MATERIALS SYSTEM FOR INTERMEDIATE TEMPERATURE (600-800°C) SOLID OXIDE FUEL CELLS BASED ON DOPED LANTHANUM-GALLATE ELECTROLYTE

Wenquan Gong, Srikanth Gopalan and Uday B. Pal
Department of Manufacturing Engineering
Boston University, Boston MA 02215, USA

ABSTRACT

AC complex impedance spectroscopy studies were conducted between 600-800°C on symmetrical cells that employed LSGM electrolyte. The objective of the study was to identify the materials system for fabrication and evaluation of intermediate temperature SOFCs. Cathode materials investigated include LSM, LSCF, LSM-LSGM, and LSCF-LSGM composites. The anode materials were Ni-GDC and Ni-LDC composites. Experiments conducted with the anode materials investigated the effect of having a barrier layer of GDC or LDC in between the LSGM electrolyte and the Ni-composite anode to prevent adverse reaction of the Ni with lanthanum in LSGM. The ohmic and the polarization resistances of the system were obtained over time as a function of temperature, firing temperature, thickness, and the composition of the electrodes. The study revealed important details pertaining to the ohmic and the polarization resistances of the electrode as they relate to stability and the charge-transfer reactions that occur in such electrode structures.

INTRODUCTION

Rare earth elements doped CeO₂ and Sr, Mg doped LaGaO₃ (LSGM) are currently considered as promising electrolyte materials for intermediate-temperature SOFCs. LSGM has generated a lot of interest in recent years after it was first reported by Goodenough et al. (1) to have significantly higher oxygen-ion conductivity than conventional yttria-stabilized zirconia (YSZ) between 600-800°C and negligible electronic conductivity over a wide range of oxygen partial pressures employed under SOFC operating conditions. On the other hand, although doped ceria has comparable oxygen-ion conductivity, it develops significant electronic conductivity under reducing conditions (fuel gas environment) between 700-800°C (2). Therefore, compared to the LSGM electrolyte, doped ceria is not as good a choice for the SOFC electrolyte above 700°C.

The electrode kinetics has a strong exponential dependence on temperature and so lower operating temperatures would result in significant polarization losses, particularly charge-transfer polarization losses at the electrode-electrolyte interfaces. This will drastically reduce the cell efficiency. Hence, if the operating temperature of the SOFC is to be lowered, an entirely new material system for the electrodes is needed as well. This paper reports the results of several prospective anode and cathode materials for application in...
Intermediate-Temperature (600-800°C) SOFCs employing LSGM electrolyte. Cathode materials that are studied include state-of-the-art electrode material for YSZ electrolyte SOFCs (Sr-doped lanthanum manganite or LSM), Sr-doped lanthanum cobalt iron oxide (LSCF), porous composite electrodes comprising LSM-LSGM and LSCF-LSGM compositions. These cathode materials have adequate electronic conductivity to function as a cathode but their interfacial polarization resistance as a function of temperature needs to be determined because that is likely to influence their selection for application in intermediate-temperature SOFCs. The choice of anode materials focused on Ni-doped ceria composite electrodes. Nickel is a well-known SOFC anode material, and acts as the fuel side electrocatalyst and current collector. Use of lanthanum or gadolinium doped ceria as the oxygen-ion-conducting oxide in the anode would buffer the thermal expansion mismatch between the anode and the electrolyte and also result in lowering the charge-transfer polarization due to its mixed-conducting property (2); La-or-Gd-doped ceria conducts both oxygen ions and electrons. It has been observed that the Ni phase in the anode reacts with the perovskite LSGM phase forming an insulating lanthanum nickelate phase and that causes the ohmic and anodic polarization resistances to increase with time. In response to this observation the concept of applying a doped (lanthanum or gadolinium) ceria barrier or buffer layer to prevent direct contact and reaction of Ni with the LSGM electrolyte is also investigated. Since the doped ceria has sufficiently high oxygen-ion conductivity and the buffer layer will be thin (< 5 μm), it is not expected to increase the ohmic polarization resistance of the cell. The purpose of this work was to identify a possible material system and structure for the intermediate-temperature SOFC.

**EXPERIMENTAL**

**Symmetrical Cell Fabrication**

Electrolyte powders of the composition $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) were synthesized by mixing and ball-milling high purity precursors of lanthanum carbonate, strontium carbonate, gallium oxide and magnesium oxide in appropriate stoichiometric ratios and calcining at a temperature of 1200°C for 4 hours in air. The calcined powders were lightly crushed using alumina mortar and pestle and the calcination step was repeated for completing the solid-state reaction. Electrode materials such as $\text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_3\text{O}_7$ (LSM), $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.2}\text{Co}_{0.3}\text{O}_3$ (LSCF), $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_2$ (GDC) and $\text{Ce}_{0.6}\text{La}_{0.4}\text{O}_2$ (LDC) were also made using the same mixing and calcination techniques. X-ray powder diffraction analysis confirmed the composition, phase and purity of the material. All the synthesized powders and NiO powder purchased from Baker were then separately ball-milled in methanol. Laser Scattering Particle Size Distribution Analyzer (Horiba LA-910) was periodically used at different intervals of the ball milling process to determine the particle size and distribution. The ball milling process was stopped when the desired particle size and distribution were obtained.

Calcined and milled LSGM powders at room temperature were die-pressed at 10000psi pressure into pellets and sintered in air at 1450°C for 4 hours. The sintered LSGM pellets were 1.4 mm thick and 2 cm in diameter. The LSGM pellets were then all finely ground to a uniform 1 mm thickness using diamond-grinding discs. LSM-LSGM, LSCF-LSGM, NiO-GDC, and NiO-LDC composite electrodes were prepared by thoroughly mixing desired amounts of the powders. The electrode powders (LSM, LSM-LSGM, LSCF, LSCF-LSGM, NiO-GDC, and NiO-LDC) were each dispersed in α-terpeniol solvent to...
form a paste. For the cathode electrodes and the anode without the buffer layer, the ground LSGM electrolyte pellets were masked with Scotch™ tape to form an outer ring on both sides and the electrode pastes were painted smoothly on the open circular surfaces. The painted LSGM electrolyte pellets were air-dried, masks removed and fired in air at elevated temperature for 2 hours. The firing temperature was 1100°C for all the cathodes and 1200-1300°C for the anodes. All electrodes had the same effective area of around 1.33 cm². When GDC or LDC buffer layers were employed between the Ni-doped-ceria composite anode and the LSGM electrolyte, very fine GDC or LDC powders were dispersed in α-terpinol solvent to form a paste which was painted on both sides of the LSGM electrolyte. They were air dried and sintered at 1200-1300°C and the anodes were then applied following the procedure described earlier. For the cathode materials, two pieces of platinum mesh were co-sintered on both electrode surfaces to act as current collectors. Lead wires of Pt were used to connect the platinum-mesh current collectors to the measuring instrument. For the anode materials, pieces of nickel mesh were pressed over the electrode surfaces and co-sintered in a reducing atmosphere. Nickel lead wires were used to connect the nickel-mesh current collectors to the measuring instrument.

**AC Impedance Characterization**

The symmetrical cell was exposed to the same oxidizing (cathodic), or reducing (anodic) atmosphere on both sides and a two-probe configuration was used to measure the impedance spectra. During measurements a constant flow of air was maintained for the cathode materials, and anode materials were maintained at forming gas (95% Argon-5% Hydrogen) bubbled through water at 25°C. Impedance measurements were made in the temperature range of 600-800°C in 50°C increments for all the samples using a Perkin-Elmer potentiostat/galvanostat (model 263A) and Solartron analytical-frequency-response analyzer (model 1250). For all samples measured in this investigation, the impedance spectra consisted of a single depressed arc. The high-frequency intercept of the impedance plot on the real axis gives the ohmic resistance of the cell (R_s). The low-frequency intercept gives the total resistance (R_s + R_p) of the cell. The total interfacial polarization resistance of the electrode (R_p) is then extracted by subtracting the high-frequency intercept from the low-frequency intercept on the impedance plot.

The impedance measurements were performed both as a function of composition for the LSM-LSGM, Ni-GDC, and Ni-LDC electrodes and as a function of electrode thickness for the LSCF electrodes. After electrochemical testing, the samples were sectioned, epoxy mounted and polished. Optical microscopy and scanning electron microscopy were used to measure the grain size, porosity and thickness of the electrodes and confirm the consistency of the microstructure. Electron microprobe analysis and wavelength dispersive spectroscopy were also used to determine diffusion profiles of the elements at the interfaces.

**RESULTS AND DISCUSSION**

**Electrode Microstructures**

The microstructure of the composite cathode and anode is crucial to achieving high power densities while operating the cell. Fine microstructure, fine connected porosity and
well dispersed ionic and electronic conductors are essential for a good electrode exhibiting low charge-transfer or interfacial polarization. It has been theoretically shown by Tanner et al. (3) that the effective charge-transfer resistance scales as the square root of the grain size of the electrode material. However, there is a limit to the acceptable pore size. When the electrode pore size is comparable to the mean free path of the gases being transported in and out of the electrodes, the cell performance is dominated by concentration (mass-transfer) polarization. To achieve a balance between these two conflicting requirements, graded electrode structures with a finer microstructure and porosity close to the electrolyte and coarser microstructure and larger porosity away from it needs to be developed for the supporting electrode. In this investigation we will focus our attention on the fine microstructure that is needed at the electrode interface with the electrolyte.

Fractured surfaces of the LSM, LSM-LSGM, LSCF, LSCF-LSGM, Ni-GDC, and Ni-LDC electrodes and their interfaces with the electrolyte/barrier layer show that these electrodes have similar microstructures in terms of their interfacial adherence with the LSGM electrolyte, porosity and grain size. The grain size is on the order of 1-2 μm and the porosity is between 50-55% measured in terms of percentage area of the pore from the micrographs using Adobe Photoshop software. As a sample, cross section of the fractured surface of the LSM-LSGM electrode/electrolyte interface along with the back-scattered electron image of the electrode is shown in Fig. 1. Based on the grain size, porosity and thickness (10-60 μm) of the electrodes, gas diffusion is not expected to control the interfacial polarization process particularly for small applied potentials that were used for the AC impedance measurements.

![Figure 1](image)

Selection of Cathode Material

In order to lower the interfacial polarization it is well known that the electrode needs to be a mixed conductor (have both electronic and oxygen ion conductivities) (2). Since, LSM is a p-type semi-conductor, it is advantageous to provide the oxygen ion conductivity by mixing it with LSGM. On the other hand, since the LSCF is already a mixed conductor, mixing it with LSGM is not expected to significantly lower the interfacial polarization. However, it is to be noted that there is a 50% mismatch in thermal expansion coefficient between the LSCF electrode material and LSGM.
electrolyte material (4,5). Therefore from the point of view of lowering the interfacial thermal stresses it is desirable to have a LSCF-LSGM composite electrode as the cathode. To explore these concepts, several cathode materials, LSM, LSCF, LSM-LSGM and LSCF-LSGM composite electrodes were studied for possible application in Intermediate Temperature (IT)-SOFCs based on the LSGM electrolyte. Fig. 2 shows a comparison of the polarization resistances of the above cathode materials as a function of temperature measured using impedance spectroscopy on symmetric cells as outlined earlier. The polarization resistance is plotted as inverse resistance versus inverse temperature.

Figure 2. Comparison of interfacial polarization resistances of various cathode materials on LSGM electrolyte.

From these studies of cathode materials compatible with LSGM electrolyte it was determined that a 50vol% LSCF-LSGM porous composite would serve as the best cathode material. As can be seen from Fig. 2, the composite LSCF-LSGM cathode has an interfacial polarization resistance that is several orders of magnitude lower than the LSM-LSGM composite cathode, although as expected the later is lower than the conventional single-phase LSM electrode. The interfacial polarization resistance of the LSCF-LSGM composite cathode is also slightly lower than the single phase LSCF cathode. In addition, considering the thermal expansion coefficient (TEC) mismatch between the LSCF cathode and LSGM electrolyte, the LSCF-LSGM composite will also be preferred over the single phase LSCF material. Our investigations of mixed-conducting cathode materials have also revealed a dependence of polarization resistance on electrode thickness. The polarization resistance of LSCF cathode on LSGM electrolyte is shown in Fig.3 as a function of thickness. The polarization of the cathode layer initially decreases sharply with increasing electrode thickness and then levels off asymptotically. The initial decrease of the cathode polarization resistance can be rationalized on the premise that increasing the electrode thickness results in an increase in the number of electrochemical reaction sites, i.e. total three-phase boundary length in the case of composite cathodes, or total pore area in the case of mixed ionic-electronic conductors. The subsequent leveling off of the polarization resistance is due to the fact that above a certain critical electrode thickness the migration of the oxygen ions from the reaction sites to the electrode/electrolyte interface become rate controlling. Thus, there is a certain critical
thickness beyond which the cathodic polarization resistance shows no further decrease with increasing thickness. This critical electrode thickness has been shown to be a strong function of the microstructure (grain size) and porosity (5), i.e. finer the microstructure and porosity, smaller is the critical thickness. Based on our cathode microstructure, a thickness of 40 µm is sufficient to minimize the interfacial polarization resistance.

**Figure 3.** Variation of LSCF interfacial polarization resistance over LSGM electrolyte as a function of thickness at 800°C.

Selection of Anode Material

Nickel is a well-known SOFC anode material, and acts as the fuel side electrocatalyst and current collector. However, Ni reacts with the LSGM and forms insulating phases (lanthanum nickelates) at elevated temperatures (6). GDC is an excellent oxygen-ion conductor, is chemically and mechanically compatible with the LSGM electrolyte and has electronic conductivity under reducing conditions (2,4). Therefore, Ni-GDC cermet is expected to be an effective anode if its reaction with the LSGM electrolyte can be prevented. Therefore the use of a layer of doped ceria between the LSGM electrolyte and Ni-GDC anode to prevent direct contact between the Ni in the anode with the lanthanum in the LSGM electrolyte was explored.

**Ni-GDC Electrodes with GDC Buffer Layer on LSGM Electrolyte**

It was apparent from the wavelength-dispersive-spectroscopy (WDS) analysis of these samples that the GDC barrier layer allowed lanthanum diffusion from the LSGM electrolytes (Fig. 4). Lanthanum diffusion from LSGM into GDC leads to the formation of Ce$_{1-x}$La$_x$Gd$_2$O$_3$ solution in the GDC buffer layer and resistive phases LaSrLa$_2$O$_7$ or LaSrGaO$_4$ at the LSGM electrolyte interface (7). The latter significantly increases the ohmic resistance of the cell. By decreasing the sintering temperature of the GDC buffer layer it is possible to decrease the lanthanum diffusion, but this leads to incomplete densification and poor interfacial adherence of the GDC buffer layer to the LSGM electrolyte. This causes penetration of the Ni-GDC anode slurry into the LSGM electrolyte surface through the porous GDC buffer layer and during testing results in a time-dependent increase of interfacial polarization resistance similar to when the GDC...
buffer layer is absent. In conclusion, it was determined that the GDC did not serve as an effective buffer layer between the LSGM electrolyte and the Ni-GDC composite anode.

**Figure 4. Diffusion profile of lanthanum in the GDC buffer layer.**

**Ni-GDC and Ni-LDC Electrodes with LDC Buffer Layer on LSGM Electrolyte**

Next, lanthanum doped ceria (LDC) was employed as the barrier layer between the LSGM electrolyte and the Ni-composite anode in order to limit or eliminate lanthanum diffusion from the LSGM electrolyte into the barrier layer. The idea was to eliminate the lanthanum chemical potential gradient at the interface that results in lanthanum diffusion. It is to be noted that unlike the LSGM electrolyte which has a perovskite phase, the LDC barrier layer has a fluorite structure. The Ni in the anode is not expected to react with the lanthanum in the LDC barrier layer as long as the La content in the LDC is below 50 mol% in the cationic site (8). It was observed that, unlike the GDC, when the LDC barrier layer had 40 mol% La in the Ce site and was sintered at 1300°C, there was no detectable La diffusion from the LSGM electrolyte. The 40 mol% Lanthanum doped ceria (LDC) likely has the same La chemical potential as in the LSGM and therefore prevented the La diffusion between LSGM electrolyte and the LDC buffer layer (8). Also since the La content was below 50 mol%, it was expected to be stable in contact with the Ni-composite anode. Since LDC was being employed as the barrier layer, it was logical to also investigate Ni-LDC composite along with the Ni-GDC composite anodes.

The temperature dependence of the interfacial polarization resistance for symmetrical cells with LSGM electrolyte and Ni-LDC and Ni-GDC (50 or 70 v% Ni) composite electrodes sintered at 1300°C over the LDC buffer layer (sintered at 1300°C) is shown in Fig. 5. As can be seen from Fig.5, the Ni-LDC (70 v% Ni) electrode has the largest interfacial polarization resistance, especially at lower testing temperatures, i.e. 600-700°C. While all other electrodes, i.e. Ni-LDC5050 (50 v% Ni), Ni-GDC7030 (70 v% Ni), and Ni-GDC5050 (50 v% Ni), had almost the same interfacial polarization resistance. At higher testing temperature, i.e. 700-800°C, the polarization resistances of all the electrodes approached one another. Moreover, for Ni-LDC5050, Ni-GDC7030 and Ni-
GDC5050 electrodes, the polarization resistance did not decrease much when the testing temperature was increased from 600°C to 800°C. This meant that from the point of view chemical reactivity and thermal expansion mismatch it would be preferable to select Ni-LDC5050 as the composite anode for the LSGM electrolyte with the LDC barrier layer.

Figure 5. Comparison of the effect of the composition of the Ni-doped ceria composite electrodes on the interfacial polarization resistance as a function of temperature.

Time dependence of the $R_p$ at 800°C of the LSGM symmetrical cells with Ni-LDC and Ni-GDC (70 v% Ni) composite electrodes with LDC buffer layer is shown in Fig. 6.

Figure 6. Time dependence of the interfacial polarization resistances of cermet anodes with and without the LDC barrier layer over LSGM electrolyte at 800°C.

Also shown in the same figure is the interfacial polarization resistance of the Ni-GDC (70 v% Ni) composite electrode without the buffer layer. The interfacial polarization resistances of both Ni-LDC and Ni-GDC electrodes with LDC buffer layer were stable over a period of two weeks, whereas the interfacial polarization resistance of the Ni-GDC electrode without the LDC buffer layer increased continuously with time due to the reaction between Ni and the lanthanum in the LSGM electrolyte.
Materials System for the Intermediate Temperature Solid Oxide Fuel Cell

Based on this investigation the desirable materials system for the SOFC with LSGM electrolyte will consist of: (a) 50% by volume of LSCF-LSGM composite cathode having a fine microstructure (1-2μm grains), porosity of 40-50% and thickness of at least 30-40 μm, (b) a dense adherent barrier layer (5μm) of lanthanum doped ceria (LDC) between the LSGM electrolyte and the anode, and (c) 50% by volume of Ni-LDC composite anode having a fine microstructure near the LDC buffer layer, coarser microstructure away from the buffer layer and a porosity of 40-50%. Since the design is based on an anode-supported cell, the anode can be 1-2 mm thick and the fine microstructure region at least 30-40 μm.

The desired cell structure is schematically shown in Fig. 7.

Figure 7. Schematic of an anode supported Intermediate Temperature Solid Oxide Fuel Cell based on LSGM electrolyte.

CONCLUSIONS

The materials system for the Intermediate-Temperature (600-800°C) Solid Oxide Fuel Cell is based on the LSGM electrolyte. Electrode materials were investigated by using impedance spectroscopy and symmetrical cell arrangement. Among the cathode materials (LSM, LSM-LSGM, LSCF and LSCF-LSGM), pure LSM electrode has the worst interfacial polarization resistance. The addition of LSGM electrolyte material to the LSM electrode increases the mixed-conducting boundary with the gas phase and lowers the interfacial polarization resistance. Mixed-conducting LSCF electrode however, has much lower polarization resistance compared to the LSM-LSGM composite electrodes. Although adding LSGM electrolyte material to the LSCF electrode doesn’t improve the cell performance very much, it can buffer the larger thermal expansion coefficient of
LSCF compared to the LSGM electrolyte. As expected, the polarization resistance of the LSCF electrode decreased asymptotically as the electrode thickness is increased. The optimum electrode thickness for the given microstructure was determined to be around 30-40μm. As Ni in the anode material reacts with lanthanum in the LSGM electrolyte it increases the interfacial polarization resistance. A buffer layer between the LSGM electrolyte and Ni-GDC anode is necessary to prevent this reaction. However, if the buffer layer is GDC, La diffusion occurs from the LSGM electrolyte. LDC appeared to serve as an effective buffer layer between the LSGM electrolyte and the Ni-composite anode. Polarization resistance of several Ni-GDC and Ni-LDC composite anodes with LSGM electrolyte and LDC buffer layer sintered at 1300°C was also investigated using impedance spectroscopy and symmetrical-cell arrangement. Ni-LDC (70 v% Ni) electrode has the largest interfacial polarization resistance, while all other electrodes, i.e. Ni-LDC (50 v% Ni), Ni-GDC (70 v% Ni), and Ni-GDC (50 v% Ni), had almost the same interfacial polarization resistance. From the point of view chemical reactivity and thermal expansion coefficients it would be preferable to select Ni-LDC as the composite anode for the LSGM electrolyte with a thin LDC barrier layer.

ACKNOWLEDGMENT

Support from US-DOE in the form of university coal research grant (grant number: DE-FG26-02NG41539) is gratefully acknowledged.

REFERENCES

1. M. Feng, and J. B. Goodenough, *Eur. J. Solid State Inorg. Chem.*, 31, 663 (1994).
2. N. Q. Minh and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, Elsevier Publishing Company Inc., New York, (1995).
3. C. W. Tanner, K. Z. Fung and A. V. Virkar, *J. Electrochem. Soc.*, 144, 21 (1997).
4. H. Hayashi, M. Suzuki, and H. Inaba, *Solid State Ionics*, 128, 131 (2000).
5. A. Petric, P. Huang, and F. Tietz, *Solid State Ionics*, 135, 719, (2000).
6. X. Zhang, S. Ohara, R. Maric, H. Okawa, T. Fukui, H. Yoshida, T. Inagaki, and K. Miura, *Solid State Ionics*, 133, 153 (2000).
7. M. Hrovat, A. Ahmad-Khanlou, Z. Samardžija, and J. Hole, *Materials Research Bulletin*, 34, 2027-2034 (1999).
8. K. Huang, J. H. Wan, and J. B. Goodenough, *J. Electrochem. Soc.*, 148, A788 (2001).