



Short communication

Anode performance of LST– x CeO₂ for solid oxide fuel cells

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ABSTRACT

La-doped SrTiO₃ (LST)– x CeO₂ ($x=0, 30, 40, 50$) composites were evaluated as anode materials for solid oxide fuel cells in terms of chemical compatibility, electrical conductivity and fuel cell performance in H₂ and CH₄. Although the conductivity of LST– x CeO₂ composite slightly decreased from 4.6 to 3.9 S cm⁻¹ in H₂ at 900 °C as the content of CeO₂ increased, the fuel cell performance improved from 75.8 to 172.3 mW cm⁻² in H₂ and 54.5 to 139.6 mW cm⁻² in CH₄ at 900 °C. Electrochemical impedance spectra (EIS) indicated that the addition of CeO₂ into LST can significantly reduce the fuel cells polarization thus leading to a higher performance. The result demonstrated the potential ability of LST– x CeO₂ to be used as SOFCs anode.

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1. Introduction

As a promising technology for high efficiency power generation system, solid oxide fuel cells (SOFCs) offer a clean and electrochemical way to convert chemical energy stored in fossil fuel into electrical power directly [1]. Directly utilizing hydrocarbon fuels to replace H₂ is the key issue to accelerate the commercialization of SOFCs [2], since H₂ is more expensive than hydrocarbon fuels such as methane, ethanol and so on, and has many problems with mass storage and transportation. It is a big challenge for the anode materials to directly utilize the hydrocarbon fuels. The traditional anode of SOFC is Ni/YSZ, which has an excellent performance in H₂ and syngas, but is not suitable for directly utilizing hydrocarbon fuels as it promotes carbon deposition [3]. Meanwhile, Ni-based anode also has many disadvantages including nickel coarsening, sulfur poisoning, volume instability upon redox cycling. Therefore it is necessary to develop an alternative anode material to resolve the problems with Ni/YSZ.

Many efforts have been made to develop new anode materials, including Cu–CeO₂, Ru–CeO₂ [4–6] and doped LaCrO₃ [7,8], etc. Among these materials, doped SrTiO₃ has attracted much interest due to its thermal and chemical stability with YSZ electrolyte in fuel cell operating environment. With the mixed electronic-ionic conductivity, SrTiO₃ has been investigated extensively as SOFCs anode materials [9–12], since it can use methane as fuels directly

and exhibit sulfur tolerance ability [13]. Unfortunately, this material shows poor electro-catalytic performance. As a good catalyst, CeO₂ may enhance the electrochemical performance of doped SrTiO₃ [14].

In this paper, a composite anode of CeO₂ and La-doped SrTiO₃ with different weight ratio was prepared. And its electronic conductivity and corresponding fuel cell performance in H₂ and CH₄ were investigated.

2. Experimental

2.1. Sample preparation

Sr_{0.6}La_{0.4}TiO₃ (LST) powders were prepared by solid-state reaction method. The start materials were as follows: SrCO₃ (99.8%, Sinopharm Chemical Regant Co. Ltd.), TiO₂ (99.8%, Hubei Xiantao Zhongxing Electronic Material Co. Ltd.), La₂O₃ (99.99%, Rare-chem Hi-Tech Co. Ltd.). First the raw materials were directly mixed in an appropriate molar ratio by ball milling for 4 h with ethanol. After drying the mixture was calcined at 1250 °C for 3 h in air. The calcined sample was then ball milled with ethanol again for 3 h with different weight ratio of CeO₂ (99.99%, Rare-chem Hi-Tech Co. Ltd.) (LST:CeO₂ was 100:0, 70:30, 60:40, and 50:50, respectively) and marked as LST, LST–30CeO₂, LST–40CeO₂, and LST–50CeO₂.

The calcining process was based on TG–DSC analysis by NETZCH SATA 449C with a heating rate of 5 °C min⁻¹. Phase identification of synthesized samples was performed by X-ray diffraction analysis (Rigaku D/max 2550 V) with Cu K α radiation and Ni filter. To study the chemical compatibility of LST with CeO₂ and LST with YSZ, LST

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and corresponding powders were mixed in a 1:1 weight ratio and then calcined at 1400 °C for 3 h in air.

For conductivity measurements, powders were pressed into bars at 200 MPa and sintered in air at 1400 °C for 4 h. The conductivity was measured by standard four-probe method in H₂ atmosphere with 3% H₂O from 600 to 900 °C. In order to get LST fully reduced the samples were initially kept at 900 °C for 10 h. The densities of these samples were measured by Archimedes method.

2.2. Fuel cell preparation

To prepare fuel cells, LST–CeO₂ slurry was prepared by mixing the LST–CeO₂ composites with terpinol and ethyl cellulose. The slurry was screen printed to the 0.3 mm thick dense YSZ electrolyte, followed by calcining at 1350 °C for 3 h. Thirty percentages of ScSZ (20 mol% Sc-doped ZrO₂) and 70% LSM (La_{0.8}Sr_{0.2}MnO₃) mixtures were used as cathode by screen printing and calcining at 1200 °C for 3 h. Pt paste was the current collector. Each cell with the cathode area of 1.33 cm² was sealed onto alumina tubes via glass ring. Thereafter, the entire cell was placed inside a furnace and heated to 900 °C. Meanwhile, H₂ or CH₄ with 3% H₂O was fed to the anode side with a flow rate of 25 mL min⁻¹ and O₂ was fed to the cathode side with the same flow rate. Before fuel cell test, the anode was reduced in H₂ at 900 °C for 3 h. The current–voltage curves and electrochemical impedance spectroscopy (EIS) were obtained by IM6e-X (ZAHNER, Germany) with ac 20 mV amplitude over the frequency range 8 mHz to 1 MHz. The fuel cell was tested in hydrogen atmosphere and CH₄. Between the two processes, N₂ was used as purge gas to sweep for at least 1 h with a flow rate of 25 mL min⁻¹. Microstructure of LST–xCeO₂ anode after cell test were examined with a JSM-6700F scanning electron microscope (SEM).

3. Results and discussion

3.1. TG–DSC and X-ray diffraction analyses

Fig. 1 shows the TG–DSC result of the synthesis process of LST. A sharp endothermic peak appears at 923.4 °C due to the decomposition of SrCO₃. The corresponding weight loss begins at 865 °C and lasts until 1000 °C. A broad exothermic peak appears at 1100 °C and ends at about 1250 °C corresponding to the solid solution of La₂O₃ with SrTiO₃. As shown in Fig. 2, LST powders calcined at 1250 °C exhibits single perovskite structure compared with the standard XRD pattern of Sr_{0.6}La_{0.4}TiO₃ (JCPDS Card No. 79-188).

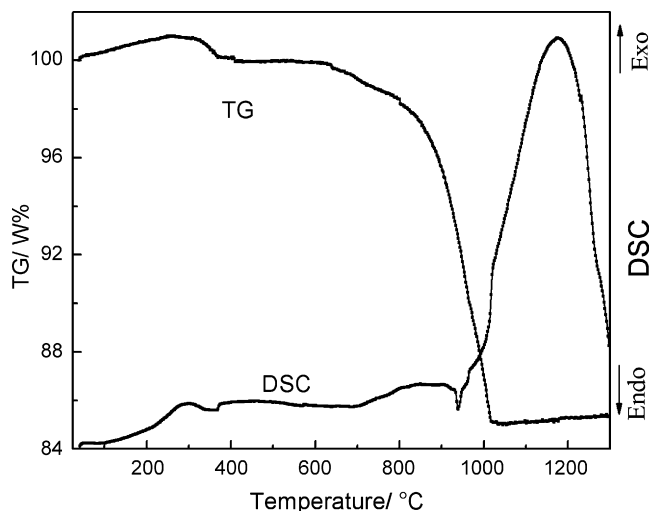


Fig. 1. TG–DSC curve of LST.

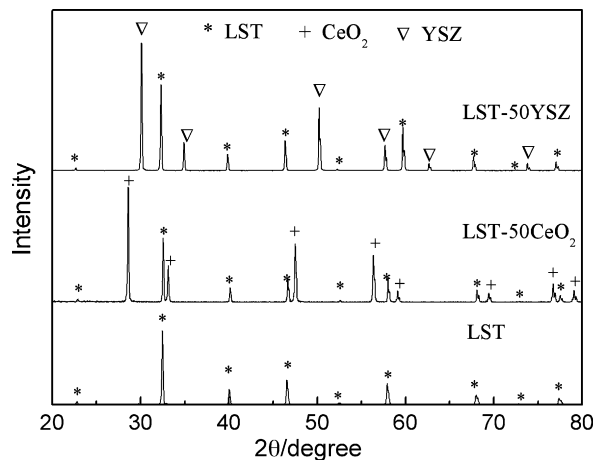


Fig. 2. XRD patterns for LST, LST–50CeO₂ and LST–50YSZ.

The X-ray diffraction analysis of LST–50CeO₂ and LST–50YSZ calcined at 1400 °C are also given in Fig. 2. These composites keep its original phase peak which indicates that there is not any severe reaction between LST with CeO₂ or YSZ.

3.2. Electrical conductivity measurements

It is very important for anode materials to have good conductivity in fuel cell environment. Many researchers have studied the conductivity of LST sintered in reducing atmosphere, which exhibits good conductivity in 700–1000 °C (about 100–500 S cm⁻¹) [10,15]. But for fuel cells, the anode materials were always sintered in oxidizing conditions. In this work, we studied the conductivity of LST and LST with different weight ratio of CeO₂ sintered at 1400 °C in air. The relative densities of these samples were 94% ($x=0$), 80% ($x=30$), 73% ($x=40$), 64% ($x=50$).

Fig. 3 shows the electrical conductivity of LST and LST with different ratio of CeO₂ as a function of temperature. Samples have to be reduced in H₂ for almost 10 h to get fully reduced. For fuel cell testing, porous anodes were easier to be reduced than the dense one. The results indicate that with the elevation of temperature, the electrical conductivities of LST decrease slightly whereas that of LST–CeO₂ composite increases. In pure LST, due to the different valence between La³⁺ and Sr²⁺, introduction of La into the lattice requires the lattice defect structure to be modified to maintain

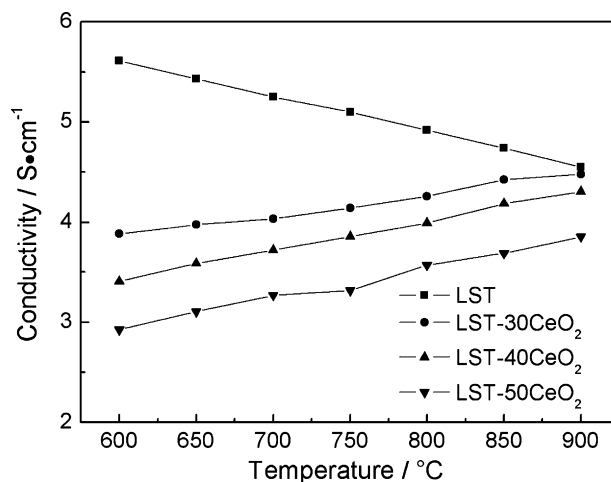


Fig. 3. Electrical conductivity of LST–xCeO₂ as a function of temperature in H₂ + 3% H₂O.

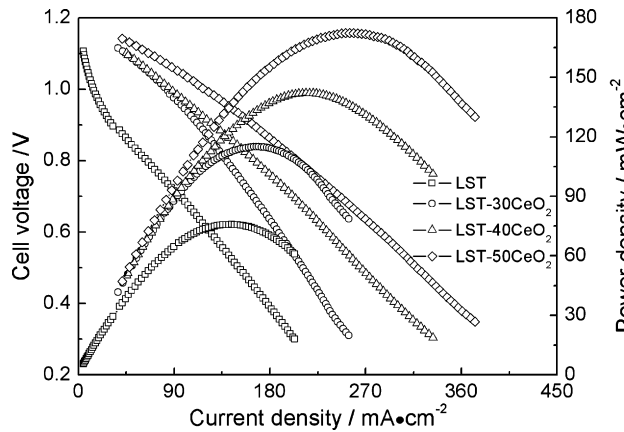


Fig. 4. Electrochemical performance of single fuel cells with LST- x CeO₂ anode operating in H₂ + 3% H₂O.

electro neutrality. In our experiment, LST was sintered in oxidizing atmosphere, so that the valence compensation may mainly depend on the formation of Sr²⁺ vacancies. During the reduction process, crystal lattice oxygen was lost, causing the change of Ti⁴⁺ to Ti³⁺. Thus, electronic conduction is the predominant conduction mechanism in LST. But for LST-CeO₂ composite, poor electronic conductivity of CeO₂ and low sintering density may depress the conductivity. The total conductivity of these materials is above 3.9 S cm⁻¹ at fuel cell operating temperature.

3.3. Fuel cell performance

The performances of fuel cell using LST and LST- x CeO₂ as anode in H₂ at 900 °C are shown in Fig. 4. Fuel cell with pure LST anode exhibits poor performance and its maximum power density is only 65 mW cm⁻². With the increase of CeO₂ content, maximum power density improves significantly from 75.8 to 172.3 mW cm⁻².

Fig. 5 shows the curves of voltage and power density versus current density while the fuel cell is running with 3% H₂O saturated CH₄. With the increase of CeO₂ content, the maximum power density increases from 54.5 to 139.6 mW cm⁻². Fuel cell performances in CH₄ are lower than that in hydrogen.

In an attempt to examine the different performances of these fuel cells, we measured the impedance spectra of fuel cells on H₂ and CH₄ as displayed in Figs. 6 and 7, respectively. Although the addition of CeO₂ slightly decreases the bulk conductivity of

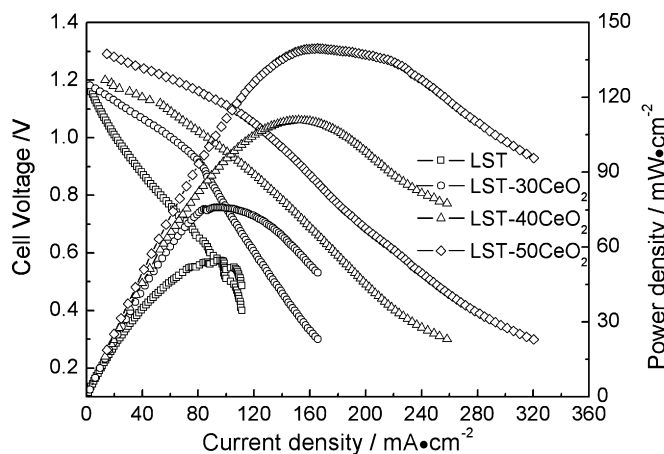


Fig. 5. Electrochemical performance of single fuel cells with LST- x CeO₂ anode operating in CH₄ + 3% H₂O.

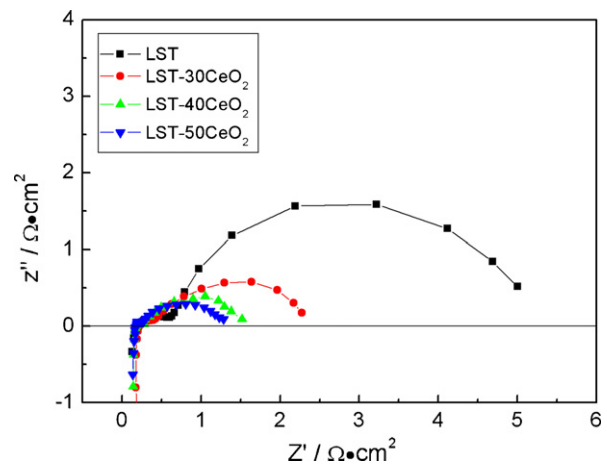


Fig. 6. Nyquist plot of the electrochemical impedance spectroscopy under open circuit conditions of the fuel cell operating in H₂ + 3% H₂O.

LST which can be seen from the impedance spectra, the real-axis intercept at high frequency is almost at the same value. Because the fuel cells made from the same electrolyte and cathode, the increase of power density must be mainly contributed from CeO₂. The impedance spectra demonstrate that the improvement of fuel cell performance is due to the change of anode polarization. With the mixed ionic and electronic conductivity, CeO₂ can enhance the ionic conductivity of the anode, which increases the efficient active area. Thus, with the increase of CeO₂ content, the lower frequency arc corresponding to mass transport process decreases. The size of low frequency impedance spectra arc in CH₄ is bigger than that in hydrogen, because the CH₄ is more difficult to crack than H₂.

3.4. SEM observation

In order to further understand the anodes performances, SEM images of LST- x CeO₂ anode are shown in Fig. 8. The thicknesses of the anodes are about 150 μm. The adding of CeO₂ can significantly suppress LST agglomeration, and increase the triple phase boundary. Comparing with pure LST anode, the adding of CeO₂ can form a more homogeneous porosity and also decrease the mismatch between the anodes and electrolyte thus improve the fuel cells performance. Further experiments are needed to optimize the anode structure and reduce the anode polarization.

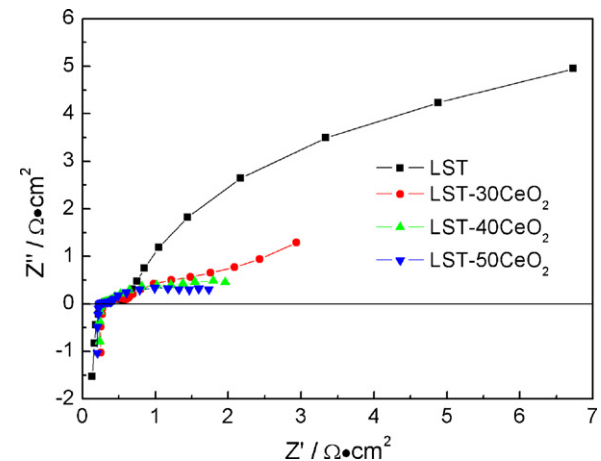


Fig. 7. Nyquist plot of the electrochemical impedance spectroscopy under open circuit conditions of the fuel cell operating in CH₄ + 3% H₂O.

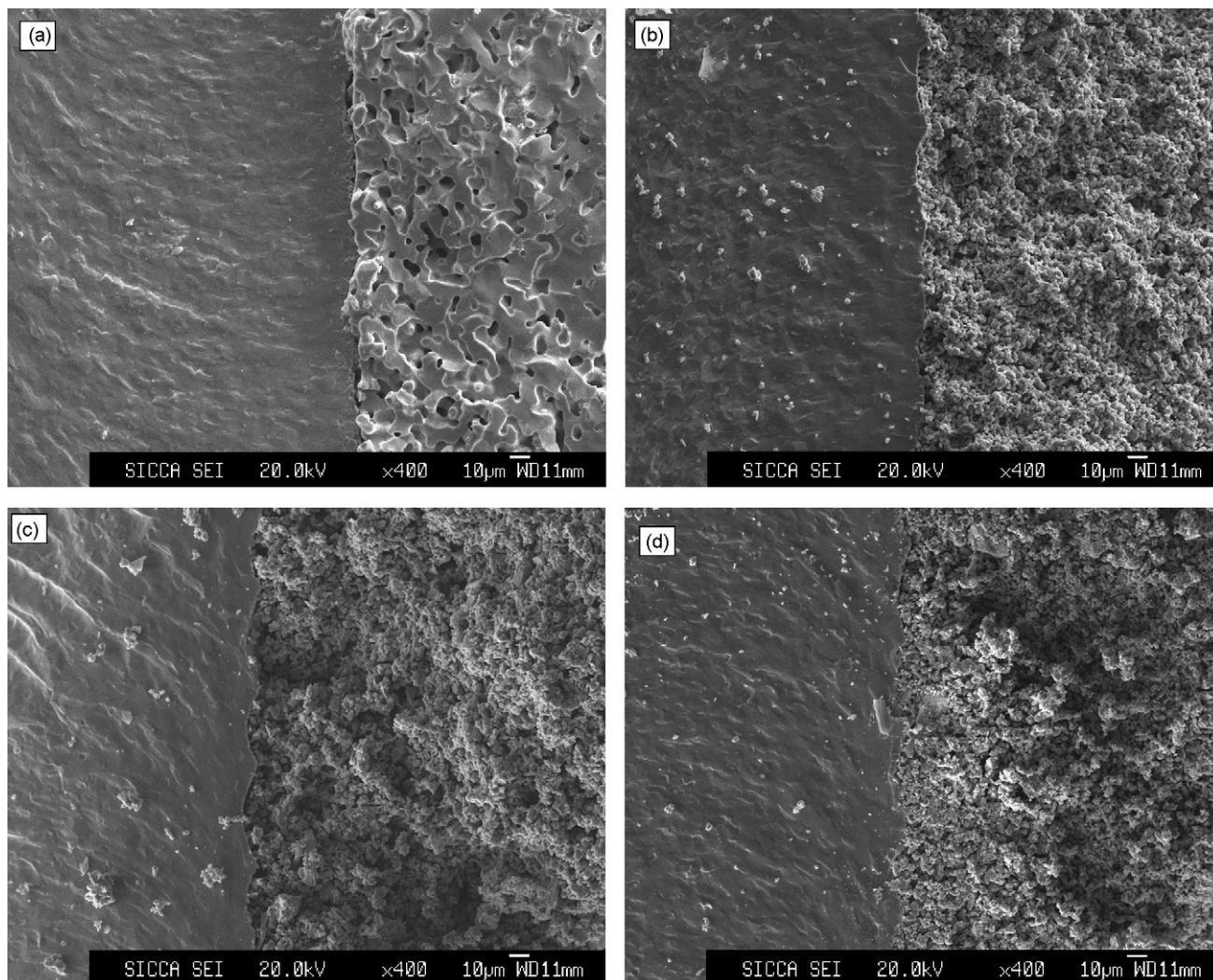


Fig. 8. SEM images of LST- x CeO₂ anode and electrolyte, (a): LST with 8YSZ electrolyte, (b) LST-30CeO₂ with 8YSZ electrolyte, (c) LST-40CeO₂ with 8YSZ electrolyte, (d) LST-50CeO₂ with 8YSZ electrolyte.

4. Conclusions

Perovskite oxide La-doped SrTiO₃ has been synthesized and its compatibility with CeO₂ and YSZ have been examined. The conductivity study of LST with different weight ratio of CeO₂ carried out in this work demonstrates that the overall conductivity of LST- x CeO₂ ($x=0, 30, 40, 50$) is above 3 S cm^{-1} at 900°C . In addition, the fuel cell performances of LST- x CeO₂ in H₂ and CH₄ have been evaluated. With the increase of CeO₂ content, the cell polarization decreases, and the maximum power density increases. The cell with LST-50CeO₂ as anode exhibits maximum power densities of about 172.3 and 139.6 mW cm^{-2} in H₂ and CH₄, respectively. SEM observation also shows that the adding of CeO₂ can significantly optimize the anode structure, and leading to higher fuel cell performances. The results demonstrate that LST- x CeO₂ composite can be considered as a potential candidate of SOFCs' anode for directly utilizing hydrocarbon fuels.

Acknowledgement

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