

Short communication

Electrochemical performance of LSCF-based composite cathodes for intermediate temperature SOFCs

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Abstract

Symmetrical electrochemical cells with various electrodes, viz. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}$ (LSCF), LSCF-($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_3$) GDC, LSCF-platinum (Pt) and LSCF-GDC-Pt, were fabricated for the purpose of investigating their potential use in intermediate temperature solid oxide fuel cells (IT-SOFCs) and the relationship between the electrocatalytic characteristics and electrode microstructure of the electrochemical cells. Both the LSCF-GDC and LSCF-Pt composite electrodes seemed to perform better than the LSCF electrode for oxygen reduction. The polarization resistance was significantly reduced in the case of the composite electrodes. The incorporation of Pt particles in the LSCF electrode was found to be effective over the entire temperature range for which measurements were taken. Adding the GDC resulted in microstructural changes taking place in the LSCF electrode, and a low polarization resistance was obtained at temperatures of 600 °C and lower. Based on the impedance spectrum data, it was considered that Pt might accelerate the oxygen adsorption at high temperature. On the other hand, GDC seemed to serve as a fast oxygen ion diffusion path at lower temperatures.

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1. Introduction

Recently, there has been a considerable amount of research and development in the field of solid oxide fuel cells (SOFCs), which have several distinct advantages over other fuel cells. In effect, SOFCs do not require noble metal catalysts such as platinum and the fact that all of the components are solids offers considerable cell design flexibility and eliminates the material corrosion problem. Moreover, SOFCs have the potential for cogeneration due to their high temperature operation and also have multi-fuel capability. In particular, the fuel diversity of SOFCs allows for the internal reformation or direct oxidation of hydrocarbon (DH) SOFCs, in which hydrocarbon fuels, such as methane, butane, LPG, etc., react electrochemically at the anode [1–3].

However, one of the disadvantages of SOFCs is their high operating temperature (800–1000 °C), which causes both physical and chemical degradation of the construction materials and limits the choice of materials that can be used for their fabrication. In addition, this high operating temperature requires lanthanum chromite-based ceramic interconnectors to be used, which are very expensive and difficult to fabricate and machine. If the operating temperature could be reduced to 600–700 °C, inexpensive ferritic stainless steel (Fe–Cr alloy) could be used for the interconnectors [4,5]. Thus, it is desirable to develop SOFCs operating at an intermediate temperature of around 600–800 °C. However, this requires not only new cathode and electrolyte materials to be used, but also sophisticated microstructure development of the cathode.

YSZ is widely used as a solid electrolyte material in SOFCs, because of its excellent mechanical, thermal, and chemical stability at high temperature. To decrease the resistance as well as the cell operating temperature, solid electrolytes which have higher ionic conductivity than

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YSZ in the intermediate temperature range must be used. Sc_2O_3 -stabilized zirconia (ScSZ) and Gd_2O_3 -doped CeO_2 ($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_3$, GDC) are considered to be candidates for intermediate temperature applications, because they show higher ionic conductivity than YSZ [6,7].

In the present study, we fabricated symmetrical electrochemical cells consisting of a GDC electrolyte and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}$, (LSCF)-based composite electrodes with fine GDC or Pt particles. LSCF is the most suitable electrode material for the GDC electrolyte, because of its high mixed ionic and electronic conductivity and its excellent thermal and chemical compatibility with GDC [8]. The electrocatalytic characteristics and microstructural evolution of the LSCF-based composite electrodes were investigated.

2. Experimental procedure

Commercially available GDC disks (22 mm in diameter and 0.5 mm thick) were used as the solid electrolyte for the present study. Symmetrical electrochemical cells were produced by using LSCF, LSCF–GDC (40 vol%), LSCF–Pt (0.5 and 1 vol%) and LSCF–GDC (40 vol%)–Pt (1 vol%) composite electrodes (cathode and anode) with the GDC electrolyte. The LSCF and GDC or PtO_2 powders were mixed by ball milling for 24 h in ethanol. After drying the powder at 80°C , the LSCF–GDC, LSCF– PtO_2 or LSCF–GDC– PtO_2 composite electrode paste was screen-printed onto both sides of the GDC disk. The electrochemical cells were then sintered at 1000°C for 1 h. The thickness of the electrode was about $30\ \mu\text{m}$. A current-collector platinum layer containing 15 wt.% GDC powder was further coated onto each of the composite electrodes. For comparison, a LSCF/GDC/LSCF cell with no GDC or Pt was prepared by the same process.

Fine platinum particles were incorporated into LSCF via the chemical precipitation technique. Fig. 1 shows the flow chart for the fabrication of the LSCF–Pt composite powder. Platinum chloride ($\text{PtCl}_4\cdot 5\text{H}_2\text{O}$) was dissolved in water, and then the LSCF powder was mixed with the platinum solution. Ammonia solution (NH_3) was added to the platinum solution to synthesize a platinum complex. Then, formaldehyde (formalin) was used as a reducing agent, and the mixture was stirred for several hours at a temperature of 100°C . After filtering and washing, the composite powder so obtained was dried using the freeze-drying method. Transmission electron microscope (TEM) observations showed that platinum particles were precipitated onto the surfaces of the matrix LSCF particles.

For the AC impedance spectroscopy and electrode polarization measurements, the electrochemical cells were held in a quartz tube and placed in a vertical furnace. Twenty percent O_2 (the balance being helium) gas from a premixed gas cylinder was supplied to the quartz tube at a flow rate of 50 mL/min. Platinum wires were connected to the Pt meshes which were in contact with the current collecting Pt layers. AC impedance spectroscopy was performed, with an excitation potential of 50 mV, over a frequency range from 1 MHz to 0.1 Hz, generated by a frequency analyzer (Model 1255B, Solartron). The microstructures of the electrodes were observed by scanning electron microscopy (SEM, JSM-6320FK, JEOL Co. Ltd., Japan).

3. Results and discussion

The cross sections of the LSCF–GDC composite electrodes sintered at 1000 and 1200°C for 2 h were observed by SEM. Typical images are shown in Fig. 2. In general, sintering the LSCF electrode at high temperature increases its grain

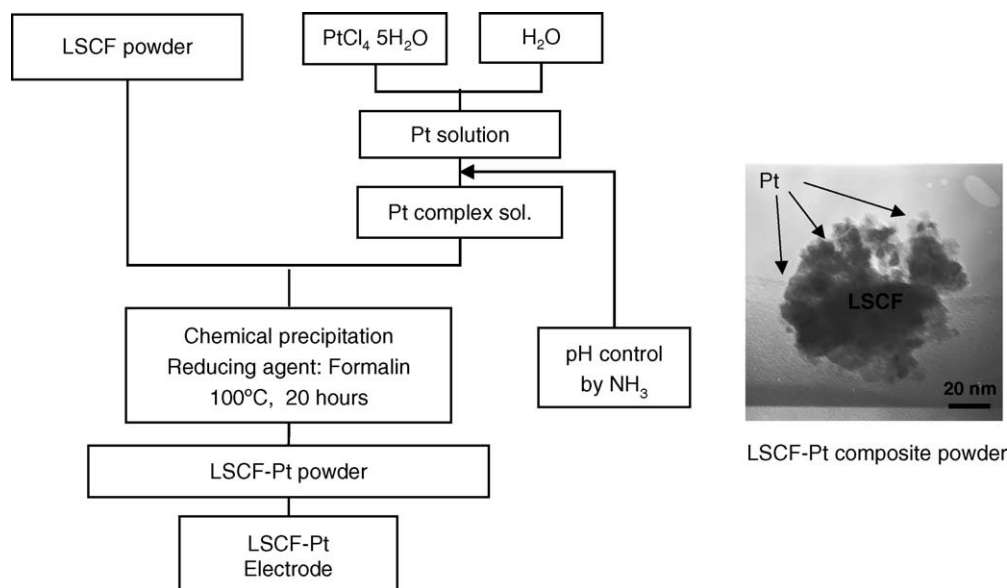


Fig. 1. Flow chart of synthesis of LSCF–Pt composite powders by chemical precipitation method.

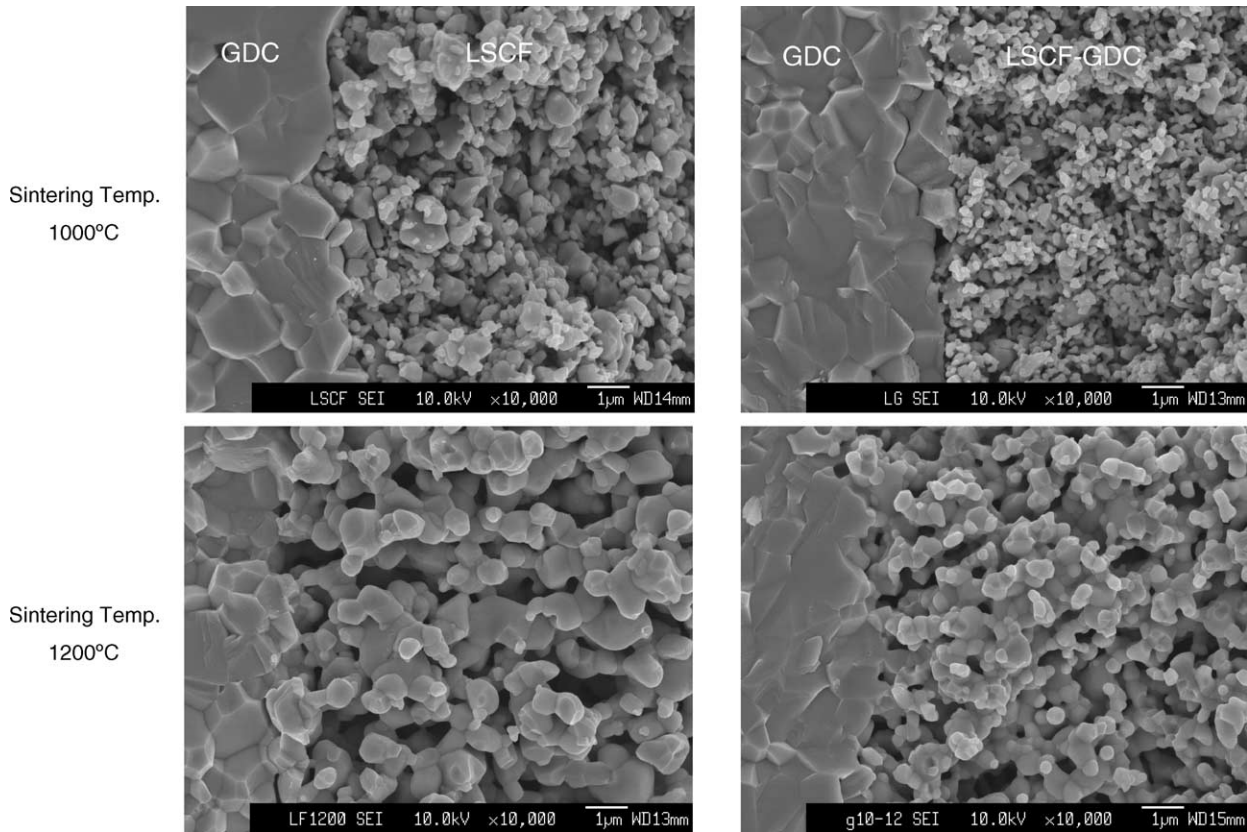


Fig. 2. SEM photographs showing cross-section of LSCF (left) and LSCF–GDC composite electrode (right) sintered at 1000 °C (upper) and 1200 °C (lower), respectively.

size and, thus, decreases the electrode surface area–gas solid interface (triple phase boundary), resulting in high polarization resistance [9]. On the other hand, due to the increase in the sintering temperature, the LSCF particles strongly adhered to the GDC electrolyte surface. Obtaining LSCF particles with a fine microstructure and their strong adhesion to the electrolyte are in a trade-off relationship with respect to the sintering temperature. The LSCF and LSCF–GDC electrodes sintered at 1000 °C showed smaller grain sizes and larger porosity, along with poorer contact to the electrolyte in comparison with the electrodes sintered at 1200 °C. As is evident in Fig. 2 (right), the addition of GDC (40 vol%) to the LSCF was able to suppress the LSCF grain growth and, as a consequence, the LSCF–GDC composite electrode sustains its fine and porous microstructure which probably resulting in the increase in triple-phase boundaries (tpbs).

Fig. 3 shows the surface microstructure (backscattered image) of the LSCF–GDC composite electrode. It would appear that relatively large LSCF grains are surrounded by fine GDC particles. The LSCF (dark phases) was found to be continuous and to form the three-dimensional framework of the composite electrode. On the other hand, the GDC (bright and spherical phases), which was homogeneously dispersed in the LSCF matrix, was fragmented or partially continuous. The GDC particles were estimated to be approximately 100 nm in size.

Fig. 4 shows the SEM micrographs of the LSCF (a), LSCF–GDC (b), LSCF–Pt (c), and LSCF–GDC–Pt (d) composite electrodes sintered at 1000 °C for 2 h. All of these electrodes show porous microstructures and are in good interfacial contact with the GDC electrolyte, with no signs of delamination. During the sintering process, the original PtO₂ is completely reduced to Pt at around 650 °C. No Pt

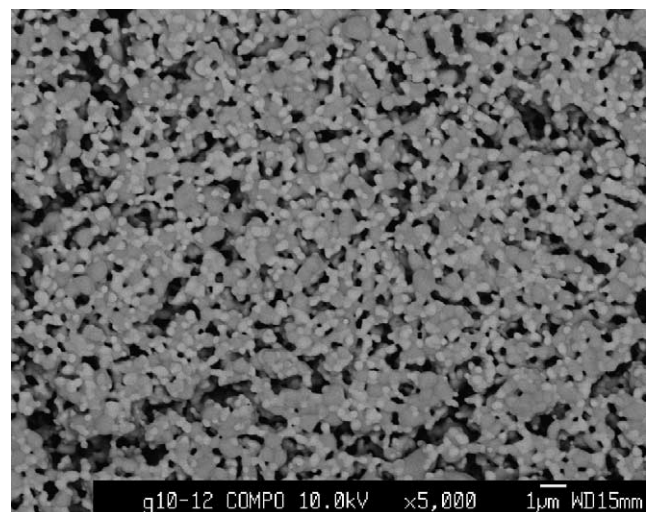


Fig. 3. Microstructure of LSCF–GDC electrode sintered at 1000 °C for 2 h.

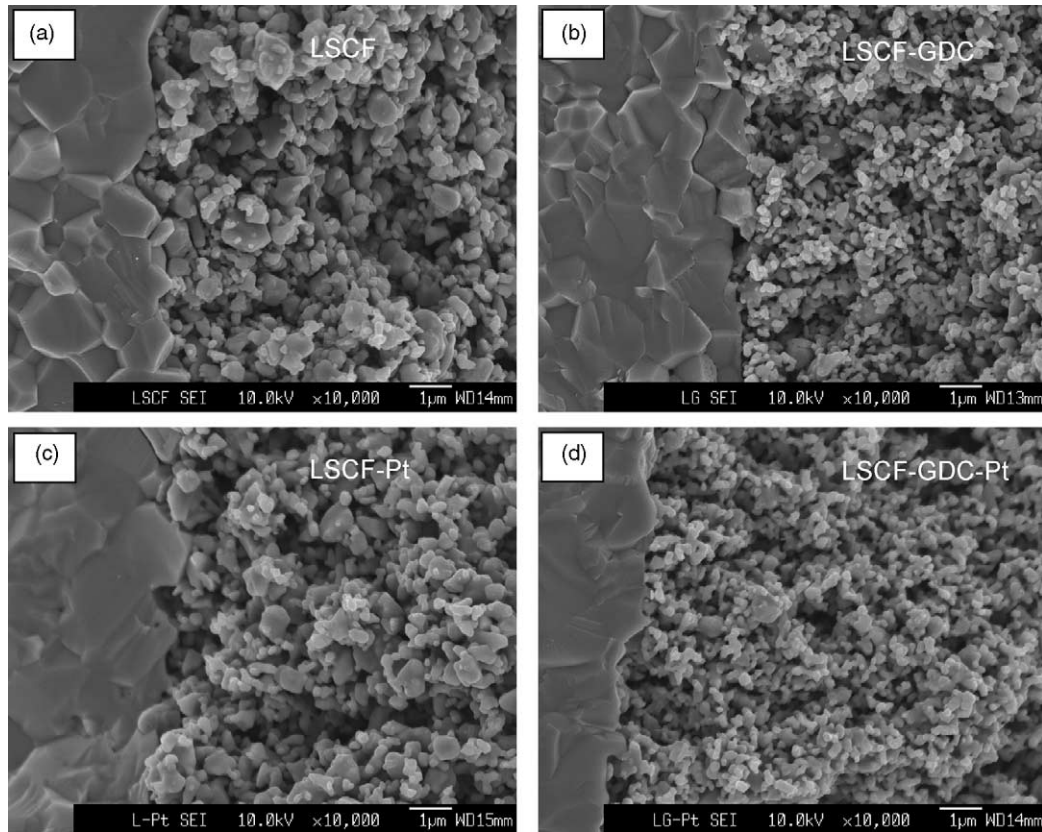


Fig. 4. Microstructures of LSCF (a), LSCF-GDC (b), LSCF-Pt (c), and LSCF-GDC-Pt (d) composite electrodes sintered at 1000 °C for 2 h.

particles can be seen in Fig. 4(c) or (d), and it was confirmed by high resolution SEM that the Pt is dispersed in the LSCF. The addition of Pt does not seem to affect the microstructure evolution of the LSCF electrode. The microstructure of the LSCF-Pt composite electrode is almost the same as that of the LSCF electrode. This phenomenon is not surprising, since the amount of Pt in the LSCF was very small (0.5 and 1 vol%).

Fig. 5 shows the impedance spectra of the LSCF and LSCF-GDC composite electrodes, measured at 700 and 500 °C, in a 20% oxygen atmosphere (the balance being helium). Above 700 °C, the shape of the impedance semicircle of the LSCF-GDC composite electrode was very similar to that of the LSCF electrode. It would seem that the addition of GDC to the LSCF does not affect the catalytic activity of the LSCF electrode. However, the LSCF-GDC composite electrode showed better electrocatalytic activity than the LSCF electrode when the operating temperature was decreased to 500 °C. The polarization resistances were estimated to be approximately 4 and 12 Ω for the LSCF-GDC and LSCF electrodes, respectively, at an operating temperature of 500 °C. From the polarization resistance versus temperature relationship, the activation energy can be calculated. The activation energy decreased from 142 kJ/mole for the LSCF to 122 kJ/mole for the LSCF-GDC composite electrodes. It can be inferred from this that the addition of GDC is more

effective at lower operating temperatures. Considering that the polarization resistances of the LSCF-GDC electrode were ~0.07 and 2 Ω at 700 and 500 °C, respectively, it can be concluded that the composite electrode is a candidate

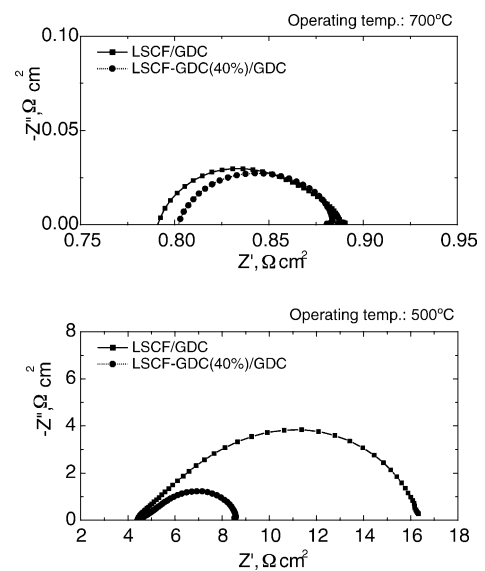


Fig. 5. Impedance spectra of LSCF and LSCF-GDC (40 vol%) composite electrodes.

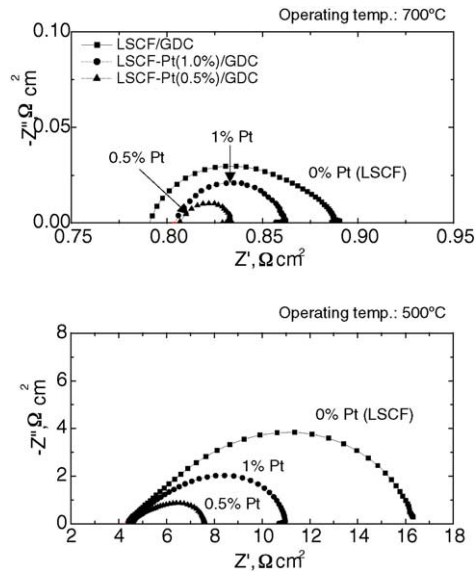


Fig. 6. Impedance spectra of LSCF and LSCF–Pt(0.5 and 1 vol%) composite electrodes.

electrode material for intermediate temperature SOFCs, a finding which is consistent with reports by other researchers [8].

The impedance spectra, measured at 700 and 500 °C, in a 20% oxygen atmosphere (the balance being helium), taken for the LSCF and LSCF–Pt composite electrodes are shown in Fig. 6. The addition of Pt was found to be very effective at 500 °C, as well as at 700 °C. An interesting feature in Fig. 6 is that the polarization resistance decreased with decreasing Pt content in the case of the LSCF–Pt composite electrode. At 500 °C, the polarization resistance of the LSCF–0.5 vol% Pt composite electrode was nearly one fifth of that of the LSCF electrode. This tendency could be observed at operating temperatures lower than 700 °C.

The dependences of the oxygen partial pressure on the polarization resistance of the LSCF electrode are shown in Fig. 7. Irrespective of the cell operating temperature (600 and 800 °C), a relatively high oxygen partial pressure dependence was observed at an oxygen partial pressure of less than 1×10^{-3} atm, and the slope was estimated to be approximately 1, which is indicative of the gas phase diffusion of oxygen being a rate-determining step at low oxygen partial pressures [10,11]. As the oxygen partial pressure increased, the oxygen partial pressure dependence sharply decreased (≈ 0.2) when the cell was operated at 600 °C, whereas it decreased only slightly (≈ 0.8) at 800 °C. These results suggest that the rate-limiting reaction of the oxygen reduction on the LSCF electrode strongly depends on the cell operating temperature.

At high temperature (>700 °C), the addition of Pt seems to be more effective than that of GDC in enhancing the catalytic activity against O_2 reduction, while, at temperatures of <700 °C, e.g., at 500 °C, the LSCF–GDC composite was found to be the better oxygen electrode. This result suggests

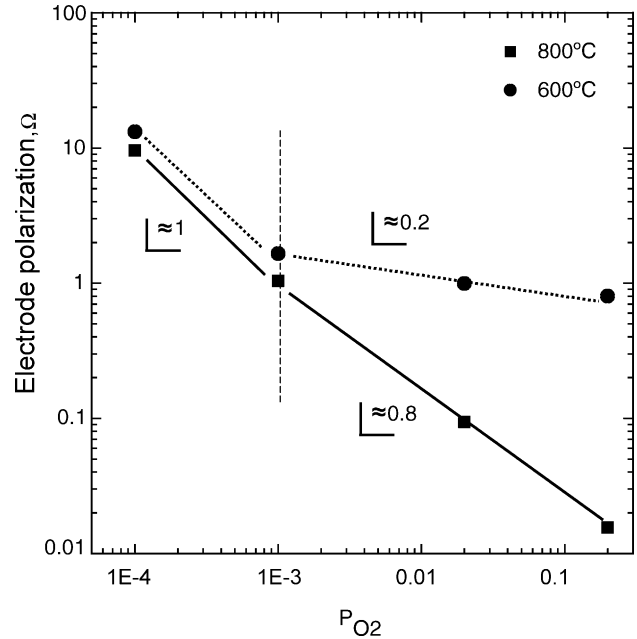


Fig. 7. The dependence of oxygen partial pressure on the polarization resistance of the LSCF electrode.

that the addition of Pt improves the catalytic activity of the LSCF electrode in a different manner from that of GDC. Watanabe et al. found that fine Pt particles had a significant depolarizing effect on an LSM electrode [12]. In their report, it was proposed that Pt promotes the dissociative adsorption of O_2 or the exchange reaction with oxygen vacancies. At low overpotential (impedance results), the LSCF–Pt composite electrode exhibits lower polarization resistance than the LSCF electrode. Therefore, the observed improvement in the catalytic activity of the LSCF–Pt composite electrode might be mainly due to the catalysis of the charge-transfer reaction, which is the rate-determining step in the reduction of oxygen at high temperature [13].

The composite of LSCF and GDC showed better catalytic activity at low temperature (<600 °C) than at high temperature. Comparing the left and right images of Fig. 2 suggests that GDC can serve as a grain growth inhibitor of LSCF. It is well known that the oxygen reduction process strongly depends on the microstructure of the electrode, in particular, the grain size of the electrode material. The low polarization resistance obtained in the LSCF–GDC composite electrode might be associated with the microstructural change induced by the addition of GDC. In addition, GDC can not only produce triple-phase boundaries, but also provide rapid mass transport (the interface between LSCF and GDC) and enhance the performance of the electrochemical cell [14].

4. Conclusion

Adding GDC or Pt to the LSCF electrode resulted in its having a lower polarization resistance than the pure LSCF

electrode. Both the LSCF and LSCF–Pt electrodes showed good electrocatalytic activity against O₂ at temperatures lower than 700 °C. A small amount (0.5 vol%) of Pt was found to be sufficient to reduce the polarization resistance of the LSCF electrode over the whole range of operating temperatures (500–800 °C). However, the addition of GDC was only effective at operating temperatures of less than 700 °C and the polarization resistance was significantly decreased at 500 °C. From the microstructural viewpoint, the addition of GDC is more effective than that of Pt, allowing a fine-grained microstructure to be obtained in the LSCF–GDC composite electrode.

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