Chinese Journal of Catalysis 36 (2015) 502–508

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journal homepage: www.elsevier.com/locate/chnjc

Article (Special Column on Electrocatalysis for Fuel Cells)

TiO_2-modified $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathode for intermediate temperature solid oxide fuel cells

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ARTICLE INFO

Article history:
Received 18 July 2014
Accepted 22 September 2014
Published 20 April 2015

Keywords:
Intermediate temperature solid oxide fuel cell
Cathode
Titanium oxide
Interfacial reaction
Zirconia-based electrolyte

ABSTRACT

A $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode modified using nanosized TiO_2 was direct prepared on the yttria stabilized zirconia (YSZ) electrolyte in an intermediate temperature solid oxide fuel cell. TiO_2 prevents reaction between LSCF and YSZ, which would have formed a $SrZrO_3$ phase. The cell with a LSCF-0.25 wt% TiO_2 cathode exhibited a current density that was 1.6 times larger than that with a pure LSCF cathode at 0.7 V and 600 °C. Electrochemical impedance spectra showed the accelerated incorporation of oxygen anions into the YSZ electrolyte with the TiO_2-modified LSCF cathode. The improvement was attributed to the suppressed formation of a non-conductive $SrZrO_3$ layer at the cathode/electrolyte interface.

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1. Introduction

Solid oxide fuel cells (SOFCs) directly convert chemical energy stored in fuels to electrical energy [1]. The traditional SOFC has the components Ni-YSZ (YSZ = yttria stabilized zirconia) anode, YSZ electrolyte, and $(La,Sr)MnO_3$-YSZ cathode and operates in the 800–1000 °C range [2,3]. To reduce the operating temperature of SOFCs, $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ (LSCF) materials with a high electronic and ionic conductivity (MIEC) and excellent catalytic activity for oxygen reduction are extensively studied as the SOFC cathode [4]. However, unlike $(La,Sr)MnO_3$ materials, $(La,Sr)(Co,Fe)O_3$ suffers significant Sr surface segregation and easily reacts with YSZ to form non-conductive phases of $SrZrO_3$ and/or $La_2Zr_2O_7$ even at 700 °C [5]. This leads to very large interfacial losses when the LSCF cathode is directly prepared on the YSZ electrolyte. Much effort has been devoted to preventing the formation of the non-conductive phases, such as adding Gd-doped CeO_2 (GDC) as an interlayer to avoid direct contact between the cathode and YSZ electrolyte [6–8] or infiltrating the cathode material (such as $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$) into the YSZ scaffold and sintering at low temperature to avoid the unwanted interfacial reaction [9]. However, these methods add to the cost and complexity of the cell fabrication and introduce new interfacial losses between the GDC interlayer and YSZ electrolyte. Therefore, it is useful to develop a new method for the direct application of an LSCF cathode on the ZrO_2-based (such as YSZ) electrolyte.

The interface between different phases can be changed by

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This work was supported by the National High Technology Research and Development Program of China (863 Program, 2011AA050704), the National Basic Research Program of China (973 Program, 2010CB732302, 2012CB215500), and the National Natural Science Foundation of China (21376238, 21306189, and 51101146).

DOI: 10.1016/S1872-2067(14)60235-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 4, April 2015

adding a proper modifier. For example, Co_3O_4 has been studied as a sintering aid to modify the microstructure of a Co-containing perovskite cathode and the interface of the cathode/electrolyte [10]. TiO_2 has been widely used as a photocatalyst because of its high stability, non-toxicity, and relatively low cost [11,12]. In the field of SOFC glass sealing materials, TiO_2 has been used to tune the crystallization temperature and microstructure of glass materials, and TiO_2-modified Bi_2O_3-BaO-SiO_2-R_xO_y (R = K, Ca, etc.) shows a good match of the thermal properties and firm adherence to the electrolyte and connector [13]. TiO_2 has been added to a CeO_2-based electrolyte to reduce the sintering temperature and improve the grain boundary conduction [14]. The addition of TiO_2 into an LSCF can prevent the reaction of LSCF with YSZ by the interaction between LSCF and TiO_2 and modify the interface of the cathode/electrolyte.

In this study, nanosized TiO_2 particles were added into an LSCF cathode by an ultrasound-assisted blending process. The TiO_2-modified LSCF cathode was directly applied on the YSZ electrolyte. The interaction of the LSCF, TiO_2, and YSZ oxides were studied by X-ray diffraction (XRD). The effects of TiO_2 addition on cell performance were studied by electrochemical analysis and scanning electron microscopy (SEM).

2. Experimental

Anode-supported single cells with a thin film YSZ (10 μm) were fabricated by the tape casting method. The anode-electrolyte bilayer assemblies were sintered at 1295 °C for 3 h. The homemade $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) powder was synthesized by a citric acid ammonium-assisted Pechini-type method [15] and sintered at 1050 °C for 3 h. The TiO_2-modified LSCF cathode was made by the ultrasound assisted process as follows. Commercial TiO_2 (Zhenjiang, China) nanoparticles were added into deionized water with a TiO_2 concentration of 0.25 mol/L. The LSCF powder was blended with various amounts of TiO_2 nanoparticles using an ultrasonic bath with a frequency of 25 kHz and a nominal power of 600 W for 30 min. The cathode slurry consisting of dried LSCF-TiO_2 composite oxides, organic binders, and solvent was coated on the YSZ electrolyte and sintered at 850 °C for 2 h. The thickness of the cathode was 35 μm.

The single cells were tested in the homemade electrochemical device. Humidified H_2 (3% H_2O) and pure O_2 flow were supplied as fuel and oxidant, respectively. The current-voltage curves and corresponding power density (*I*-*V*-*P*) of single cells were measured using the two-electrode four-wire method at 600–750 °C. Electrochemical impedance spectra were measured under open circuit condition using a Solartron 1260 frequency response analyzer with a Solartron 1287 electrochemical interface. The frequency ranged from 1×10^6 to 0.08 Hz with an amplitude of 10 mV.

Powder XRD patterns were collected in the 2θ range of 20°–80° on a Rigaku D/Max-2500/PC X-ray diffractometer operated at 40 kV and 200 mA using Cu K_α (λ = 0.15406 nm) radiation. The average crystallite size of the cubic phase was calculated from the Scherrer equation, where the Scherrer constant (particle shape factor) was taken as 0.89. The SEM photographs of the TiO_2-modified LSCF cathode were taken with a JSM7800F microscope equipped with a field emission gun at 5 kV.

3. Results and discussion

3.1. XRD characterization

The interaction between LSCF and TiO_2 was investigated by powder reaction. LSCF powder and TiO_2 powder were mixed in a mass ratio of 4:1 and then calcined at various temperatures for 2 h. Figure 1 shows the XRD patterns of the LSCF-TiO_2 composite oxide calcined at 750–1050 °C. For the LSCF-TiO_2 composite oxide calcined at 750–800 °C, the characteristic peaks can be assigned to the perovskite LSCF phase and anatase phase of TiO_2. For the LSCF-TiO_2 composite oxide calcined at 850–1050 °C, the characteristic peaks of $SrTi_{21}O_{38}$ and $CoFe_2O_4$ started to appear in addition to the diffraction peaks of LSCF and TiO_2. These results suggested that the LSCF started to react with TiO_2 at 850 °C. The average size of nano-crystallite TiO_2, $SrTi_{21}O_{38}$, and $CoFe_2O_4$ from the LSCF-TiO_2 mixture that was sintered at 850 °C was calculated by the Scherrer equation to be 35, 28, and 33 nm, respectively. In addition, $SrTiO_3$ can be formed from the reaction between LSCF and TiO_2. Surface strontium enrichment on the LSCF, in the form of SrO or $Sr(OH)_2$, is well known [16–20]. Sr-enriched LSCF can react with TiO_2 to $SrTiO_3$. However, the $SrTiO_3$ phase cannot be detected by XRD in the presence of the LSCF phase because of the same peak position of the perovskite LSCF phase and $SrTiO_3$ phase. In order to show $SrTiO_3$ formation, TiO_2 was blended with $Sr(NO_3)_2$ and calcined at 850 °C for 2 h. Figure 2 shows the XRD patterns of the TiO_2-$Sr(NO_3)_2$ composite with different molar ratio of Ti:Sr after calcination. For the molar ratios of Ti:Sr = 1:1, the diffraction peaks of the $SrTiO_3$ and Sr_2TiO_4 phases can be identified, indicating that $SrTiO_3$ can be easily formed by the reaction of TiO_2 with SrO. A similar conclusion was given for the reaction of Sr oxalate with TiO_2 at 800 °C [21]. When the molar ratio of Ti:Sr was increased to 4:1, $Sr_2Ti_6O_{13}$ phases were also identified besides the $SrTiO_3$ and Sr_2TiO_4 phases. These observations indicated that $SrTiO_3$ could be

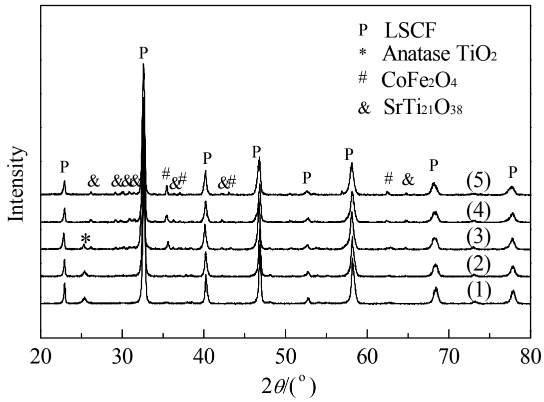

Fig. 1. XRD patterns of the LSCF-TiO_2 composite oxide calcined at 750 (1), 800 (2), 850 (3), 950 (4), and 1050 °C (5) for 2 h.

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