



Short communication

Low-temperature solid oxide fuel cells with $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ as the cathodesRuifen Tian^{a,b}, Jue Fan^{a,c}, Yali Liu^a, Changrong Xia^{a,*}^a Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China^b College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, China^c Chemistry Department, Clark University, Worcester, MA 01610, USA

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ABSTRACT

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) has been widely developed as the cathode material for high-temperature solid oxide fuel cells (SOFCs) due to its chemical and mechanical compatibilities with the electrolyte materials. However, its application to low-temperature SOFCs is limited since its electrochemical activity decreases substantially when the temperature is reduced. In this work, low-temperature SOFCs based on LSM cathodes are developed by coating nanoscale samaria-doped ceria (SDC) onto the porous electrodes to significantly increase the electrode activity of both cathodes and anodes. A peak power density of 0.46 W cm^{-2} and area specific interfacial polarization resistance of $0.36 \Omega \text{ cm}^2$ are achieved at 600°C for single cells consisting of Ni-SDC anodes, LSM cathodes, and SDC electrolytes. The cell performances are comparable with those obtained with cobalt-based cathodes such as $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, and therefore encouraging in the development of low-temperature SOFCs with high reliability and durability.

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1. Introduction

It is desirable to develop low-temperature SOFCs because of their potential to dramatically reduce the cost of the materials and cell fabrication in addition to improved reliability, portability, and operational life. Low-temperature SOFCs are usually constructed on doped-ceria electrolytes using cathodes consisting of cobalt-based perovskites rather than strontium-doped lanthanum manganites (LSM), which are commonly used as the cathode materials for high-temperature SOFCs. For example, with $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) as the cathodes, fuel cells could generate power density as high as 0.4 W cm^{-2} at 600°C [1–3]. It has been recently proved that cobalt-based perovskites such as SSC, LSCF, and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) [4–6] are much more electrochemical active than LSM. Therefore, cobalt-based perovskites are considered as the primary choice for low-temperature SOFCs. However, the thermal expansion coefficients of SSC (20×10^{-6}), LSCF (16×10^{-6}), and BSCF (24×10^{-6}) do not match those of the doped-ceria electrolytes (12×10^{-6}). The mismatch suggests low reliability when SOFCs are operated in harsh conditions such as thermal cycles. Deep decrease in electrode performance has been exper-

imentally shown on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ electrodes when they were operated under thermal cycle and long-term operational conditions [7]. On the contrary, the thermal expansion coefficient of LSM and those of the electrolytes are well matched. Thus, LSM has been extensively investigated and developed as an electrode material for high-temperature as well as intermediate-temperature SOFCs. But its application to low-temperature SOFCs is limited since its electrochemical performance decreases dramatically with temperature, especially when the operational temperature is below 600°C [8,9].

The electrode performance could be substantially increased by microstructure optimization. Coating with nanosized ceria has been experimentally and theoretically proved to be an effective route to improve the performance significantly [10–15]. LSM coated with samaria-doped ceria (SDC) reduced the interfacial polarization resistance from 0.75 to $0.23 \Omega \text{ cm}^2$ at 700°C [14]. The anode performance could also be improved by SDC coating. For instance, SDC-coated Ni anode generated power density of 0.57 W cm^{-2} (600°C), much higher than that obtained with a composite Ni-SDC anode [12]. In this work, to develop low-temperature SOFCs using LSM as the cathodes, both the cathodes and anodes were coated with SDC. High fuel cell performances were achieved, which are comparable to those with cobalt-based cathodes. Up to date, cell performance with both electrodes coated with doped ceria is not available in the literature.

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2. Experimental

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC), A-site non-stoichiometric $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_{3-\delta}$ (LSM), and NiO powders were prepared with a glycine–nitrate method [16]. A solution of $\text{Sm}(\text{NO}_3)_3$ and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ were prepared at 1:4 of concentration ratio. Glycine was then added at glycine to nitrate ratio of 2:1. The solution was subsequently heated until self-combustion occurred. The resulted ash was fired at 600 °C for 2 h to form SDC powders with fluorite structure as confirmed by X-ray diffraction (D/Maxra X diffractometer with Cu $K\alpha$ radiation). LSM powder were prepared using $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Mn}(\text{NO}_3)_4$ as the precursors and fired at 800 °C for 4 h to form the perovskite structure. To prepare anode-supported single cells, NiO and SDC powders were mixed and milled as the precursors for the anode substrates. The mass ratio for SDC and NiO was 1:9, and SDC was used to enhance the bonding between the substrate and electrolyte (SDC) film. Starch (10 wt.%) was applied as pore former. The 1:9 SDC–NiO powder was pre-pressed then co-pressed with SDC powder to form bi-layer pellets with diameter at 13 mm. The pellets were fired at 1250 °C in air for 5 h to form dense SDC layer supported on porous NiO–SDC substrates [12]. Slurry consisting of LSM and starch (10 wt.%) was then applied and fired at 900 °C for 2 h to form porous LSM frames on dense SDC electrolytes. The anode substrate, electrolyte, and LSM layer were about 380, 30, and 100 μm thick, respectively.

SDC coating was conducted by impregnating the pellets with the SDC solution under vacuum condition. After drying, they were fired for 2 h at different temperatures (600, 700, 800, and 900 °C). The impregnation–firing cycle was repeated until the impregnated SDC and LSM had equal mass [14]. The cells were then sealed onto alumina tubes, heated to 600 °C. NiO was in situ reduced to Ni, and stabilized at 600 °C for 2 h before conducting the electrochemical characterizations, which were performed under ambient pressure.

The cells were sealed onto an alumina tube with silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins). Humidified (3% H_2O) hydrogen was used as the fuel and ambient air as the oxidant. Hydrogen was humidified through a water bubbler at room temperature and the flow rate was 50 mL min^{-1} . Electrochemical impedance spectra were measured with an Electrochemical Workstation (IM6e, Zahner) under open circuit conditions in a typical frequency range from 1 MHz to 100 mHz with 5 mV as AC amplitude. The morphologies of the cells were characterized with a scanning electron microscope (JSM-6700F, JEOL).

Single cells with different electrodes were also prepared for comparison with impregnated electrodes. Cell I had a normal structure with a composite NiO–SDC anode substrate, a thin film SDC electrolyte (30 μm in thickness), and a composite LSM–SDC (1:1 mass ratio) cathode. The anode–electrolyte bi-layer was prepared by the same co-pressed and co-fired procedures. The cathode was applied by printing and firing at 900 °C for 2 h. Cell II had the same anode and electrolyte as cell I but the cathode was LSM coated with SDC.

3. Results and discussions

3.1. Performances for cells with both electrodes coated with SDC

Shown in Fig. 1a are the cell voltage and power density as a function of current density for a single cell with both electrodes impregnated with SDC. At 500 °C, the cell exhibited open-circuit voltage (OCV) of 0.934 V, which is close to those reported for H_2/air fuel cells with doped-ceria electrolytes. The reported values are 0.950, 0.92, and 0.98 V for single cells with LSCF, SSC, and ANLC-1 as cathodes, respectively [1,3,17]. The closeness in OCVs indicates

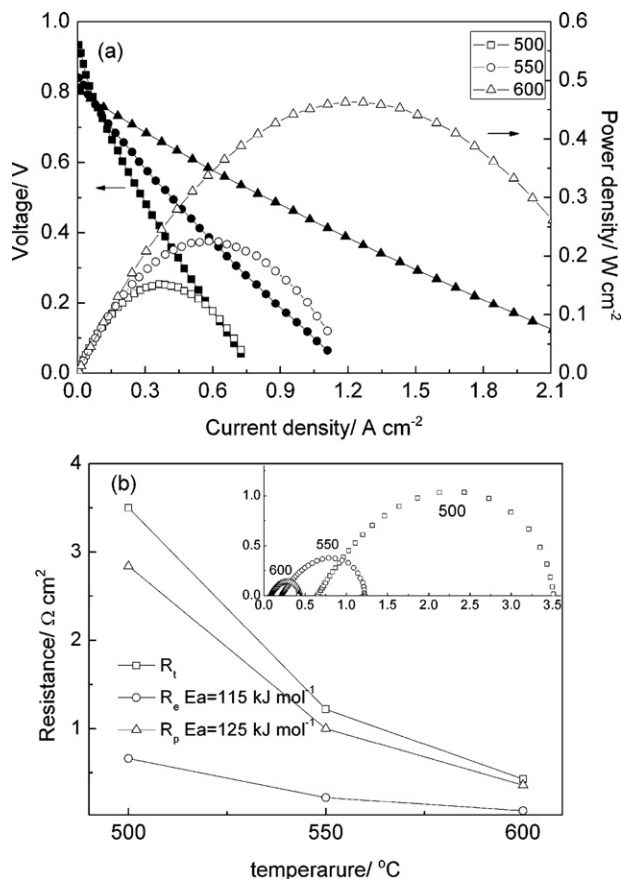


Fig. 1. Electrochemical performances for a single cell (Ni-SDC/SDC/LSM) with both electrodes coated with SDC. (a) Voltages (solid symbols) and power densities (open symbols) versus current densities measured at 500, 550, and 600 °C. (b) Impedance spectra measured under open circuit conditions and the electrolyte resistance (R_e), interfacial polarization resistance (R_p), and total cell resistance (R_t) as determined from the spectra.

that LSM-based cathodes exhibit similar electrochemical activity to those based on cobaltites when SOFCs are operated at temperature below 600 °C. A poor electrode usually causes a low OCV for fuel cells based on mixed-conducting electrolytes [18,19]. The maximum power densities ranged from 0.152 W cm^{-2} at 500 °C to 0.463 W cm^{-2} at 600 °C. The power exports are very high for low-temperature SOFCs and comparable with those obtained with ceria-based fuel cells using SSC and LSCF cathodes (see Table 1). Shown in Fig. 1b are the corresponding impedance spectra measured under open-circuit conditions. The interfacial polarization resistances (R_p), electrolyte resistances (R_e), and total cell resistances (R_t) as determined from the spectra are also shown in Fig. 1b. It is clear that the performance is essentially determined by R_p , to which is contributed by both the cathode and anode. The apparent activation energy of R_p is 125 kJ mol^{-1} , close to those (115 kJ mol^{-1}) reported for ceria-based single cells with LSCF [3] and SSC [1,2] as the cathodes. This further indicates that the SDC-coated LSM cathode has similar activity to those of LSCF and SSC composite electrodes. In addition, this infers that the interfacial polarization resistance in our cell seems to be dominated by the cathode. It is found that at low operating temperature, the effect of the electrode resistances pre-dominates the total cell impedance.

The power density, OCVs, R_p , and activation energy for R_p of the single cell with SDC-coated LSM cathode are comparable to those reported for similar cells with LSCF, SSC, and ANLC-1 cathodes. Therefore, it is promising to use LSM as the cathodes for

Table 1
Peak power densities for low-temperature SOFCs with doped-ceria electrolytes.

Cell component			Power density (mW cm^{-2})			Ref.
Cathode	Electrolyte	Anode	500 °C	550 °C	600 °C	
SSC-GDC	26 μm GDC	Ni-GDC	145	205	270	[1]
SSC-GDC	20 μm GDC	Ni-GDC	145	270	240	[2]
SSC-SDC	30 μm SDC	Ni-SDC	188	140	345	[2]
LSCF-GDC	10 μm GDC	Ni-GDC	167	345	578	[3]
LSM impregnated with SDC	30 μm SDC	Ni-SDC impregnated SDC	152	226	463	This work

low-temperature SOFCs. High reliability in performance is expected for the use of LSM instead of SSC and LSCF because LSM is believed to be more thermally stable and mechanically compatible with the electrolytes than the cobaltite perovskites.

3.2. Performances for cells with different electrodes

Shown in Fig. 2a are the cell voltages and power densities measured at 600 °C for cells with different electrodes. Fig. 2b shows their impedance spectra measured under open circuit conditions. Cell I had two normal composite electrodes, i.e. Ni-SDC and LSM-SDC electrodes. A peak power density of 0.168 W cm^{-2} was obtained and R_p was $1.15 \Omega \text{ cm}^2$. Cell II had the same anode with Cell I but different cathode, which was SDC-coated LSM. Impregnation SDC to LSM resulted in substantial reduction of R_p , which was only $0.58 \Omega \text{ cm}^2$ at 600 °C. Meanwhile, the peak power density increased to 0.203 W cm^{-2} . The power density increased further to 0.463 W cm^{-2} when both the cathode and anode were coated with SDC (Cell III). At the same time, R_p was reduced to $0.36 \Omega \text{ cm}^2$. It is noted that the shapes of the impedance spectra are similar, which demonstrates SDC impregnation does not change the electrode processes.

Shown in Fig. 3a is the SEM image for the fractured cross-section of SDC-coated LSM cathode consisting of a porous LSM framework and SDC nanoparticles. The framework was composed of porous LSM particles at micro-scale. After being impregnated

with SDC solution and heated at 800 °C, nanoscale SDC particles (about 100–200 nm) were formed on the inner surfaces of the framework. The SDC nanoparticles were deposited on the surface of LSM particles and at the electrode/electrolyte interface. Triple-phase boundary, where the electrochemical reaction occurs, as well as bonding between the electrode and electrolyte were therefore enhanced [10,11]. Consequently, R_p decreased and the power density increased. When the anode was impregnated with SDC, increased anodic triple-phase boundary was also expected since SDC nanoparticles were also deposited onto the inner surface as well as at the anode/electrolyte interface (see Fig. 3b). In addition, doped CeO_2 is catalytically active for the H_2 oxidation under SOFC operating conditions [20]. Therefore, the fuel cell performance was further improved.

It is clear that the improvement of cell performance is primarily due to the decrease of polarization resistance as an effect of pronounced triple-phase boundary caused by the coating of SDC nanoparticles. In addition to the decrease in polarization resistance, the ohmic resistance was also reduced when SDC was loaded (Fig. 2b). It is possibly accounted for the enlargement of contact area at the electrode/electrolyte interface by means of the impregnation process. Fig. 3c shows the cross-sectional view of a cathode/electrolyte interface. It seems that SDC deposition has an effect on enhancing the bonding between the electrode and electrolyte. Ding et al. [15] reported that the nanosized SDC particles, loaded by the impregnation method, could enlarge significantly the contact area between the ionic phase and electronic phase and thus reduced the ohmic resistance. Vanberkel et al. [21] also pointed out that smaller particles at the electrode/electrolyte interface could make for larger area, which was involved in faster reaction kinetics and higher currents that could be drawn through the electrode. Therefore, coating nanoscale SDC particles to the electrodes could reduce not only R_p , but also R_e and thus increase the cell performance dramatically so that the cell could be operated at low temperatures with high power exports.

3.3. Performances for cells with impregnated SDC fired at different temperatures

Fig. 4a shows the impedance spectra of single cells with impregnated SDC fired at different temperatures. The corresponding total resistances and peak power densities at 600 °C are shown in Fig. 4b. The measured ohmic resistances decreased with firing temperature from $0.26 \Omega \text{ cm}^2$ at 600 °C to $0.09 \Omega \text{ cm}^2$ at 800 °C. As mentioned early, the ohmic resistance can be affected by the bonding at electrode/electrolyte interface. High temperature might increase the bonding and thus reduce the resistance. However, it seems very likely that increasing temperature beyond 800 °C does not further decrease the resistance, which was $0.10 \Omega \text{ cm}^2$ at 900 °C.

The shapes of the impedance spectra are almost the same, inferring that the electrode processes have not been much changed by the firing temperature. When the electrodes were fired below 800 °C, R_p was almost not changed by the firing temperature. The average value was $0.32 \Omega \text{ cm}^2$. When the firing temperature was

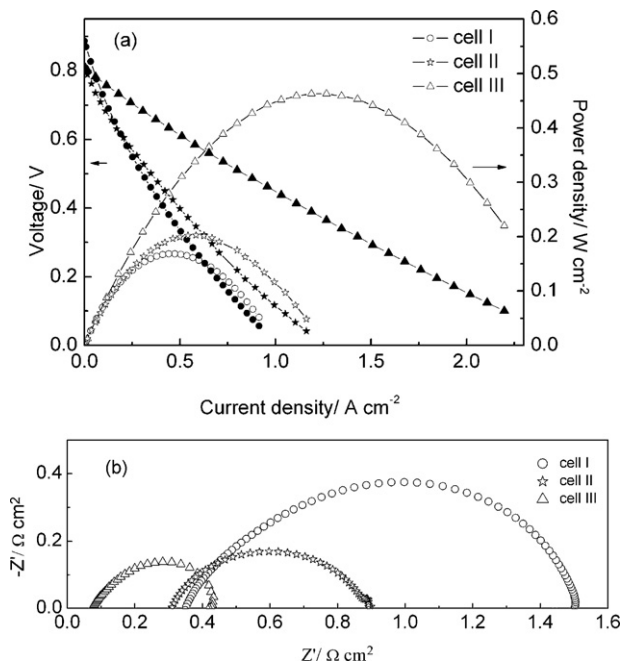


Fig. 2. Cell performances (a) and impedance spectra (b) for cell I with composite electrodes where impregnation was not performed, cell II with SDC-coated LSM cathode, and cell III with both electrodes coated with SDC.

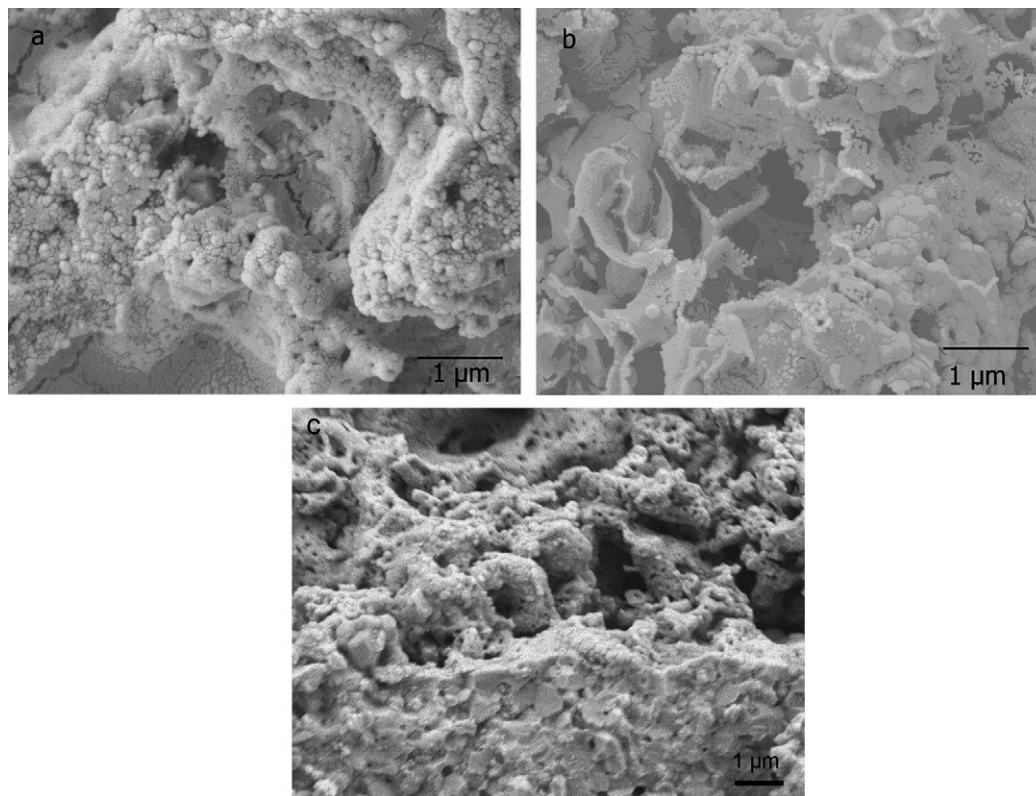


Fig. 3. SEM micrographs for the cross-section views of (a) SDC-coated cathode, (b) SDC-coated anode, and (c) cathode/electrolyte interface.

900 °C, R_p increased to $0.47 \Omega \text{ cm}^2$. The reason may be that the SDC particles grew too large at a high temperature as 900 °C. This is consistent with the previous results obtained with symmetric LSM-SDC cathodes that were prepared with the ion-impregnation

method and fired at different temperatures [14]. The effect of firing temperature on the ohmic and interfacial polarization resistances leads to the lowest total cell resistance, $0.46 \Omega \text{ cm}^2$, and thus highest peak power density, 0.463 W cm^{-2} , when the cell was fired at 800 °C (see Fig. 4b).

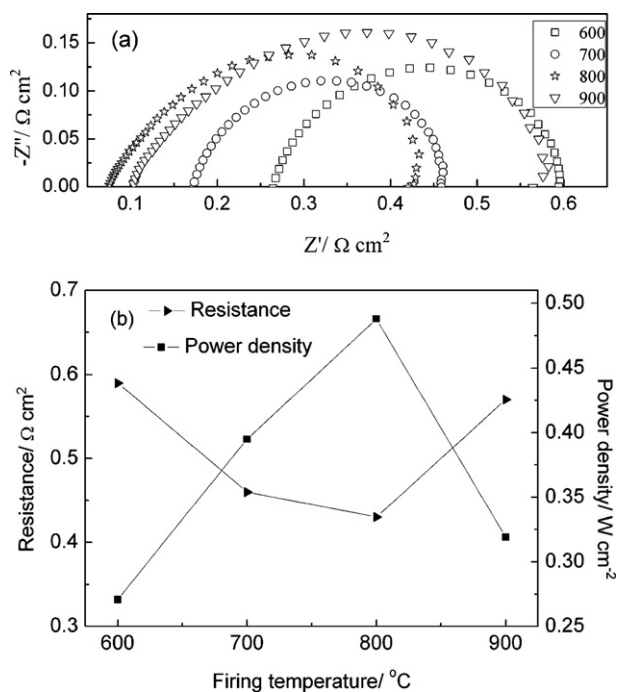


Fig. 4. (a) Impedance spectra measured at 600 °C under open circuit conditions and (b) total resistances and peak power densities for cells with impregnated SDC fired at different temperatures.

4. Conclusion

SOFC single cells with Ni-cermet anodes and LSM cathodes both coated with nanosized ceria particles have been prepared by using an ion-impregnation process. SDC-coating had significant effect on improving the electrode performance: the interfacial polarization resistance at 600 °C was reduced from 1.15 to $0.36 \Omega \text{ cm}^2$. Meanwhile, peak power density of 0.463 W cm^{-2} was achieved at 600 °C. The performance is comparable to those obtained with LSCF and SSC as the cathodes. Additionally, the performance could be further increased by optimizing the microstructures with means such as change the firing temperature. The high performance suggests that it is of great promise to develop low-temperature SOFCs by using LSM cathode materials.

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