



Short communication

Enhanced electrochemical performance of solution impregnated $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ cathode for intermediate temperature solid oxide fuel cells

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ARTICLE INFO

Article history:

Received 15 June 2011

Received in revised form 14 July 2011

Accepted 15 July 2011

Available online 22 July 2011

Keywords:

Solid oxide fuel cells

Solution impregnation

Electrochemical impedance

Polarization resistance

ABSTRACT

Solution impregnated $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$ + Gd-doped CeO_2 (LSCN+GDC) cathodes for intermediate temperature solid oxide fuel cells (IT-SOFC) are prepared and their electrochemical properties are evaluated and compared with the conventional LSCN cathodes. The results indicate that the cathode performance can be enhanced by the presence of the nanosized microstructure produced with the solution impregnation method. It is determined that the amount of LSCN loading in the LSCN + GDC composite cathode needs to be higher than 35 wt% in order to achieve a performance superior to that of the conventional LSCN cathode. The optimum amount of LSCN loading is in the range of 45–55 wt% with an activation energy near 1.32 eV for oxygen reduction. At temperatures between 600 and 750 °C, the polarization resistance of the 55 wt% LSCN loaded LSCN + GDC cathode is in the range of 1.07 and 0.08 $\Omega\text{ cm}^2$, which is only about one half of that for the conventional cathode.

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1. Introduction

As the operating temperature of solid oxide fuel cells is reduced from conventional high temperature range around 1000 °C to the intermediate temperature range between 600 and 800 °C, the state-of-the-art cathode material, Sr-doped LaMnO_3 (LSM), is facing challenges of high overpotential and low electrochemical activity [1]. Up to 60% of the cell voltage loss is attributable to the polarization resistance associated with oxygen reduction reaction in the cathode [2]. This problem has stimulated intensive studies on alternative cathode materials, aiming to reduce the cathode polarization loss in the intermediate temperature solid oxide fuel cells (IT-SOFCs). The most frequently investigated alternative cathode materials for IT-SOFCs are the mixed electron-oxygen ion conducting perovskite ceramics such as Sr-doped LaCoO_3 and LaFeO_3 [2,3]. They possess excellent electrical and electrochemical properties with a thermal expansion coefficient (TEC) that is adjustable by element doping, and extends the oxygen reduction reaction away from the triple phase boundary in the cathode.

By integrating the good electrical property of Sr-doped LaCoO_3 (LSC) [4,5] and the high stability of Sr-doped LaFeO_3 (LSF) [6,7], $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) has received extensive attention due

to its sufficiently high mixed conductivity and suitably adjusted TEC; and polarization resistances as low as 0.24 $\Omega\text{ cm}^2$ can be achieved by using $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ as the cathode at 726 °C [8]. Furthermore, it has been demonstrated that, with partial substitution of Co by Ni in LSC, the mixed conductivity can be further increased and a more favorable TEC match to the electrolyte can be obtained at the same time [9], which makes $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_{3-\delta}$ a promising alternative cathode material for IT-SOFCs. More recently, Chen et al. [10] has studied the chemical compatibility, electrical conductivity, TEC and electrochemical performance of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Ni}_{0.2}\text{O}_3$ (LSCN). It is found that the LSCN reacts with Y_2O_3 doped ZrO_2 (YSZ) electrolyte at temperatures above 900 °C but is inert to Gd-doped CeO_2 (GDC) electrolyte such as $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$; and it has a conductivity of 1243 S cm^{-1} at 800 °C and an average TEC of $16.7 \times 10^{-6} \text{ K}^{-1}$ between 30 and 1000 °C. Polarization resistances of 0.30 and 0.10 $\Omega\text{ cm}^2$ at 700 and 750 °C have been achieved with the porous LSCN cathode on the GDC interfaced YSZ. Hjalmarsson et al. [11,12] have also evaluated a variety of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_{3-\delta}$; and even higher electrical conductivity (over 1500 S cm^{-1} at 800 °C) and lower TEC ($16.5 \times 10^{-6} \text{ K}^{-1}$) have been reported.

In order to enhance the cathode performance and circumvent thermal and chemical incompatibility between cathode and electrolyte materials, impregnation or infiltration technique, instead of the conventional method involving high temperature sintering, is extensively employed for preparation of the composite

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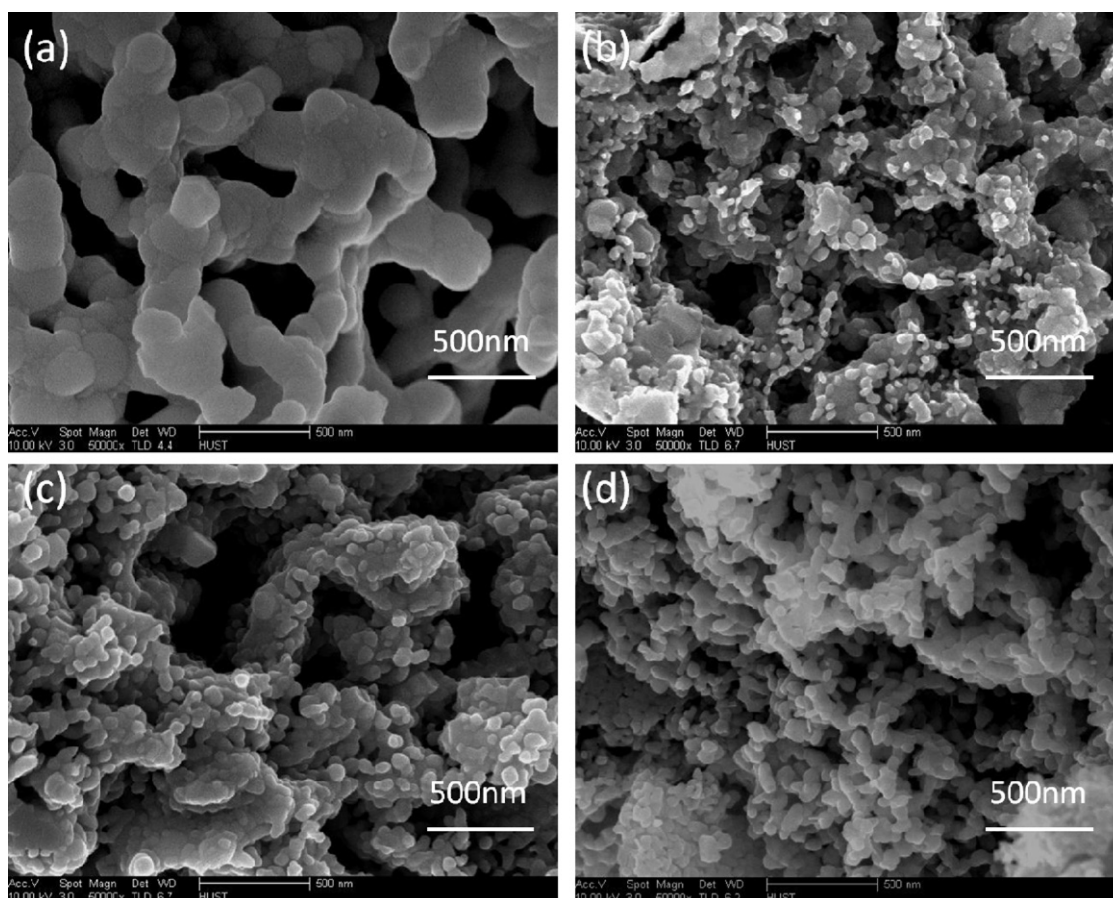


Fig. 1. SEM micrographs of the porous GDC structure and LSCN cathodes: (a) GDC scaffold; (b) 35 wt% LSCN loaded; (c) 55 wt% LSCN loaded; (d) screen-printed LSCN.

cathodes that consist of mixed conducting perovskite and electrolyte [13–16]. The impregnated LSM–YSZ [17–20] and LSCF–YSZ nano composite cathodes [21,22] have demonstrated higher than usual performance. In the present study, the impregnated LSCN+GDC composite cathodes with various LSCN loadings are evaluated and compared with that prepared by the conventional method.

2. Experimental

A 0.5 mol L^{-1} solution for LSCN impregnation was prepared by dissolving stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into distilled water. A part of the above solution, with addition of glucose and acrylamide (99.9%, Sinopharm Chemical Reagent Co. Ltd) as the fuel and dispersant [10], was dried in an oven at 180°C for 10 h and calcined at 800°C for 2 h to obtain LSCN powder for fabrication of the conventional cathode. The GDC ($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$) powder, which was used for making the buffer layer between the LSCN and YSZ (TZ-8Y, Tosoh, Japan), was synthesized by the same method as that used for making the LSCN powder but at a higher calcining temperature of 900°C . Dense YSZ electrolyte disks with a dimension of $\Phi 20 \times 1.2 \text{ mm}$ were prepared by sintering the die-pressed YSZ green disks at 1500°C for 4 h in air. The phase formation of the LSCN and GDC was confirmed in the previous study [10].

For preparation of the half cell with impregnated LSCN+GDC cathode, the GDC slurry was screen printed onto the YSZ electrolyte substrate and sintered in air at 1200°C for 2 h to form a porous GDC, into which the prepared LSCN solution was impregnated. The LSCN-impregnated GDC was then dried and sintered at 750°C in air for

2 h. The LSCN loading in the cathode was increased by repeating impregnation/drying cycles. For preparation of the half cell with conventional LSCN cathode, a GDC interlayer was slurry printed on the dense YSZ electrolyte substrate and sintered at 1250°C in air for 2 h to form the buffer, on which the LSCN slurry was screen printed and sintered at 1000°C in air for 2 h. All the cathodes prepared have a thickness in the range of $8\text{--}10 \mu\text{m}$ and an active area of 0.5 cm^2 .

In order to electrochemically evaluate the prepared cathodes, a Pt paste was painted symmetrically on the opposite side of the YSZ electrolyte as the counter and reference electrodes. The distance between the circular-shape counter electrode and the ring reference electrode was 4 mm (3 times larger than the thickness of the electrolyte), avoiding the possible interference of electrical field on the electrochemical measurement [23]. Using an impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface analyzer (Solartron 1287), the electrochemical impedance of the half cell was measured in static air in a frequency range of 0.1 Hz to 100 kHz with 10 mV signal amplitude in the temperature range of $600\text{--}750^\circ\text{C}$ at open circuit. A cathodic current of 200 mA cm^{-2} was applied for different periods of time to characterize the cathode stability. The electrode interface resistance (R_E) was determined by the difference between the low- and high-frequency intercepts on the real impedance axis.

3. Results and discussion

Fig. 1 shows the cross-sectional views of the porous GDC layer, the LSCN impregnated and conventional LSCN cathodes. The porous GDC was well sintered at 1200°C in air for 2 h, forming a three-dimensional rigid network with a porosity of $\sim 45\%$ (Fig. 1a). With

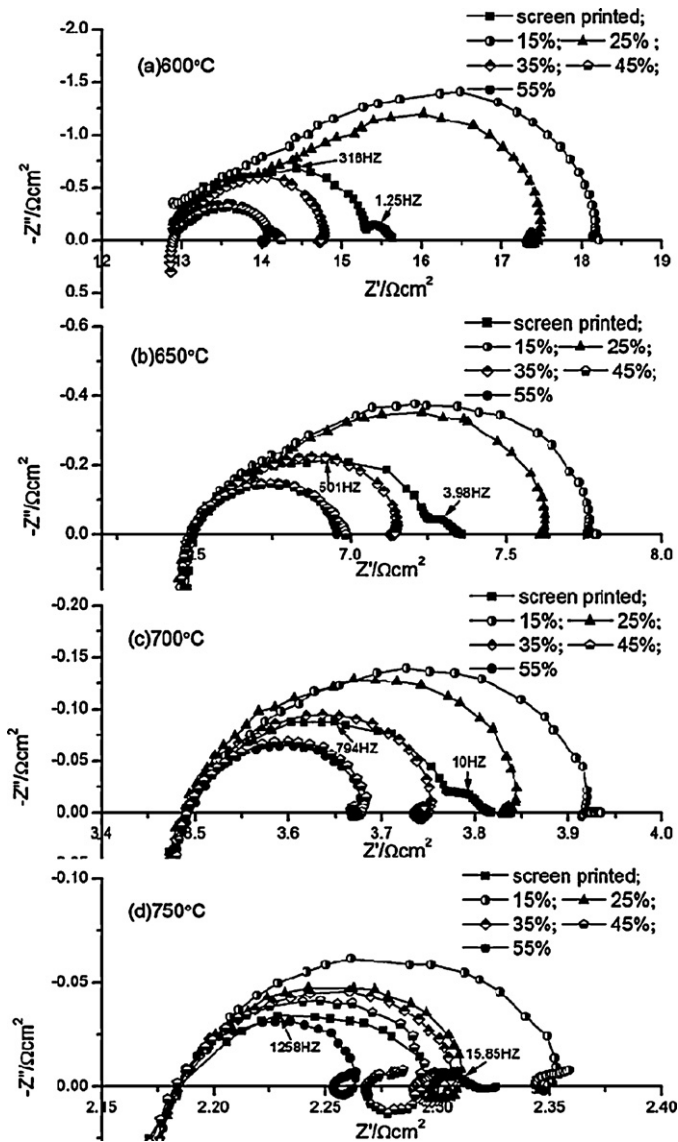


Fig. 2. Electrochemical impedance spectra of LSCN+GDC cathodes with various LSCN loadings measured in air at open circuit, in comparison with that of the conventional LSCN cathode, at (a) 600 °C, (b) 650 °C, (c) 700 °C and (d) 750 °C.

repeated impregnation of the LSCN solution, the amount of LSCN loading in the porous GDC scaffold, which is defined by the weight ratio of LSCN to GDC, was increased gradually, as typically seen in Fig. 1b and c for loadings of 35 wt% (impregnated twice) and 55 wt% (impregnated three times), respectively. The impregnated LSCN particles, averagely smaller than 60 nm, were well connected and uniformly distributed on the GDC backbone. The cross-sectional view of the conventional screen printed LSCN cathode is shown in Fig. 1d for comparison.

Fig. 2 illustrates the electrochemical impedance spectra of oxygen reduction in the cathodes measured under the condition of open circuit at various temperatures between 600 and 750 °C in air for the LSCN cathodes prepared via the solution impregnation and conventional methods, respectively. The impedance spectra of the conventional cathode at various temperatures were characterized by two distinguished arcs with labeled peak frequency. The low-frequency polarization resistance decreased from 0.43 Ωcm^2 to 0.03 Ωcm^2 as temperature increased from 600 °C to 750 °C, even though its contribution to the overall polarization resistance

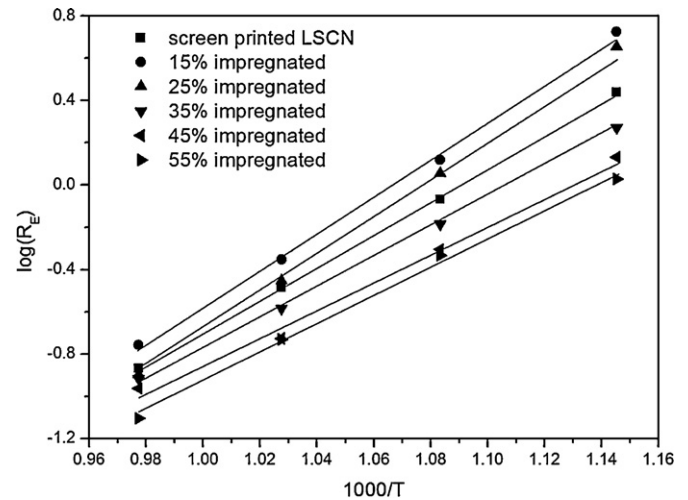


Fig. 3. Temperature dependence of R_E for LSCN+GDC cathodes with various LSCN loadings and conventional LSCN cathode, derived from Fig. 2.

increased from 15.8% at 600 °C to 23.9% at 750 °C. This phenomenon was similar to the impedance behaviour of LSCN cathode reported previously [12]. The overall electrode polarization resistance R_E was 2.74, 0.85, 0.33 and 0.14 Ωcm^2 at 600, 650, 700 and 750 °C, respectively. These values were smaller than those of the conventional LSCF cathodes reported in the literature [24]. The electrochemical impedance spectra of the impregnated LSCN+GDC cathodes at various temperatures showed a feature of a flattened arc. With increase of the measurement temperature, the size of the arc decreased and the inductance loop in the fourth quadrant became increasingly larger at lower frequencies. Such inductance loop has been frequently observed for the impregnated cathodes [21,22,24–27] and is considered to be related to the enhanced adsorption/desorption of oxygen species on the surface of nano-structure electrodes at higher temperature, but clarification of the detailed mechanisms requires further studies.

Fig. 3 shows the dependence of the polarization resistance of various prepared cathodes on temperature, which was derived from Fig. 2. With 15 and 25 wt% loadings of LSCN, the R_E of the impregnated LSCN+GDC cathode was higher than that of the conventional cathode at various temperatures measured, but the difference became less significant as measurement temperature increased. For example, at 750 °C, the R_E for the 25 wt% loaded LSCN+GDC cathode was 0.13 Ωcm^2 , which was comparable with that for the conventional cathode at 0.14 Ωcm^2 . The R_E for the LSCN+GDC cathodes with a loading at 35 wt% or above was considerably smaller than that for the conventional LSCN cathode, especially at temperatures below 700 °C. As the amount of the LSCN loading increased in the composite cathode, the R_E decreased dramatically. For instance, at 750 °C, it decreased from 0.14 to 0.08 Ωcm^2 as the amount of loading increased from 15 to 55 wt%. It can also be seen from Fig. 3 that the R_E of each prepared cathode decreased linearly with increase in the measurement temperature, suggesting that the Arrhenius relation was obeyed. The activation energy determined in this study for the conventional LSCN cathode was 1.54 eV, which was somewhat smaller than that reported previously [10,11]. The activation energy for the LSCN+GDC cathodes varied in the range of 1.32–1.83 eV, with a minimum occurring in the neighborhood of 45–55 wt% loading. These results suggest that the cathode performance is enhanced by the nanosized microstructure via solution impregnation of LSCN and the amount of LSCN loading for the optimum electrochemical performance of the LSCN+GDC cathode is in the range of 45–55 wt%.

4. Conclusions

Nanostructured LSCN+GDC composite cathodes and conventional LSCN cathode were successfully fabricated by solution impregnation and screen printing-sintering processes, respectively; and their electrochemical performance was evaluated by electrochemical impedance at various temperatures. Based on the results obtained, the following conclusions are made.

- (1) Solution impregnation is an effective method for the enhancement of electrochemical performance of the LSCN cathodes those are featured with nanosized LSCN particles formed at relatively low temperature and uniformly distributed on the scaffold of well sintered GDC.
- (2) For obtaining electrochemical properties superior to those of the conventional LSCN cathode, the amount of LSCN loading in the LSCN+GDC composite cathode should be higher than 35 wt%; and the optimum amount of LSCN loading is in the range of 45–55 wt%.
- (3) At temperatures between 600 and 750 °C, the R_E for the 55 wt% LSCN loaded LSCN+GDC cathode is in the range of 1.07 and 0.08 Ωcm^2 , which is approximately only one half of that for the conventional cathode.

Acknowledgements

This research was financially supported by National “863” project 2011AA050702, Natural Science Foundation of Hubei Province (2008CDA004) and Fundamental Research Funds for Central Universities (HUST2010ZD012). SEM characterization was assisted by the Analytical and Testing Center of Huazhong University of Science and Technology.

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