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Performance of Solid Oxide Fuel Cell With La and Cr Co-Doped SrTiO_3 as Anode

The $\text{La}_{0.3}\text{Sr}_{0.55}\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_{3-\delta}$ (LSTC10) anode material was synthesized by citric acid-nitrate process. The yttria-stabilized zirconia (YSZ) electrolyte-supported cell was fabricated by screen printing method using LSTC10 as anode and $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_{3-\delta}$ (LSM) as cathode. The electrochemical performance of cell was tested by using dry hydrogen as fuel and air as oxidant in the temperature range of 800–900 °C. At 900 °C, the open circuit voltage (OCV) and the maximum power density of cell are 1.08 V and 13.0 $\text{mW}\cdot\text{cm}^{-2}$, respectively. The microstructures of cell after performance testing were investigated by scanning electron microscope (SEM). The results show that the anode and cathode films are porous and closely attached to the YSZ electrolyte. LSTC10 is believed to be a kind of potential solid oxide fuel cell (SOFC) anode material. [DOI: 10.1115/1.4026144]

Keywords: solid oxide fuel cell (SOFC), doped strontium titanate, perovskite, anode

1 Introduction

Solid oxide fuel cell (SOFC) is mainly composed of porous anode and cathode, a dense electrolyte layer and bipolar plate or connection materials. In the cell, the anode provides the site for the electrochemical reaction of the fuel, transfers electrons and gases, and furthermore it must possess good catalytic properties for the oxidation of the fuel. Therefore, the performance of anode materials plays a vital role in the performance of cell [1,2].

Ni/yttria-stabilized zirconia (YSZ) cermet is currently used as the anode in SOFC because it meets most of the requirements: mixed conductivity, thermal and chemical stability under operating conditions and also good catalytic activity to promote the oxidation of the fuel. But it also subjects to the following limitations: (1) propensity of Ni to catalyze carbon formation when operating the SOFC with hydrocarbon fuels [3,4], (2) sensitivity to sulfur in fuels [5,6], and (3) sintering of Ni particles and large Ni-NiO volume change during the redox cycling at SOFC operating temperature, which results in a significant degradation of cell performance [7,8].

Nowadays, therefore, the search of alternative materials to the Ni/YSZ cermet as efficient anodes for SOFC is one of the main research trends in solid state electrochemistry. The doped strontium titanate with a perovskite structure is considered as a promising candidate anode material for SOFC owing to its excellent mixed ionic-electronic conductivity [9,10], ability to be resistant to carbon depositing [11] and sulfur poisoning [12,13], and higher structural stability than Ni/YSZ cermet at high temperature [14,15].

According to literatures [14,16,17], donor-doping such as La or Y on Sr site of SrTiO_3 can remarkably increase the electronic conductivity of the materials at high temperature in the low-oxygen partial pressure, and A-site deficiency of perovskite oxides is an effective way to enhance the oxygen ionic conductivity of the materials via extra oxygen vacancy generation. In addition, LaCrO_3 has a good structural stability in a wide range of oxygen

partial pressure [18], and the doping of Cr can increase the stability of perovskite oxides [19]. So, in our preliminary work [20], a La and Cr co-doped SrTiO_3 (LSTC) with A-site deficiency was prepared by citric acid-nitrate process and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS). The results show that the LSTC can be considered as a potential candidate anode material for SOFC with YSZ as electrolyte. In this paper, the YSZ electrolyte-supported cells were fabricated by screen printing method using LSTC as anodes. With a view to researching the performance of cell with La and Cr co-doped SrTiO_3 as anode.

2 Experimental

2.1 Raw Materials. In addition to chemically pure tetrabutyl titanate, all reagents used in experiments were of analytical grade. YSZ disks and $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_{3-\delta}$ (LSM) cathode powders were purchased from Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science. The slurries of gold and platinum, gold and platinum wires were from Sino-platinum Metals CO., Ltd.

2.2 Anode Material Preparation. The $\text{La}_{0.3}\text{Sr}_{0.55}\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_{3-\delta}$ (LSTC10) powders were prepared by citric acid-nitrate process. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ were dissolved into de-ionized water to make a nitrate solution, which was marked as solution A. Stoichiometric amount of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dissolved into dilute nitric acid solution to make solution B. Solutions A and B were mixed into a uniform mixture. Citric acid in a 1.3:1 molar ratio with respect to the total amount of cations was added into the mixture. The pH value of the resulting solution was adjusted to 7–8 with appropriate quantities of $\text{NH}_3\cdot\text{H}_2\text{O}$ under continuous stirring at 70 °C and a homogeneous solution was thus formed. With the evaporation of water, a viscous gel of metal-citrate complexes was obtained. The gel was heated up to 200 °C in oven to generate a foamlike black precursor, it was then ground in a mortar and calcined in air at 800 °C for 5 h to produce the LSTC10 powders.

2.3 Cell Fabrication. In the cell fabrication, commercial YSZ disks were used as the electrolyte. Their thickness and

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Fig. 1 XRD pattern of LSTC10 powders calcined at 800 °C for 5 h

diameter were 260 μm and 20 mm, respectively. The anode slurry was prepared by mixing the LSTC10 powder and nanographite with a binder consisting of ethylcellulose and α -terpineol in a mortar. After that, a circular pattern was screen-printed on one side of the YSZ disk as the anode, which was then sintered in air at 1200 °C for 2 h. The cathode slurry was prepared from mixture of LSM powder, ethylcellulose, and α -terpineol. In the same way, the slurry was screen-printed on the other side of the YSZ disk as the cathode. The sandwich structure was sintered in air at 1100 °C for 2 h. The active area of working electrode was 1 cm^2 . Gold and platinum paste grids were sintered onto the anode and cathode sides, respectively, at 900 °C to serve as current collectors, with gold and platinum wires attached on the anode and cathode respectively as leads and sintered simultaneously with the paste as mention above.

2.4 Phase Structure and Morphology Analysis. The phase composition of LSTC10 anode material was determined by XRD using a BRUKER D8 ADVANCE diffractometer with Cu-K α source ($\lambda = 0.154056 \text{ nm}$) in the Bragg angle range of 20–80 deg. The microstructures of LSTC10 anode powders and cell after performance testing were investigated using a ZEISS ULTRA 55 scanning electron microscope.

2.5 Cell Performance Test. The prepared cell was bonded on the end of the Al_2O_3 tube with high temperature inorganic binder. Cell performance test was performed in a tube furnace at temperatures from 900 to 800 °C using a two-electrode setup. Dry hydrogen at room temperature was used as fuel with a set flow rate of 80 $\text{cm}^3 \cdot \text{min}^{-1}$. Ambient air was maintained on the cathode side. Before testing, the anode was heated to 900 °C in nitrogen. After the temperature reaching steady state, the atmosphere of anode chamber was switched to hydrogen for reducing the anode of cell. After an hour of reduction, the steady state performances of cell were recorded from open circuit voltage (OCV) to 0 V by linear sweep voltammetry at a scan rate of 10 $\text{mV} \cdot \text{s}^{-1}$ with an electrochemical instrument (AUTOLAB PGSTAT302N).

3 Results and Discussion

3.1 Phase Analysis of LSTC10 Anode Powder. Figure 1 is the XRD pattern of LSTC10 powders calcined at 800 °C for 5 h. It can be seen from Fig. 1 that LSTC10 powders exhibits a single-phase perovskite structure similar to the standard XRD pattern of undoped SrTiO_3 (PDF35-0734), implying that doping has negligible effect on the structure of SrTiO_3 . The average crystallite size

Fig. 2 SEM pictures of LSTC10 powders with different magnification: (a) 4950 $\times$; (b) 50,000 $\times$

(d_{avg}) of LSTC10 powders can be estimated from the XRD diffractograms using Scherrer Eq. (1)

$$d_{\text{avg}} = \frac{\kappa \lambda}{\beta \cos(\theta)} \quad (1)$$

where κ , λ , β , and θ are Scherrer constant (taken as 0.89), wavelength of the Cu-K α radiation (0.154056 nm), full width at half maximum (FWHM) of the (110) reflection, and Bragg angle of the (110) reflection, respectively. The average crystallite size (d_{avg}) of LSTC10 powders was estimated to be 24 nm.

3.2 Microstructure Analysis of LSTC10 Powders. Figure 2 shows SEM pictures of LSTC10 powders calcined at 800 °C for 5 h. Figure 2 reveals that the powders are loose and porous and these particles are homogeneous and mostly regularly spherical, which is in favor of die forming and sintering processes. Figure 2 also gives an average particle size of about 50–70 nm in diameter, which is larger than that calculated from the XRD diffractograms using Scherrer Eq. (1). This difference might be due to the larger particle formation by agglomerated crystallites, resulting in a larger particle size as observed from SEM. This small crystallite size of nanolevel is very important for the improved electrocatalytic activity of SOFC anode. So we have reasons to believe that LSTC10 is promising as a kind of SOFC anode material.

3.3 Performance Test of Cell. Figure 3 illustrates the variations of cell voltage and power density as a function of current densities under steady state. It can be seen from Fig. 3. The OCV are 1.08, 1.06, and 1.00 V at 900, 850, and 800 °C, respectively, indicating that the sealing and separating performance of the cell is good. The maximum power density is 13.0 $\text{mW} \cdot \text{cm}^{-2}$ at 900 °C

Fig. 3 Performances of cell with LSTC10 as anode at different temperatures. Dry H_2 as fuel gas with a flow rate of $80 \text{ cm}^3 \cdot \text{min}^{-1}$, static air on the cathode side.

Fig. 4 Performances of cell with LSTC20 as anode at different temperatures. Dry H_2 as fuel gas with a flow rate of $80 \text{ cm}^3 \cdot \text{min}^{-1}$, static air on the cathode side.

and it decreases with decreasing temperature, with only $2.8 \text{ mW} \cdot \text{cm}^{-2}$ at 800°C . Such a temperature dependence of maximum power density is obviously due to the increasing overpotential with decreasing temperature.

In order to investigate the effect of the dopant content of chromium on the cell performance, the $\text{La}_{0.3}\text{Sr}_{0.55}\text{Ti}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$ (LSTC20) powder was also used as the anode material for cell. The preparation and characterization of LSTC20 material can be found in literature [20]. The performances of cell with LSTC20 as anode at 900 , 850 , and 800°C are shown in Fig. 4. The maximum power density of cell is $11.5 \text{ mW} \cdot \text{cm}^{-2}$ at 900°C . The slightly lower value may indicate that the dopant content of chromium in the range of 10 – $20 \text{ mol}\%$ has an insignificant effect on the cell performance.

As can be seen from the above test results, the power density of cell is low, which may be due to the following two reasons. First, the ohmic resistance of cell increases significantly with increasing the thickness of electrolyte layer [21]. The electrolyte layer with a thickness of $260 \mu\text{m}$ in this study is too thick so that the ohmic resistance of cell is high. Second, the doped titanates show low electrocatalytic activities for oxidation of hydrogen and hydrocarbon fuels [22]. Accordingly, for the sake of improving the output performance of cell, it is necessary to prepare an anode-supported cell with YSZ thin film as electrolyte and incorporate some

Fig. 5 SEM pictures of cell after performance testing: (a) surface of anode; (b) cross section of anode; (c) cross section of cell; and (d) interface between anode and electrolyte

catalytic materials into LSTC so as to optimize the catalytic properties of the anode.

3.4 Microstructure Analysis of Cell. SEM images of cell with LSTC10 as anode after performance testing are shown in Fig. 5. The expected structure with a dense YSZ layer, porous anode and cathode layers can be clearly seen from Fig. 5. It can also be seen from the surface and cross section of anode (Figs. 5(a) and 5(b)) that the grains are connected to form three-dimensional network structure and, hence, obtain massive open pores which is beneficial to the diffusion of fuel gas reducing the concentration polarization. The network structure is also in favor of the electronic transmission. However, from Fig. 5(a) it can be seen that the distribution of pores in the anode is nonuniform. This may also be one of the reasons for the low power density of cell. So the composition and preparation of anode slurry should be further optimized to improve the anode microstructure.

As seen in Fig. 5(c), the thickness of anode is about $65 \mu\text{m}$ and that of cathode is about $21 \mu\text{m}$. Figures 5(c) and 5(d) show good contact and good adhesion of the interfaces between the anode or cathode and the YSZ electrolyte. This indicates that the preparation process of electrodes in this study is feasible, which lays the foundation for our subsequent studies and provides a reference for similar studies.

4 Conclusions

- (1) LSTC10 was proved to be a potential anode material for SOFC, with which as an anode and dry hydrogen as fuel, the maximum power density of cell is $13.0 \text{ mW} \cdot \text{cm}^{-2}$ at 900°C .
- (2) The rather thick electrolyte layer, low electrocatalytic activity and nonuniform pore distribution of anode are probably the main reasons for the low power density of cell. Therefore, the configuration of cell must be changed and the catalytic properties and microstructure of anode need to be further improved.

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