New Two-layer Ruddlesden-popper Cathode Materials for Protonic Ceramics Fuel Cells

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Abstract

New two-layer Ruddlesden-popper (RP) oxide La$_{0.25}$Sr$_{2.75}$FeNiO$_7$-$\delta$ (LSFN) in the combination of Sr$_3$Fe$_2$O$_7$-$\delta$ and La$_3$Ni$_2$O$_7$-$\delta$ was successfully synthesized and studied as the potential active single-phase and composite cathode for protonic ceramics fuel cells (PCFCs). LSFN with the tetragonal symmetrical structure (I4/mmm) is confirmed, and the co-existence of Fe$^{3+}$/Fe$^{4+}$ and Ni$^{3+}$/Ni$^{2+}$ couples is demonstrated by XPS analysis. The LSFN conductivity is apparently enhanced after Ni doping in Fe-site, and nearly three times those of Sr$_3$Fe$_2$O$_7$-$\delta$, which is directly related to the carrier concentration and conductor mechanism. Importantly, anode supported PCFCs using LSFN-BZCY composite cathode achieved high power density (426 mW·cm$^{-2}$ at 650°C) and low electrode interface polarization resistance (0.26 $\Omega$ cm$^2$). Besides, relaxation time distribution function (DRT) technology was further used to analysis the electrode polarization processes. The observed three peaks (P1, P2, P3) separated by DRT shifted to the high frequency region with the decreasing temperature, suggesting that the charge transfer at the electrode-electrolyte interfaces become more difficult at reduced temperature. Preliminary results demonstrate new two-layer PR phase LSFN can be a promising cathode candidate for PCFCs.

1. Introduction

Protonic ceramics fuel cells (PCFCs) possess several advantages of high proton conductivity electrolytes with low activation energy and high fuel efficiency, receiving more attractive at reduced operating temperature [1–4]. However, As the temperature reduced, the corresponding challenge for the oxygen reduction reaction is the reduced cathodic catalytic activity, causing the large electrode polarization loss and fast degradation of cell performance [5–7]. Therefore, great efforts have been devoted to developing new cathode materials and modifying high performance conventional cathode materials that can own high catalytic activity at reduced temperature.

New cathodes with mixed conductivity based on simple perovskite (doped LaCoO$_3$, BaCoO$_3$ and LaFeO$_3$) have been extensively studied [7–12]. Considering high oxygen-ion defect concentration, oxygen diffusion anisotropy and cation ordered-structure, several recent studies have highlighted the promising of the Ruddlesden-Popper (RP) series, A$_{n+1}$BnO$_{3n+1}$, for cathode application, where the special sandwich structure consists of n ABO$_3$ perovskite and two A0 rock salt layers[13–17]. The Sr$_3$Fe$_2$O$_7$-$\delta$-based systems, belonging to the n = 2 series, have been widely investigated owing to their high oxygen deficiency, excellent water-intercalation property and prominent catalytic activity [18–20]. The partial substitution of Ni for Fe in Sr$_3$Fe$_2$O$_7$-$\delta$ can increase the electrical conductivity and the oxygen permeability without structural transformation [21–22]. In our previous works, the introduction of La into Sr-site forming La$_x$Sr$_{3-x}$Fe$_2$O$_7$-$\delta$ can enhance thermo-chemical stability as well as large oxygen deficiency [23–24]. Moreover, another RP phase, La$_3$Ni$_2$O$_7$-$\delta$ (n = 2), showed large electrical conductivity, acceptable stability and similar thermal expansion coefficient to electrolytes [25–27]. Therefore, in this work, we combine two RP phase oxides of Sr$_3$Fe$_2$O$_7$-$\delta$ and La$_3$Ni$_2$O$_7$-$\delta$ thanks to their similar ionic radii and chemical properties, expecting to enhance the conductivity and electrochemical activity without structural
transformation. Here, La$_{0.25}$Sr$_{2.75}$FeNiO$_{7-\delta}$ (LSFN) was successfully prepared and investigate the electrochemical performance to verify the possibility for using as cathode material for PCFCs. In addition, LSFN incorporated with BZCY to form a composite cathode for PCFCs were also examined. The polarization processes for PCFCs under working condition were detailly analyzed by relaxation time distribution function (DRT) method.

2. Experimental

LSFN, NiO-BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY), and BZCY powders were synthesized by EDTA- citric acid combustion method, and the primary powders were calcined at 1200°C, 1100°C and 1100°C for 3 h, respectively [28]. X-ray diffraction (XRD) was used to perform all prepared powders as well as LSFN-BZCY mixtures calcined at different temperatures. X-ray photoelectron spectrometer (XPS) was used to analyze the elemental chemical state of LSFN, and then the conductivity measurement by H.P. multimeter using the standard DC four-probe technique was investigated from 800 to 300°C in air.

Anode supported PCFCs with LSFN single-phase and composite cathode were used to investigate the electrochemical performance. The NiO-BZCY-starch / NiO-BZCY / BZCY anode supported half cells were prepared by the dry pressing, and then sintering at 1400°C for 3h. Finally, LSFN and LSFN-BZCY (7:3) cathode slurry were brushed onto BZCY electrolyte surface severally, and then calcined at 900°C for 3 h in air. Anode supported PCFCs were evaluated by cell-testing system with humidified (~3% H$_2$O) H$_2$ fuel at 650°C-500°C. The impedance spectra (Chi604E, Shanghai Chenhua) under open-current conditions were investigated with the frequency range of 100kHz-0.01Hz and AC amplitude of 10mV at 650°C-500°C, of which the microstructure was performed using scanning electron microscopy (SEM).

3. Result And Discussion

XRD pattern of prepared LSFN powder was presented in Fig. 1(a), which clearly shows defined the tetragonal symmetry with the space group of I4/mmm in the light of standard powder diffraction information for Sr$_3$Fe$_2$O$_{7-\delta}$, indicating that the partial replacement of Fe with Ni can't affect the single RP phase structure [18-20]. Rietveld analysis (GSAS) was performed and the XRD Rietveld refinement results are also given in Fig. 1(a) and Fig. 1(b) (magnified results with 2θ of 25-50 °), where low refinement reliability factors (wRp=12.90%, Rp=9.84%, $\chi^2=2.05$) were obtained. The calculated lattice parameters a and c based on this model are 3.8364(50) and 20.0376(93) Å, respectively, and one can clearly be seen that two perovskite layers are sandwiched by the rock-salt layer along the c-axis in the typical two-layer RP phase structure sandwiched as illustrated in Fig. 1(c) . In addition, LSFN sample with high crystallinity and well-defined crystalline fringes was observed in Fig. 1(d), and the lattice spacing of 0.2658nm corresponds to the lattice spacing of the (110) plane in the tetragonal symmetry in selected-angle diffraction in Fig. 1(b). All results together demonstrate the well maintained single RP phase structure after the combination of two RP phase oxides of Sr$_3$Fe$_2$O$_{7-\delta}$and La$_3$Ni$_2$O$_{7-\delta}$. 
The elemental chemical state was characterized by XPS, and La3d, Sr3d, Fe2p and Ni2p peaks in XPS spectra for LSFN sample at room temperature were shown in Fig. 2. The peaks of binding energies of La 3d5/2 (at 834.4 and 838.1 eV) and La3d 3/2 (at 851.5 eV) represent La3+ as revealed in Fig. 2(a). Fig. 2(b) proves Sr in LSFN sample displays a +2 valence state with the binding energies of Sr 3d5/2 (at 132.8 eV) and Sr 3d 3/2 (at 134.6 eV). Fig. 2(c) shows the Fe 2p binding energy region of LSFN sample, where the location of 710.5/724.1 eV and 712.5/725.9 eV peaks are related to the Fe2p 3/2 /Fe2p 1/2 signals for Fe3+ and Fe4+, respectively, and the proportion of Fe4+/Fe3+ is about 0.898 without the peaks of Fe2+ [29-30]. Fig. 2(d) reports the Ni 2p XPS spectra of LSFN sample, and the Ni 2p peaks that envelope the Ni2+ and Ni3+ valence states are fitted. One can clearly observed that four characteristic peaks with the binding energy of 855.8, 862.7, 873.5 and 880.5 eV, which related to Ni3+ 3d 5/2 and 3d 3/2, respectively, while the peaks of 2p 1/2 at 872.1 and 877.8 eV and 2p 3/2 at 854.4 and 860.7 eV can be attributed to Ni2+, where the proportion of Ni3+ /Ni2+ is about 1.25[31-33]. The XPS results conform the fact that Fe3+/Fe4+ and Ni3+/Ni2+ couples are co-existed in the LSFN sample. Moreover, the conductivity of LSFN can be considered to be affected in LSFN sample as follows:

$$Fe^{4+} + Ni^{2+} \leftrightarrow Fe^{3+} + Ni^{3+}$$  (1)

Therefore, the introduction Ni3+/Ni2+ couples would be expected to enhance the conductivity and electrochemical properties of the LSFN sample.

The electrical conductivity for Sr3Fe2O7-δ sample increases to a peak of about 60.4 S·cm⁻¹ at around 500 °C, and then reduces as the temperature increases from 300 °C to 800 °C as shown in Fig. 3, exhibiting typical semi-conductor-like behavior[19, 20]. Fig. 3 also gives the electronic conductivity of LSFN sample measured at 300-800 °C in air, and LSFN sample presents typical metallic behavior as well as La3Ni2O7-δ, of which the conductivities increase with the decrease of temperatures (223 S·cm⁻¹ at 300°C[27]). The charge carriers, Fe3+/Fe4+ and Ni3+/Ni2+ redox couples, directly affect the change from the semiconductor-like to metallic conducting behavior, indicating that Ni doping into Fe-site causes the 3d electron delocalized [21, 22]. Therefore, LSFN sample presents improved conductivity and is superior to both Sr3Fe2O7-δ and La3Ni2O7-δ.

Before the electrochemical performance of LSFN single-phase and composite cathode for anode supported PCFCs was measured, the chemical compatibility behavior of LSFN-BZCY mixture was evaluated. LSFN-BZCY mixture with the same mass calcined in air at 800-1100 °C for 10h, respectively. There are no any reaction between LSFN and BZCY before 1000°C as shown in Fig. 4. Although a small amount of (BaSr)FeO3-δ was observed, the vast majority of the LSFN-BZCY composite were very stable after calcined at 1100 °C. Meanwhile, (BaSr)FeO3-δ-based cathode owns high catalytic activity and exhibits excellent electrochemical performance (696 mW·cm⁻² at 700 °C[34]). Therefore, anode supported PCFCs based on LSFN single-phase and composite cathode have been measured at 650-500°C, and I-V-P
curves were given in Fig. 5. The open-circuit voltage values of LSFN and LSFN-BZCY at 650°C are 1.02 and 1.04 V, indicating the highly dense microstructure of BZCY electrolyte. The maximum power densities of LSFN single-phase cathode are 348.0, 219.6, 136.2, and 71.7 mW·cm⁻² at 650, 600, 550 and 500°C. With the incorporation of BZCY, the maximum power densities of LSFN-BZCY composite cathode increase to 426.0, 332.3, 188.8, and 94.5 mW·cm⁻² at the same operation temperature. Obviously, LSFN-BZCY composite cathode exhibits much higher performance than Co-doped La₃Ni₂O₇-δ (398 mW·cm⁻²[27]), but still lower than Sr₃Fe₂O₇-δ-5wt.%BZCY composite cathode (583 mW·cm⁻²[19]).

To evaluate the catalytic performance of LSFN-BZCY composite cathode for oxygen reduction reactions, electrochemical impedance spectroscopy (EIS) measurements was used to perform anode supported PCFCs under open-circuit conditions as shown in Fig.6 (a). Electrode polarization resistance (Rp) and the ohmic resistance (Rb) can be calculated from the impedance as well as the total resistance (Rt), and then presented in Fig. 6(b). Temperature has a significant effect on the Rp and Ro at the working temperatures, and the Rp value increased from 0.26 to 1.72 Ω·cm² with the reduce temperature, while corresponding Rb only changes from 0.47 to 1.23 Ω·cm², indicating that the Rp is the rate-limiting step for PCFCs at low temperatures. LSFN-BZCY composite cathode exhibits low Rp than Co-doped La₃Ni₂O₇-δ (7.6 Ω·cm² [27]), but much larger than Sr₃Fe₂O₇-δ-5wt.%BZCY composite cathode (0.15 Ω·cm² [19]).

As to further detailly investigate the electrode polarization process of anode supported PCFCs with LSFN composite cathode under OCVs conditions, the impedance spectrum analysis using the relaxation time distribution (DRT) method can be characterized as the peaks in the $F(\tau)$ vs. $-\log_{10}(2\pi \tau)$ curves as follows [35-38]:

$$F(\tau) = \tau G(\tau) \ln(10) = \frac{-\ln(10)}{\pi} \left[ Z''\left(e^{-\ln r+\frac{j\pi}{2}}\right) + Z''\left(e^{-\ln r-\frac{j\pi}{2}}\right) \right]$$

where $F(\tau)$ is the distribution function of the relaxation time. As shown in Fig. 7(a), The calculated DRT plots exhibit several polarization processes. It clearly can be seen that there exist three (P1, P2, P3) main peaks at different operation temperatures, suggesting there are three rate-limiting steps. Meanwhile, all the peaks shift to high frequency with the reduced temperatures, suggesting the charge transfer with electron and oxygen-ion at reduced temperature becomes more difficult at the electrode-electrolyte interfaces. Simulated resistances correspond to P1, P2 and P3 are presented in Fig. 7(b, c). P1 observed at the high frequency decreases with the increasing temperature, and therefore P1 is considered to be proton incorporation and diffusion at cathode-electrolyte interface [36, 37]. As can be seen from Fig. 7(b), the proportion of P1 is much larger than P2 and P3, indicating that P1 is the rate-limiting step for the reaction. Since LSFN single-phase cathode has ignorable proton conductivity and the mix of BZCY can dramatically improve the proton conducting behavior. P2 is the processes of H₂ adsorption, dissociation and proton formation at anode and the proportion of P2 is almost the same as temperature reduced. Certainly, P3 also decreases with the increasing temperature and locates at the low frequency. Therefore,
P3 is supposed to oxygen dissociation, adsorption and diffusion in cathode with low proportion of about 19% at 500°C owing to excellent conductivity of LSFN.

Fig. 8 shows the stability test of LSFN composite cathode with a 50 mA·cm⁻² discharge current density at 700°C in humidified H₂ fuel. The output voltages varied with test time were recorded, and results indicated that the voltage remained a stable value at 0.96 V within 50 h test. Fig. 9(a) shows cross-sectional images of anode-supported PFCFs with LSFN-BZCY cathode after long-term testing. The 30 µm-thickness proton BZCY electrolyte is dense enough and adheres well with LSFN-BZCY cathode under the cover of silver, preventing the gas leakage and ensuring efficient proton transmission. Besides, there are countless microporous at the approximate 35µm-thick anode functional layer from the reduction of NiO and macroporous at anode substrate as shown in Fig. 9(b), leading to a better interfacial contact between anode substrate and electrolyte. Preliminary results demonstrated new two-layer RP structure LSFN must be a promising cathode candidate for PCFCs, and catalytic activity and proton conductivity of LSFN single-phase cathode can be further enhanced by incorporation with BZCY.

4. Conclusions

In this work, we successfully synthesized two-layer Ruddlesden-popper oxide La₀.₂₅Sr₂.₇₅FeNiO₇₋δ (LSFN) and then was evaluated as the active single-phase and composite cathode for proton ceramics fuel cells (PCFCs). LSFN with the tetragonal symmetrical structure (I4/mmm) is confirmed by the XRD Rietveld refinement. Furthermore, the XPS results obviously prove the co-existence of Fe³⁺/Fe⁴⁺ and Ni³⁺/Ni²⁺ couples in the combination of two RP phase oxides of Sr₃Fe₂O₇₋δ and La₃Ni₂O₇₋δ, and directly affect the change from the semiconductor-like to metallic conducting behavior confirmed by the conductivity measurement. Importantly, anode supported PCFCs using LSFN-BZCY cathode achieved maximum power densities of 426.0, 332.3, 188.8, and 94.5 mW·cm⁻² at 650 – 500°C, respectively, with corresponding Rp of 0.29, 0.43, 0.79, and 1.72 Ω·cm². The electrode polarization processes were further analyzed using the relaxation time distribution function (DRT), and thus three polarization peaks (P1, P2, P3) observed in DRT curves shifted to the right at high frequency with the decreasing temperature, suggesting that the charge transfer at the electrode-electrolyte interfaces become more difficult at reduced temperature. Preliminary results demonstrated two-layer RP structure LSFN can be a promising cathode candidate for PCFCs.

Declarations

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