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Electrocatalytic Properties of Intermediate Temperature-SOFC Cathode/LSGMC Interfaces

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Electrocatalytic properties of the interfaces between $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ (LSGMC) electrolyte and various cathodes: comprised of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC), and $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) in composite forms (70wt.%) with LSGMC (30wt.%) were investigated under both oxygen reduction and evolution conditions. All the oxides were synthesized using the glycine-nitrate process (GNP). Symmetrical electrochemical cells were investigated with three-electrode linear *dc* polarization and *ac* impedance spectroscopy. For the composite SSC-LSGMC cathode/LSGMC interface, the cathodic overpotential under 1 A/cm^2 current density was as low as 0.085 V at 700°C, 0.062V at 750°C and 0.051V at 800°C in air. Composite LSCF-LSGMC cathode/LSGMC interfaces were found to have about twice the exchange current density of composite SSC-LSGMC/LSGMC interfaces at 700°C.

1. Introduction

Solid oxide fuel cell (SOFC) systems are of particular interest as electrochemical power generators that can operate on various hydrocarbon fuels with high fuel-to-electrical energy conversion efficiency. The traditional materials set used in SOFC systems is based upon a yttria-stabilized zirconia (YSZ) electrolyte that has proven performance and stability characteristics at operating temperatures up to 1000°C (1). Reducing the operating temperature of an SOFC system could result in significant cost and degradation reduction benefits, which could in turn significantly improve SOFC commercialization potential (2).

Most of the SOFC manufacturers are developing systems on the basis of SOFC stacks that can operate in the intermediate temperature (IT) range of 700-850°C (2). This can be achieved by optimizing powder features, materials processing and microstructural parameters of the traditional YSZ materials set or by using other materials sets. $La_{1-x}Sr_xGa_{1-y-z}Mg_yO_{3-\delta}$ perovskite (LSGM) is regarded as a promising electrolyte material for SOFC systems because of its high ionic conductivity in the intermediate temperature range and because it has exhibited thermal and chemical stability in full fuel cell tests. Kuroda et al. (3) reported on a low-temperature SOFC using the perovskite-type oxide of doped $LaGaO_3$ as an electrolyte. In particular, $LaGaO_3$ where Sr was substituted on the La-site and Mg and Co on the Ga-site ($La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2-x}Co_xO_{3-\delta}$: LSGMC) (4-6) was highly interesting because of its high oxide ion conductivity that at 650°C LSGMC was

found to be comparable to that of YSZ at 1000°C, and the high transference number of oxide ion (over 0.8).

Xia et al. have found good performance of strontium-doped samarium cobaltite, $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC), for use as a cathode material for SOFCs with YSZ, LSGM, and doped ceria electrolytes (7, 8). SSC-LSGM composites synthesized using the solid-state reaction method exhibited acceptable activity for oxygen reduction as cathodes for IT-SOFC based on LSGM electrolytes (9). Koyama et al. prepared an SSC powder by the co-precipitation method and reported an electrode resistance of about $0.04\Omega cm^2$ at 800^oC (10). Wang and Zou (11) investigated SSC powders that were synthesized using the glycine–nitrate process and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{3-\delta}$ (LSGMC5) powders that were synthesized using a sol-gel method. The electrode resistance of composite SSC-LSGMC5 was about 0.07 Ωcm^2, and the overpotential under 1 Acm^{-2} current density was 0.077 V at 700^oC in oxygen (11). In addition to SSC-LSGMC composites, strontium- and iron-doped lanthanum cobaltite (LSCF) has also been widely studied as a promising cathode material for IT-SOFC based on LSGM electrolytes (12-17).

The current research focuses on development of good cathode-electrolyte interface performance in the intermediate temperature operating range using a LSGMC-based materials set. $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ (LSGMC) has been chosen as the composition because of its good oxide ion conductivity at intermediate temperatures (4). All electrode and electrolyte materials were synthesized in-house using GNP. GNP was followed by a unique powder processing (including ball-milling with sufficient binders, surfactants and plasticizers), screen-printing and sintering procedure designed to effectively produce cathode-electrolyte interfaces for study. The focus is on characterizing the interfacial electrocatalytic properties of the cathode/LSGMC interfaces produced. SSC with LSGMC and LSCF with LSGMC composites cathodes were produced on LSGMC electrolyte substrates for this study.

2. Experimental

2.1 Materials Synthesis

Cathode and electrolyte materials of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC), $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ (LSGMC) were synthesized by GNP method as presented in Figure 1.

Using LSGMC as an example, the LSGMC powder was prepared by dissolving the proper stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa Aesar), $Sr(NO_3)_2$ (98%, Alfa Aesar), $Ga(NO_3)_3 \cdot xH_2O$ (99.999%, Alfa Aesar), $Mg(NO_3)_2 \cdot 6H_2O$ (98.0-102.0%, Alfa Aesar), and $Co(NO_3)_2 \cdot 6H_2O$ (98.0-102.0%, Alfa Aesar) into distilled water to form an aqueous solution. Then a particular amount of glycine was added to produce a molar ratio of 0.75 of glycine to NO_3^- group. Spontaneous combustion of the solution was facilitated in a glass beaker sitting on a hotplate. The resultant ash was calcined in air at 900°C for 2 h to remove carbon residue and to produce the desired phase of the $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ perovskite structure. In a similar procedure, $Sm_{0.5}Sr_{0.5}CoO_3$ and $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ powders were synthesized.
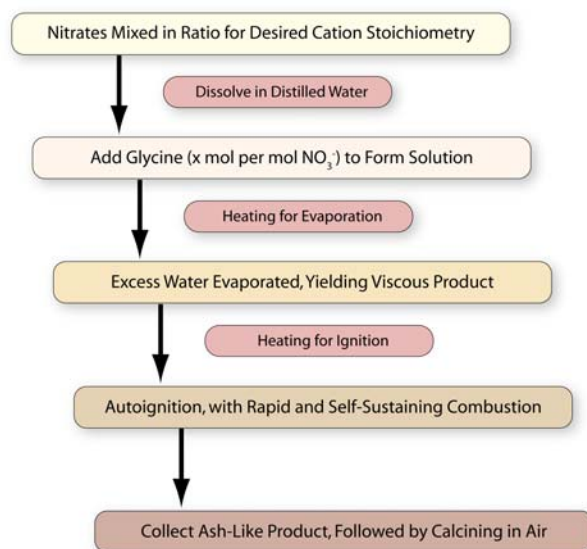
Figure 1. Flow chart of the glycine–nitrate process (GNP) use to synthesize perovskite-type oxides

2.2 Material Properties Characterization

The phase and purity of the materials produced by GNP were determined by normal X-ray diffraction (XRD) technique with *Bruker* D5000. The microstructural features of electrolytes, cathodes and cathode/electrolyte interfaces were characterized by Scanning Electron Microscopy (SEM, Zeiss Ultra55).

2.3 Electrochemical Characterization

For conductivity measurement of the electrolyte materials produced, LSGMC powder (calcined at $900^{o}C$ for 2 h) was pressed into disks. The sintering temperature of the LSGMC disks was $1400°C$ for 5 h in air to obtain a density greater than 97.5% of the theoretical value. Resulting pellet disks were 0.9 cm in diameter and 0.12 cm thick. Pt paste (Engelhard, A3788A) was brush painted onto both sides of the pellet and Pt gauze (Alfa Aesar, 52 mesh woven from 0.1 mm dia wire, 99.9% Pt) was buried in the Pt paste for current-collection. The disks with Pt electrodes were fired at $1050^{o}C$ in air for 0.5 h. Pt wires were welded to the platinum gauze in a four-probe configuration. The conductivity measurements were conducted in air using a Solartron 1260A frequency analyzer and 1480A electrochemical interface. The *AC* impedance spectra in the frequency range of 100 kHz to 0.1 Hz with excitation voltage amplitude of 5 mV were taken to ensure a linear response.

Symmetric electrode cells, as shown in Figure 2, were prepared to study the electrochemical properties of the composite SSC and LSCF cathodes on LSGMC electrolyte substrates. Electrolyte substrate disks were made with the same procedure to be approximately 300 µm thick and 2 cm in diameter after sintering. Cathode inks were made for screen printing by adding an organic binder (Heraeus, V006) into cathode powders and grinding the mixture with an agate mortar and pestle. The samples with symmetric cathodes were manufactured by screen-printing cathode inks as 1cm x 1cm

square shaped patterns that were accurately aligned on opposite sides of the LSGMC electrolyte substrates, following by firing at 1100°C in air for 2 h.
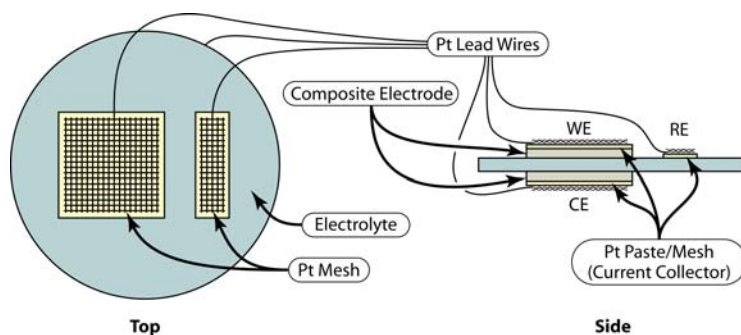

Figure 2. Schematic diagram of 3-electrode configuration used for *dc* polarization measurements (not drawn to scale)

The sintered cathode thickness was around 20–30 μm. Then Pt paste was brush-painted on both sides of the cathode layers and in a 0.3cm x 1cm rectangular shaped reference electrode, placed at least 3 mm away from the cathode electrode on one side of the cell for use as the reference electrode. Pt gauzes (Alfa Aesar, 52 mesh woven from 0.1 mm dia wire, 99.9% Pt) spot-welded with Pt wires were buried in the Pt pastes on the working, counter and reference electrodes (see Figure 2), following by firing at 950°C in air for 1 h. DC polarization measurements were performed at temperatures of 700°C, 750°C and 800°C in air, using the same electrochemical testing instrument as in the conductivity measurements. The current density vs. overpotential plots were done by applying stepwise + and - DC voltages across the working and reference electrodes while collecting AC impedance spectra, in which ohmic resistances were obtained and the ohmic drops were subtracted from the cell voltages to calculate the overpotentials.

3. Results and discussion

3.1 XRD Phase Analysis

The XRD patterns for SSC and LSCF powders calcined at 900°C for 2 h and an LSGMC pellet sintered at 1400°C for 4 h are shown in Figure 3. The XRD results show that each of the oxides has been produced with high phase purity with no evidence of intermediates or contaminants. The theoretical patterns well match the measurements for each of the results presented in Figure 3. These XRD results demonstrate that the current GNP method can well synthesize SSC, LSCF and LSGMC in the desired phase purity.

3.2 Microstructure Characterization

SEM images of two composite cathodes on LSGMC electrolyte substrates are presented in Figure 4. Note that both cathode layers have similar thickness (~ 30 μm) and that there is no obvious reaction zone in the interfacial region. However, the microstructural characteristics of the two composite cathodes are dramatically different. The composite SSC-LSGMC cathode has a much larger pore and particle size and their distribution is not uniform. The overall microstructure of composite LSCF-LSGMC is relatively more uniform and comprised of typically smaller pore and particles. Note that all of these composite cathode materials were synthesized and processed under the same
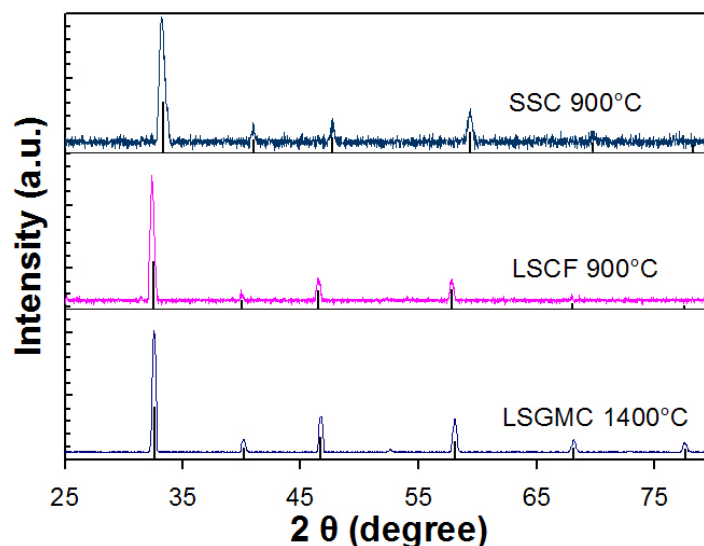
Figure 3. XRD patterns of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ powders calcined at 900°C for 2 h in air, and a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ pellet sintered at 1400°C for 4 h in air; solid bars represent the theoretical XRD patterns of each of the oxides obtained from CrystalMaker simulation results

conditions and both cathodes are comprised of 30wt.% LSGMC. Nonetheless, it is likely that the LSCF cathode powder was produced with smaller original particle size and is more prone to confinement by LSGMC during the cathode sintering process, leading to the significant differences presented in Figure 4.
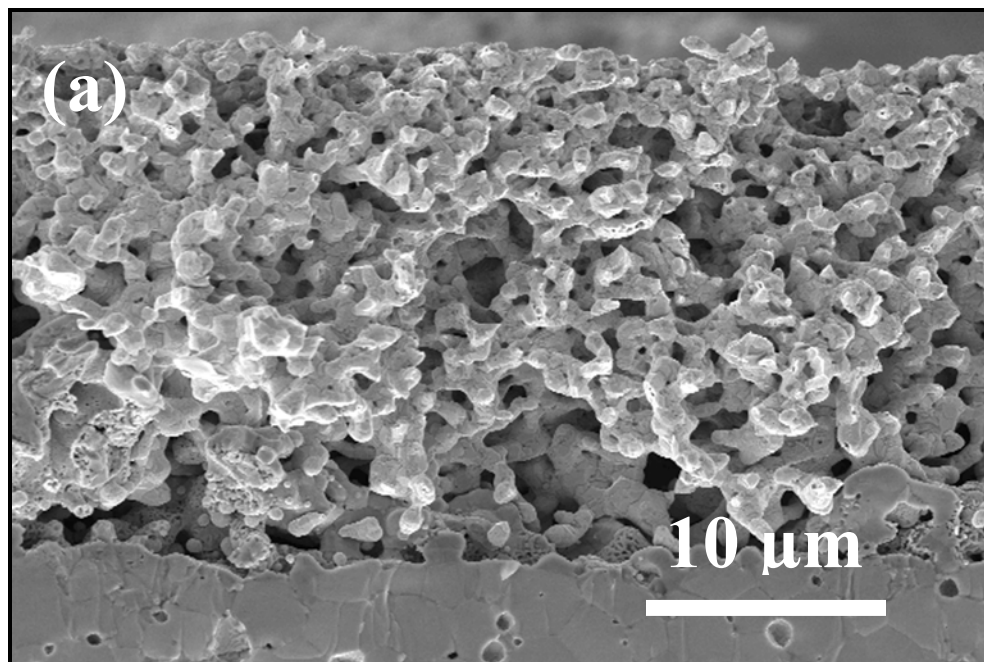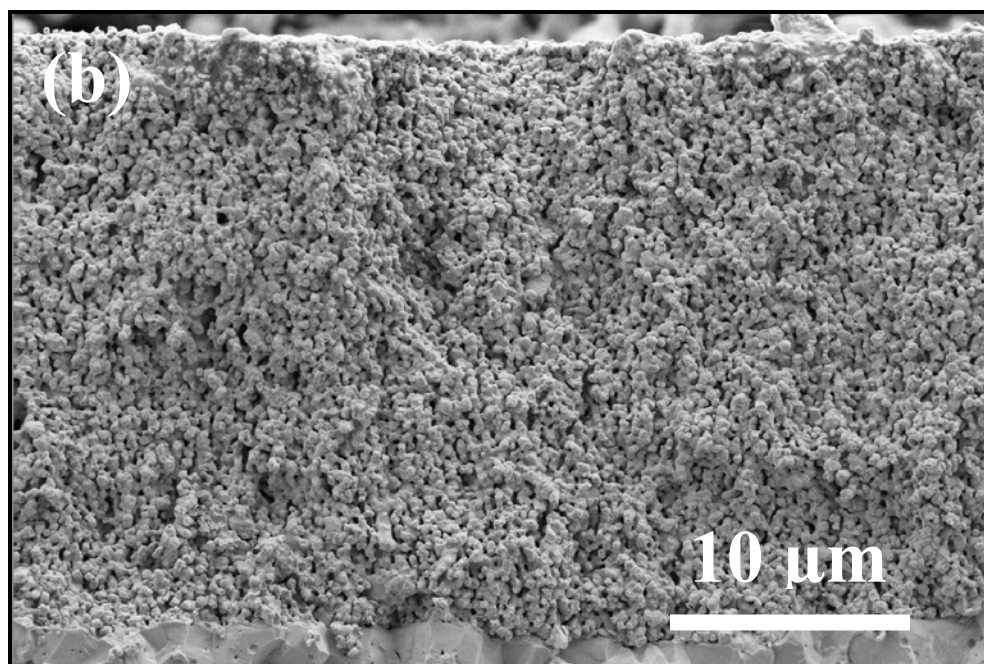
Figure 4. Cross-sectional views of composite cathode-LSGMC interfaces: (a) Composite SSC0.7LSGMC0.3 (b) Composite LSCF0.7LSGMC0.3
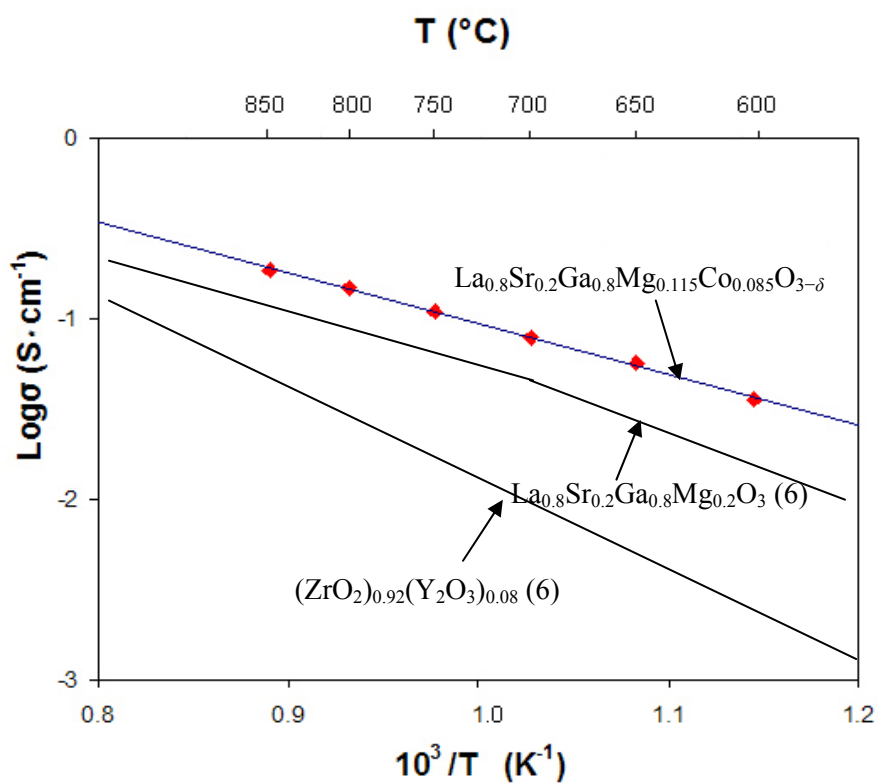
3.3 Conductivity Measurement of LSGMC

Figure 5. Electrical conductivity comparison as a function of temperature (Note: LSGMC plot is experimental result; $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ and $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ data are from Ishihara et al. (6).)

Ishihara et al. have reported that an optimized composition of LSGMC is $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ to achieve high ionic conductivity and resultant SOFC power density (6). Based primarily on these reported results and on initial conductivity measurements of various dopant compositions in LSGMC, this specific composition of LSGMC was chosen for the current study. Figure 5 presents the measured conductivity of the $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ disks that were produced in this study, confirming that high quality LSGMC pellets were produced in the current effort. Note that the current LSGMC material exhibits high conductivity in the intermediate-temperature range (700-800°C), which is comparable to the performance of conventional SOFC electrolyte materials at 1000-1100°C (6).

3.4 DC Polarization Test

Figure 6(a) shows the impedance spectra of the composite $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ − $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ (70wt.% SSC-30wt.% LSGMC) electrode at zero DC polarization in air under various temperatures. The total resistance corresponding to the low-frequency intercept of the impedance spectra decreases with increasing temperature. Also the loops of impedance spectra shrink when temperature is raised, showing a clear temperature-dependent trend. Similar results were obtained in the composite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ (70wt.% LSCF-30wt.% LSGMC) electrode under the same conditions as shown in Figure 6(b).
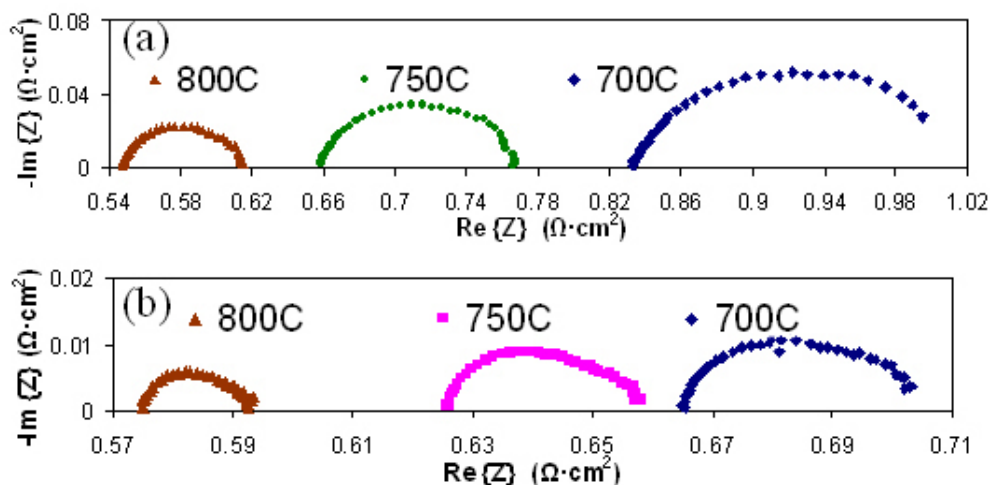

Figure 6. Impedance spectra of symmetric cell with different composite cathodes on a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.115}Co_{0.085}O_{3-\delta}$ electrolyte. Cathode area of the cell is approximately 1×1 cm^2 in each case: (a) 70wt.% SSC+30wt.% LSGMC composite cathode; (b) 70wt.% LSCF+30wt.% LSGMC composite cathode.

Figure 7 presents polarization curves for a composite SSC-LSGMC electrode/LSGMC electrolyte interface with comparison to a composite LSCF-LSGMC electrode/LSGMC electrolyte interface measured using a three-electrode configuration. The composite SSC-LSGMC electrode results are presented for three temperatures (700°C, 750°C, and 800°C). The trends of the curves are in agreement with typical Butler-Volmer relationship. The composite SSC-LSGMC electrode/LSGMC cell also demonstrates good performance. The measured cathodic overpotential under 1 A cm^{-2} current density was

as low as 0.051V in air at 800°C compared to a recent literature reported value of 0.087 V in pure oxygen at 800°C (9).

However, the composite LSCF-LSGMC electrode exhibited even better performance than the composite SSC-LSGMC cathode. As shown in Figure 7, at 700°C under the same overpotential conditions, the current density of the composite LSCF-LSGMC/LSGMC interface is about 3 times higher than that of the composite SSC-LSGMC/LSGMC interface under both cathodic and anodic polarization conditions. The composite LSCF-LSGMC electrode could have lower charge transfer resistance due to higher conductivity of LSCF. In addition, the significant difference in microstructure (as seen in Figure 4) may also dramatically affect the polarization results, which will be further investigated in the future efforts. Nevertheless, both the composite SSC-LSGMC and LSCF-LSGMC electrodes have demonstrated satisfactory performance to remain candidate cathode materials for LSGMC electrolyte systems used in intermediate-temperature SOFC applications.
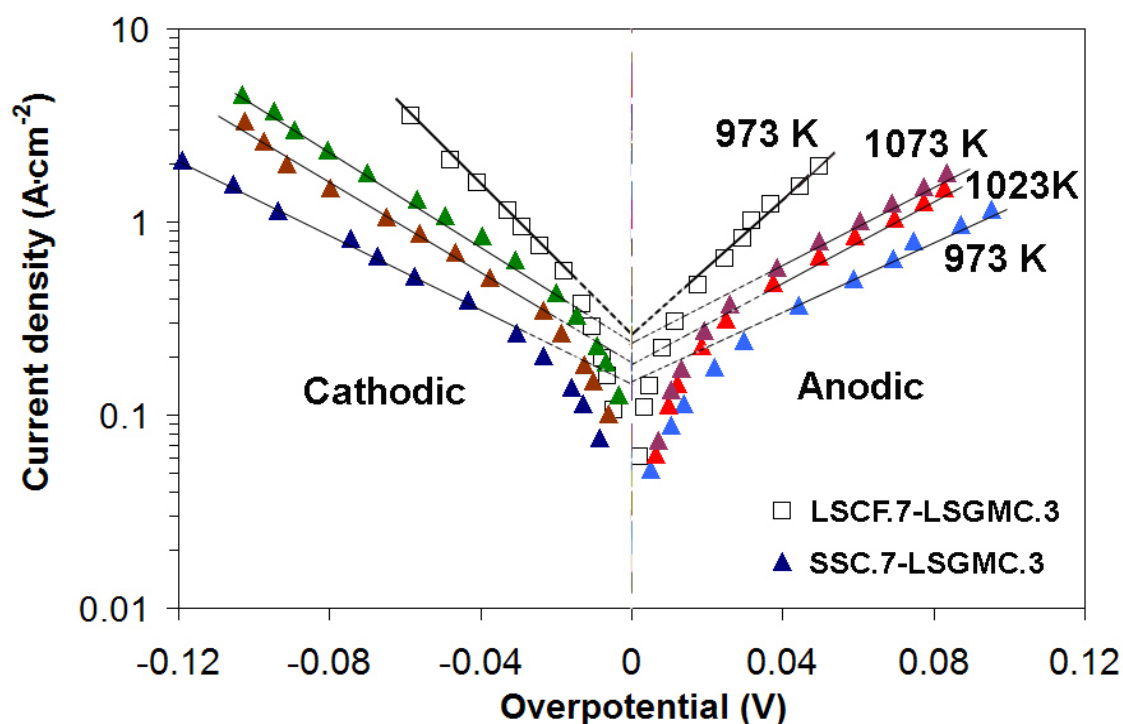

Figure 7. Overpotential vs. current density curves obtained at 700°C (973K), 750°C (1023K) and 800°C (1073K) for SSC–LSGMC composite cathodes compared to LSCF–LSGMC composite cathodes at 700°C in air.

TABLE I. Tafel Coefficients (α_a, α_c) and Exchange Current Densities (i_0, A• cm^{-2}) of Various Samples in Air at Different Temperatures.

Samples	700°C (973 K)			750°C (1023 K)			800°C (1073 K)		
	α_a	α_c	i_0	α_a	α_c	i_0	α_a	α_c	i_0
SSC0.7-LSGMC0.3	0.9	1.1	0.13	0.9	0.8	0.18	1.0	0.9	0.21
LSCF0.7-LSGMC0.3	1.0	1.0	0.28						

Table I summarizes the calculated exchange current densities and anodic and cathodic charge transfer coefficients obtained from a linear fit of the polarization curves in the Tafel region (high DC field). The composite LSCF-LSGMC/LSGMC interface has about twice the exchange current density of that of the composite SSC-LSGMC/LSGMC interface, which indicates that the current composite LSCF-LSGMC/LSGMC interface has much greater electrocatalytic activities. The results in Table I also present the calculated anodic and cathodic charge transfer coefficients, which are consistent with those determined by others studying similar materials sets (9).
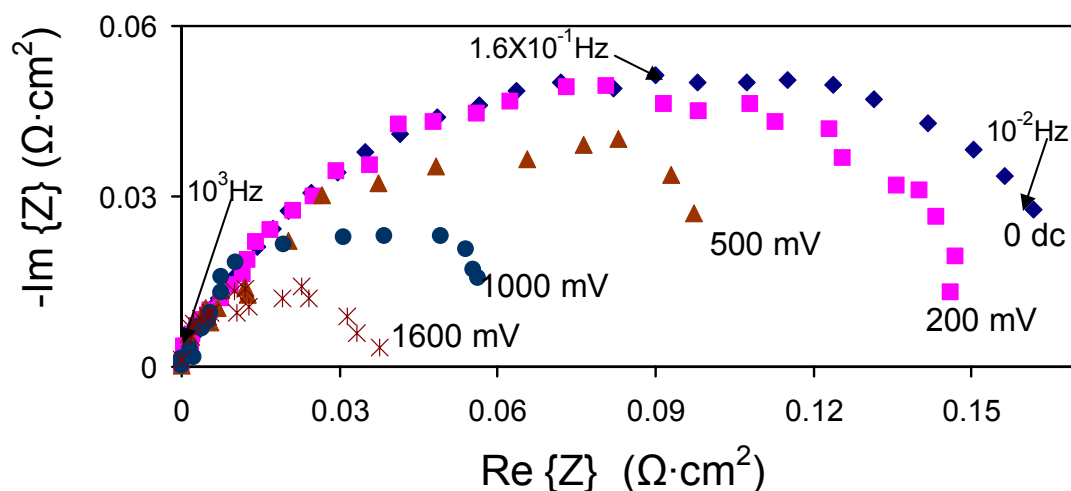

Figure 8. Impedance spectra of composite 70wt.%SSC+30wt.%LSGMC cathode on LSGMC under various applied *dc* potential conditions at 700°C in air

Shown in Figure 8 are impedance spectra of a composite 70wt.% SSC-30wt.% LSGMC electrode/LSGMC interface under varying applied *dc* potential conditions. The loops of the spectra shrink with increasing applied *dc* potential. The fact that polarization resistance decreases with increasing applied potentials indicates that the charge transfer process is the rate-determining-step (*r.d.s.*) under high field *dc* polarization.

4. Conclusions

Perovskite-type oxides (for both electrode and electrolyte) for use in intermediate temperature solid oxide fuel cells have been synthesized by using the glycine–nitrate combustion process. The produced powders were found to have good phase purity with negligible intermediate or contaminant phases. These powders were used to manufacture LSGMC pellets for measurement of conductivity and testing of various composite electrodes/LSGMC interfaces. The measured LSGMC conductivity is consistent with that found in the literature. Symmetrical cells of composite SSC-LSGMC/LSGMC and LSCF-LSGMC/LSGMC interfaces were manufactured. Microstructural characterization and electrochemical analysis of the interfacial properties were studied by scanning electron microscopy and three-probe dc polarization techniques. The electrochemical performance for both the SSC-LSGMC and LSCF-LSGMC composite electrode materials on LSGMC confirm their potential for use in intermediate temperature SOFC applications. The composite LSCF-LSGMC electrode exhibited much higher current

density than the composite SSC-LSGMC electrode in the current *dc* polarization measurements.

Acknowledgments

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