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TiO₂-modified La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode for intermediate temperature solid oxide fuel cellsWeixing Liu ^{a,b}, Zhe Zhao ^a, Baofeng Tu ^a, Daan Cui ^a, Dingrong Ou ^a, Mojie Cheng ^{a,*}^a Division of Fuel Cells, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

A La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) cathode modified using nanosized TiO₂ was directly prepared on the yttria stabilized zirconia (YSZ) electrolyte in an intermediate temperature solid oxide fuel cell. TiO₂ prevents reaction between LSCF and YSZ, which would have formed a SrZrO₃ phase. The cell with a LSCF-0.25 wt% TiO₂ 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 TiO₂-modified LSCF cathode. The improvement was attributed to the suppressed formation of a non-conductive SrZrO₃ 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)MnO₃-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-δ} (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)MnO₃ materials, (La,Sr)(Co,Fe)O₃ suffers significant Sr surface segregation and easily reacts with YSZ to form non-conductive phases of SrZrO₃ and/or La₂Zr₂O₇ 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 CeO₂ (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-δ}) 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 ZrO₂-based (such as YSZ) electrolyte.

The interface between different phases can be changed by

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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 ($\text{R} = \text{K}, \text{Ca}$, 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 $^\circ\text{C}$ for 3 h. The homemade $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) powder was synthesized by a citric acid ammonium-assisted Pechini-type method [15] and sintered at 1050 $^\circ\text{C}$ 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 $^\circ\text{C}$ 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 $^\circ\text{C}$. 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 $^\circ$ on a Rigaku D/Max-2500/PC X-ray diffractometer operated at 40 kV and 200 mA using $\text{Cu } K\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation. The average crystallite size of the cubic phase was calculated from the Scherrer equation, where the Scherrer con-

stant (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 $^\circ\text{C}$. For the LSCF- TiO_2 composite oxide calcined at 750–800 $^\circ\text{C}$, 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 $^\circ\text{C}$, the characteristic peaks of $\text{SrTi}_{21}\text{O}_{38}$ 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 $^\circ\text{C}$. The average size of nano-crystallite TiO_2 , $\text{SrTi}_{21}\text{O}_{38}$, and CoFe_2O_4 from the LSCF- TiO_2 mixture that was sintered at 850 $^\circ\text{C}$ 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 $\text{Sr}(\text{OH})_2$, 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 $\text{Sr}(\text{NO}_3)_2$ and calcined at 850 $^\circ\text{C}$ for 2 h. Figure 2 shows the XRD patterns of the TiO_2 - $\text{Sr}(\text{NO}_3)_2$ 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 $^\circ\text{C}$ [21]. When the molar ratio of Ti:Sr was increased to 4:1, $\text{Sr}_2\text{Ti}_6\text{O}_{13}$ 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 $^\circ\text{C}$ (5) for 2 h.

Fig. 2. XRD patterns of $\text{TiO}_2\text{-Sr}(\text{NO}_3)_2$ composites with Ti:Sr molar ratios of 1:1 (1) and 1:4 (2) at 850 °C for 2 h.

formed at 850 °C by the reaction of LSCF with TiO_2 .

The reaction of LSCF with YSZ was characterized by XRD. LSCF powder and YSZ powder were mixed at a mass ratio of 2:1 and then calcined at various temperatures for 2 h. Figure 3 shows the XRD patterns of the LSCF-YSZ composite oxides calcined at 800–900 °C for 2 h. When the LSCF-YSZ composite oxide was calcined at 800 °C, all the peaks can be assigned to the perovskite LSCF phase and fluorite YSZ phase. With an increase of the calcination temperature, besides the characteristic peaks of LSCF and YSZ, diffraction peaks of SrZrO_3 and CoFe_2O_4 were also found with the LSCF-YSZ composite oxide calcined at 850 and 900 °C, indicating that LSCF started to react with YSZ at 850 °C.

LSCF, TiO_2 , and YSZ powder were mixed in a mass ratio of 4:1:2.5 and then calcined at various temperatures for 2 h. Figure 4 shows the XRD patterns of the LSCF-YSZ- TiO_2 composite oxide calcined at 800–900 °C for 2 h. When the LSCF-YSZ- TiO_2 composite oxide was calcined at 800 and 850 °C, the peaks can be assigned to the perovskite LSCF, fluorite YSZ, anatase TiO_2 , and $\text{SrTi}_{21}\text{O}_{38}$ phases, respectively, indicating that TiO_2 effectively prevented the formation of SrZrO_3 from the reaction between LSCF and YSZ. When the calcination temperature was increased to 900 °C, besides the peaks of the LSCF, YSZ, TiO_2 and $\text{SrTi}_{21}\text{O}_{38}$ phases, small peaks of SrZrO_3 were also found,

Fig. 3. XRD patterns of the LSCF-YSZ composite oxide calcined at 800 (1), 850 (2), and 900 °C (3) for 2 h.

Fig. 4. XRD patterns of the LSCF-YSZ- TiO_2 composite oxide with the mass ratio of 4:1:2.5 calcined at 800 (1), 850 (2), and 900 °C (3) for 2 h.

but the intensity was obviously smaller than that of the SrZrO_3 from the LSCF-YSZ composite calcined at 900 °C. These results showed that TiO_2 could prevent or suppress the reaction between LSCF and YSZ to form the SrZrO_3 phase.

3.2. SEM characterization

Figure 5(a) shows the SEM micrograph of the LSCF cathode sintered at 850 °C for 2 h. The average size of the primary LSCF particles was 150 nm. The LSCF particles were well connected and constituted porous agglomerates (ca. 0.4 μm). Figure 5 (b–d) shows the SEM micrographs of the LSCF-0.25 wt% TiO_2 , LSCF-0.5 wt% TiO_2 , and LSCF-2 wt% TiO_2 cathodes sintered at 850 °C for 2 h. The commercial TiO_2 powder had irregular shapes on the nanoscale with grain sizes of 7–8 nm. The size of TiO_2 in the cathode was increased due to high temperature sintering at 850 °C. Nanosized particles (30 nm) on the surface of LSCF were TiO_2 and/or the reaction product of TiO_2 with LSCF, as shown Fig. 1.

Fig. 5. SEM micrographs of the LSCF cathode (a) and LSCF-0.25 wt% TiO_2 (b), LSCF-0.5 wt% TiO_2 (c), and LSCF-2 wt% TiO_2 (d) composite cathodes.

Fig. 6. Current-voltage curves and the corresponding power densities (I - V - P) of single cells with LSCF, LSCF-0.25 wt% TiO_2 , LSCF-0.5 wt% TiO_2 , LSCF-1 wt% TiO_2 , and LSCF-2 wt% TiO_2 composite cathodes at 600–750 °C.

3.3. Cell performance

Figure 6 shows the current-voltage curves and correspond-

ing power density of single cells with LSCF, LSCF-0.25 wt% TiO_2 , LSCF-0.5 wt% TiO_2 , LSCF-1 wt% TiO_2 , and LSCF-2 wt% TiO_2 composite cathode at 600–750 °C. The current density of the cells with the LSCF cathode was 0.14 A/cm² at 0.7 V and

Fig. 7. Electrochemical impedance spectra (EIS) of the cells with LSCF, LSCF-0.25 wt% TiO_2 , LSCF-0.5 wt% TiO_2 , LSCF-1 wt% TiO_2 , and LSCF-2 wt% TiO_2 cathodes at 600–750 °C.

600 °C. The cell with the TiO₂-modified LSCF cathode showed better performance. The current density of the cells with LSCF-0.25 wt% TiO₂, LSCF-0.5 wt% TiO₂, and LSCF-1 wt% TiO₂ were 0.23, 0.21, and 0.18 A/cm² at 0.7 V and 600 °C, respectively. The significant segregation of Sr on the surface of LSCF in the form of SrO or Sr(OH)₂ is well known [16–20]. Sr-enriched LSCF easily reacts with YSZ electrolyte to SrZrO₃ and/or La₂Zr₂O₇. As a result, the cell with LSCF on YSZ gave very poor performance. For the TiO₂-modified LSCF cathode, TiO₂ can react with Sr-enriched LSCF to give SrTiO₃ and Sr₂TiO₄, which prevents or suppresses the formation of the non-conductive SrZrO₃ layer at the cathode/electrolyte interface. Unlike SrZrO₃, SrTiO₃ and Sr₂TiO₄ improved the LSCF/YSZ interface due to good conductivity and improved cell performance [22]. With a further increase of TiO₂ amount up to 2 wt% in the cathode, the current density of the cells with LSCF-2 wt% TiO₂ was 0.12 A/cm² at 0.7 V and 600 °C, which was lower than that of the cell with the LSCF cathode. When the content of

TiO₂ was too high, TiO₂ reacted with LSCF to SrTi₂O₃₈ as shown by the XRD results, which led to the drop of cell performance.

3.4. Electrochemical impedance analysis

Figure 7 shows electrochemical impedance spectra (EIS) of the cells with LSCF, LSCF-0.25 wt% TiO₂, LSCF-0.5 wt% TiO₂, LSCF-1 wt% TiO₂, and LSCF-2 wt% TiO₂ cathodes at 600–750 °C. The ohmic resistance of cell showed very small differences, but the cell polarization resistance significantly varied with cathode composition. The polarization resistance (*R_p*) of the cells with the LSCF cathode was 9.5285 Ω cm² at 600 °C. The *R_p* of the cells with LSCF-0.25 wt% TiO₂, LSCF-0.5 wt% TiO₂, and LSCF-1 wt% TiO₂ were 5.1342, 7.1998, and 7.8421 Ω cm², respectively, which decreased by 44%, 24%, and 18% compared with that of the cell with the LSCF cathode at 600 °C (Table 1). With a further increase of TiO₂ to 2 wt% in the cathode, the *R_p*

Table 1
Comparison of ohmic resistance and polarization resistance of the cell with various cathodes at 600–750 °C.

Cathode composition	Ohmic resistance (Ω cm ²)				Polarization resistance (Ω cm ²)			
	750 °C	700 °C	650 °C	600 °C	750 °C	700 °C	650 °C	600 °C
LSCF	0.2027	0.2172	0.2654	0.3743	0.9493	1.6820	3.5981	9.5285
LSCF-0.25 wt% TiO ₂	0.2051	0.2175	0.2620	0.3707	0.5917	0.9878	1.9817	5.1342
LSCF-0.5 wt% TiO ₂	0.1980	0.2076	0.2482	0.3532	0.7135	1.2284	2.6326	7.1998
LSCF-1 wt% TiO ₂	0.2062	0.2160	0.2632	0.3690	0.7747	1.3051	2.8435	7.8421
LSCF-2 wt% TiO ₂	0.2155	0.2342	0.2956	0.4059	1.1328	2.0406	4.3568	12.0989

Fig. 8. Bode plots of the cells with LSCF, LSCF-0.25 wt% TiO₂, LSCF-0.5 wt% TiO₂, LSCF-1 wt% TiO₂, and LSCF-2 wt% TiO₂ composite cathodes at 600–750 °C.

Fig. 9. Resistances of the cells with LSCF, LSCF-0.25 wt% TiO₂, LSCF-0.5 wt% TiO₂, LSCF-1 wt% TiO₂, and LSCF-2 wt% TiO₂ cathodes at 600 °C based on the model circuit.

of the cell with LSCF-2 wt% TiO₂ was 12.0989 Ω cm² at 600 °C, which was larger than that of the cell with the LSCF cathode.

The EIS results are also further shown in the form of Bode plots (Fig. 8). The impedance spectra of the cell with the LSCF and TiO₂-modified LSCF cathode consisted of three arcs: a high frequency arc (summit frequency $f_{\text{summit}} > 1000\text{Hz}$), intermediate frequency arc ($f_{\text{summit}} = 100\text{ Hz}$), and low frequency arc ($f_{\text{summit}} = 2.5\text{Hz}$), reflecting at least three rate determining steps in the electrochemical reaction. The electrochemical impedance spectra at 600 °C were fitted by an equivalent circuit as shown in Fig. 9, which consisted of a high frequency arc R_H , intermediate frequency arc R_i , and low frequency arc R_L . It can be seen that R_H dramatically decreased with TiO₂ addition, indicating that the corresponding process was accelerated by TiO₂. R_i increased with TiO₂ addition. R_L was unchanged with cathode composition. On the basis of the frequency of the impedance arcs and reported results [15,23,24], the corresponding processes of the cell with the LSCF cathode in the impedance spectra were identified. The high frequency arcs R_H was related to the incorporation of oxygen anions into the electrolyte across the cathode/electrolyte interface. The intermediate frequency arc R_i correlated with the dissociative adsorption of oxygen. The low frequency arc R_L showed very little change with temperature and oxygen partial pressure and was due to gas diffusion with a very low activation energy in the anode. TiO₂ mainly caused the change in the high frequency arc and affected the incorporation of oxygen anions into the electrolyte across the cathode/electrolyte interface. TiO₂ suppressed the formation of the inactive SrZrO₃ layer at the interface of the cathode/electrolyte and decreased interfacial losses.

3.5. Stability of the LSCF-TiO₂ composite cathode

The stability of the TiO₂-modified LSCF cathode is very important for its application. Figure 10 shows the current density of the cell with the LSCF-0.25 wt% TiO₂ cathode as a function of time at a constant voltage of 0.8 V and 700 °C. It can be seen that the cell performance slightly degraded in the first 20 h of operation and then became stable over the next 60 h operation. The corresponding current density losses were 1.2 mA/h for

Fig. 10. Current density of the cell with the LSCF-0.25 wt% TiO₂ cathode as a function of time at a constant voltage of 0.8 V and 700 °C.

the first 20 h operation and decreased to 0.2 mA/h over the next 60 h operation. Further work is needed to study the long term stability of the TiO₂-modified LSCF cathode for its practical application.

4. Conclusions

A TiO₂-modified LSCF cathode was prepared directly on a YSZ electrolyte. TiO₂ prevented the reaction between LSCF and YSZ, which suppressed the formation of the non-conductive SrZrO₃ phase. The electrochemical performance of the TiO₂-modified LSCF cathode was better than that of the blank LSCF cathode. The electrochemical impedance spectra showed that there was accelerated incorporation of oxygen anion into the YSZ electrolyte on the TiO₂-modified LSCF cathode. The improvement was ascribed to the suppressed formation of the non-conductive SrZrO₃ layer at the cathode/electrolyte interface. This work provided new possibilities to apply highly active Co-containing perovskite cathodes such as (La,Sr)(Co,Fe)O₃ on a ZrO₂-based electrolyte by adding an appropriate amount of TiO₂.

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Graphical Abstract

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TiO₂-modified La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} cathode for intermediate temperature solid oxide fuel cells

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A TiO₂-modified La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) cathode directly prepared on the YSZ electrolyte improved the fuel cell performance. This was attributed to the suppressed formation of a non-conductive SrZrO₃ layer at the cathode/electrolyte interface.

11946

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TiO₂修饰La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}用于中温固体氧化物燃料电池的阴极

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摘要: 纳米TiO₂修饰的La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF)阴极被直接应用于YSZ电解质电池上。TiO₂可阻止LSCF和YSZ间的化学反应, 抑制SrZrO₃的形成。LSCF-0.25 wt% TiO₂阴极电池在0.7 V和600 °C下的电流密度是LSCF阴极电池的1.6倍。电化学阻抗谱结果表明, TiO₂修饰显著加快了氧离子注入电解质的过程, 这可能与TiO₂抑制了阴极/电解质界面处高电阻SrZrO₃层的形成有关。本文为在ZrO₂基电解质上使用高性能的(La,Sr)(Co,Fe)O₃阴极材料提供了一种简单有效的方法。

关键词: 中温固体氧化物燃料电池; 阴极; 二氧化钛; 界面反应; 氧化锆基电解质

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