Journal of Power Sources 195 (2010) 8094–8096

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Electrochemical performances of $NdBa_{0.5}Sr_{0.5}Co_2O_{5+x}$ as potential cathode material for intermediate-temperature solid oxide fuel cells

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ARTICLE INFO

Article history:
Received 28 April 2010
Received in revised form 18 June 2010
Accepted 18 June 2010
Available online 25 June 2010

Keywords:
Solid oxide fuel cell
Cathode
Layered perovskite
Electrochemical performance

ABSTRACT

Layered perovskite oxide $NdBa_{0.5}Sr_{0.5}Co_2O_{5+x}$ is investigated as a cathode material for intermediate-temperature solid oxide fuel cells. The NBSC cathode is chemically compatible with the electrolyte $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) at temperatures below 1000 °C. It is metallic in nature and the maximum and minimum conductivities are $1368\ S\ cm^{-1}$ at 100 °C and $389\ S\ cm^{-1}$ at 850 °C. The area specific resistance (ASR) value for the NBSC cathode is as low as $0.023\ \Omega\ cm^2$ at 850 °C. The electrolyte-supported fuel cell generates good performance with the maximum power density of 904, 774 and $556\ mW\ cm^{-2}$ at 850, 800 and 750 °C, respectively. Preliminary results indicate that NBSC is promising as a cathode for IT-SOFCs.

1. Introduction

In recent years, the focus of the solid oxide fuel cells (SOFCs) is shifting towards operating them at intermediate temperatures. However, the reduction of operating temperature leads to a significant decrease in electrode activity. For example, the traditional SOFC cathode, $La_{1-x}Sr_xMnO_{3-\delta}$, is not suitable for intermediate-temperature (IT) SOFCs due to its low activity in this temperature regime [1]. For the further improvement of cell performance, the development of high performance cathode material is critical.

Recently, many simple perovskite-type mixed ionic and electronic oxides, such as $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [2], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [3] and $Pr_{0.7}Sr_{0.3}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [4] are the most commonly used cathode materials for IT-SOFCs due to their high-electrocatalytic activity for the oxygen-reduction reaction [5]. It has been reported that the oxygen kinetics in perovskites with an ordered structure type, such as the double perovskites, are significantly faster than in the corresponding disordered perovskites [6], suggesting the potential application of ordered perovskites as cathodes in IT-SOFCs. $LnBaCo_2O_{5+x}$ (Ln = rare-earth) [6–9], has been reported to adopt an oxygen-deficient double-perovskite structure in which Ba cations do not have a random distribution on the A perovskite sites but are ordered in alternating lanthanide and alkali-earth planes. Moreover, the oxygen vacancies are mainly located in the LnO rare-earth planes. The particular distribution of vacancies in these oxides could greatly enhance the diffusivity of oxide ions in the bulk of the material and possibly supply surface defect sites with enhanced reactivity towards molecular oxygen compared with a simple cubic perovskite with randomly occupied A-sites [10]. Kim and Manthiram [7] have shown that layered perovskite $NdBaCo_2O_{5+x}$ exhibited high electrical conductivity, reasonable oxygen content and good cell performance.

Recently, some initial researches have investigated the substitution of the Ba cation with Sr to form a double-layered perovskite. When Ba site is partially substituted by Sr, it could potentially improve the conductivity of layered perovskite oxides [11]. Kim et al. [12] reported the Sr-doped layered perovskite oxide system $LnBa_{0.5}Sr_{0.5}Co_2O_{5+x}$ (Ln = Pr, Sm, and Gd) showed a lower polarization resistance based on doped ceria electrolyte, and could be potentially employed as cathode material for IT-SOFCs. To date, there appears to be no published study on the application of $NdBa_{0.5}Sr_{0.5}Co_2O_{5+x}$ (NBSC) as cathode material in SOFC settings. In this work, the performances of the NBSC cathode material were studied, including the chemical compatibility with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolyte, electrical conductivity, cathodic polarization resistance and single-cell performance.

2. Experimental

$NdBa_{0.5}Sr_{0.5}Co_2O_{5+x}$ (NBSC) oxides were synthesized by a conventional solid-state reaction. Briefly, Nd_2O_3, $BaCO_3$, $SrCO_3$ and Co_2O_3 were weighed in the stoichiometric proportions of NBSC. The mixture was ground thoroughly and pressed, then fired repeatedly at 1000, 1050, and 1100 °C for 12 h in air. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$

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doi:10.1016/j.jpowsour.2010.06.061

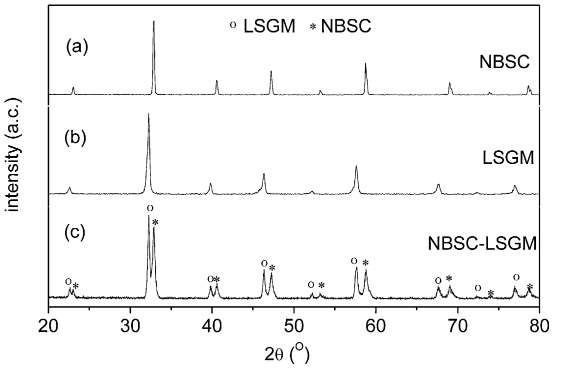

Fig. 1. XRD patterns of (a) NBSC powders, (b) LSGM powders and (c) NBSC–LSGM mixture sintered at 1000 °C for 10 h.

(LSGM), $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) and NiO powders were synthesized using the glycine–nitrate combustion method.

Symmetrical electrochemical cells with the configuration of electrode/LSGM/electrode were applied for the impedance studies. The LSGM powder was dry-pressed into pellets about 13 mm in diameter and 1 mm thick under 200 MPa, and sintered at 1450 °C for 10 h in air to obtain a dense electrolyte substrate. Suitable slurries were made up by mixing NBSC powders with an organic solvent (10% ethyl cellulose + 90% terpineol) and screen printed onto both sides of LSGM electrolyte pellet (the thickness of electrode is ~40 μm), followed by calcination at 950 °C for 2 h. Then silver paste was applied to electrode surfaces to serve as current collectors.

Electrolyte-supported fuel cells were fabricated using a screen printing method. The sintered LSGM ceramic disks were polished to become thin and smooth, the thickness was controlled to 300 μm. In order to prevent interdiffusion of ionic species between NiO–GDC (65:35 by weight) and LSGM, a thin buffer layer of GDC was screen printed onto the anode side of the LSGM electrolyte. After heating the buffer layer at 1300 °C for 1 h, the NiO–GDC anode was screen printed onto the GDC layer and heated at 1250 °C for 4 h. The NBSC cathode layer was subsequently screen printed onto the cathode side of the LSGM electrolyte and heated at 950 °C for 2 h. The single-cell made in this way was then sealed onto one end of an alumina tube with silver paste.

The phase structure of synthesized powders was characterized with an X-ray diffractometer (XRD, Rigaku-D-Max γA system with Cu Kα radiation). Electrical conductivity was measured as a function of temperature by the standard dc four-terminal method. Impedance spectra of the symmetrical cells were measured over the frequency range of 0.1–10^5 Hz under open circuit conditions, using an electrochemical system (CHI604C). The single-cell performance was tested under dry H_2 and ambient air.

3. Results and discussion

Fig. 1 shows an XRD pattern of NBSC–LSGM mixtures (50:50 by weight). For comparison, the patterns of NBSC and LSGM are also shown in the same figure. It can be seen that the NBSC cathode material synthesized by the solid-state reaction method is pure layered perovskite phase with an orthorhombic structure. The structure of the LSGM is the cubic fluorite structure. After the NBSC–LSGM mixture has been sintered at 1000 °C for 10 h, the NBSC and LSGM still retain their own structures. This suggests that there are no obvious reactions between NBSC and LSGM and NBSC is a chemically stable cathode material for SOFCs based on LSGM when the operating temperature is below 1000 °C.

Fig. 2 shows the temperature dependence of the electrical conductivity of the dense NBSC pellet in air. The conductivity of NBSC gradually increases with decreasing temperature and reaches 1368 S cm^{-1} at 100 °C, indicating a metallic behavior. This is consistent with a previous report [13]. The apparent metallic conductivity behavior of NBSC maybe due to an energy band overlap between Co-3d and O-2p and the presence of Co^{4+} ions from thermally generated charge disproportion of Co^{3+} [14]. For cathode materials of SOFC, the general required value for the electrical conductivity is about 100 S cm^{-1} at the operating temperature [15]. The lowest electrical conductivity of NBSC at 850 °C is still above 389 S cm^{-1} and therefore the material is adequate for application as a cathode in IT-SOFC. The conductivity of $NdBa_{0.5}Sr_{0.5}Co_2O_{5+x}$ (NBSC) cathode is much higher than that of the $NdBaCo_2O_{5+x}$ (NBC). For example, the highest electrical conductivity of the NBC was only ~150 S cm^{-1} at 450 °C [8]. Sr substitution results in a significant increase of conductivity. As described previously with the $YBa_{1-x}Sr_xCo_2O_{5+\delta}$ ($0 \le x \le 1$) system [11], the conductivity value of partial Sr-substituted is much higher than the pure Ba one, probably due to the smaller lattice volume.

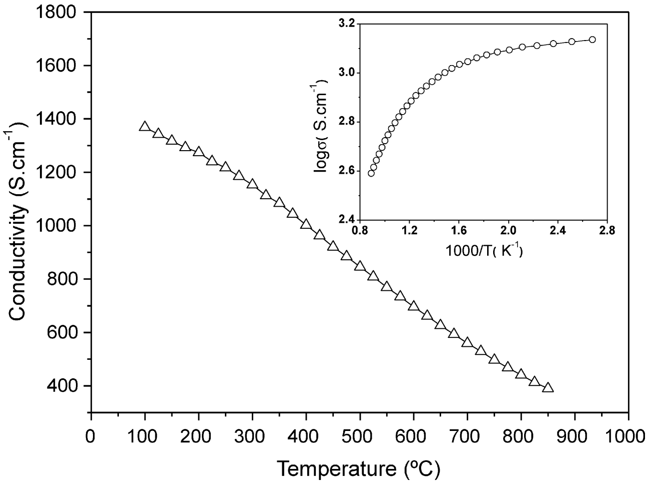

Fig. 2. Temperature dependence of the conductivity for NBSC sample.

Fig. 3(a) shows the impedance spectra of NBSC cathode on LSGM electrolyte measured at different temperatures in air. The ac impedance is made up of both ohmic and interfacial resistances. The intercept with the real axis at high frequency represents the resistance of the electrolyte and lead wires. The arc observed at lower frequency can be associated with the interfacial impedance between the NBSC cathode and the LSGM electrolyte. As expected, an increase of the measurement temperature resulted in a significant reduction of the ASR. The ASRs of NBSC cathode on LSGM electrolyte are 0.069, 0.039 and 0.023 Ω cm^2 at 750, 800, 850 °C, respectively. These values are much lower than that expected for the ASR of the cathode, which is lower than 0.15 Ω cm^2 at operating temperature [16]. Moreover, the ASR of NBSC is lower than that of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ [17], $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [2] and $Sm_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{3-\delta}$ [18] (x = 0, 0.2, 0.6 and 0.8). The low ASR values indicated that NBSC cathode has high-electrocatalytic activity for oxygen-reduction reactions at intermediate temperatures. This excellent cathode performance of NBSC maybe related to fast oxygen diffusion in the bulk and high surface kinetics on the surface of electrode for double-perovskite structure. Moreover, as a MIEC oxide, NBSC provides multiple pathways for the oxygen ions to migrate to the electrode/electrolyte interface. Fig. 3(b) shows the Arrhenius plot of the polarization resistance for NBSC cathode. The activation energy calculated from the slope of the fitted line is 114.4 kJ mol^{-1}, which is close to that of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode reported by Shao and Haile [3].

Fig. 4 shows the power density and voltage as a function of current density for Ni–GDC/GDC/LSGM/NBSC cell using H_2 as the fuel

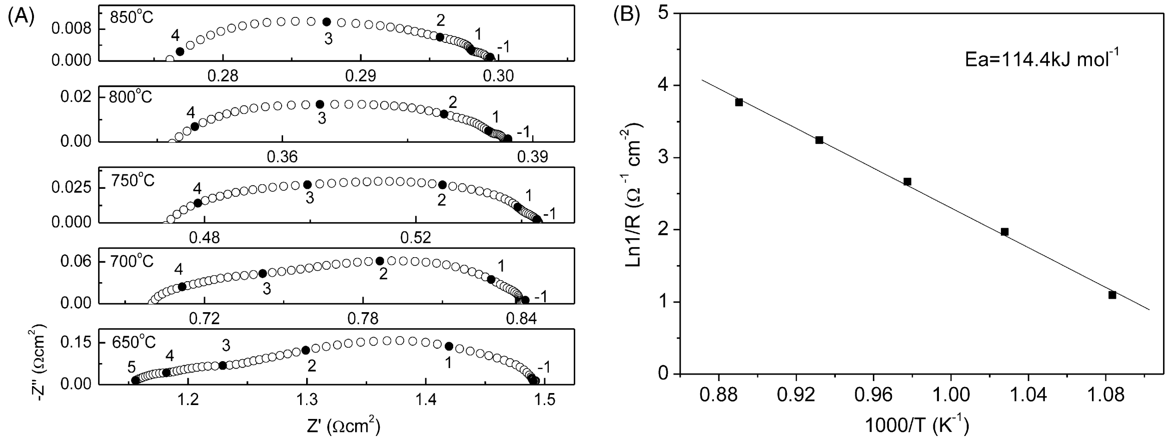

Fig. 3. (a) Impedance spectra of the NBSC cathode (sintered at 950 °C) measured at 650–850 °C. The numbers in these plots correspond to logarithm of frequency. (b) Arrhenius plot of the polarization resistance of NBSC cathode on LSGM electrolyte sintered at 950 °C for 2 h.

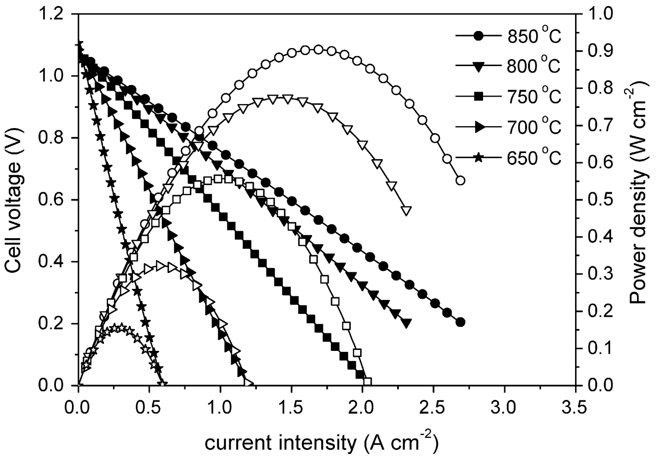

Fig. 4. Cell voltage and power density as functions of current density with NBSC cathode.

and static air as the oxidant in the temperature range of 650–850 °C. Peak power densities are 904, 774 and 556 mW cm^{-2} at 850, 800 and 750 °C, respectively. Obviously, the performance of the cell with a NBSC cathode is well compared with other cathodes measured under the same conditions, such as: $LaBaCuMO_{5+x}$ (M = Co, Fe) [19] and $GdBaCuMO_{5+x}$ (M = Co, Fe) [20] cathodes. These results demonstrate that NBSC may be a promising cathode material for IT-SOFCs, although its long-term stability on single-cell needs to be further investigated.

4. Conclusions

NBSC cathode material synthesized with a solid-state reaction had a pure layered perovskite phase structure. It also revealed a good chemical compatibility with the LSGM electrolyte. The NBSC cathode exhibited metallic behavior with electrical conductivities of 1368 S cm^{-1} at 100 °C and 398 S cm^{-1} at 850 °C. The lowest ASR of 0.023 Ω cm^2 was achieved at 850 °C. The maximum power density of a single-cell was 904, 774 and 556 mW cm^{-2} at 850, 800 and 750 °C, respectively. All results considered, NBSC cathode is a promising material for IT-SOFC based on LSGM electrolyte, whose stability and performance on single-cell will be investigated in the future.

Acknowledgement

This work was supported by the Natural Science Foundation of China (no. 10604020).

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