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K_2NiF_4 type $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$ as the cathodes for solid oxide fuel cells

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Abstract

K_2NiF_4 structured $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$ is an oxygen overstoichiometric oxide with high oxygen diffusion and oxygen surface exchange coefficients at temperature range 450–800 °C. In this work, composites consisting of $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$ (LSCN, $x=0$, 0.4, 0.8, 1.2, 1.6) and $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) have been investigated as the cathodes for low-and-intermediate temperature solid oxide fuel cells (SOFCs). AC impedance spectroscopy on symmetric cells indicated that among the series of LSCN–GDC composites, $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$-based electrode had the lowest interfacial polarization resistance, which was 1.36 Ω cm^2 at 600 °C when the electrode was not activated. Significant activation effect was observed with a single cell when current treatment was performed at 200 mA cm^{-2} within 30 min. The single cell with $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC as the cathode generated power density up to 350 mW cm^{-2} at 600 °C. In addition, the performance was pretty stable when a constant output voltage of 0.5 V was set for 36 h. These results suggest that $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$ could be promising materials as the cathodes for SOFCs that operated at low-and-intermediate temperatures.

Keywords: Solid oxide fuel cell; $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$; K_2NiF_4 type oxide; Composite cathode; Doped ceria

1. Introduction

Mixed electronic–ionic conducting oxides have drawn much attention because of their potential applications in various technologies, including dense membranes for oxygen separation and porous electrodes for solid oxide fuel cells (SOFCs). Much work for the application as SOFC cathodes focused on perovskite type oxides such as $La_{1-x}Sr_xMnO_{3-\delta}$, $La_{1-x}Sr_xCoO_{3-\delta}$, $Sm_{1-x}Sr_xCoO_{3-\delta}$, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [1,2], which are usually oxygen understoichiometric oxides. Recently, there has been considerable interest in the oxygen overstoichiometric $La_2NiO_{4+\delta}$ based compounds as novel mixed conductors for oxygen separation membranes [3,4]. These oxides have a K_2NiF_4 type structure and are usually formulated as $A_2BO_{4+\delta}$, which can be regarded as ABO_3 perovskite and AO rock-salt layers arranged one upon the other in the *c*-direction. There is sufficient space in the AO layer. This structure allows for the accommodation of oxygen overstoichiometry as oxygen interstitial species with negative charges, which are balanced through the oxidation of the B site cations [5]. Previous studies have shown that these $A_2BO_{4+\delta}$ materials exhibit good characteristics in terms of electronic conductivity due to the mixed valence of B site metal, of the oxygen ionic transport properties due to the oxygen overstoichiometry, of electrocatalysis for the oxygen reduction, and of moderate thermal expansion properties [4–6]. Of greater interest are the high oxygen diffusion coefficient (~10^{-8} cm^2 s^{-1}) and oxygen surface exchange coefficient (~10^{-6} cm s^{-1}) of the series of materials $La_2Ni_{1-x}Co_xO_{4+\delta}$, particularly the high cobalt content materials over the temperature range 450–650 °C [5]. The high oxygen–ion diffusion and surface exchange coefficients are desired properties for SOFC cathodes. Further, the thermal expansion

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coefficients (TEC) are around $11.0\sim14.0\times10^{-6}$ K^{-1} [6], which match well with those of SOFC electrolytes. Therefore, these desired properties make them promising candidate materials as the cathodes for low-and-intermediate temperature SOFCs. In this work, $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$ was characterized as the cathodes for SOFCs with doped ceria as the electrolytes. In addition, A site was doped with Sr to improve the electrode performance. Emphasis was laid on the optimization of Sr-doped $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$ composite cathodes.

2. Experimental

Oxide powders including $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$ (LSCN, x=0, 0.4, 0.8, 1.2, 1.6) and $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) were synthesized with a glycine–nitrate combustion method using nitrate precursors of $La(NO_3)_3$, $Sr(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Gd(NO_3)_3$, and $(NH_4)_2Ce(NO_3)_6$. Stoichiometric amount of the nitrates were dissolved in distilled water to form a precursor solution. Glycine was then added to the solution with a molar ratio of glycine to nitrate of 0.5. The solution was subsequently heated until it was ignited, producing oxide powders. The powders were heated in air at 1250 °C for 12 h to form LSCN solid solutions and 600 °C for 2 h to form fluorite structured GDC. All chemicals were of analytical grade.

Electrolyte substrates were fabricated by dry-pressing ceria powder at 300 MPa, followed by sintering at 1400 °C for 5 h. The substrates were ceramic disks 13 mm in diameter and 0.75 mm thick. Cathode slurry consisted of LSCN (70 wt.%) and GDC was prepared by overnight ball-milling with an ethyl cellulose binder and a terpineol-based solvent. The slurry was applied onto both sides of the substrates with a screen-printing method, and subsequently fired at 1100 °C in air for 2 h to form symmetrical cells for electrochemical testing. The electrode thickness was about 50 μm and the area was 1.28 cm^2. Anode-supported single cells with GDC as the electrolytes were prepared by co-pressing and co-firing techniques [7]. Anode precursor powders consisted of 60 wt.% NiO and GDC were pre-pressed at 60 MPa, and GDC powder was then added and co-pressed at 300 MPa to form a bilayer. The green bilayer was fired at 1250 °C in air for 5 h to densify the GDC membrane. The cell was 12 mm in diameter with a 40-μm thick electrolyte and 0.40-mm thick anode. Cathode was also applied with the screen-printing technique. Ag paste and silver wires were used as electron collectors. The interfacial polarization resistances were measured using a Zahner IM6e electrochemical workstation in the frequency range of 10^{-2}–10^6 Hz with a bias voltage of 10 mV.

3. Results and discussion

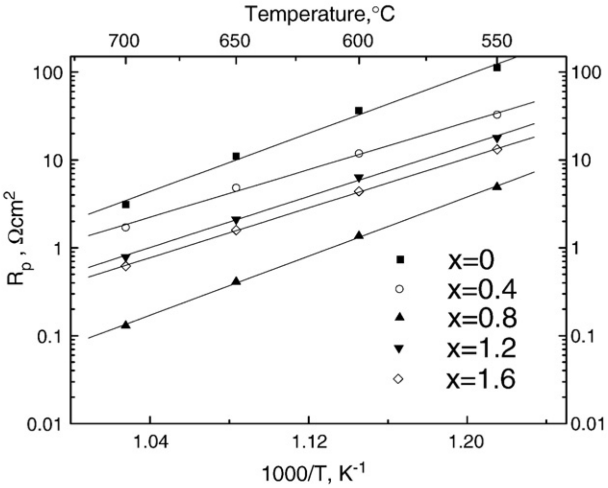

Fig. 1. Temperature dependence of interfacial polarization resistances (Rp) for symmetrical cells with $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$–GDC ($x$=0, 0.4, 0.8, 1.2, 1.6) electrodes.

Shown in Fig. 1 is the temperature dependence of interfacial polarization resistances (Rp) for $La_{2-x}Sr_xCo_{0.8}Ni_{0.2}O_{4+\delta}$–GDC ($x$=0, 0.4, 0.8, 1.2, 1.6) electrodes measured with symmetrical cells. Rp is the area-specific polarization resistance obtained via electrochemical impedance spectroscopy (EIS) testing, i.e. the difference between the real axis intercepts of the impedance arcs [2,7]. As expected, the resistance increased with decreasing temperature. At 600 °C, it was 36.5 Ω cm^2 for an $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC composite. The resistance was much higher than that of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$–GDC (0.6 Ω cm^2), $Sm_{0.5}Sr_{0.5}CoO_3$–$Sm_{0.2}Ce_{0.8}O_{1.9}$ (0.2 Ω cm^2), $La_{0.8}Sr_{0.2}MnO_3$–GDC (4.44 Ωcm^2) and $La_{0.8}Sr_{0.2}MnO_3$–$Sm_{0.2}Ce_{0.8}O_{1.9}$ (4.68 Ω cm^2) [7–9]. The performance of an SOFC cathode is strongly dependent on the oxygen surface exchange and oxygen–ion diffusion coefficients of the electrode materials. High coefficients are generally favorable for low Rp. The coefficients of cobaltite based perovskites are much higher than that of $La_{0.8}Sr_{0.2}MnO_3$ (LSM). Therefore, Rp of cobaltite composites is known to be much lower than that of LSM-based electrodes. Accordingly, the performance of $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC composite could be dramatically improved since $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$ has much higher coefficients than that of cobaltite and manganite perovskites. However, present study showed the reverse result. Composition and microstructure optimization should be an effective way for the improvement since the rate of oxygen reduction for the cathode is believed to be a strong function of microstructural variables such as the size of the electrocatalyst, the use of porous mixture of the electrocatalyst and electrolyte. The optimization was reported to be very successful for the perovskite cathodes in promoting their performance [7,9]. Future work will be thus focused on the structure modification.

To improve the performance, Sr was doped to the A site of $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$. As shown in Fig. 1, A site doping with Sr had a significant effect on reduction of Rp. When x=0.8, the composite showed the lowest Rp, which was 1.36 Ω cm^2 at 600 °C. It was twenty-six times lower than the interfacial polarization resistance of the $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC electrode. A decrease of Rp could be the result of an increasing electron hole concentration as the Sr-doping content is increased. However, an increase of Rp was observed with increasing the amount of Sr-doping beyond x=0.8, which may be assumed as the result of lattice distortion associated with more substitution of La^{3+} by Sr^{2+} [3,4,10]. It should be noted

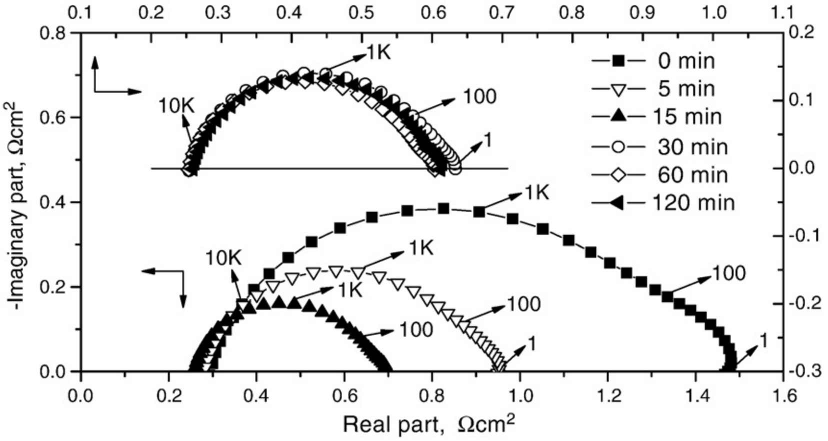

Fig. 2. Impedance response as a function of current passage time for an anode-support cell with $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC as the cathode. The current density was 200 mA cm^{-2}. The measurement was carried out immediately after the current passage at 600 °C under open circuit conditions, and the numbers are the frequencies in hertz.

that further reduction in Rp is possible by varying Sr content in the range $0.4<x<1.2$.

Shown in Fig. 2 is the impedance spectra for a single cell with $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC cathode. The cell was operated at 600 °C with humidified hydrogen (~3% H_2O) as the fuel and ambient air as the oxidant. The interfacial polarization resistance as shown in Fig. 2 was contributed from both the cathode and anode. Comparing with the cathodic contribution, the resistance derived from the anode was usually neglectable for a Ni-ceria cermet anode [11]. The interfacial polarization resistance was 1.18 Ω cm^2 under open circuit condition when no current was passed through the cell. It has been shown that leakage current always exists when doped ceria is used as the electrolyte. The leakage current might have an effect on activating the electrode. Therefore, the resistance measured with the single cell was lower than that with the symmetric cell. Meanwhile, the lower resistance indicates that the electrode material might be activated when the cell is operated. To investigate the activation effect, current (200 mA cm^{-2}) was thus passed through the cell. The measurement of EIS was carried out at 600 °C under open circuit conditions immediately after the current passage. The impedance response as a function of current passage time is shown in Fig. 2. Before passing current, the cell impedance was characterized by a small low frequency arc with a large and depressed arc at high frequency. With the current passage time running, the impedance arcs were reduced significantly and the interfacial polarization resistance decreased from 1.18 Ω cm^2 to 0.35 Ω cm^2. Significant activation effect was observed within 15 min. After 30 min current passing, the total arc size kept almost constant. The analysis of the impedance responses indicates that the effect of the cathodic polarization is primarily on the reduction in the high-frequency impedance. This is similar with the polarization behavior of an $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$–GDC composite cathode [12].

Shown in Fig. 3 is the cell performance measured at 600 °C when $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC was used as the cathode. The data was recorded after the cell was stabilized for 2 h. As shown in Fig. 3a, maximum power density up to 350 mW cm^{-2} was achieved. The power generation was relatively lower than those with perovskite $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ as the cathode. The latter usually generated power density above 400 mW cm^{-2} at the same temperature with the same anode and electrolyte [13]. The cell resistance calculated from the I–V curve was 0.367 Ω cm^2, which is consistent with that shown in Fig. 2 when the cell was fully activated.

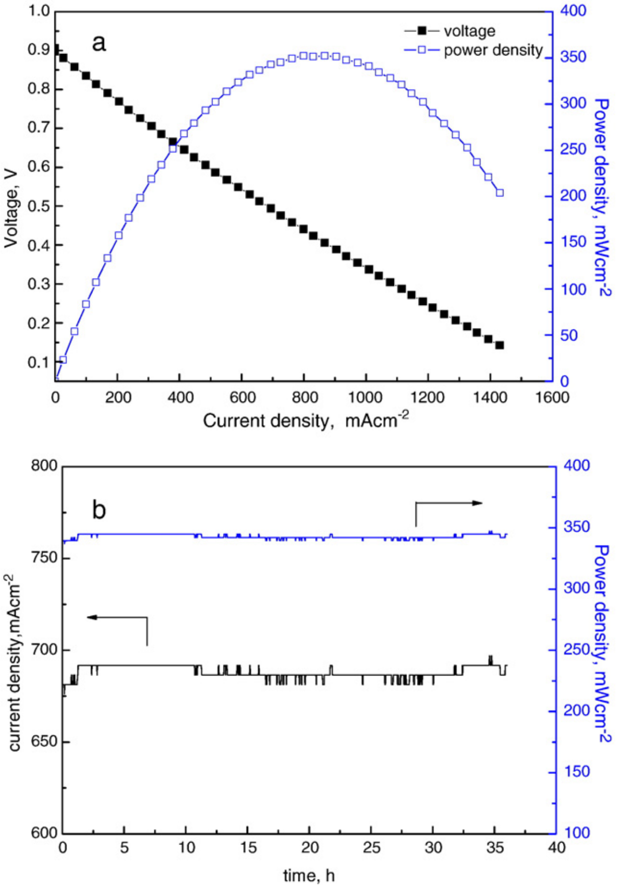

Fig. 3. Performance of a single cell with $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC as the cathode. Measurement was conducted at 600 °C with humidified H_2 (3% H_2O) as the fuel and ambient air as the oxidant. (a) Cell voltage and power density as a function of current density; (b) Stability with a constant output voltage of 0.5 V.

Shown in Fig. 3b is the stability of the single cell with a constant output voltage of 0.5 V. The current density increased slightly in the initial 1 h and then fluctuated with the operating time, indicating the electrode was activated first and no substantial declining in the cell performance was observed within the following 35 h operating. Only 1% fluctuation of the current density was observed in the stability test, indicating $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC composite was pretty stable as the cathode for SOFC operated at 600 °C. The observed stability together with the coming electrode optimization suggests a promising application of $La_2Co_{0.8}Ni_{0.2}O_{4+\delta}$-based composites as the cathodes for SOFC that operated at intermediate and low temperatures.

4. Conclusions

LSCN–GDC composites were investigated as the cathodes for SOFCs. The interfacial polarization resistance was much higher than that of cobaltite perovskites. A single cell with $La_{1.2}Sr_{0.8}Co_{0.8}Ni_{0.2}O_{4+\delta}$–GDC as the cathode generated power density up to 350 mW cm^{-2} at 600 °C. And the cell performance was quite stable in the period investigated. Further work will focus on improving the electrochemical activity of the LSCN–GDC composites by changing the GDC content, by decreasing the fabrication temperature leading to greater surface area, and by optimizing the amount of Sr-dopant.

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