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Synthesis of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}-x\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ cobalt-free composite cathodes by a one-pot method for intermediate-temperature solid oxide fuel cells

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ABSTRACT

Cobalt-free composite cathodes consisting of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}-x\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ (PSFO-xCPO, $x = 0-50$ wt%) have been synthesized using a one-pot method. X-ray diffraction, scanning electron microscopy, thermal expansion coefficient, conductivity, and polarization resistance (R_p) have been used to characterize the PSFO-xCPO cathodes. Furthermore the discharge performance of the Ni-SSZ/SSZ/GDC/PSFO-xCPO cells has been measured. The experimental results indicate that the PSFO-xCPO composite materials fully consist of PSFO and CPO phases and possess a porous microstructure. The conductivity of PSFO-xCPO decreases with the increase of CPO content, but R_p of PSFO-40CPO shows the smallest value amongst all the samples. The power density of single cells with a PSFO-40CPO composite cathode is significantly improved compared with that of the PSFO cathode, exhibiting 0.43, 0.75, 1.08 and 1.30 W cm^{-2} at 650, 700, 750 and 800 °C, respectively. In addition, single cells with the PSFO-40CPO composite cathode show a stable performance with no obvious degradation over 100 h when operating at 750 °C.

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Introduction

Solid oxide fuel cells (SOFCs) are advanced energy conversion systems that have attracted significant attention due to their high energy conversion efficiency, fuel flexibility and low pollutant emissions [1–3]. To expand the commercial applications of SOFCs, it is necessary to develop intermediate-temperature SOFCs (IT-SOFCs) that can operate at temperatures between 600 and 800 °C [4,5]. However, the decrease of operating temperature leads to lower oxygen diffusivity and slower surface exchange reactions, which together decrease the rate of the oxygen reduction reaction (ORR) at the cathode [6–8]. The conventional $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) demonstrates high stability and compatibility with most of the SOFCs electrolytes, but has low electrocatalytic activity [9]. Thus, a study of new cathode materials is of great importance for IT-SOFCs development.

Cobalt-based cathodes have been intensely studied, the results of which have shown that these materials have good electrochemical properties [10–12]. This interest is due to the fact that cobalt-based materials exhibit good catalytic activity for the ORR and high electrical conductivity in the intermediate-temperature range [13,14]. However, the expense of elemental cobalt together with the high thermal expansion coefficients of the cathode materials and unacceptable chemical stability have been significant obstacles to further development [15–17]. Therefore, a new move is underway to develop cobalt-free cathode materials. Ferrite-based oxides such as $\text{La}_{0.5}\text{Bi}_{0.3}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ [18], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ [19], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Mo}_{0.1}\text{O}_{3-\delta}$ [20], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ [21] have attracted attention due to their lower TEC, better stability and lower cost. However, the electrochemical activities of these materials for the ORR are generally lower than that of cobalt-based materials at intermediate temperatures [22]. In addition, development of composite cathodes has also now proven to be an effective strategy for improving the electrochemical performance of the IT-SOFCs [23]. These new composite cathodes can exhibit higher ORR activity when compared with single-phase cathodes, as the second phase may be able to increase the number of triple phase boundaries (TPBs) in the electrode [24–27]. The general approach for preparing these composite cathodes is based on mechanical mixing of different phases or use of an impregnation technique [28]. However these methods normally require multiple steps and are time-consuming. As a result, a simple, easier method for fabricating high performance IT-SOFCs composite cathodes would be highly desired.

Facile one-pot methods are timesaving and have had a wide range of applications in the preparation of oxygen membranes [29]. Moreover, one-pot methods can attain more uniform mixtures of two phases than alternative powder blending methods, packing methods and loading methods, resulting in more catalytic reaction sites and longer TPBs [30]. A useful method should allow for good compatibility between the ionic conducting phase and the perovskite phase. Zirconia reacts easily with perovskite oxides to produce zirconates which can block the transport of ions and electrons. Therefore doped ceria ($\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-\delta}$ (Ln: rare earth metal, $0.05 \leq x \leq 0.2$)) is a good choice. The low

tolerance factor of 0.87 gives Sr^{2+} a higher chemical potential in SrCeO_3 than in $\text{Ln}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$ ($0.2 \leq y \leq 0.8$), so SrCeO_3 does not emerge in dual phase composite materials. Therefore, composite cathodes can be obtained using a composition of $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-\delta}$ – $\text{Ln}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$ [31]. According to reports in the literature, the cobalt-free ferrite-based composite membrane material $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ – $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ has shown good phase stability in a CO_2 atmosphere at high temperatures [32,33]. In addition, the oxygen permeation flux of the $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ – $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ membrane is greater than that of the single-phase perovskite-type membrane $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ and dual phase-type membranes (e.g., $\text{Gd}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ – $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{2-\delta}$) under similar conditions. $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ prepared by impregnation methods or doping methods was reported to use as cathode materials for SOFCs [34,35]. However, there are no systematic reports about $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ – $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ composite prepared by the novel one-pot methods as cathode materials for IT-SOFCs. In this study, $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ – $x\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}$ (PSFO- x CPO, $x = 0$ –50 wt%) composite cathodes were prepared by a one-pot method. The effect of composite cathode on cell performance can be improved by changing the volume fraction of the cathode component. The phase structure and microstructure of the materials were characterized with X-ray diffraction and scanning electron microscopy, respectively. In addition, their performance was further studied, including conductivity, electrochemical impedance spectroscopy and discharge performance of the resulting cells.

Experimental

Materials preparation

PSFO- x CPO composite powders were synthesized using a one-pot method. The synthesis process is illustrated in Fig. 1. Stoichiometric amounts of $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were employed as the precursors. The preparation procedure began with dissolving the metal nitrates in deionized water. Next, EDTA and citric acid were then mixed into the solution as complexing agents using a molar ratio of total metal nitrates to EDTA to citric acid of 1:1:2. The next step involved addition of NH_4OH to adjust the solution pH value to approximately 7. Following evaporation of the water at 80 °C, a transparent gel was obtained. This gel was heated at 250 °C until the composite gel combusted. The resulting ash was further calcined at 1000 °C for 5 h under an air atmosphere to obtain CPO and PSFO- x CPO ($x = 0, 20, 30, 40$, and 50 wt%) composite powders. Other materials used in this procedure included 10% Sc_2O_3 -stabilized ZrO_2 (SSZ, Tosoh Co., Japan), NiO (High Purity Chemicals, Japan) and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC, Fuel cell materials Co., USA). The PSFO- x CPO powders were pressed into a rectangular bar with a size of $25 \times 5 \times 5 \text{ mm}^3$ under a pressure of 200 MPa, and then sintered at 1400 °C for 5 h in air. The thermal expansion coefficient (TEC) and the electronic conductivity (σ) measurements were performed on samples of these materials.

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