Short communication

# Electrochemical performance of La$_{1.6}$Sr$_{0.4}$NiO$_4$–Ag composite cathodes for intermediate-temperature solid oxide fuel cells

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## ARTICLE INFO

## ABSTRACT

La$_{1.6}$Sr$_{0.4}$NiO$_4$–Ag (LSN–Ag) composite cathodes are prepared and characterized by XRD and SEM, respectively. The electrochemical properties of the composite cathodes are investigated using AC impedance and DC polarization methods from 500 to 700 °C under different oxygen partial pressures. The polarization resistance ($R_p$) decreases with the increase of Ag content in the composite electrode. The addition of 5 vol.% Ag in LSN results in the lowest $R_p$ of 0.21 Ω cm$^2$ at 700 °C in air. Oxygen partial pressure dependence study indicates that the charge transfer process is the reaction rate limiting step, while the diffusion process has no sensitive to the Ag loading. LSN–5Ag cathode exhibits the lowest overpotential of about 32 mV at a current density of 144 mA cm$^{-2}$ at 700 °C in air.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) are considered as a promising next-generation electric power source because of their high efficiency, environmental friendliness and fuel flexibility. There has been considerable effort in recent years to reduce the operating temperature of SOFCs to an intermediate range of 500–800 °C [1,2]. However, the reduced operating temperature leads to a decrease in the catalytic activity of the cathode for the oxygen reduction reaction. One method to improve the cathode performance is to modify the oxide electrode with noble metals. The addition of Pt or Pd into porous cathodes can enhance the electrocatalytic activity, while maintaining adequate amount of reaction sites, e.g. the triple phase boundary TPB [3–5]. Ag metal is a promising electrocatalytic material for oxygen reduction reaction. Several kinds of oxide-Ag cermet cathodes were found to show good electrochemical performances [6–9]. For example, Sakito et al. [7] studied the electrochemical properties of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$–Ag composite cathode. They found the peak power density of the test cell increased to 0.42 W cm$^{-2}$ at 530 °C by the addition of 18 vol.% Ag. Wang and Barnett [8] observed that the addition of silver to La$_{0.7}$Sr$_{0.3}$CoO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ cathodes resulted in significant improvement of electronic conductivity and electrocatalytic activity for oxygen reduction reaction. Studies have also proved that Ag particles with relatively small size and homogeneous dispersion always produce enlarged reaction area, which leads to improved catalytic activity [10,11]. These results demonstrate that the nano-Ag catalyst-infiltrated material can be an effective and low-cost cathode for IT-SOFCs.

From the literature, we noticed that current study in this field is focused mainly on the perovskite oxide-Ag cermet. Oxides with the K$_2$NiF$_4$-type structure have not been considered for such application. In previous studies, Sr doped La$_2$NiO$_4$ was found to exhibit high electronic conductivity and promising cathodic properties [12,13], due to their relatively high oxygen diffusion and surface exchange coefficients [14,15]. The electrochemical properties of La$_{2-x}$Sr$_x$NiO$_4$ (LSN) were further enhanced by the addition of suitable amount of Ce$_{0.9}$Gd$_{0.1}$O$_{1.9}$ [16].

In this paper, we extend our study by investigating the electrochemical properties of La$_{1.6}$Sr$_{0.4}$NiO$_4$ (LSN)–Ag cermet. Ag is added based on the following considerations: (1) silver is a good electronic conductor and it should improve the electronic conductivity of the cathode; (2) as the melting point of silver is low, it might aid to sinter the cathode at lower temperature; (3) by improving the activity of the oxygen exchange reaction with Ag doping, a good performance of the cathode is expected.

## 2. Experimental

La$_{1.6}$Sr$_{0.4}$NiO$_4$ (LSN) powder was synthesized using the glycine-nitrate process (GNP) according to Ref. [17]. Ce$_{0.9}$Gd$_{0.1}$O$_{1.9}$ (CGO) powder was prepared according to Ref. [18]. The CGO powders were uniaxially pressed at 220 MPa and then sintered at 1400 °C for 10 h to form a dense pellet. The LSN powder was first mixed with ter-

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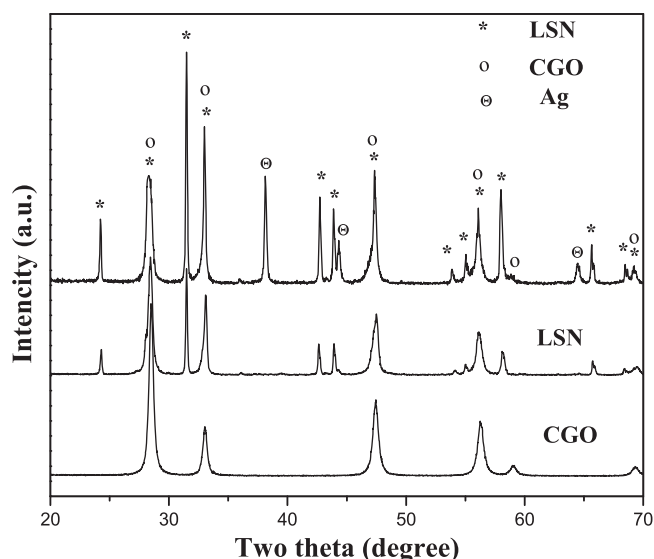E-mail address: zhaohui98@yahoo.com (H. Zhao).

**Fig. 1.** XRD patterns of the as-prepared LSN, CGO and the LSN–CGO–Ag mixed powders after sintering at 800 °C, for 72 h, in air.

pineol to form a slurry, and subsequently painted on one side of the CGO electrolyte to form an electrode area of 0.5 cm$^2$. The cathode was first heated at 400 °C for 2 h to eliminate organic binders, followed by sintering at 1000 °C for 4 h in air. For the modification of LSN cathode with silver, a method of nitrate decomposition was applied [19]. In general AgNO$_3$ solution with the concentration of 0.05 mol L$^{-1}$ was dropped by a suction pipette with an accuracy of ±0.01 mL and soaked into the porous LSN cathode layer, and then heated over a hotplate to evaporate the water, followed by firing at 800 °C for 4 h to form the working electrode (WE). Platinum paste was painted on the other side of the CGO pellet in symmetric configuration, as the counter electrode (CE). A Pt wire with diameter of 0.1 mm was used as reference electrode (RE). This Pt wire was welded on the same side of the working electrode with Pt paste, to form a point contact (less than 0.5 mm in diameter) on the edge of CGO electrolyte. The RE was normally placed 5 mm away from the WE, ensuring that this distance was more than three times the thickness of the electrolyte [20]. Five kinds of electrodes were prepared, in which the volume percentage of Ag to LSN oxide was 0.5, 2, 3, 5 and 7 vol.%, and they were noted as LSN–05Ag, LSN–2Ag, LSN–3Ag, LSN–5Ag and LSN–7Ag, respectively.

Structural features and phase stability of the materials were investigated by X-ray powder diffraction on a Rigaku D/max-2550 diffractometer (Cu $K_\alpha$ radiation, operated at 40 kV, 200 mA, $\lambda$ = 0.15418 nm). The morphology and microstructure of the sintered electrodes were examined with Hitachi S-4700 FEG-SEM. AC impedance spectroscopy was performed using an Autolab PGStat30 (Holland) in the frequency range of 1 MHz to 0.1 Hz at temperatures ranging between 500 and 700 °C. Oxygen partial pressure was varied between $1.0 \times 10^{-4}$ and $1.0 \times 10^{-1}$ atm. by using O$_2$/N$_2$ gas mixtures and monitored by oxygen sensor (ZIROX, Greifswald/Germany). The DC polarization experiments were performed by the chronoamperometry method described in a previous publication [21].

## 3. Results and discussions

### 3.1. Chemical stability of the cathode material

XRD experiments were first performed to check the phase purity of the as-prepared powders. Fig. 1 shows the XRD patterns of LSN and CGO powders; compared to the literature [22], LSN crystallizes
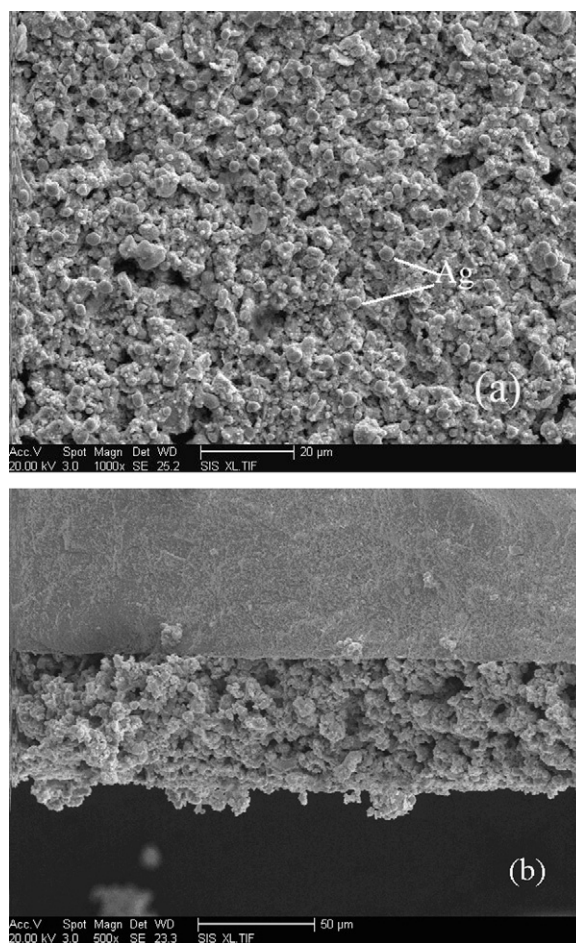


**Fig. 2.** SEM images of LSN–5Ag composite cathode on CGO electrolyte (a) surface; (b) cross-section.

in a single phase with K$_2$NiF$_4$-type structure and CGO with the cubic fluorite structure. No impurity phase was found. In order to study the chemical stability of LSN with CGO and Ag materials at high temperature, the sample was prepared by mixing LSN thoroughly with CGO and Ag powders in a 1:1:1 weight ratio, and then heat-treated at 800 °C for 72 h in air. It was observed from Fig. 1 that LSN, CGO and Ag remained their structures unchanged, no new diffraction patterns were detected except those of LSN, CGO and Ag. This result reveals that LSN has a good chemical compatibility with CGO electrolyte and Ag material.

### 3.2. Electrochemical properties of the cathode material

Fig. 2(a) and (b) shows the images of the surface and cross-section microstructures of LSN–5Ag composite cathode sintered on CGO electrolyte at 800 °C for 4 h, respectively. The microstructure of the composite cathode exhibits very fine particles and moderate porosity. The silver spherical particles obtained by the decomposition of AgNO$_3$ adhere to the surface of the LSN layer, and have an average particle size of 1.2 μm. From the cross-sectional view, it can be seen that the cathode with thickness of about 40 μm has a good contact with CGO electrolyte (see Fig. 2(b)). This kind of microstructure is benefit for the improved cathode property because the silver with high number of electrochemical active sites, high catalytic activity for electrochemical reaction on cathode, is helpful to the electrochemical performance of cathode [23]. It could be anticipated that the polarization resistance of cathode is reduced by the modification.
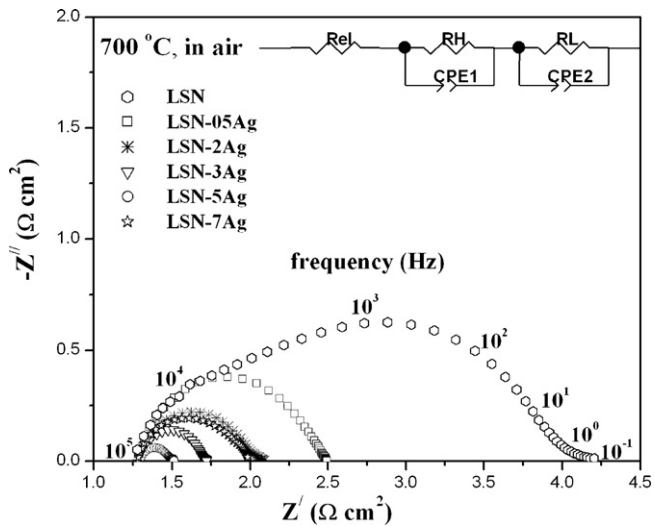
**Fig. 3.** Impedance spectrum of the LSN–Ag composite cathodes at 700 °C in air.



**Fig. 4.** Temperature dependence of the polarization resistance $R_p$ for various LSN–Ag composites measured in air.

Fig. 3 shows the impedance spectra of LSN–Ag composite cathodes measured at 700 °C in air. From the impedance spectra, it was observed that for all the cathodes with vary amount of silver contents, the impedance spectra could be separated into two arcs located in the high frequency zone and the low frequency zone, respectively. This suggests that the oxygen reduction reaction over the electrodes was composed of at least two different processes. In order to clarify this point, an equivalent circuit was used to fit the measurement data (Fig. 3, inset). Here $R_{el}$ represents the intercept value of the impedance spectrum at high frequency side with the real axis, which corresponds to the resistance of the electrolyte and lead wires. $R_H$ and $R_L$ are the resistance corresponding to the arc1 and arc2, respectively. CPE is a constant phase element. The total polarization resistance ($R_p$) is the sum of $R_H$ and $R_L$. It was observed that $R_H$ decreased first as the Ag concentration increased up to 5 vol.%, and then it increased rapidly with the further increasing of Ag content. $R_L$ had almost no dependency on Ag concentration. The variation of polarization resistance with Ag doping concentration can be understood. It is known that the performance of cathodes is strongly influenced by both the electronic and oxygen ionic conductivities of the electrode materials. The initial improvement with Ag incorporation (up to 5 vol.%) is due to the increase of the catalytic activity while maintaining adequate amount of reaction sites, e.g. the TPB. In contrast, when the content of silver is over 5 vol.%, the LSN network structure may be broken so that oxygen ion cannot be transferred successfully and valid TPB decreases. This will reduce the active sites for oxygen reduction reaction and consequently results in a decrease of electrochemical performance [24]. The similar result has been reported before in the investigation of $Nd_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_3$–Ag and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$–Ag composite cathodes [10,25].

Fig. 4 shows the behaviour of polarization resistance as a function of temperature for the LSN–Ag composite cathodes. A linear relationship between the $log(R_p)$ and $1000\,T^{-1}$ was obtained. From the Arrhenius plot of the polarization resistance, the activation energy (determined by the slope of the interpolated straight lines) can be calculated. The values are around 1.15–1.45 eV for all the studied composite cathodes. LSN–5Ag (with 5 vol.% Ag) composite cathode gave the lowest polarization resistance value of 0.21 Ω cm$^2$ at 700 °C in air. This value is ten times smaller than that of pure LSN cathode [13], similar to the one reported for $La_{0.7}Sr_{0.3}CoO_3$–Ag and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$–Ag composite cathode [8,26]. Therefore, in the experiments below, only the optimum composite electrode LSN–5Ag was further studied.
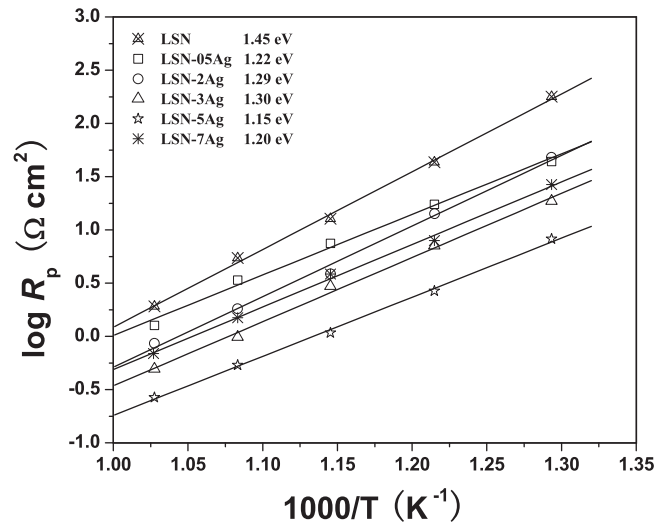
In order to determine the reaction rate limiting step, the effect of oxygen partial pressure on the polarization resistance of LSN–5Ag composite cathode was further studied. Fig. 5 is a typical impedance spectrum of the LSN–5Ag cathode measured at 700 °C under various oxygen partial pressures ($P_{O_2}$). From the fitting results, it can be found that the resistance of the high frequency arc ($R_H$) is much larger than that of the low frequency one ($R_L$). This means that the $R_H$ related process is the reaction rate limiting step. The corresponding capacitances (obtained from the relaxation frequency of the two arcs, according to the relation $f = 1/2\pi RC$) are about $10^{-4}$ and $10^{-1}$ F, respectively. These values are similar to that reported for the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$–Ag composite electrode [26]. It was consistent with electrochemical reaction mechanism that occurred on electrode [27]. These results further prove that two arcs exist in the impedance spectrum, and they represent two different electrochemical processes occurred on electrode.

The electrode polarization resistances ($R_p$) of LSN–5Agat 700 °C under various $P_{O_2}$ are shown in Fig. 6, from which the $P_{O_2}$ dependence of the $R_p$ can be calculated.
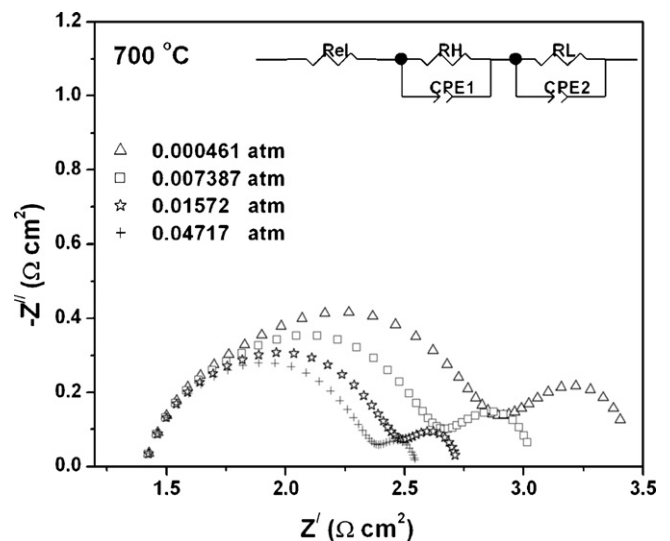


**Fig. 5.** Impedance spectrum for the LSN–5Ag composite cathode measured at 700 °C under different oxygen partial pressures.
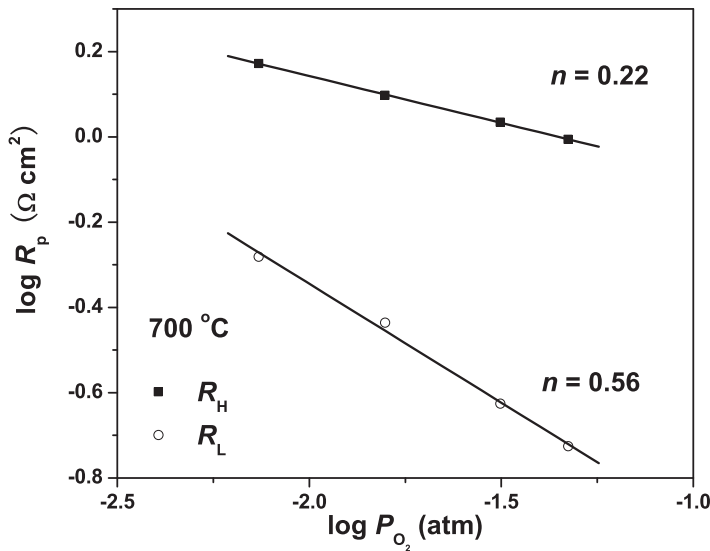
**Fig. 6.** Dependence of polarization resistance on oxygen partial pressure for LSN–5Ag composite cathode at 700 °C.



**Fig. 7.** Polarization curves for LSN–Ag composite electrode obtained at 700 °C in air.

Generally, $R_p$ varies with the oxygen partial pressure according to the following equation

$$R_p = R_p^0 (P_{O_2})^n$$

$$n = 1, \quad O_2(g) \Leftrightarrow O_{2,ads.}$$
$$n = \frac{1}{2}, \quad O_{2,ads.} \Leftrightarrow 2O_{ads.}$$
$$n = \frac{1}{4}, \quad O_{ads.} + 2e^{/} + V_O^{\bullet\bullet} \Leftrightarrow O_O^{x}$$

The value of $n$ may give useful information about the type of species involved in the electrode reactions [28,29]. For metal oxide electrodes on solid electrolytes, $n = 0.25$ has been attributed to the charge transfer process at the TPB, occurring at the current collector/electrode and the electrode/electrolyte interfaces, respectively. $n = 0.5$ related to the oxygen adsorption–desorption process, involving oxygen diffusion at the gas cathode surface interface and surface diffusion of intermediate oxygen species related, and $n = 1$ to gaseous diffusion of oxygen molecules in the porous structure. As can be seen from Fig. 6, a 0.56 $P_{O_2}$ dependency of $R_L$ was observed. We propose that the low frequency arc be assigned to the oxygen adsorption–desorption process. The characteristic of $R_H$ showed 0.22 $P_{O_2}$ dependency, which could be related to the charge transfer process at the TPB. Compared with the results obtained in Fig. 5, it is clear that the charge transfer process is the major rate limiting step for LSN–5Ag composite cathode in the whole range of measurement oxygen partial pressure. The similar behaviour has been observed in our previous study of pure LSN cathode materials [13].

Cathodic polarization and overpotential are important factors affecting the electrode performance. Fig. 7 shows the cathodic polarization curves for LSN–Ag composite cathodes measured at 700 °C in air. It can be seen that at the same cathodic overpotential, the current density increases with the addition of Ag, and the best performance is reached at 5 vol.% Ag content. The overpotential of about 32 mV is obtained at a current density of 144 mA cm$^{-2}$ at 700 °C in air. This value is similar to that of $Y_{0.25}Bi_{0.75}O_{1.5}$–Ag composite cathode material previously reported in the literature [30]. Clearly the electrode performance has been improved with the addition of Ag to LSN. Based on the impedance spectra analysis (Figs. 3 and 4), the reduction in the cathodic overpotential caused by Ag impregnation could be attributed possibly to the high catalytic activity of Ag rather than simply to the reduction in the ohmic resistance. In order to gain a more in depth understanding
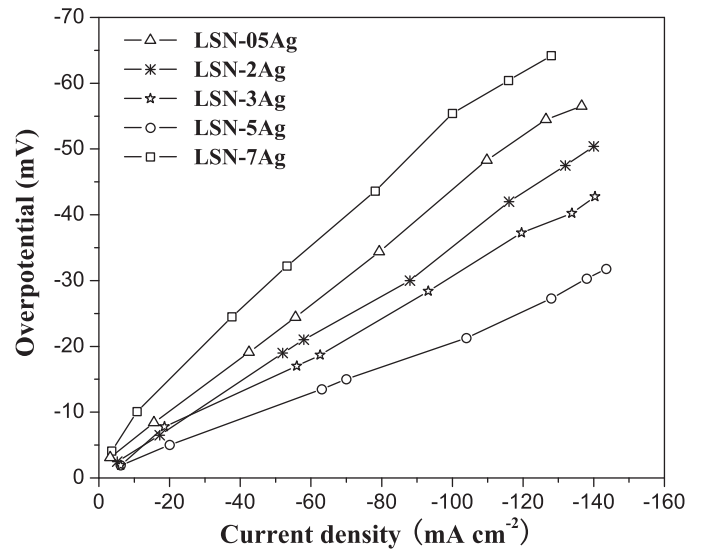
of the positive effects of the silver, further studies are obviously required.

It should be noted that although the addition of silver can greatly promote the cathode performance, the long-term stability of silver and hence the cathode performance is a critical issue that should be addressed [31]. In order to gain a more in depth understanding of the positive effects of the silver, and its long-term stability in the LSN–Ag composite cathode, further studies are obviously required.

## 4. Conclusions

$La_{1.6}Sr_{0.4}NiO_4$–Ag composite materials have been prepared and their cathode properties were studied below 700 °C. The lowest polarization resistance, 0.21 Ω cm$^2$ at 700 °C in air, was found for the 5 vol.% Ag composite cathode. Impedance analysis and oxygen partial pressure dependence study indicate that the charge transfer process is the reaction rate limiting step. The electrochemical performance of LSN–5Ag for the oxygen reduction reaction was superior to the LSN, which obviously results from the impregnated silver that enhances the oxygen reduction performance of LSN.

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