

# Characteristics of $La_{0.85}Sr_{0.15}MnO_{3-\delta}$ Powders Synthesized by a Glycine-Nitrate Process

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#### Abstract

The amount of glycine added, i.e., the glycine/oxide molar ratio, k, is optimized for synthesizing  $La_{0.85}Sr_{0.15}MnO_{3-\delta}$  (LSM) powders by a glycine-nitrate process. The specific surface area of the resultant LSM powders increases with this ratio, which indicates the deviation of the required glycine from the stoichiometric reaction. The powder is further characterized as a precursor for LSM-SDC (samarium-doped ceria) composite electrodes for solid oxide fuel cells. The electronic conductivity of the LSM-SDC composite increases with increases in the glycine/oxide ratio. In addition, the ratio has an effect on the interfacial polarization resistance of the LSM-SDC electrodes, as determined with symmetric cells using AC impedance spectroscopy. The lowest resis-

#### 1 Introduction

Reducing the cathodic interfacial polarization resistance is critical to the development of practical solid oxide fuel cells (SOFC). Generally, a lower resistance can be achieved by using novel electrode materials with a high electrochemical activity and/or by increasing the number of reactive sites on conventional electrodes through microstructural modification [1]. Oxygen reduction at the cathode can be realized at triplephase boundaries (TPBs) at the electrode, electrolyte, and oxygen, where gaseous O<sub>2</sub>, and electrons and oxide ions can percolate through pores, and catalytic and electrolyte materials, respectively [2]. TPBs are related to the number of reactive sites, which is determined by the microstructure of the electrode. Consequently, it is believed that electrodes with different microstructures result in different performances, due to the competition between the mass transfer and charge transfer reactions [3]. Therefore, the optimization of the microstructure would be helpful in reducing the interfacial polarization resistance.

tance is achieved using a LSM powder prepared with 20% more glycine than the stoichiometric requirement (k = 1.2). The activation energies for electrochemical oxygen reduction are about 1.3 eV, when the ratio is below 1.2, and about 1.0 eV, when it exceeds 1.2. The activation energy suggests that oxygen ion transfer is the rate determining process for the LSM-SDC electrode when  $k \ge 1.2$ , whereas both mass transfer and charge transfer are the rate limiting steps when k < 1.2.

**Keywords**: Composite Cathodes, Glycine Nitrate Process, Interfacial Polarization Resistance, SOFCs, Solid Oxide Fuel Cells

Strontium doped lanthanum manganite (LSM) is known as a classical cathode material due to its high stability in oxidizing atmospheres, the good compatibility with the coefficient of thermal expansion of the ceramic electrolyte, and sufficient electrical conductivity at 1,000 °C [4]. However, the interfacial polarization resistance of LSM electrodes increases rapidly with a reduction in temperature (below 800 °C), even exceeding the resistance of the electrolyte films, to become the major source of inter-resistance for SOFCs [5]. Composite electrodes, consisting of LSM and electrolyte materials, such as yttria stabilized zirconia and doped ceria, have been proven to have a better performance than pure LSM electrodes. This is by virtue of the extension of the TPBs, which shift from 2-dimensional interfaces between the electrolyte and the electrode to the 3-dimensional bulk of the electrode. Moreover, it has been found that the electrode composition, as well



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as the properties of the starting powders, may affect the electrode microstructure and subsequently the resistance [6–9].

The glycine-nitrate process (GNP) is a fast and cost effective technique for preparing fine and homogeneous LSM powders [10–13]. The GNP is a self-sustaining combustion synthesis technique with metal nitrates as the oxidizers and glycine as the fuel. Therefore, the amount of glycine is of great importance for the completion of the oxidation-reduction reaction, and thus has a great effect on the characteristics of the resulting LSM powders, and furthermore on the microstructure and performance of the composite electrode. In this work, LSM powders are prepared using the GNP method, with various amounts of glycine added. The powders are characterized as precursors for SOFC cathodes, by investigating the electronic conductivity of the LSM-SDC (samarium doped ceria) composites and the interfacial polarization resistance of LSM-SDC electrodes on SDC electrolytes.

#### 2 Experimental Procedures

 $La_{0.85}Sr_{0.15}MnO_{3-\delta}$  (LSM) powders were prepared using a glycine-nitrate process. Assuming that the sole gaseous products were H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub>, and that glycine is stoichiometrically oxidized with nitrates, the combustion reactions can be expressed as follows:

$$6La(NO_3)_3 + 10NH_2CH_2COOH = 3La_2O_3 + 14N_2\uparrow + 25H_2O\uparrow + 20CO_2\uparrow$$
(1)

$$9Sr(NO_3)_2 + 10NH_2CH_2COOH =$$
  
 $9SrO + 14N_2^2 + 25H_2O^2 + 20CO_2^2$  (2)

$$2Mn(NO_3)_2 + 2NH_2CH_2COOH =$$

$$Mn_2O_3 + 3N_2\uparrow + 5H_2O\uparrow + 4CO_2\uparrow$$
(3)

Therefore, the stoichiometric molar ratio of glycine to the LSM product should have been 2.425, when no additional oxygen was required.  $k = r/r_0$ , where  $r_0$  is the stoichoimetrical molar ratio, r the practical ratio, and k the relative glycine/oxide molar ratio.

To carry out the glycine-nitrate process,  $La(NO_3)_3$ ,  $Sr(NO_3)_2$ , and  $Mn(NO_3)_2$  were dissolved in distilled water and then glycine was added with k = 0.5, 0.7, 1.0, 1.2, and 1.6. The aqueous solution was heated while stirring and converted to a viscous gel. When the free water had evaporated and the temperature reached the burning point of glycine, spontaneous ignition occurred, resulting in a fine LSM 'ash', which was brown in color. The resultant ash was fired in air at 800 °C for 4 hours to remove possible carbon residues and to form perovskite LSM. The resultant LSM was simplified to k05LSM, k07LSM, k10LSM, k12LSM, and k16LSM, which related to the various relative ratios of k mentioned earlier. Samarium doped ceria (Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub>) powders were also prepared with the glycine nitrate process, as reported previously [12]. LSM was mechanically mixed with SDC in a 1:1 weight ratio, to form a composite powder. The powder was then uniaxially cold-pressed at 220 MPa into a bar sample for electrical conductivity measurements. The green bar was sintered at 1,200 °C for 4 hrs at a heating rate of 3 °C min<sup>-1</sup>.

SDC powders were cold-pressed at 220 MPa into pellets, 15 mm in diameter and 0.6 mm thick, and sintered at 1,400 °C for 5 hrs to form the electrolyte substrates. A slurry, consisting of the composite powders and organic binders, was produced by ball milling and screen-printing onto both sides of the pre-sintered SDC substrates. After drying at room temperature, the samples were sintered at 950 °C for 4 hrs to form the symmetric cells. Ag paste was applied to the surface of the symmetrical electrodes and fired at 600 °C for 30 min to form current collectors. The active electrode area on each side of the cell was approximately 1.23 cm<sup>2</sup>.

Phase identification was performed with powder X-ray diffraction, using CuK<sub>a</sub> radiation (D/Max- $\gamma_A$ ). The specific surface areas of the LSM powders were measured by the iso-thermal nitrogen adsorption-desorption (BET, Omnisorp100cx) technique. The conductivities were measured between 500 and 850 °C in air, using the DC 4-point method with a HP34401A multimeter. The electrode microstructure was studied using a scanning electron microscope (HITA-CHIX-650 and JSM6700F). The electrode/electrolyte interfacial resistances of the symmetrical cells were determined using AC impedance spectroscopy (CHI604A) in air from 550 to 800 °C. The frequency range was between  $10^{-2}$  Hz and  $10^5$  Hz.

#### 3 Results and Discussion

# 3.1 Characteristics of LSM Prepared with Different Glycine to Oxide Ratios

Figure 1 shows X-ray diffraction patterns for LSM powders, prepared with different glycine/oxide ratios. All of the LSM powders exhibited a well-defined perovskite structure after firing at 800 °C, which was not affected by the amount of glycine added. It can be seen that the peak positions and their relative intensities are similar. Therefore, the use of different amounts of glycine did not affect the crystalline structure. However, the glycine to oxide ratio had an obvious effect on the specific surface area of the LSM powders, as shown in Table 1. The specific surface area increased with *k*, suggesting that the particle size was smaller when more glycine was used. In the glycine-nitrate process, glycine acts as the reductant in the redox reaction at high temperature. Meanwhile, at low temperature, it forms a chelate complex with cations such as La<sup>3+</sup>. When less than the stoichiometric amount of glycine is used, the cation cannot be fully chelated. Consequently, the un-chelated nitrates crystallize during heating and evaporation. The crystallization might lead to the aggregation of the resultant particles, since the redox combustion and nitrate decomposition occur at different temperatures. In contrast, when more than the stoichiometric amount

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Fig. 1 XRD patterns of LSM powders prepared with different glycine/ oxide ratios.

Table 1 Specific surface areas of LSM powders synthesized with different glycine/oxide ratios and fired at 800 °C for 4 hrs.

| k   | 0.5   | 0.7   | 1.0   | 1.2   | 1.6   |
|---|-------|-------|-------|-------|-------|
| Specific Surface<br>Area / m <sup>2</sup> g <sup>-1</sup> | 8.241 | 8.998 | 12.03 | 15.31 | 20.56 |

of glycine is used, the metal ions are fully chelated. Only combustion occurs during heating. Simultaneously, large amounts of gases, such as  $CO_2$  and  $N_2$ , are released, resulting in weak bonds in the porous powders. The nitrates are not sufficient for the oxidization of glycine if the amount of glycine is further increased. In this case, ambient oxygen may assist the reaction. Therefore, more gas is expected and thus the particle size is reduced. This is possibly the reason that the specific surface area decreased with the amount of glycine when  $0.5 \le k \le 1.6$ .

#### 3.2 Electrical Conductivity of LSM-SDC Composites

The conductivity (electronic and ionic) of the LSM-SDC composites is shown in Figure 2; the LSM was synthesized with different glycine/oxide ratios. It can be seen that the conductivity is below 10 S cm<sup>-1</sup>. This is much lower than that of pure La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3- $\delta}$  (x  $\approx$  0.2), which is approximately 44.7 S cm<sup>-1</sup> at 500 °C [4]. The lower conductivity of the composites is likely to be attributable to the SDC phase. The conductivity of SDC was only 0.006 S cm<sup>-1</sup> at 500 °C, about 4 orders of magnitude lower than that of LSM. Thus, the SDC particles could be regarded as a non-conductive medium amongst the LSM particles. After blending with the LSM, the SDC particles partially interfered with the LSM particles, obstructing the connection between them, eventually limiting electron transport through the LSM phase.</sub>

Composites consisting of k12LSM and k16LSM are more conductive than the others, as shown in Figure 2. Since the SDC powders were the same, the difference in conductivity could be attributed to distinct characteristics of the LSM powders, synthesized at different *k*. When conducting particles



Fig. 2 Electrical conductivity of porous LSM-SDC cathodes with different glycine/oxide ratios.

are blended with insulating particles, the conducting threshold increases with the particle size of the conductive phase, provided that its volume ratio is fixed [14], i.e., more conducting paths are built with smaller particles at the fixed volume ratio. Since the particle size decreased with k, the composites consisting of k12LSM and k16LSM were more conductive than the others.

# 3.3 Interfacial Resistance and Microstructure of the Composite Electrodes

The electrode performance depends critically on its microstructure, which is strongly affected by the characteristics of the starting powders. Thus, it is of great importance to optimize the LSM synthesis parameters, especially the relative ratio k, with respect to its effect on electrode performance. The impedance spectra, measured at 750 °C, are shown in Figure 3. The impedance spectra are normalized by the electrode/electrolyte contact surface unit. Whatever the relative ratio, each impedance spectra approximately corresponded to two overlapping arcs (depressed semicircles), indicating two rate processes, oxygen reduction and oxygen ion incorporation, at the electrodes [15].

The high frequency intercept at the real axis denotes the electrolyte and lead-wire resistance,  $R_{\rm s}$ , and the resistance determined by the impedance arc,  $R_{\rm i}$ , is twice the interfacial polarization resistance under open circuit conditions, due to the construction of the symmetric cells.  $R_{\rm s}$  remains almost constant with increasing *k*. Whereas,  $R_{\rm i}$  decreases sharply with *k*, suggesting that the microstructure of the composite electrodes meliorates with the LSM powders synthesized at a high glycine/oxide ratio. The interfacial polarization resistances at 800 °C were 1.43, 1.24, 0.66, 0.26, and 0.44  $\Omega$  cm<sup>2</sup> at the relative ratios of 0.5, 0.7, 1.0, 1.2, and 1.6, respectively. It should be noted that the lowest resistance was achieved using the LSM powder prepared with 20% more glycine than the stoichiometric requirement.

Figure 4 presents the reciprocal temperature dependence of the interfacial polarization resistance. The linear curves

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Fig. 3 Impedance spectra at 750 °C for symmetric cells with electrodes consisting of LSM synthesized with different ratios of k. k = (a) 0.5; (b) 1.0; (c) 1.6.

indicate that there is no change in the electrode reaction mechanism for each cell, within the temperature range studied. The resistances were largely related to the glycine/oxide ratio, k, owing to its significant influence on the properties of the LSM powders. The resistance decreased with k and reached a minimum value at k = 1.2. This is consistent with the electrical conductivity measured, as shown in Figure 2.



Fig. 4 Arrhenius plots of the interfacial resistance of LSM-SDC symmetrical electrodes in which LSM was prepared with different glycine/oxide ratios.

The activation energies for interfacial polarization resistances are also shown in Figure 4. The activation energies for k12LSM-SDC and k16 LSM-SDC were about 1.0 eV, and about 1.3 eV for k05LSM-SDC, k07LSM-SDC, and k10LSM-SDC.

Oxygen reduction is often considered to take place at triple-phase boundaries (TPBs) for porous LSM composite electrodes, in which the dissociative adsorption of oxygen onto the LSM surface and the transfer of oxygen ions from the triple-phase boundary to the electrolyte lattice may be the two rate determining steps. The activation energy for oxygen dissociation on a pure LSM electrode is approximately 2.0 eV, while the activation energy for mass transfer is about 1.0 eV [16]. The proximity of the activation energy to that of oxygen



Fig. 5 SEM images of LSM-SDC cathodes in which LSM was prepared with different glycine/oxide ratios. k = (a) 0.5; (b) 0.7; (c) 1.0; (d) 1.2; (e) 1.6.

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ion transfer suggests that, with the addition of SDC to the LSM electrode, the electrochemical activity of the electrode is improved substantially by the enlargement of the TPBs and that the dissociative adsorption of oxygen becomes less rate determining on the electrode. Also, it was found that the transfer of the oxygen ion was the only rate-determining step on the k12LSM-SDC and k16LSM-SDC composite electrodes. The improvement in the electrochemical performance with the increase of the relative ratio was mainly due to the spatial enlargement of the TPB area by the smaller LSM particles synthesized with larger k, which increased the electrochemically active sites for oxygen adsorption.

#### 3.4 Microstructure of the Composite Electrodes

The surface microstructure of the composite electrodes is shown in Figure 5. It can be seen that, although their composition is the same, their microstructures are obviously different when the LSM precursors were prepared with different glycine/oxide ratios. When the ratio was below 1.0, the electrodes consisted of grains, several micrometers in size. The grains were not uniform and were badly aggregated. On the contrary, when the ratio exceeded 1.2, the electrodes were composed of small, submicron size, grains. The average grain sizes of k12LSM-SDC and k16LSM-SDC were about 0.2 and 0.1 µm, respectively. The grains were very uniform and well dispersed. Compared with k05LSM-SDC, k07LSM-SDC, and k10LSM-SDC, the previous two samples had a smaller grain size, proper microstructure, and thus high TPBs. Consequently, k12LSM-SDC and k16LSM-SDC had much lower interfacial polarization resistances, as shown in Figure 4.

### 4 Conclusions

 $La_{0.85}Sr_{0.15}MnO_{3-\delta}$  powders were synthesized by a glycinenitrate process. The glycine/oxide ratio was optimized for the preparation of LSM-SDC composites as cathodes for SOFCs. The interfacial resistances at 800°C for the LSM-SDC cathodes were 1.4, 1.2, 0.66, 0.26, and 0.44  $\Omega$  cm<sup>2</sup> when the LSM powders were synthesized at ratios of 0.5, 0.7, 1.0, 1.2, and 1.6, respectively. The activation energies for oxygen reduction at the electrodes were about 1.3 eV, when the ratio was lower than 1.2, and about 1.0 eV for k = 1.2 and 1.6.

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