



Improving electrochemical performance of lanthanum strontium ferrite by decorating instead of doping cobaltite



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ABSTRACT

Cobalt oxide is usually used as a dopant to improve the catalytic activity of Mn and Fe based perovskites such as lanthanum strontium ferrite (LSF) for solid oxide fuel cells. This work presents the catalytic improvement by decorating LSF surface with cobalt oxide, Co₃O₄, using infiltration technique. X-ray diffraction and high resolution electron microscopy analysis indicate that Co₃O₄ is chemically compatible with LSF at the intermediate-temperature range for solid oxide fuel cells. Electrochemical impedance spectrum demonstrates substantial reduction in interfacial polarization resistance, from 0.22 to 0.083 Ωcm² at 700 °C when 5.84 wt. % Co₃O₄ is infiltrated into the bare LSF electrodes. Further analysing the impedance spectrum with distribution of relaxation time calculation suggests that the performance improvement is associated with the charge-transfer processes of the surface reaction. Meanwhile, the electrochemical conductivity relaxation measurement shows that Co₃O₄ particles can improve the surface reaction kinetics, increasing the oxygen surface exchange coefficient by a factor of about 5 at 700 °C. In addition, Co₃O₄ particles can increase the peak power density of the single cells from 0.865 Wcm⁻² to 1.3 Wcm⁻² at 800 °C with LSF based cathodes. The results clearly demonstrate an alternative mean to use cobalt oxide in improving the catalytic performance of Mn and Fe based perovskites.

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1. Introduction

Solid oxide fuel cells (SOFCs) are extensively investigated as an environmentally friendly energy-conversion technique [1]. Their efficiency is primarily determined by the overpotential associated with oxygen reduction reaction (ORR) at the cathode, where oxygen molecular is electrochemically transferred to oxygen ions. Accordingly, it is necessary to reduce the cathodic overpotential by accelerating the ORR kinetics, particularly for SOFCs operated at intermediate temperatures of 600–800 °C. Although cobalt-based perovskite cathodes have the high ORR kinetics at intermediate temperatures, their relative high thermal expansion coefficients, which are higher than the typical electrolytes such as yttria-stabilized zirconia and samaria-doped ceria (SDC), limit the wide application [2]. As a cobalt-free electrocatalyst for ORR, lanthanum

strontium ferrite (LSF) materials have been investigated due to its good electrochemical performance and the similar thermal expansion coefficients to the electrolytes in SOFC [2,3]. However, comparing with the cobalt based perovskite cathode, LSF exhibits relatively low electrochemical performance. For instance, the interfacial polarization resistance (R_p) at 700 °C for a LSF electrode on a SDC electrolyte is ~1.0 Ωcm² [4], about twice as that for La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} under the similar conditions [5]. In addition, R_p is 28.5 Ωcm² at 600 °C for a LSF electrode [4], which is much higher than 2.5 Ωcm² for Sm_{0.5}Sr_{0.5}CoO₃ [6]. Obviously, it is critical to improve the performance of LSF cathode by accelerating the ORR kinetics.

Doping metallic oxide to A site or B site of the ABO₃ crystalline is often used to improve the electrochemical performance. Cobalt oxide is often used as the doping material for Mn and Fe based electrocatalysts with the perovskite structure. Doping Co to the Fe site of the (La, Sr)FeO₃ crystal can improve their catalytic activity. For instance, at 700 °C, R_p of La_{0.8}Sr_{0.2}FeO₃ is about 44 Ωcm², when 20% Co is doped to Fe site, forming La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O₃, the ORR

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kinetics is improved and R_p is reduced to $3.4 \Omega \text{cm}^2$ with YSZ electrolyte [7]. Nevertheless, the thermal expansion coefficient is also increased with the doping of Co, resulting in increased thermal expansion mismatch between the electrode and electrolyte materials. For example, 20% Co doping to the Fe site to form $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ causes about 21.3% increase in the thermal expansion coefficient, from 12.2 to $14.8 \times 10^{-6} \text{K}^{-1}$, which is much higher than the electrolyte materials, such as $10.5 \times 10^{-6} \text{K}^{-1}$ for YSZ [2].

This work reports that the performance is improved by introducing the cobalt oxide onto the LSF surface rather than into the crystalline bulk. Depositing cobaltite to a pre-sintered porous LSF frame will not change the thermal expansion coefficient while could affect the surface reaction.

2. Experimental

2.1. Powder Synthesis

Symmetrical cells are supported on dense samaria-doped ceria electrolytes with identical $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (LSF) electrodes. The LSF powders were synthesized using a combustion process with ethylenediaminetetraacetic acid (EDTA) and citric acid as the combustion agents. Stoichiometric amounts of the cation precursors $\text{Sr}(\text{NO}_3)_2$ (99.5%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%), and $\text{La}(\text{NO}_3)_3$ (99.9%) were dissolved in distilled water. The combustion agents were subsequently added to the nitrate solution with a molar ratio of 1:1:2 for the total metal ions, EDTA (99.5%), and citric acid (99.5%), respectively. Then, ammonia solution was dropped to adjust pH to about 6.0. The precursor solution was subsequently heated on a hot plate till self-combustion occurred, resulting in black ashes, which were subsequently collected and heated at 800°C for 2 h to form the desired LSF phase with a well-defined crystalline perovskite structure.

$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) as the electrolyte of the symmetrical cells was prepared using the carbonate co-precipitation method [8]. $\text{Sm}(\text{NO}_3)_3$ (99.95%) and $\text{Ce}(\text{NO}_3)_3$ (99%) were used as the cation sources while ammonia carbonate (99.7%) as the precipitant. The white precipitates were dried at 90°C and then heated at 600°C for 2 h to obtain SDC powders with the fluorite structure.

2.2. Symmetrical Cell Fabrication

The SDC powders were uniaxially pressed into disk-shaped pellets at 250 MPa, using a 13 mm diameter stainless steel die, and then sintered at 1400°C for 5 h in air to form dense SDC pellets with a diameter of ~ 10.0 mm and thickness of ~ 0.5 mm. To prepare the electrode layers, LSF slurry, which was prepared by mixing LSF powders with α -terpineol and ethyl cellulose, was symmetrically deposited onto both sides of the pellets using the screen-printing technique. After drying under an infrared lamp, the sandwich fresh bodies were heated at 900°C for 2 h to form symmetrical cells consisting of dense SDC electrolyte supports and porous LSF electrodes, where cobaltite could be infiltrated.

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.5%) was dissolved in distilled water to form the infiltration solution with the metal ion concentration of 0.1 mol L^{-1} . The infiltration solution was then dropped slowly onto the porous LSF using milliliter syringe. Each infiltration step was followed by drying and heating at 800°C for 2 h to form Co_3O_4 nano-particles. The mass of the samples before and after each infiltration treatment was measured to estimate the infiltration loading, which was expressed as the mass ratio of Co_3O_4 to the LSF backbones. The dropping-drying-heating cycle was repeated to increase the loading. All chemicals were from Sinopharm Chemical Reagent Co. Ltd.

2.3. Oxygen Surface Exchange Coefficient Measurement

The oxygen surface exchange coefficient was measured by electrical conductivity relaxation (ECR) method. LSF bar specimens (approximately $20.0 \times 5.0 \times 0.89 \text{ mm}^3$) were prepared for the measurements of chemical surface exchange coefficient (K_{chem}). LSF powders were isostatically pressed into rectangular bars at 300 MPa, followed by sintering at 1350°C for 5 h in air, resulting in dense LSF bars with relative density higher than 95% as determined with Archimedes method. Co films were deposited on the LSF bar surfaces using sputter coater (JFC-1600, JEOL) at 20 mA and under the vacuum of 10 Pascal, which were conducted for 10, 20 and 30 s, and the films were then heat-treated at 800°C for 2 h to form Co_3O_4 nano-particles. The K_{chem} values were determined using the ECR method [9–11] with oxygen partial pressure changed from 0.21 to 1.0. The specific process to conduct the ECR measurement and the equations used to calculate K_{chem} have been represented in the previous work [4]. A digital multimeter (Keithley, 2001-785D) was used to record the resistance of the bars with a four-probe method.

2.4. Single Cell Fabrication

Single cells have a configuration of an Ni-Zr_{0.85}Y_{0.15}O_{1.925} (YSZ) anode support, a thin layer of YSZ electrolyte, a SDC interlayer, and a LSF based cathode. YSZ and NiO used for single cells were prepared by glycine-nitrate method [12]. Stoichiometric amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were dissolved in distilled water to form an aqueous solution with a total metal concentration of 0.1 M. The combustion agent (glycine, 99.5%) was subsequently added to the nitrate solution. The molar ratio of metal ion to glycine was 2:1. The solution was stirred for 2 h with magnetic stirring apparatus, and then heated on a hot plate until self-combustion occurred. NiO was synthesized with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98.0%) with the same process as YSZ. The as-prepared ashes of YSZ and NiO were then collected and heated at 850°C for 4 h to obtain the desired powders. The anode-supported single cells were prepared for electrochemical characterization. NiO and YSZ were mixed homogeneously with a weight ratio of 6: 4 as the anode materials, and then were pressed into the pellets at 250 MPa. The anode pellets were heated at 1000°C for 2 h, followed by applying YSZ slurry (alcohol: YSZ: dispersant = 20: 2:1) using dip-coating method and sintering at 1400°C for 5 h to form dense electrolyte thin layers. SDC buffer layer was applied on the surface of the YSZ electrolyte via dip-coating method, and then heated at 1200°C for 2 h. The details of fabrication process have been represented by Wu et al. [13] for tubular solid oxide fuel cells. Finally, cathode slurry was screen printed on the SDC surface, followed by drying and heating at 900°C for 2 h. Finally, Ag paste was printed on the surface of cathode to collect current, then five-layered pellet was sealed onto the top of a ceramic tube with the cathode side exposing in ambient air and the anode side flowing with humidified ($\sim 3\% \text{ H}_2\text{O}$) hydrogen at 50 mL min^{-1} .

2.5. Characterization

The phase structures were investigated using X-ray diffraction (XRD, Rigaku TTR-III diffractometer) with Cu-K α radiation source. The XRD patterns were obtained in the range of 20 – 80° with a 0.02° step size and a scan speed of $10^\circ/\text{min}$ at 40 kV and 200 mA. A thermogravimetry analyzer (SDT Q600) was used to determine the decomposition behavior of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in air and explore the chemical compatibility between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and LSF. The morphologies of the samples were characterized using high resolution electron microscope (HRTEM), (JEM-2010, 200 kV). The interfacial polarization resistance of the cells was determined from ac impedance spectrum using a Solartron 1260 Frequency

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