Study on anode material of Co$_{\delta}$Fe$_{1-\delta}$O$_x$-Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ for solid oxide fuel cell

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Abstract

This paper mainly explores the anode properties of Co$_{\delta}$Fe$_{1-\delta}$O$_x$-Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (SDC) ($\delta=0$, 0.2, 0.5, 0.8, and 1) for solid oxide fuel cell (SOFC). The composite anode materials were synthesized by sol-gel method, and the XRD technique was used to characterize structural properties. After H$_2$ reduction at 700 ℃, the Co$_{\delta}$Fe$_{1-\delta}$O$_x$ oxides were reduced to Co, Fe metal or Co-Fe alloy. The symmetric cells were fabricated with Co$_{\delta}$Fe$_{1-\delta}$O$_x$-SDC as the electrodes and SDC-carbonate as the electrolyte. At 700 ℃, the symmetric cell with Co$_{0.5}$Fe$_{0.5}$O$_x$-SDC electrodes showed the lowest polarization resistance and the symmetric cell with Co$_{0.2}$Fe$_{0.8}$O$_x$-SDC showed the largest polarization resistance.

1. Introduction

Solid oxide fuel cell (SOFC) is an efficient electrochemical energy conversion technology that can convert chemical energy into electrical energy [1,2] with the advantages of cleanliness, high efficiency and no noise [3,4]. SOFC consists of anode, cathode and electrolyte. Through the action of the catalyst, the fuel is oxidized on the anode. With H$_2$ as fuel, hydrogen molecules are oxidized into hydrogen ions and generate electrons. The catalytic activity of the anode material plays an important role in cell performance. Therefore, it is very important to explore the catalytic activity of anode materials.

The selection of anode materials is helpful to improve the performance of the cell. Zhu et al. [5] found that the maximum power density of the cell with Co$_{0.5}$Fe$_{0.5}$-SDC as the anode, La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_3$ as the electrolyte, and Au mesh and Pt mesh as the anode collector can reach 1.07 and 1.20 W cm$^{-2}$, respectively. Zhang et al. [6] used Ba$_x$MMoO$_y$ ($M =$ Fe, Co, Mn, Ni) as the anode of SOFC, both Ba$_2$FeMoO$_6$ and Ba$_2$CoMoO$_6$ showed good electrochemical properties, and the maximum power density of Ba$_2$FeMoO$_6$ could reach 605 mW cm$^{-2}$. Xie et al. [7] found that the cell with Fe$_{0.25}$Co$_{0.25}$Ni$_{0.5}$-SDC anode had a higher power density than the cell with Ni-SDC as the anode. Moreover, Co and Fe can also inhibit the carbon deposition of Ni-SDC anode and further improve the stability of the cell [8,9]. Zhang et al. [10] found that Co-Fe alloy can precipitated from Pr$_{0.4}$Sr$_{0.6}$Co$_{0.2}$Fe$_{0.7}$Nb$_{0.1}$O$_{3+\delta}$ in H$_2$ atmosphere at 900 ℃. The existence of Co-Fe alloy improved the cell performance when using propane as the fuel. In addition, Fu et al. [11] found the addition of Co and Fe could improve the conductivity of the Gd$_{0.1}$Ce$_{0.9}$O$_{2.5}$ (GDC). Furthermore, Lai and Manthiram...
found the in-situ exsolution of Co-Fe alloy from La$_{0.3}$Sr$_{0.7}$Cr$_{0.3}$Fe$_{0.6}$Co$_{0.1}$O$_{3-\delta}$ could also improve the H$_2$S tolerance, redox reversibility and long-term stability of the SOFC. Therefore, it can be inferred that Co-Fe alloy plays an important role in improving the catalytic activity of the anode. However, the relationship between the Co/Fe ratio in Co-Fe alloy and cell performance is still unclear, and further research is urgently needed.

Herein, in this work, we prepared Co$_{0.4}$Fe$_{0.6}$O$_x$-SDC composite materials as the anode of SOFC. The crystal structure and the effect of the Co/Fe ratio on the performance of SOFC were described in detail.

2. Materials and Methods

2.1 Material preparation and characterization

Co$_{0.8}$Fe$_{0.2}$O$_x$ ($\delta=0$, 0.2, 0.5, 0.8, and 1) powders were synthesized through a sol-gel process [13] using Co(NO$_3$)$_2$·6H$_2$O (99%, Shanghai Aladdin Bio-Chem Technology Co., Ltd) and Fe(NO$_3$)$_3$·9H$_2$O (99.9%, Shanghai Aladdin Bio-Chem Technology Co., Ltd) as the raw materials. The nitrate mixture was heated at 5 °C/min to 350 °C and calcined for 4 hours, then heated to 700 °C and calcined for 6 hours to obtain Co$_x$Fe$_{1-x}$O$_x$ ($\delta=0$, 0.2, 0.5, 0.8, and 1). SDC was prepared by hydrothermal method [14] using Ce(NO$_3$)$_3$·6H$_2$O (99%, Shanghai Aladdin Bio-Chem Technology Co., Ltd) and Sm(NO$_3$)$_3$·6H$_2$O (99.9%, Shanghai Aladdin Bio-Chem Technology Co., Ltd) as the raw materials. SDC and Co$_x$Fe$_{1-x}$O$_x$ were mixed at a molar ratio of 1:1, and then calcined at 700 °C for 2 h to form the composite anode Co$_x$Fe$_{1-x}$O$_x$-SDC ($\delta=0$, 0.2, 0.5, 0.8 and 1). The electrolyte material (SDC-LN) consisted of 70 wt% SDC and 30 wt% (Li$_{0.67}$Na$_{0.33}$)$_2$CO$_3$. First, mixed sodium carbonate and lithium carbonate in a ball mill with a molar ratio of 1:2 for 5 hours, heated up to 700 °C and calcined for 1 hour, and ground and screened to make (Li$_{0.67}$Na$_{0.33}$)$_2$CO$_3$. The SDC was mixed with (Li$_{0.67}$Na$_{0.33}$)$_2$CO$_3$ with a mass ratio of 7:3 in a ball mill for 5 hours and then calcined at 700 °C for 1 hour to make the SDC-LN electrolyte. The symmetric cells with the structure of Co$_{0.4}$Fe$_{0.6}$O$_x$-SDC|SDC-LN|Co$_{0.4}$Fe$_{0.6}$O$_x$-SDC were fabricated and the catalytic activities of various anode materials on hydrogen oxidation reaction were explored. The electrolyte powder was first pressed into pellet with a thickness of 0.65 mm, and then the pellet was sintered in air at 700 °C for 1 h. The anode slurry was screen-printed onto both sides of the electrolyte pellet. The symmetrical cell was calcined at 700 °C for 1 hour and the schematic diagram of symmetrical cell.

In addition, in order to explore the structural changes of the anode materials before and after reduction, the Co$_{0.4}$Fe$_{0.6}$O$_x$-SDC powders were reduced in H$_2$ atmosphere at 700 °C for 2 hours and labeled as R-Co$_{0.4}$Fe$_{0.6}$O$_x$-SDC. And the X-ray diffraction (XRD) technique was used to characterize the structural properties of the anode materials before and after reduction. The XRD was operated by a Rigaku (Smartlab) instrument under the conditions of Cu-Kα radiation in the 2θ range of 20°-80°.

2.2 Testing

The performance of symmetrical cells was tested by an electrochemical workstation (CHI 660E). Before test, both sides of the cell were reduced in pure H$_2$ atmosphere at 700 °C for 2 hours. Then the electrochemical impedance spectra (EIS) were tested under various hydrogen partial pressures ($P_{H2}$ = 100 %, 80 %, 60 %, 40 %, 20 %) using N$_2$ as the balance. All the spectra were recorded under open circuit voltage (OCV) in the frequency range from 1 M to 0.01 Hz with amplitude of 10 mV.

3. Results and Discussion

3.1 Material characteristics

The XRD patterns of Co$_{0.4}$Fe$_{0.6}$O$_x$-SDC are shown in Fig. 1(a). It was found that Co$_2$O$_4$ (PDF #74-2120) existed in CoO$_x$-SDC; with the Fe content increased to 20%, Co$_2$O$_4$ and Fe$_2$O$_3$ (PDF #75-0033) exist in Co$_{0.8}$Fe$_{0.2}$O$_x$-SDC. When further increase the Fe content to 50%, the substance existing in Co$_{0.5}$Fe$_{0.5}$O$_x$-SDC is the same as Co$_{0.8}$Fe$_{0.2}$O$_x$-SDC. With Fe content higher than 50%, (CoFe)$_2$O$_4$ (PDF #
and Fe₂O₃ (PDF #89-0596) existed in Co₀.₂Fe₀.₈Oₓ-SDC. The and only Fe₂O₃ (PDF #89-0596) peaks are observed in FeOₓ-SDC. It should be mentioned that the existence of Fe in FeOₓ-SDC and Co₀.₂Fe₀.₈Oₓ-SDC are Fe₂O₃ (PDF #89-0596), which was different from that in Co₀.₈Fe₀.₂Oₓ-SDC and Co₀.₅Fe₀.₅Oₓ-SDC.

Furthermore, the XRD patterns of R-Co₀.₂Fe₀.₈Oₓ-SDC are shown in Fig. 1(b). After reduction, Co and Fe oxide peaks are disappeared instead of the formation of metal Co (PDF #15-0806) in R-CoOₓ-SDC and metal Fe (PDF #06-0696) in R-FeOₓ-SDC. when the Fe content increased to 20%, both Co₀.₇Fe₀.₃ (PDF #48-1818) and metal Co exist in R-Co₀.₈Fe₀.₂Oₓ-SDC. With further increase the Fe content to 50%, CoFe (PDF #49-1568) peaks are observed in R-Co₀.₅Fe₀.₅Oₓ-SDC. As the Fe content increased to 80%, Co₃Fe₇ (PDF #48-1816) peaks are appeared in R-Co₀.₅Fe₀.₈Oₓ-SDC. Therefore, different Co/Fe ratios display different Co-Fe alloys in R-Co₀.₂Fe₀.₈Oₓ-SDC. In addition, there is no change for SDC (PDF #75-0158) peaks before and after reduction in H₂, indicating the structure of SDC is stable in both oxidation and reduction atmosphere.

3.2 Electrochemical performance

The EIS results of symmetric cells with R-Co₀.₂Fe₀.₈Oₓ-SDC as the electrode are shown in Fig. 2. The intercepts of the Nyquist plots on the real axis correspond to the ohmic resistances and the polarization resistances (R_p) are represented by the arcs. The ohmic resistances of the cells were deduced from the results for a better comparison, and the R_p values of the cell follow an order of R-Co₀.₅Fe₀.₅Oₓ-SDC < R-Co₀.₇Fe₀.₃Oₓ-SDC < R-Co₀.₈Fe₀.₂Oₓ-SDC < R-FeOₓ-SDC < R-Co₀.₂Fe₀.₈Oₓ-SDC. R-Co₀.₅Fe₀.₅Oₓ-SDC has the smallest R_p, while the R-Co₀.₂Fe₀.₈Oₓ-SDC has the largest R_p. It probably due to the different alloys formed on different anode materials. From the XRD results, it can be inferred that CoFe alloy formed in R-Co₀.₅Fe₀.₅Oₓ-SDC shows the highest catalytic activity toward H₂ oxidation and Co₇Fe₇ alloy formed in R-Co₀.₂Fe₀.₈Oₓ-SDC showed the lowest catalytic activity. Therefore, the proper addition of Fe can improve the electrocatalytic activity [15]. In addition, by comparison R-CoOₓ-SDC and R-FeOₓ-SDC, it could be found that the catalytic activity of R-CoOₓ-SDC was higher than that of R-FeOₓ-SDC, indicating that Co has more positive significance for improving electrocatalytic activity than Fe. R-Co₀.₈Fe₀.₂Oₓ-SDC exhibits lower catalytic activity than R-Co₀.₅Fe₀.₅Oₓ-SDC but higher catalytic activity than R-Co₀.₂Fe₀.₈Oₓ-SDC, suggesting that the catalytic activity of Co₀.₇Fe₀.₃ alloy is higher than that of Co₇Fe₇, but lower than that of CoFe alloy.
Fig. 2. EIS spectra of the symmetric cells with R-CoO_x-SDC as the electrode at 700 °C with H_2 as the fuel.

The EIS results of R-CoO_x-SDC and R-Co_{0.5}Fe_{0.5}O_x-SDC materials under different hydrogen atmospheres (P_{H_2} = 100 %, 80 %, 60 %, 40 %, 20 %) are shown in Fig. 3(a). With the increase of H_2 pressure, the R_p values increased. That was, the larger the proportion of hydrogen in the fuel, the more sufficient fuel could be improved, which was more conducive to the reaction on the anode side and improved the catalytic activity of the anode. By studying the relationship between R_p and P_{H_2}, we could better understand the electrochemical oxidation process of hydrogen on the anode. The power exponents(α) of R-CoO_x-SDC, R-Co_{0.8}Fe_{0.2}O_x-SDC, R-Co_{0.5}Fe_{0.5}O_x-SDC, R-Co_{0.2}Fe_{0.8}O_x-SDC, and R-FeO_x-SDC are -0.54, -0.47, -0.51, -0.49 and -0.39, respectively, as shown in Fig. 3(b). It has been reported that H_2 mainly has four reaction steps in the anodic electrochemical oxidation process, and these four reaction steps are related to the α value. The value of α determines the rate-determining step(RDS). The α value is mainly divided into -1, 0.5 and 0, which means that RDS is dissociating the adsorbed H_2 on the surface to adsorbed H atoms, transferring the adsorbed H transfers to the reaction site, and transferring oxygen ions generated on the oxygen electrode from the electrolyte to the three-phase boundary, respectively [16]. Therefore, it can be known that the adsorbed H transferring to the reaction site is the RDS of these five samples.

Fig. 3. (a) EIS of R-CoO_x-SDC, R-Co_{0.5}Fe_{0.5}O_x-SDC sample at 700 °C under different atmospheres; (b) R_p of the symmetric cells versus P_{H_2} at 700 °C

4. Conclusion
Sol-gel method was used to synthesis the anode materials of Co_{δ}Fe_{1-δ}O_x-Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) (δ=0, 0.2, 0.5, 0.8, and 1) for solid oxide fuel cell (SOFC). Before reduction, the Co and Fe elements in all the samples existed as oxides and after H_2 reduction at 700 °C, the Co_{δ}Fe_{1-δ}O_x oxides were reduced to Co, Fe metal or Co-Fe alloy. To clear the catalytic activity of anode materials toward H_2 electrochemical...
oxidation reaction, the symmetric cell tests were operated. The symmetric cells were fabricated with Co$_{0.5}$Fe$_{0.5}$O$_x$-SDC as the electrodes and SDC-carbonate as the electrolyte. At 700 °C, the symmetric cell with Co$_{0.5}$Fe$_{0.5}$O$_x$-SDC electrodes showed the lowest polarization resistance, indicating that Co$_{0.5}$Fe$_{0.5}$O$_x$-SDC exhibits the highest catalytic activity for H$_2$ electrochemical oxidation reaction.

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