



Original Research Paper

Effects of A-site deficiency on the electrical conductivity and stability of (La, Co) co-doped SrTiO₃ anode materials for intermediate temperature solid oxide fuel cells

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ABSTRACT

Improved anode materials are required for intermediate temperature operation of solid oxide fuel cells (SOFCs). (La, Co) co-doped SrTiO₃ was synthesized via solid state reaction in this study. The results have demonstrated remarkable improvement of the ionic electrical conductivity and the thermal stability of (La, Co) co-doped SrTiO₃ anode materials with A-site deficiency. The ionic conductivity of (La_{0.3}Sr_{0.7})_{0.95}Co_{0.07}Ti_{0.93}O_{3-δ} sample is 0.7–1.9 × 10⁻² S cm⁻¹ from 500 °C to 900 °C and 1.4 × 10⁻² S cm⁻¹ at 700 °C in 5% H₂/Ar. These values are nearly ten times higher than that of La_{0.3}Sr_{0.7}TiO_{3-δ} at 700 °C. A-site deficiency improves the thermal stability of (La, Co) co-doped SrTiO₃ and ensures stable electrical performance in different atmospheres. The possible charge compensation mechanism of (La_{0.3}Sr_{0.7})_{0.95}Co_{0.07}Ti_{0.93}O_{3-δ} multicomponent system was also discussed.

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1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical device that converts the energy of a chemical reaction directly into electrical energy. It shows many advantages over conventional power-generating systems in terms of efficiency, reliability, modularity, fuel flexibility, and environmental friendliness [1]. It is thus considered as a very important power technology in the future. At present, the Ni/YSZ is widely used as anode material. However, this material still has many problems related to its longevity or long term stability due to its high operation temperature of around 1000 °C [2,3]. These difficulties can be minimized by developing intermediate temperature SOFCs (IT-SOFCs) that can operate in the intermediate temperature range of 500–800 °C [4–6].

SrTiO₃-based perovskites are potential mixed ionic–electronic conductors for solid oxide electrolysis cells, solid oxide fuel cells and separation membranes due to its excellent chemical stability, thermal stability, and carbon and sulfur tolerance [7]. However, the un-doped stoichiometric SrTiO₃ cannot be used for anode materials due to its lower electrical conductivity. Therefore, many efforts have been made to enhance the mixed conductivity of SrTiO₃-based material. Donor-doping such as Y or La on Sr site

and acceptor-doping such as Co or Sc on Ti site of SrTiO₃ can remarkably increase the electronic conductivity and the ionic conductivity [8,9]. In addition, A-site deficiency of perovskite oxides has been reported as an effective way to increase the oxygen ionic conductivity via the generation additional oxygen vacancies [10,11]. On the other hand, the A-site nonstoichiometry in ABO₃ perovskites has also a strong impact on the sinterability, the structure stability and the thermal expansion coefficient (TEC), which is of great importance to anode materials [12–14].

Li and co-workers' research [8,11] indicated that La-doped SrTiO₃ has high electronic conductivity while (La, Co) co-doped SrTiO₃ has better ionic conductivity. In the present work, certain degree of A-site nonstoichiometry is introduced into La_{0.3}Sr_{0.7}Co_{0.07}Ti_{0.93}O_{3-δ} in an effort to improve the ionic conductivity and the structural stability. This study particularly focuses on the effects of A-site deficiency on electrical conductivity, including both electronic and ionic conductivities, sinterability and thermal stability of conductivity. The performances of YSZ-based fuel cells using La_{0.3}Sr_{0.7}TiO_{3-δ}, La_{0.3}Sr_{0.7}Co_{0.07}Ti_{0.93}O_{3-δ} or (La_{0.3}Sr_{0.7})_{0.95}Co_{0.07}Ti_{0.93}O_{3-δ} as anodes were investigated, respectively. A possible charge compensation mechanism caused by A-site deficiency was proposed and discussed.

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2. Experimental

A-site deficient $(\text{La}_{0.3}\text{Sr}_{0.7})_{1-x}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ ($x = 0, 0.05, 0.10$) and stoichiometric $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_{3-\delta}$ perovskite oxides were synthesized via solid state reaction among intimately mixed high-purity La_2O_3 , SrCO_3 , Co_3O_4 and TiO_2 in 5% H_2/Ar at 1300 °C for 10 h. Then the pre-reacted powder was ball-milled for the second time and uniaxially pressed at 200 MPa into pellets (13 mm in diameter and 2–3 mm in thickness) and bars (40 mm–7 mm–3 mm). The doped $\text{SrTiO}_{3-\delta}$ pellets were sintered at 1500 °C for 10 h in 5% H_2/Ar before electrochemical characterizations. XRD (X-ray diffraction, Rigaku D/max-A X-ray diffractometer, using $\text{Cu K}\alpha$ radiation) was employed to examine the phase purity of the sintered samples. The total electrical conductivity was measured by the standard four terminal DC methods in the temperature range of 50–900 °C in 5% H_2/Ar or air, and the ionic conductivity was determined by electron-blocking method in the temperature range of 500–900 °C in 5% H_2/Ar saturated with room-temperature water. Details of the experiment can be found in Ref. [15]. The total electrical and ionic conductivities data were taken in an interval of 50 °C. At each temperature the cell was held for at least 30 min to ensure thermal and phase equilibrium within the sample.

The electrode materials used in this study include Pt (intended for cathode) and doped $\text{SrTiO}_{3-\delta}$ composite (intended for anode). The densed $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) was used as electrolyte (20 mm in diameter and about 0.2 mm in thickness). The Pt electrodes were prepared from commercial Pt paste whereas homemade $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$, $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$, $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_{3-\delta}$ composites were prepared by mixing the individual powders with ethyl cellulose as binder in a weight ratio of 2:3. An electrode was fabricated by painting the prepared paste on the two surfaces of an LSGM pellet and firing in 5% H_2/Ar at 1300 °C for 2 h. Ag paste and Ag-leads served the current collectors. The cell was sealed to an Al_2O_3 tube with glass ring and cement. The cell has an effective surface area of 0.8 cm^2 . The flow rates of air and H_2 (containing 3% H_2O) were set to 50 cc min^{-1} and 40 cc min^{-1} , respectively.

3. Results and discussion

3.1. Phase development and the effect of A-site deficiency on sintering process

The $(\text{La}_{0.3}\text{Sr}_{0.7})_{1-x}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ ($x = 0, 0.05$ and 0.10) samples with $x \leq 0.05$ shows a single cubic perovskite structure and no impurity peaks are detected, while for the sample with $x = 0.10$ a trace amount of impurity (TiO_2) could be observed by XRD after sintering at 1500 °C for 10 h in 5% H_2/Ar (Fig. 1). The limit of A-site deficiency in $(\text{La}_{0.3}\text{Sr}_{0.7})_{1-x}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ at 1500 °C in 5% H_2/Ar is below 10 mol%. Thus, $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.90}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ was not investigated in this study. SEM images of fracture surfaces of $(\text{La}_{0.3}\text{Sr}_{0.7})_{1-x}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ samples are shown in Fig. 2. The porosity and the grain size show no obvious change with the tiny A-site deficiency doping.

According to the previous research [9], A-site deficiency in SrTiO_3 tends to increase pellet density, on the other hand, increase of A-site deficiency will lead to the increase of Co content in perovskite oxide, which, in turn, will cause density decrease. Thus, the effect of A-site deficiency on pellet density is not obvious.

3.2. Effects of A-site deficiency on the ionic and total electrical conductivity of (La, Co) co-doped SrTiO_3 mixed conductors

The total electrical and the ionic of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ and $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ samples as a function of temperature

are shown in Figs. 3 and 4, respectively. With increasing temperature, $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ sample shows a similar behavior with $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ in electrical conductivity, increasing first to a maximum and then decreasing (Fig. 3), indicating a small-polaron conduction mechanism [11,16,17]. It also shows that the total electrical conductivity of $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ is lower than that of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$, which indicates that the total electrical conductivity has been decreased by the A-site deficiency, as shown in Fig. 3. However, the ionic conductivity of $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ is $0.7\text{--}1.9 \times 10^{-2} \text{ S cm}^{-1}$ from 500 °C to 900 °C and $1.4 \times 10^{-2} \text{ S cm}^{-1}$ at 700 °C, about 2.3 times that of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ and nearly ten times higher than that of $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_{3-\delta}$. Thus, the ionic conductivity can be improved by appropriate B-site doping, and it can be further improved by A-site deficiency. The results also show that the (La, Co) co-doped SrTiO_3 anode is more promising to improve ionic conductivity than the (Y, In) co-doped SrTiO_3 anode published recently by Shan and co-workers [18] and the (La, Sc) co-doped SrTiO_3 anode published a few years ago by Li and co-workers [15]. It is worth noting that although the electrical conductivity decreases slightly, but the ionic conductivity of $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ increases significantly. According to previous studies [11,14], the power performance of anode material is the synergistic effect of electrical conductivity and ionic conductivity, the ionic conductivity is the bottleneck that limits the power performance when the conductivity is much higher than ionic conductivity. The influence of the ratio of electrical conductivity and ionic conductivity on the power performance will be intensively investigated in future work.

According to charge the compensation mechanism, the concentrations relationship between positive charges and negative charges in $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ at a constant oxygen partial pressure can be expressed as Eq. (1):

$$[\text{La}'_{\text{Sr}}] + 2[\text{V}''_{\text{O}}] = 2[\text{V}''_{\text{Sr}}] + [\text{Co}'_{\text{Ti}}] + [\text{Ti}'_{\text{Ti}}] \quad (1)$$

Compared to the sample of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$, the content of $[\text{La}'_{\text{Sr}}]$ decreases and $[\text{V}''_{\text{Sr}}]$ increases when the presence of A-site deficiency. The charge imbalance by A-site deficiency will result in the increase of $[\text{V}''_{\text{O}}]$ and/or the decrease of $[\text{Ti}'_{\text{Ti}}]$ to keep the charge balance. A-site deficiency will lead to the decrease of $[\text{Ti}'_{\text{Ti}}]$ and the increase of $[\text{V}''_{\text{O}}]$, considering the decreasing of the total electrical conductivity and the increasing of the ionic conductivity after A-site deficiency and B-site doping as shown in Figs. 3 and 4. Therefore, the charge imbalance caused by A-site deficient $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ is compensated by both the increase of oxygen vacancy concentration and the decrease of Ti^{3+} concentration.

3.3. Effects of A-site deficiency on the thermal stability of $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ in air

In order to achieve good sealing and fuel saving in the testing process of SOFC, typically the fuel cell is firstly raised to a certain temperature in air, then the fuel gas is allowed. This means good thermal stability in air is also very important for mixed ionic–electronic conductor.

Temperature and atmosphere dependence of the electrical conductivity of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ and $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.95}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ are shown in Fig. 5. It was found that $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\delta}$ showed a sudden decrease in conductivity in air above 800 °C, but it did not occur in 5% H_2/Ar . It is considered that the oxidation of Ti (changing from Ti^{3+} to Ti^{4+}) is responsible for the sudden change of conductivity in air at high temperature, which cause not only the decrease of Ti^{3+} concentration but also the formation of impurity phase. Correspondingly, the distinct attenuation of electrical conductivities is not observed for A-site deficient

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