



Short communication

High performance layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ cathode for intermediate-temperature solid oxide fuel cells

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ARTICLE INFO

Article history:

Received 21 May 2009

Received in revised form 17 June 2009

Accepted 17 June 2009

Available online 24 June 2009

Keywords:

Solid oxide fuel cells

Cathode

Layered perovskite

Interfacial polarization resistance

ABSTRACT

The layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (SBSC) perovskite oxide is synthesized by the Pechini method and investigated as a novel cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs). A laboratory-sized $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC)-based tri-layer cell of NiO-SDC/SDC/SBSC is operated from 500 to 700 °C fed with humidified H_2 (~3% H_2O) as a fuel and the static ambient air as oxidant. A maximum power density of 1147 mW cm^{-2} is achieved at 700 °C. The interfacial polarization resistance is as low as 1.01, 0.38, 0.16, 0.06 and 0.03 $\Omega \text{ cm}^2$ at 500, 550, 600, 650 and 700 °C, respectively. The experimental results indicate that SBSC is a very promising cathode material for IT-SOFCs.

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1. Introduction

A solid oxide fuel cell (SOFC), one of the most efficient energy conversion devices, enables the conversion of chemical energy of hydrogen into electrical energy directly [1,2]. The traditional SOFC is generally operated at temperature conditions of 800–1000 °C. While high temperature operating condition may result in advantages such as high reaction kinetics and high efficiency, it also leads to a series of problems, typically including high degradation rate of SOFC material systems, a limited choice of interconnect materials for stack, as well as thermal expansion mismatch and solid state reactions among cell components, etc. [3–5]. In order to widen the materials chosen, decrease material degradation, prolong the lifetime and reduce the cost, the reduction of the working temperature of SOFCs becomes the urgent demand. These difficulties can be minimized by reducing the operating temperature to an intermediate temperature range of 500–800 °C. Accordingly, intermediate-temperature SOFCs (IT-SOFCs) have attracted much attention in recent years [6–9].

The development of proper cathode materials for SOFCs in order to improve materials compatibility and interfacial polarization resistances remains a challenge [10,11]. Many simple perovskite-type mixed ionic–electronic conductors such as doped LaCoO_3 [12], BaCoO_3 [13] or LaFeO_3 [14] have been extensively studied as possible cathodes, however, more complicated perovskite materials

with double or layered structures received little attention. Layered $\text{SmBaCo}_2\text{O}_{5+\delta}$ (SBCO) perovskite with an intermediate lanthanide-ion radius ($r_{\text{Sm}^{3+}} = 0.964 \text{ \AA}$) may provide a suitable tradeoff of material properties between the catalytic activity and the value of thermal expansion coefficient (TEC) [15]. Zhou and Lin et al. [16,17] have shown the potential of layered SBCO for cathode application and evaluated the performance of this material working as a cathode in SOFCs. Recently, Irvine and co-workers [18] reported a novel layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (SBSC) perovskite, which shows advanced electrochemical properties in doped ceria electrolyte settings, and could be potentially employed as cathode material for IT-SOFC applications. However, to the best of our knowledge, SBSC as cathode material in SOFC settings has not been reported yet. In this work, layered SBSC perovskite was examined as a new cathode for SOFCs based on oxide ion conductor of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC).

2. Experimental

Powders of SDC electrolyte were synthesized by glycine–nitrate process (GNP). Stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) were dissolved in distilled water and then glycine was added with the glycine/metal molar ratio of 2:1. The solution was heated under stirring conditions. After converted into a viscous gel, the solution was ignited to flame, resulting in the ash. The resulting ash-like material was afterwards calcined in air at 800 °C for 2 h to form fluorite SDC powders. The anode-supported SDC bilayer ($\varnothing 15 \text{ mm}$) was prepared by a dry-pressing method. NiO + SDC + starch mixture (60%:40%:20% in weight) was pre-pressed at 200 MPa as an anode substrate. Then loose SDC

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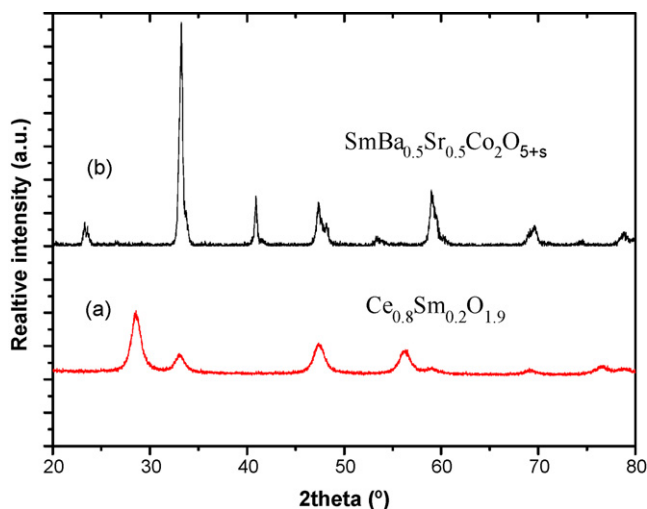


Fig. 1. XRD patterns for (a) the layered $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+s}$ (SBSC) perovskite powders and (b) $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) powders.

powders synthesized above were uniformly distributed onto the anode substrate, co-pressed at 250 MPa and sintered subsequently at 1400 °C for 5 h to densify the SDC membrane.

Layered SBSC powder was synthesized by the Pechini process using $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (99.9%), $\text{Sr}(\text{NO}_3)_2$ (99.9%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%) as precursors, followed by calcinations at 1000 °C for 10 h. Fine SBSC powders were mixed thoroughly with a 6 wt% ethylcellulose–terpineol binder to prepare the cathode slurry, which was then painted on SDC electrolyte films, and sintered at 1000 °C for 3 h in air to form single cells of Ni–SDC/SDC/SBSC.

The phase identification of the sintered anode–electrolyte bilayer and prepared cathode powders was carried out with the powder X-ray diffraction by Cu-K α radiation (D/Max-gA, Japan). Single cells were tested from 500 to 700 °C in an in-house developed cell testing system with humidified hydrogen ($\sim 3\%$ H_2O) as a fuel and the static air as an oxidant. The flow rate of fuel gas was about 40 ml min^{-1} . The cell voltages and output currents of the cells were measured with a digital multimeter (GDM-8145). AC impedance spectroscopy (Chi604c, Shanghai Chenhua) was performed on the cell under open-circuit conditions from 550 to 700 °C. A scanning electron microscope (SEM) was used to observe the microstructure of the cells after testing.

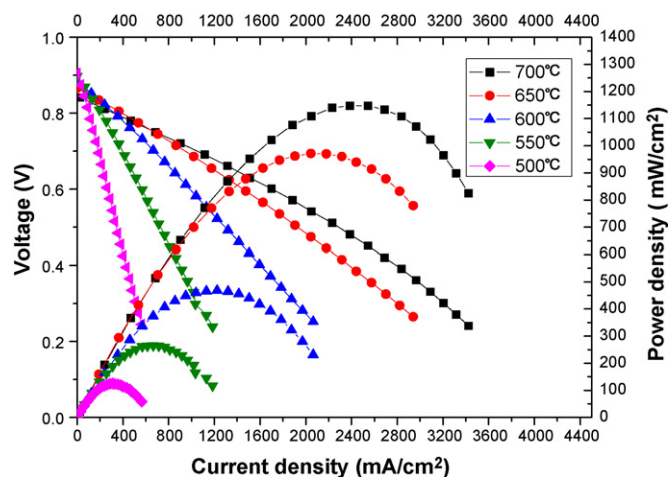


Fig. 3. Performance of the as-prepared cell with hydrogen at different temperatures.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared SBSC powder exhibits a layered perovskite phase without peaks attributable to impurities [18]. Fig. 1(b) presents the XRD spectra of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) calcined at 800 °C for 2 h. It could be clearly seen that there were only peaks corresponding to the fluorite phase [19].

Fig. 2(a) is the SEM image of surface morphology of SDC electrolyte on the porous anode support after testing. It can be seen that the SDC membrane is completely dense. There are no pores and cracks on the surface. It can also be found that the thickness of SDC membrane is about 20 μm from the cross-section view of the SDC electrolyte (Fig. 2(b)).

Fig. 3 presents the I – V and I – P characteristics of the as-prepared Ni–SDC/SDC/SBSC cell using H_2 as the fuel and static ambient air as the oxidant in the temperature range of 500–700 °C. The open-circuit voltage (OCV) is lower than 1.0 V, and increases with the decrease of the operation temperature since doped ceria is not a pure oxide ion conductor [20]. The reduction of Ce^{4+} to Ce^{3+} in the SDC electrolyte film causes an internal current which reduces the OCV of the cell. Peak power densities were 1147, 971, 467, 265 and 125 mW cm^{-2} at 700, 650, 600, 550 and 500 °C, respectively. The cell performance is very encouraging and suggests that SBSC is a very promising cathode material for IT-SOFCs.

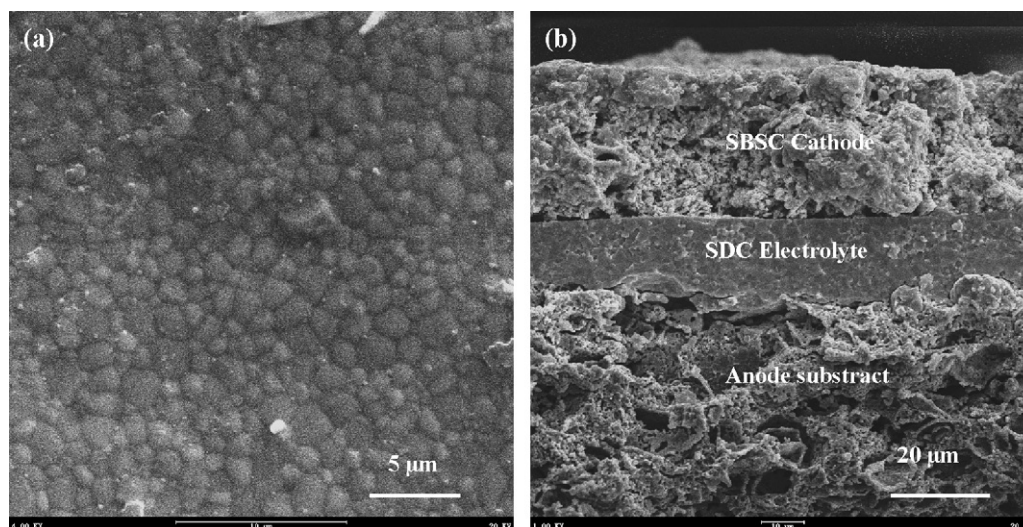


Fig. 2. SEM images of cell after testing: (a) the surface of electrolyte and (b) the cross-section of cell with a 20 μm -thick SDC membrane.

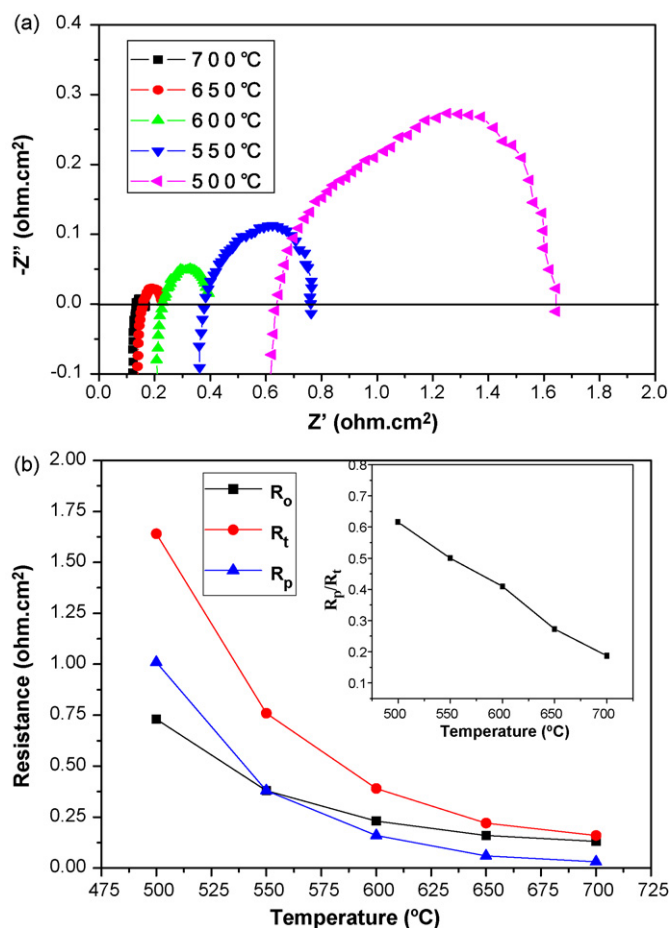


Fig. 4. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures. R_p/R_t is also shown in (b).

In order to evaluate the performance of layered SBSC perovskite working as a cathode in a single cell setting, the impedance spectra of the as-prepared cells were obtained under open-circuit conditions at different temperatures (Fig. 4(a)). The total cell resistance (R_t), ohmic resistance (R_o), and interfacial polarization resistance (R_p) determined from the impedance spectra at different temperatures are shown in Fig. 4(b). As expected, the increase of the measurement temperature resulted in a significant reduction of R_p , typically from $1.01 \Omega \text{ cm}^2$ at 500°C to $0.03 \Omega \text{ cm}^2$ at 700°C . It is worth noting that the R_p value at 500°C for SBSC cathode is even lower than that of a cell with a BSCF–SDC composite cathode at the same operating temperature ($1.1 \Omega \text{ cm}^2$ at 500°C) [21]. The low polarization resistances indicated that the SBSC cathode is a good candidate for operation at or below 700°C . Further analysis shows

that R_t is primarily dominated by R_p . The ratio of R_p to R_t increases with a decrease of the operating temperature, from 18% at 700°C to 62% at 500°C , implying that the cell performance is greatly limited by interfacial polarization resistance at low temperature conditions. It is dominated by the cathode–electrolyte interface whereas the resistance of the anode–electrolyte is negligible. At 500°C , the polarization resistance of the electrodes is $1.01 \Omega \text{ cm}^2$ whereas the resistance of the electrolyte is only $0.73 \Omega \text{ cm}^2$. Clearly it is worth to perform further studies in the future to reduce cathode–electrolyte interfacial resistance.

4. Conclusions

In order to develop IT-SOFCs with a SBSC cathode, a dense electrolyte was fabricated on a porous anode support by a simple dry-pressing/co-firing process. A laboratory-sized tri-layer cell of NiO–SDC/SDC/SBSC was operated from 500 to 700°C fed with humidified H_2 ($\sim 3\% \text{ H}_2\text{O}$). A high maximum power density of 1147 mW cm^{-2} was achieved at 700°C . The polarization resistance of the electrodes was as low as $0.03 \Omega \text{ cm}^2$ at 700°C . The results indicate that the layered SBSC perovskite cathode is a good candidate for IT-SOFC cathode, and NiO–SDC/SDC/SBSC is a promising material system for the next generation SOFCs.

Acknowledgements

The authors gratefully acknowledge the support of this research by National Natural Science Foundation of China under contract no. 50572099, and partially support from US DOE under contract no. DE-FG36-08G088116.

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