



Short communication

Layered $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ as a cathode for intermediate-temperature solid oxide fuel cells

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ABSTRACT

The layered $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (GBSC) perovskite oxides are synthesized by Pechini method and investigated as a novel cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The single cell of NiO–SDC ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$)/SDC ($\sim 20 \mu\text{m}$)/GBSC ($\sim 10 \mu\text{m}$) is operated from 550 to 700 °C fed with humidified H_2 as fuel and the static air as oxidant. An open circuit voltage of 0.8 V and a maximum power density of 725 mW cm^{-2} are achieved at 700 °C. The interfacial polarization resistance is as low as 0.88, 0.29, 0.13 and $0.05 \Omega \text{ cm}^2$ at 550, 600, 650 and 700 °C, respectively. The ratio of polarization resistance to total cell resistance decreases with the increase in the operating temperature, from 60% at 550 °C to 21% at 700 °C, respectively. The experimental results indicate that GBSC is a promising cathode material for IT-SOFCs.

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1. Introduction

Solid oxide fuel cell (SOFC) is the most efficient device among the energy technology invented so far for the conversion of chemical fuels directly into electrical power [1,2]. In order to widen the materials chosen, decrease material degradation, prolong the lifetime and reduce the cost, considerable efforts are focusing on reducing the operating temperature of SOFCs to an intermediate range of 500–800 °C [3,4]. Accordingly, intermediate-temperature SOFCs (IT-SOFCs) have attracted much attention in recent years [5–8].

It has been widely recognized that cathode is the dominant component controlling cell performance, especially for IT-SOFCs. The development of proper cathode materials still remains a challenging issue in that the interfacial polarization resistances should be as small as possible. In the mean time, the materials between cathode and electrolyte should keep chemical and mechanical compatibility [9,10]. Many simple perovskite-type mixed ionic-electronic conductors such as $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ [3,11], BaCoO_3 [12,13] or LaFeO_3 [14] have been extensively studied as possible cathode materials, however not much attention has been paid to the perovskite related structures such as the layered perovskite. In general, layered perovskite oxide exhibits lower activity energy for oxide ionic mobility compared with simple perovskite-type conductors. Tarancón et

al. [15,16] and Lin et al. [17,18] have shown the potential of layered $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO) for cathode application and evaluated the performance of this material working as a cathode in SOFCs. The total conductivity of GBCO in air reaches the maximum value (10^3 S cm^{-1}) at 673 K. The value of thermal expansion coefficient (TEC) is $16.4 \times 10^{-6} \text{ K}^{-1}$ in the 300–1073 K range [19]. Recently, Irvine et al. [20] reported a layered $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (GBSC) perovskite, which showed advanced electrochemical properties based on doped ceria electrolyte, and could be potentially employed as cathode material for IT-SOFCs. However, to the best of our knowledge, GBSC as a cathode in SOFC settings has not been reported yet. In this work, layered GBSC perovskite was examined as a new cathode for SOFCs based on oxide ion conductor of SDC.

2. Experimental

Powders of SDC electrolyte were synthesized by glycine-nitrate process (GNP). Stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water and then glycine was added with the glycine/metal molar ratio of 2:1. The mixture was heated on a hot plate, converted to a viscous gel and ignited to flame, resulting in the ashes which were afterwards calcined at 850 °C for 2 h to form fluorite SDC powders. The anode-supported SDC layer was prepared by a dry-pressing method. NiO, SDC and starch (65%: 35%: 15% in weight) were mixed and ball-milled for 24 h. The mixed powders were pre-pressed at 250 MPa as a substrate. Then loose SDC powder was uniformly distributed onto the anode substrate, co-pressed at 300 MPa and sintered subsequently at 1350 °C for 4 h to densify the SDC film.

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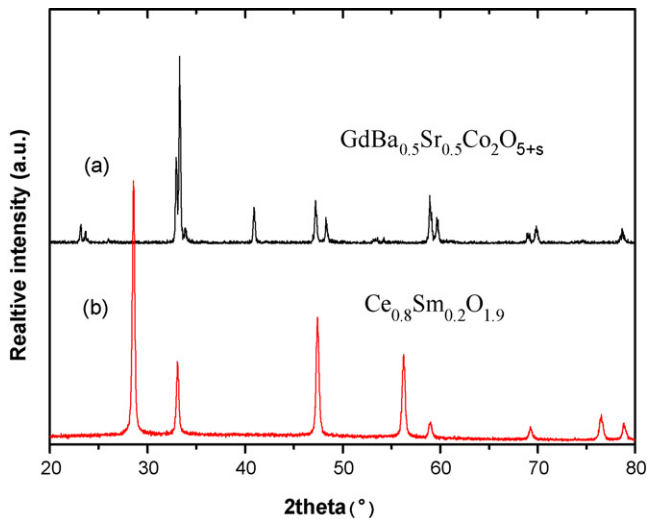


Fig. 1. XRD diffraction patterns for (a) the layered GdBa_{0.5}Sr_{0.5}Co₂O_{5+s} (GBSC) perovskite powders and (b) Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) powders.

Layered GBSC powder was synthesized by the Pechini process using Gd₂O₃, Ba(NO₃)₂·9H₂O (99.9%), Sr(NO₃)₂ (99.9%) and Co(NO₃)₂·6H₂O (99.9%) as precursors, followed by calcination at 1000 °C for 5 h. The GBSC powders were mixed ethyl cellulose and terpineol to obtain well-distributed cathode slurry, which was then painted on SDC films, and sintered at 1000 °C for 5 h in air to form single cells of NiO–SDC/SDC/GBSC. The final geometry of cell pellets is about 12 mm in diameter and active area of cathode is about 0.5 cm².

The crystal structure of prepared SDC electrolyte and GBSC cathode powders were studied with the powder X-ray diffraction by Cu-Kα radiation. After being sealed, the single cells were tested in an electrical furnace with humidified hydrogen (~5% H₂O) as fuel and the static air as oxidant, respectively. The power output performance and ac impedance spectroscopy under open-circuit condition were obtained from 550 to 700 °C. The frequency range was 0.01–10⁵ Hz with the signal amplitude of 10 mV. The morphology of the single cell after the electrochemical tests was characterized by a scanning electron microscope (SEM).

3. Results and discussion

As shown in Fig. 1(a), the GBSC powder exhibits a layered perovskite phase without peaks attributable to other impurities [20]. Fig. 1(b) presents the XRD spectra of Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) calcined at 850 °C for 2 h. It could be clearly seen that there were only peaks corresponding to the fluorite phase [21].

Fig. 2 shows the cross-sectional view of the single cell after testing. As can be seen, the SDC membrane is about 20 μm in thickness, and adheres very well to the anode substrate and the cathode layer. The effective contact indicates that GBSC is compatible with SDC electrolyte in TEC even after several thermal cycles.

Fig. 3 presents the *I*–*V* and *I*–*P* characteristics of Ni–SDC/SDC/GBSC cell using H₂ as the fuel and static air as the oxidant in the temperature range of 550–700 °C. The open circuit voltage (OCV) is lower than 1.0 V (from 0.8 V at 700 °C to 0.92 V at 550 °C) since doped ceria is not a pure oxide ionic conductor [22]. It is well known that the reduction of Ce⁴⁺ to Ce³⁺ causes an internal current in SDC electrolyte. Peak power densities were 725, 585, 344 and 156 mW cm^{−2} at 700, 650, 600 and 550 °C, respectively.

The impedance spectra of the as-prepared cells are obtained under open-circuit conditions at different temperatures, and are shown in Fig. 4. The total cell resistance (*R*_t), ohmic resistance (*R*_o),

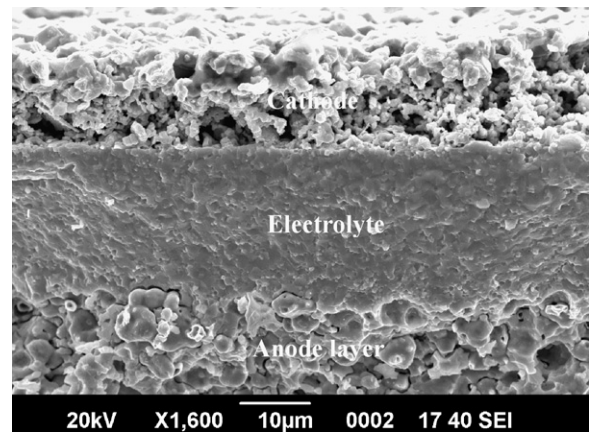


Fig. 2. Cross-section view of the cell with a 20 μm-thick SDC membrane after testing.

and interfacial polarization resistance (*R*_p) as determined from the impedance spectra at different temperatures are shown in Fig. 5. The high frequency intercept is corresponded to *R*_o which includes ionic resistance of the electrolyte, electronic resistance of the electrodes and some contact resistances associated with interfaces [23]. The low frequency intercept corresponds to *R*_t. It is obvious that increase operating temperature resulted in a significant reduction of *R*_p, typically from 0.88 Ω cm² at 550 °C to 0.05 Ω cm² at 700 °C. The low polarization resistances indicated that the GBSC cathode

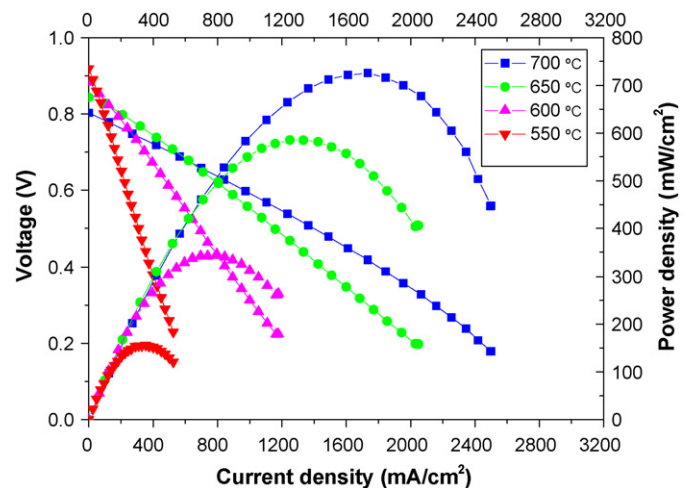


Fig. 3. Performance of the single cell under humidified hydrogen atmosphere at different temperatures.

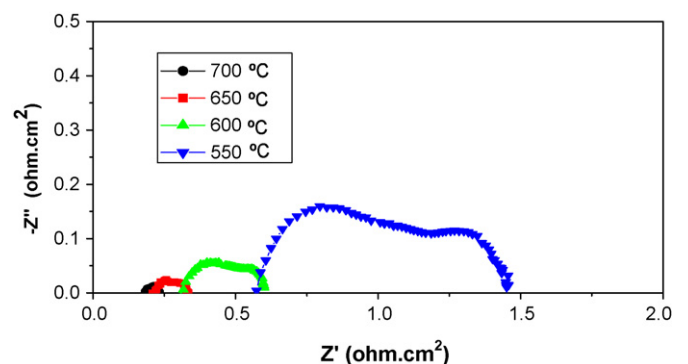


Fig. 4. Impedance spectra of the cell measured under open-circuit conditions at different temperatures.

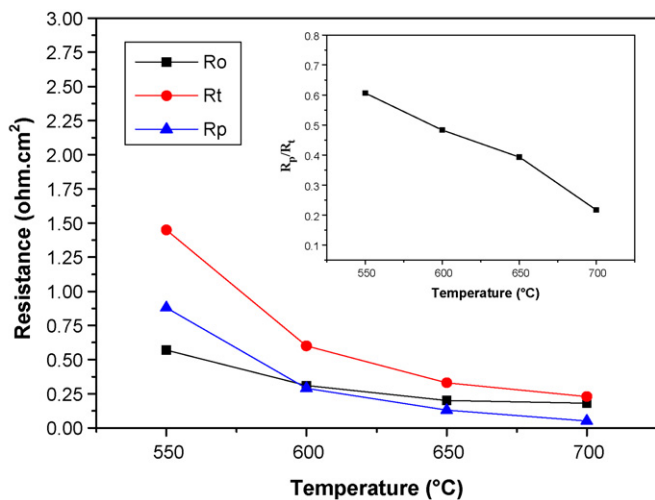


Fig. 5. The interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra. R_p/R_t is also shown.

is a good candidate for operation at 700 °C. Further analysis shows that R_t is mainly dominated by R_p . The ratio of R_p to R_t increases with the decrease in operating temperature, from 21% at 700 °C to 60% at 550 °C. The results imply that the cell performance is greatly limited by R_p at low temperature range. It is noted that the interfacial polarization resistance including anode/electrolyte (R_a) and cathode/electrolyte resistance (R_c) is greatly higher than ohmic resistance at 550 °C. R_p is dominated by R_c since R_a is negligible. At 550 °C, the polarization resistance of the electrodes is 1.45 Ω cm² whereas the resistance of the electrolyte is only 0.57 Ω cm². So it is deserved to reduce the R_c for improving the performance of the cells in the further studies.

4. Conclusions

In this work, layered $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ cathode was employed as a cathode for IT-SOFCs with a structure of NiO-SDC/SDC/GBSC. A tri-layer single cell of NiO-SDC/SDC/GBSC was operated from 550 to 700 °C fed with humidified H_2 (~5%

H_2O). The cell shows a maximum power density of 725, 585, 344 and 156 mW cm^{-2} at 700, 650, 600 and 550 °C, respectively. The polarization resistance of the electrodes was as low as 0.05 Ω cm² at 700 °C. The results indicate that the layered GBSC perovskite is a potential cathode for operation below 700 °C, and that SDC electrolyte with GBSC cathode is a promising material system for IT-SOFCs.

Acknowledgements

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