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Thermal cycling durability improved by doping fluorine to $PrBaCo_2O_{5+\delta}$ as oxygen reduction reaction electrocatalyst in intermediate-temperature solid oxide fuel cells

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HIGHLIGHTS

- F is successfully doped to $PrBaCo_2O_{5+\delta}$ (PBC) by combustion method.
- F doping significantly reduces the thermal expansion coefficient of PBC.
- The thermal cycling durability is remarkably improved by doping F to PBC.
- F doping enhances PBC's oxygen transport property & catalytic activity of ORR.

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ABSTRACT

Double perovskite $PrBaCo_2O_{5+\delta}$ (PBC) has received much attention as cathode material for solid oxide fuel cells (SOFCs) due to its excellent catalytic activity for oxygen reduction reaction (ORR), especially at intermediate temperature up to 800 °C. However, its high thermal expansion coefficient (C_{TE}), about twice as the electrolytes, usually results in poor durability. This work presents the effect of C_{TE} reduction by doping fluorine ion to the oxygen-site of $PrBaCo_2O_{5+\delta}$. The fluorine doping, which is confirmed with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy investigations, can substantially reduce C_{TE}, from $24.03 \times 10^{-6}\,K^{-1}$ down to $16.78 \times 10^{-6}\,K^{-1}$ as determined with dilatometry while from $26.52 \times 10^{-6}\,K^{-1}$ to $17.46 \times 10^{-6}\,K^{-1}$ with high-temperature XRD. Consequently, the durability is improved by a factor of ~3.0 when the electrodes are subjected to 200–800 °C thermal cycles. In addition, the fluorine doping does not deteriorate but maintains or even improves the oxygen transport properties and electrochemical performance for ORR of PBC, demonstrating that fluorine doping is very attractive for the development of promising cathode materials for intermediate-temperature SOFCs.

1. Introduction

Oxygen reduction reaction (ORR) is the key step in the processes for solid-state electrochemical devices operating at elevated temperatures, such as fuel cells [1,2], metal-air batteries [3–5], and oxygen pumps [6–8], which find potential applications in efficient, environmental friendly conversions for renewable energy sources. The slow ORR kinetics and the high cost of noble-metal catalysts have led to limited use of these energy conversion devices. Thus, finding a viable high performance electrocatalyst with low over-potential, i.e. low interfacial polarization resistance for ORR is still the focus of much research [9].

Particular interests are paid to ABO_3 perovskite materials, which are usually mixed ionic-electronic conductors [10–13]. Particularly, the double perovskite $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Gd, Sm etc.) oxides have shown very fast oxygen transport kinetics, i.e. high bulk diffusion coefficient D and oxygen surface exchange coefficient k, consequently high electrochemical performance for ORR [14,15]. For example, D at 500 °C is $2.8 \times 10^{-10}\,cm^2\,s^{-1}$ for $GdBaCo_2O_{5+\delta}$ (GBC) as measured using isotopic exchange method [16]. The bulk diffusion coefficient is about two orders of magnitude higher than $1.2 \times 10^{-12}\,cm^2\,s^{-1}$ at the same temperature for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\text{-}\delta}$ (LSCF), which is the state-of-the-art electrocatalyst for ORR at intermediate temperature [17].

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And it is about six orders of magnitude higher than 10^{-16} cm^2 s^{-1} at 600 °C for $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM), the conventional perovskite oxide for ORR at high temperature up to 1000 °C [18]. Meanwhile, k at 500 °C is 7.4×10^{-8} cm s^{-1} for GBC [16], much higher than 2×10^{-8} cm s^{-1} at 500 °C for LSCF [17] and 10^{-10} cm s^{-1} at 600 °C for LSM [18]. In the $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Gd, Sm etc.) groups, $PrBaCo_2O_{5+\delta}$ (PBC) presents the highest values in both D and k as demonstrated by Kim et al. [19]. Thus, PBC has been carefully investigated as the ORR electrocatalyst, especially for solid oxide fuel cells (SOFCs). However, applications of these cobalt-based double perovskites are challenged by their high thermal expansion coefficients (C_{TE}), which is associated with the reduction of Co ions and the formation of oxygen vacancies [20]. For instance, C_{TE} is 24.1×10^{-6} K^{-1} for PBC [21], about twice as high as those for the electrolyte and interconnect materials, typically $\sim 11 \times 10^{-6}$ K^{-1}. The large mismatch in C_{TE} must result in serious degradation in electrode performance, especially under the conditions of thermal cycle.

In order to reduce C_{TE}, the B-site ion Co has been partially substituted with other transition metals such as Sc [20], Mn [22], Fe [23], Ni [24], and Cu [21]. For example, when 50% Co in PBC is replaced with Cu, forming $PrBaCoCuO_{5+\delta}$, C_{TE} is reduced to 15.2×10^{-6} K^{-1} [21]. Meanwhile, 75% Co substitution with Fe, $PrBaCo_{0.5}Fe_{1.5}O_{5+\delta}$, results in about 25% reduction in C_{TE} [23]. However, the B-site substitution reduces the electronic conductivity, oxygen surface exchange coefficient and bulk diffusion coefficient, thus decreases the electrochemical performance. The Cu substitution decreases the conductivity from 176 S cm^{-1} to 131 S cm^{-1} at 650 °C [21]. When 75% Co is substituted with Fe, the conductivity decreases about 90% while the interfacial polarization resistance increases about 30% at 650 °C [23]. The Fe substitution also reduces the oxygen diffusion rate. For instance, the oxygen permeation flux at 900 °C decreases from 1.89×10^{-7} mol cm^{-2} s^{-1} for PBC to 1.32×10^{-7} mol cm^{-2} s^{-1} for $PrBaCo_{0.5}Fe_{1.5}O_{5+\delta}$ [25]. Moreover, efforts have been made to reduce C_{TE} by partial replacement of A-site Pr and Ba with Ca or Sr. For instance, 30% Pr substitution with Ca reduces C_{TE} to 19.1×10^{-6} K^{-1}. Meanwhile, the conductivity is decreased from 936 S cm^{-1} for PBC to 470 S cm^{-1} for $Pr_{0.7}Ca_{0.3}BaCo_2O_{5+\delta}$, and the interfacial polarization resistance is increased about 15% at 650 °C [26].

This work presents a new strategy for C_{TE} reduction by doping fluorine to the O-site of PBC. The fluorine doping is found to be able to reduce C_{TE}, thus enhance the thermal cycling durability of PBC cathodes. However, different from the A-site and B-site doping in PBC, F doping could maintain or even improve the oxygen transport properties and electrochemical performance for ORR of PBC.

2. Experimental

2.1. $PrBaCo_2O_{5+\delta}F_x$ powder synthesis and characterization

The nominal composition of fluorine doped material was $PrBaCo_2O_{5+\delta}F_x$, abbreviated as PBC, PBC-F1, and PBC-F2 for x = 0, 0.1, and 0.2, respectively. $PrBaCo_2O_{5+\delta}F_x$ powders were synthesized via an ethylene diamine tetraacetic acid (EDTA) and citric acid combustion process [21,23,27], using EDTA (99.5%) and citric acid (99.5%) as complex and combustion agents. In a typical synthetic process, $Pr(NO_3)_3·6H_2O$ (99.9%), $Ba(NO_3)_2$ (99.5%), $Co(NO_3)_2·6H_2O$ (98.5%), and BaF_2 (99.0%) with molar ratio to the nominal composition were dissolved into deionized water to form an aqueous solution with a total metal ion concentration of 2.0 mol L^{-1}. EDTA and citric acid were subsequently introduced, with the molar ratio of 1.5: 1: 1 for EDTA, citric acid and the total metal ions. Then, ammonia solution was dropped to adjust pH to about 7.0. The solution was stirred with a magnetic stirrer for about 2 h in room temperature and then heated on hot plate till self-combustion occurred, resulting in black ashes, which were subsequently collected and heated at 1100 °C for 3 h to obtain $PrBaCo_2O_{5+\delta}F_x$ powders. All chemicals were from Sinopharm Chemical Reagent Co. Ltd. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to investigate the valence states of the elements in $PrBaCo_2O_{5+\delta}F_x$. The change in oxygen content with temperature was revealed using oxygen temperature-programmed deposition (O_2-TPD, TPDRO 1100) analysis. The powder samples were measured in the range of 50–1000 °C with a ramp rate of 20 °C min^{-1} and a helium flow rate of 30 mL min^{-1}.

2.2. Thermal expansion and oxygen transport properties

Dense $PrBaCo_2O_{5+\delta}F_x$ bar samples were prepared to determine thermal expansion coefficient C_{TE} and the oxygen transport properties including electrical conductivity σ, chemical oxygen surface exchange coefficient k_{chem} and chemical oxygen diffusion coefficient D_{chem}. The as prepared $PrBaCo_2O_{5+\delta}F_x$ powders were grounded, isostatic pressed into rectangular bars at 300 MPa, and sintered at 1200 °C for 5 h in air to form dense bars with a size of about $30.00 \times 5.50 \times 0.50$ mm^3. The relative density was estimated to be about 97.8% of the theoretical value as determined with Achimedes method. C_{TE} was determined by a dilatometer (Netzsch DIL 402C) from 100 to 800 °C using Al_2O_3 as a reference with a heating rate of 5 °C min^{-1} in air. C_{TE} was also determined with high-temperature X-ray diffraction (XRD, SmartLab, 9 kW) with a temperature control unit (Anton Paar, TCU 1000N). The XRD patterns were obtained in the range of 20–80° with a step size of 0.02° and a scan speed of 3° min^{-1} at 40 kV and 200 mA. Rietveld refinement was performed to obtain the crystalline parameters. The conductivity, was measured in air using a four-probe method with a digital multimeter (Keithley, 2001-785D) at temperatures in the range from 100 °C to 800 °C. D_{chem} and k_{chem} were obtained using electrical conductivity relaxation (ECR) method. The measurement was performed at 700 °C, 650 °C, 600 °C and 550 °C. $PrBaCo_2O_{5+\delta}F_x$ bar samples were placed into a quartz tube, heated in air to the set temperature with a heating rate of 5 °C min^{-1} and then stabilized for about 1.0 h to make sure they were completely equilibrated with $P(O_2) = 0.21$ atm. After reaching equilibration at each temperature, the atmosphere was abruptly changed to pure oxygen, $P(O_2) = 1.0$ atm. The gas flow rate was 200 mL min^{-1} to ensure the gas switches were realized in less than 1 s. The increase in $P(O_2)$ led to electrical conductivity change, which was recorded, normalized and fitted according to the liner diffusion equations (Fick's second law) to calculate D_{chem} and k_{chem} [28].

2.3. Cell fabrication and electrochemical performance

The ORR performance was investigated using symmetrical cells with $PrBaCo_2O_{5+\delta}F_x$ electrodes supported on gadolinia doped ceria ($Gd_{0.1}Ce_{0.9}O_{2-\delta}$, GDC) electrolyte substrates. GDC powders from Ningbo SOFCMAN Energy Technology Co. Ltd. were used without further treatment. The powders were uniaxially pressed into disk-shaped pellets at 250 MPa, using a 13 mm diameter stainless steel die. Then, the green pellets were sintered at 1500 °C for 5 h in air to form dense pellets with a diameter of about 10.0 mm and thickness of about 0.4 mm. To prepare the electrode layers, $PrBaCo_2O_{5+\delta}F_x$ slurry was prepared by mixing $PrBaCo_2O_{5+\delta}F_x$ powders with ethyl cellulose and α-terpineol. The slurry was symmetrically deposited onto both sides of the GDC pellets via screen-printing technique. After drying, the green sandwich bodies were heated at 1000 °C for 2 h to form symmetrical cells.

The electrochemical performance was further investigated using anode supported single cells with Ni-GDC anodes, thin layer of GDC electrolytes, and $PrBaCo_2O_{5+\delta}F_x$-GDC composite cathodes. NiO powders was synthesized by glycine-nitrate process (GNP) and the specific fabrication details were previously reported [29]. NiO, GDC and Poly Methyl Methacrylate (PMMA) were mixed homogeneously with a weight ratio of 60: 40: 20, and then pressed into the pellets at 250 MPa. The anode pellets were subsequently heated at 1100 °C for 4 h. The GDC electrolyte films were fabricated by dip-coating GDC slurry onto the anode pellets and then sintering at 1500 °C for 5 h to obtain anode/