Journal of Power Sources 342 (2017) 623–628

Contents lists available at ScienceDirect

Journal of Power Sources

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

A CO_2-tolerant $La_2NiO_{4+\delta}$-coated $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ cathode for intermediate temperature solid oxide fuel cells

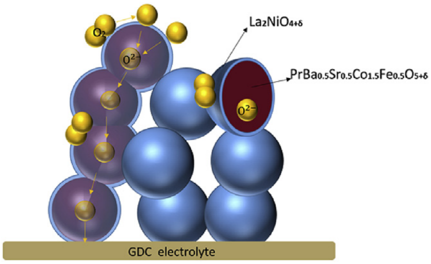
Jin Li, Qian Zhang, Peng Qiu, Lichao Jia, Bo Chi, Jian Pu, Jian Li*

Center for Fuel Cell Innovation, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, China

HIGHLIGHTS

- LN-coated PBSCF cathode is prepared by solution infiltration.
- Higher catalytic activity is achieved by functional shell's introduction.
- Two current collectors Ag and Pt pastes are used and investigated respectively.
- LN-coated PBSCF cathode's stability in a CO_2-rich atmosphere is confirmed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form
22 December 2016
Accepted 26 December 2016

Keywords:
Solid oxide fuel cell
LN-coated PBSCF cathode
Double perovskite
Ruddlesden-Popper
CO_2 tolerance

ABSTRACT

$La_2NiO_{4+\delta}$ (LN)-coated $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) composite cathode, designated as PBSCF-LN, for the intermediate temperature solid oxide fuel cells (IT-SOFCs) is prepared by solution infiltration, and investigated comparatively with single phase PBSCF cathode in the half and full cells using Ag and/or Pt paste as the current collector. Compared with Pt, Ag current collector results in a decrease of cathode polarization resistance (R_P) by an order of magnitude, which suggests that Ag is electrocatalytically active and not suitable for the use of studying the cathode performance of IT-SOFCs. The R_P value of PBSCF-LN cathode is significantly lower than that of PBSCF cathode, no matter whether Pt or Ag current collector is used for the measurement. High power densities ranging from 0.24 to 0.94 W cm^{-2} at temperatures between 600 and 750 °C are achieved using a full cell with PBSCF-LN cathode. Upon exposure to a CO_2-rich atmosphere, carbonate particles are formed on the surface of PBSCF cathode, causing irreversible degradation of electrochemical performance. In contrast, the surface of PBSCF-LN cathode remains clean, and its performance degradation due to CO_2 adsorption is recoverable.

1. Introduction

Solid oxide fuel cell (SOFC) has been regarded as a highly efficient and clean power generation system, benefiting both energy supply and environment [1]. To circumvent the issues of high maintenance cost and system instability, lowering SOFC's operating temperatures to the intermediate temperature (IT) range between 600 and 800 °C is of great significance [2]. However, this approach leads to the decrease of electrocatalytic activity of the cathode for the oxygen reduction reaction (ORR). Although the state-of-the-art cathode material $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) possesses high electronic conductivity, it cannot function effectively at the intermediate temperatures due to its negligibly low ionic conductivity [3,4]. Even in the case of LSM-Y_2O_3 stabilized ZrO_2 (LSM-YSZ) composite cathode, the area specific resistance is as high as 3.25 Ω at 750 °C [5]. To tackle this difficulty, simple perovskite (SP) oxides, such as

---

* Corresponding author.
E-mail address: lijian@hust.edu.cn (J. Li).

http://dx.doi.org/10.1016/j.jpowsour.2016.12.106
0378-7753/

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) [6] and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [7], which are mixed ionic and electronic conductors (MIEC), have been explored as cathode materials for the IT-SOFCs. The active site for the ORR is not restricted to the three-phase boundary in this type of SP materials. Their activity depends on their surface oxygen exchange coefficient (k^*) and bulk oxygen diffusion coefficient (D^*) [8]. For example, The BSCF has the highest value of k^* among SP cathode materials [9] and shows superior electrode performance to that of the LSM at intermediate temperatures [10]. But, its performance is adversely affected by phase transformation-related degradation [11], thermal and chemical incompatibility with YSZ electrolyte material [12] and CO_2 poisoning [13–15].

In addition to SP oxides, some double perovskite (DP) and Ruddlesden-Popper (RP) oxides are also developed as cathode materials for the IT-SOFCs. These perovskite-related materials have a layered structure and shown a low polarization resistance and a high catalytic activity [9]. In particular, the cation-ordered $LnBaCo_2O_{5+\delta}$ series have attracted extensive interests due to their fast oxygen ion diffusion (high D^*) and high electrical conductivity (σ_e) [16–18]. Furthermore, element doping, such as Sr and Fe in $PrBaCo_2O_{5+\delta}$, further improves their thermal expansion behavior and electrocatalytic activity for the ORR [19]. However, they are susceptible to degradation in CO_2-containing atmospheres because of the presence of alkaline-earth elements such as Ba and Sr [20]. In contrast, the typical RP oxides $Ln_2NiO_{4+\delta}$ (Ln = Nd, La or Pr) are CO_2 resistant [21] with high k^* value.

To take the advantages of high D^* and σ_e of the DP and high k^* and CO_2 resistance of the RP, we developed a novel RP-coated DP cathode via solution infiltration in the present study. $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) was used as the porous scaffold and $La_2NiO_{4+\delta}$ (LN) as the coating based on the consideration that pure LN phase can be easily formed at relatively lower temperatures and is also chemically compatible with PBSCF at temperatures investigated (Fig. S1). In order to make the results of this study comparable with those reported in literatures, both Ag and Pt pastes were used as current collectors in the measurements of electrochemical impedance spectra.

2. Experimental

PBSCF powder was synthesized by a polymer-assisted combustion synthesis method. Stoichiometric amounts of $Pr(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (Aladdin Industrial Corporation, purity > 98.5%) were dissolved into deionized water, and then glucose and acrylamide (Sinopharm Chemical Reagent, purity 99.5%) were added as the chelant. The molar ratio of metal ions: glucose: acrylamide was 1:2:3. The pH value of the solution was adjusted to between 8 and 9 by adding ammonia. This solution was subsequently heated to 80 °C under stirring to form a viscous gel, which was dried at 180 °C for 12 h. The dried gel was ball-milled and then calcined in air at 900 °C for 4 h to form single-phase PBSCF powder with an average particle size of ca. 500 nm.

For comparative performance evaluation of PBSCF and LN-coated PBSCF (PBSCF-LN) cathodes by the three-electrode method, half-cells were fabricated using dense $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC, Ningbo SOFCMAN Energy Technology Co.) as the electrolyte. GDC electrolyte disc ($\phi 22 \times 1.2$ mm) was made by die-pressing under 10 MPa and sintering in air at 1550 °C for 5 h. PBSCF powder slurry was prepared using terpilenol as the solvent and ethyl cellulose as the binder and screen-printed on one side of the electrolyte disc, followed by sintering in air at 1000 °C for 2 h to form a porous PBSCF cathode (~10 μm × 0.5 cm^2). To fabricate PBSCF-LN cathode, a solution was prepared using $La(NO_3)_3$ and $Ni(NO_3)_2$ (Aladdin Industrial Corporation, 99.5%) as the precursors, isopropanol as the solvent, glycine as the chelant and polyvinylpyrrolidone as the surfactant. This solution was dropped on the top of and soaked into the PBSCF scaffold in a negative pressure vessel, and calcined in air at 850 °C for 2 h to form a LN coating on the PBSCF scaffold. A part of the solution was dried and calcined in air at 850 °C for 2 h to form LN powder for phase identification. On the other side of the electrolyte disc, round-shaped counter and ring-like reference electrodes were made symmetrically opposite to the cathode using Ag and Pt pastes, respectively, by screen-printing and baking in air at 850 °C for 2 h. The electrochemical impedance spectra (EIS) of such prepared cells were measured in air and CO_2-containing atmosphere at open circuit voltage using an impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface analyzer (Solartron 1287) in a frequency range from 10^6 to 10^{-1} Hz with a voltage amplitude of 10 mV.

For further evaluation of the cathodes, anode-supported (Ni-YSZ) full cells were prepared by tape casting-screen printing-sintering process described in detail in Ref. [4]. A GDC buffer layer was used between YSZ electrolyte and the cathode to prevent their reaction. The current (I)-voltage (V)-power (P) responses of the full cells were measured using an impedance/gain phase analyzer (Solartron 1260) and an electrochemical interface analyzer (Solartron 1287). X-ray diffraction (XRD, PANalytical B.V. X'Pert PRO) and electron scanning microscopy (SEM, FEI Sirion 200) were employed for phase identification of the synthesized materials and microstructure examination of the as prepared and tested cathodes.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized PBSCF (a) and LN (b) powders. According to References [19,22] it was confirmed that pure phase PBSCF and LN were obtained by the solution method used. Fig. 2 shows the cross-sectional microstructures of the PBSCF and PBSCF-LN cathodes in the half-cells. It is seen that homogeneously porous PBSCF (Fig. 2a) and PBSCF-LN (Fig. 2b) cathodes were formed, and the thickness of the LN coating on the PBSCF scaffold was approximately 25 nm (Fig. 2c and d).

The EIS of these two cathodes were acquired in air at temperatures from 600 to 800 °C using Ag and Pt as the current collectors, respectively. Fig. 3 shows the typical EIS at 700 °C with Pt (Fig. 3a) and Ag (Fig. 3b) as current collectors, respectively, and the cathode polarization resistance (R_P) derived from the EIS at various temperatures (Fig. 3c). It is seen that the values of R_P of the PBSCF-LN were lower than those of the PBSCF, no matter what current collector was used. Deconvoluting the EIS at 700 °C into the high- and low-frequency arcs using an equivalent circuit shown in Fig. 3a, two corresponding polarization resistances, R_{PH} and R_{PL}, were obtained, which are listed in Table 1. R_{PH} is generally considered to be related to the charge transfer process of the reaction associated with the high frequency arc and R_{PL} to the reaction steps of oxygen adsorption, dissociation and diffusion associated with the low frequency one. Therefore, the much higher value of R_{PL} in comparison with that of R_{PH} for the PBSCF indicates that the low-frequency processes of the ORR in the cathode was sluggish, and the corresponding high-frequency process was relatively faster due to its high D^* (1.18×10^{-7} cm^2 s^{-1} at 600 °C [23]) and σ_e (420 S cm^{-1} at 600 °C [19]). And the significantly reduced R_{PL} of the PBSCF-LN demonstrates that the low-frequency processes of the ORR were greatly enhanced owing to the high k^* of the LN ($k^* = 7 \times 10^{-9}$ cm s^{-1} at 500 °C [9]), which resulted in dynamic oxygen surface exchange, and the rough surface of LN coating (Fig. 2b), which provided more active sites for O_2 adsorption [24]. It is known that single phase LN is not a proper cathode material for IT-SOFCs because its polarization resistance is much higher than