.1 \times 10^{-6} ^\circ C$ for LSGM. The LSCM sample fired at 1500°C had approximately $0.5 \times 10^{-6} ^\circ C$ larger TEC than that fired at 1450°C.

X-ray Diffraction

To examine the interactions start conditions and identify any reaction products between the LSCM and LSGM, XRD patterns were obtained from the pellets fired at 1300, 1400, 1450 and 1500°C for 2 h, and 1500°C for 6, 12 and 72 h, as shown in Figure 4. There were no reactions in samples fired under 1500°C for 2 h. The XRD results indicate reactions occurred in the samples sintered at 1500°C and dwelled for 6 h and longer.
Figure 3. Linear thermal expansion and TECs of LSCM and LSGM samples.

Figure 4. XRD Patterns of LSCM and LSGM Mixture (50:50 wt%) fired at various firing temperatures and dwell times. Interaction phases appeared in the samples fired at 1500°C for 6 h and above.
Energy Dispersive Spectrometry

Reflecting the XRD results, we can see the interfacial zone from the SEM images and EDS results (Fig. 5-6). EDS were run on all the samples. Figure 5 shows the line scan results on the sample fired at 1500°C for 72 h. It indicates the compositions changed gradually through the interfacial layer. To clearly see the element changes, and also compare with the starting compositions, a multipoint scan on the same sample, but in a wider range (larger scale) was conducted. The results (Fig. 6) gave the same trends as the line scans with an interlayer thickness of approximately 100 µm. Out of the interlayer region, the compositions were close to the start compositions of the powders. Element mappings of the sample were consistent with the line scan and point-scan results.

![Figure 5. EDS Line scan results of the LSCM-LSGM bi-layer sample fired at 1500°C for 72 h.](image)

It was noticed that the bi-layered sample fired at 1400°C for 2 h also had an interlayer zone (approximately 50µm), although the XRD data indicated there were no interactions. This may be due to the formation of a thin layer mixture of LSGM and LSCM powders at the surfaces when the bi-layer sample was pressed. Pre-firing the LSGM and LSCM...
pellets separately, and then annealing them with polished contacting surfaces would eliminate this effect.

Figure 6. EDS Multipoint scan results of the LSCM-LSGM Bi-layer sample fired at 1500°C for 72 h. The group points on the far left-hand side were the LSGM powder start compositions while the group points on the far right-hand side were the LSCM compositions.

**Microstructure**

From the SEM images of LSCM and LSGM mixture samples (Figure 7), one can see that there were large and small grains. LSCM particles may sinter first at lower temperatures (comparing to LSGM) and leave the later-sintered LSGM particles in the LSCM interface boundaries. Further EDS analysis is underway to determine the compositions of the two groups of grains.
Anode support tubes were extruded and fired at various temperatures to optimize the microstructures for LSGM electrolyte coating. Figure 8 shows the microstructural changes in the LSCM anode during firing. Extruded and dried green body (Fig. 8 (a)) was reasonably dense. With the increase of firing temperatures, ceramic bonds were formed. At 1200-1300°C, a good anode microstructure with sufficient porosity can be obtained. However, further increase in firing temperature, for example to 1400°C or even 1500°C, showed a significant decrease in porosity. This indicates that if the electrolyte layer needs to be co-sintered with the anode at temperatures above 1400°C, pore former is necessary in the start LSCM anode powder to maintain sufficient porosity after sintering.

![Figure 8](image_url)

**Figure 8. SEM images of the LSCM anode green body during firing (a) extruded and dried green body, (b) extruded and dried anode at 1100°C, (c) extruded and dried anode at 1200°C, (d) extruded and dried anode at 1300°C, (e) extruded and dried anode at 1400°C, and (f) extruded and dried anode at 1500°C.**

**CONCLUSIONS**

LSCM anode material is chemically compatible with the LSGM electrolyte under 1500°C for 2 h in air; interfacial reactions were detected in the samples prepared at 1500°C for 6 h and above. The interface zone was 100-150 μm in the pressed bi-layered LSGM/LSCM samples. The TEC of LSCM is $1 \times 10^{-6}$/°C smaller than that of LSGM; however the firing shrinkages of LSGM samples are 15%~20% higher than that of LSCM prepared under the same conditions. Further study on long term durability especially under reducing environments is needed and a pore former to increase the LSGM anode porosity after cofiring with the LSGM electrolyte is necessary.
Figure 8. SEM images of LSCM tubes at (a) green stage and fired at various temperatures for 2 h: (b) 1100°C, (c) 1200°C, (d) 1300°C, (e) 1400°C, and (f) 1500°C.

REFERENCES

1. N. Q. Minh and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, Elsevier Science B.V., Amsterdam, (1995).
2. T. Ishihara, H. Matsuda and Y. Takita, *J. Am. Chem. Soc.*, 116, 3801-3803 (1994).
3. M. Feng and J. B. Goodenough, *Eur. J. Solid State Inorg. Chem.*, 31, 663-672 (1994).
4. K. Huang, R. S. Tichy, J. B. Goodenough, *J. Am. Ceram. Soc.*, 81, 2565-2575 (1998).
5. P. M. T. Mathews, M. P. Antony, J. R. Sellar, B. C. Muddle, *Solid State Ionics*, 135, 397-402 (2000).

6. P. Huang, A. Horky and A. Petric, *J. Am. Ceram. Soc.*, 82, 2402-2406 (1999).

7. X. Zhang, S. Ohara, R. Maric, H. Okawa, T. Fukui, *Solid State Ionics*, 133, 153-160 (2000).

8. X. Zhang, S. Ohara, H. Okawa, R. Maric and T. Fukui, *Solid State Ionics*, 139, 145-152 (2001).

9. N. Maffei and G. Silveira, *Solid State Ionics*, 159, 209-216 (2003).

10. K. Yamaji, T. Horita, M. Ishikawa, H. Sakai and H. Yokokawa, *Solid State Ionics*, 121, 217-224 (1999).

11. Y. Du and N. M. Sammes, *J. Power Sources*, 136, 66 (2004).

12. I. Taniguchi, R. C. v. Landschoot and J. Schoonman, *Solid State Ionics*, 160, 271 (2003).

13. M. Joseph, P. Manoravi, H. Tabata, T. Kawai, *J. App. Physics*, 92, 997-1001 (2002).

14. N. R. T. Mathews, J. R. Sellar, B. C. Muddle, *Solid State Ionics*, 128, 111-115 (2000).

15. P. Majewski, M. Rozumek, C. A. Tas, F. Aldinger, *J. Electroceramics*, 8, 65 (2002).

16. S. Hui, X. Ma, Z. H., J. Dai, J. Roth, T. D. Xiao and D. E. Reisner, in *SOFC-VIII*, S. C. Singhal and M. Dokiya, Editors, *PV2003-07*, p. 330, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).

17. N. Q. Minh, *J. Am. Ceram. Soc.*, 76, 563-588 (1993).

18. K. S. J. R. H. Song, D. R. Shin, H. Yokokawa, *J. Chemical Engineering of Japan*, 34, 154-157 (2001).

19. H. Yokokawa, N. Sakai, T. Kawada and M. Dokiya, *Solid State Ionics*, 52, 43 (1992).

20. S. Tao and J. T. S. Irvine, *Nature Materials*, 2, 320 (2003).

21. S. Tao and J. T. S. Irvine, *J. Electrochem. Soc.*, 151, A252 (2004).

22. K. Huang, M. Feng, J. B. Goodenough and M. Schmerling, *J. Electrochem. Soc.*, 143, 3630 (1996).

23. T. Horita, K. Yamaji, N. Sakai, H. Yokoawa, A. Weber and E. Ivers-Tiffe, *Solid State Ionics*, 138, 143 (2000).

24. M. Koyama, C. Wen, T. Masuyama, J. Otomo, H. Fukunaga, K. Yamada, K. Eguchi and T. Takahashi, *J. Electrochem. Soc.*, 148, A795 (2001).

25. F. Lecarpentier, H. L. Tuller and N. Long, *J. Electroceramics*, 5, 225 (2000).

26. S. J. B. M. Sahibzada, R. A. Rudkin, J. A. Kilner, *Solid State Ionics*, 113-115, 285 (1998).

27. T. K. S. Wang, S. Nagata, T. Honda, T. Kaneko, N. Iwashita, M. Dokiya, *Solid State Ionics*, 146, 203 (2002).

28. N. M. Sammes, Y. Du, N. Padture, M. Wei, X. Huang, G. Ju, J. Wu and K. Reifsnider, in *First International Conference on Fuel Cell Development and Deployment*, (2004).