

Electrode Material of Ceria-Substitution Lscm for Symmetric Solid Oxide Fuel Cells Exposed to H₂ Fuel Containing H₂S

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Abstract—10 at.% ceria-substitution on A-site for La_{0.75}Sr_{0.15}Ce_{0.1}Cr_{0.5}Mn_{0.5} (noted as LSCCM) was synthesized by the sol-gel process. The characterizations were done by XRD and SEM. The structures, before and after exposure to 5% H₂S-5% wet H₂ at 900 °C, were demonstrated using X-ray diffraction (XRD). And best sulfur tolerance of LSCCM was studied. It also demonstrated that LSCCM had good structural compatibility with electrolyte YSZ. SEM test exhibits a homogeneous distribution of pores. The results of electric performance test prove that the maximal power density was 16.03 mW·cm⁻² in 5% H₂S-5% wet H₂ at 900 °C.

Index Terms—Symmetrical electrode, ceria-substitution, sulfur tolerance, electrochemical performance.

I. INTRODUCTION

Symmetric Solid Oxide Fuel Cells (SFCs) [1] as a new concept of Solid Oxide Fuel Cells (SOFC), using the same material as both anode and cathode, has attracted attention because they could reduce such strains greatly, enhance the ease of co-sintering and decrease the fabrication costs derived from the simpler fabrication process considerably and address problems such as reversible sulphur poisoning [1]-[3]. However, there is great challenge for SFCs, replacing the traditional SOFC configuration, due to the choice of electrode material needs to be stricter. For example, in this configuration, the electrode materials should have both good oxidability (as anode) and particular reducibility (as cathode). Furthermore, they should exhibit an adequate degree of porosity and an acceptable electronic conductivity in both oxidising and reducing atmospheres, dimensional stability and chemically and physically compatible with the other fuel cell components, and catalytically active towards oxygen reduction and fuel oxidation without using external reformers [1], [3]-[9].

Despite the requirements over the materials choice are certainly demanding, the SFC concept has already been proposed and proved using (La,Sr)(Cr,Mn)O(LSCM)-based electrodes under humidified H₂ and CH₄ [10]-[12]. Doped lanthanum chromite has been proposed as a single oxide anode due to their relatively good stability, high electronic conductivity and a certain degree of ionic conductivity. Back in 2001, Sfeir et al. studied (LaA)(CrB)O₃ system (A=Ca, Sr and B=Mg, Mn, Fe, Co, Ni) as alternative anode materials, of which thermodynamic stability and catalytic activity under simulated SOFC operation conditions [13], [14]. Meanwhile,

strontium-substituted manganites such as La_{0.8}Sr_{0.2}MnO₃ (LSM) have been regarded as the most common cathode material due to their excellent electronic conductivities at a certain temperature and good catalytic behavior towards oxygen reduction [15]. It is important to note that lanthanum chromites, as potential electrode materials for SFCs, has been recently proposed and verified by J. C. Ruiz-Morales research groups in 2006 [1], [2], [16]-[18]. La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) is a good option for such symmetrical configuration, rendering fuel cell performances in excess of 500 mW·cm⁻² using pure H₂ as fuel at 950 °C [16]. Additionally, several other systems have been explored in seeking for potential SFC electrodes such as titanates activated under oxidizing conditions [1], composites of chromium-manganites and gadolinium-doped ceria (CGO) [17] and La_{0.7}Ca_{0.3}CrO_{3-δ} [18].

Our group has been intensively studying La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM55) running on hydrogen sulfide-containing fuel, which can exhibit acceptable electrocatalytic activity, and furthermore intensification of poisoning effects [19], [20]. In the work presented herein, a new material La_{0.75}Sr_{0.15}Ce_{0.1}Cr_{0.5}Mn_{0.5} (LSCCM), ceria-substitution at A-site, was prepared and investigated for potential SFC electrodes. The effect of ceria -substitution partly in A-site on catalytic activity even in H₂S-containing fuel would be focused. We researched that LSCCM can be considered as a good electrode material in H₂S-SFCs mainly due to its better electrochemical performances exposed to H₂ fuel containing H₂S.

II. EXPERIMENTAL SECTIONS

A. LSCCM Powders Preparation

La_{0.75}Sr_{0.15}Ce_{0.1}Cr_{0.5}Mn_{0.5} (noted as LSCCM) powder was synthesized by the sol-gel process [21]. Briefly, the procedure commenced by dissolving admixing stoichiometric amounts of the nitrate salts La(NO₃)₃, Sr(NO₃)₂, Ce(NO₃)₃·6H₂O, Cr(NO₃)₃·9H₂O and Mn(NO₃)₂ in an ethylenediaminetetraacetic acid(EDTA)-ammonia aqueous solution (pH 8–9) with stirring. After added citric acid, ammonia aqueous solution was then added to balance the pH to 7–8. A dark purple solution was obtained, and mixture was stirred further on a magnetic stirrer (IKA) with a certain shear rate at 80 °C for several hours. After that, the temperature increased to 200 °C to form the gel. Then the resulting gel was heated at 500 °C to carry out combustion on a hot plate in the fume hood. After burning out the organic components, the porous ash formed was finely grinding and

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then calcined under airflow in a high-temperature furnace (NABERTHERM) at 1100 °C for 5 h to form the black powder.

LSCCM-YSZ was prepared by physically mixing the pure LSCCM and YSZ with an equal molar ratio, and then calcined at 900 °C for 4h. The well-calcined powders and LSCCM powders were identified by X-ray diffraction (XRD, Bruker D8 ADVANCE, Germany) using Cu K α radiation ($\lambda=0.15406$ nm) at room temperature. And the diffraction patterns were registered over a 2θ range between 20 and 80 degree.

The microstructure and the composition of the coating were analyzed using scanning electron microscopy (FE-SEM, Hitachi, S-4200, Japan).

B. SFCs Fabrication

Symmetric cells of LSCCM|8YSZ|LSCCM researched in the work were electrolyte (YSZ) supported. The 8YSZ is 8 mol%-yttria stabilized zirconia from Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science. And the electrolyte substrate (13 mm outer diameter, 1 mm thick) was formed by die-pressing YSZ powder under 100 MPa, then calcined under airflow in the high-temperature furnace at 1350 °C for 5 h at a ramping rate of 2 °C/min to form a dense pellets.

Besides, LSCCM powders were ground using a mortar and pestle, dispersed in α -terpineol to form a paste, and screen-printed onto the well-sintered YSZ electrolyte pellets. The membrane assembly was fired at 1200 °C in air for 5 h and had an effective area of 0.33 cm².

C. Cell Characterization

A series of YSZ electrolyte-supported SFCs LSCCM|YSZ|LSCCM with 13 mm outer diameter were produced. Then we test their electrical performance at different temperature, and 5%.vol%H₂S-5%.vol% wet H₂ was the fuel, while another electrode was exposed to the ambient atmosphere.

III. RESULTS AND DISCUSSION

A. Phase Structure and Morphology of LSCCM

The combustion powders were calcined in air at 1100 °C for 5 h to investigate the crystalline phase of LSCCM. As shown in Fig. 1, the product has strongly crystallinity of LSCCM perovskite phase. Nearly all the peaks were indexed by comparison with the orthorhombic perovskite-type structure of strontium lanthanum manganese oxide La_{0.8}Sr_{0.2}MnO₃ (PDF card no.53-0058) and lanthanum manganese oxide La_{1-x}Mn_{1-z}O₃ (PDF card no.51-1516). Thus a single perovskite phase is formed completely after calcining at 1100 °C. It is also found that LSCCM was directly suffered in 5%H₂S-5% wet H₂ at 900 °C for 4 h, good peak shapes for typical perovskite structure are still narrow. No obvious changes were observed when comparing the XRD patterns of fresh and spent samples, which confirm that sample is a certain tolerant to sulfur.

B. Microstructure of LSCCM

SEM was used to observe the microstructure images of LSCCM powders. Fig. 2 shows the surface morphology of

LSCCM powders sintered at 1100 °C with different magnification times (the left is $\times 5K$ and the right is $\times 10K$), and reveals LSCCM powders likely a little agglomerated during sol-gel synthesis process, but still exhibit a homogeneous distribution of pores. The observed porous electrode, uniform particle distribution gives rise to sufficient availability of oxygen-ion and electron transfer.

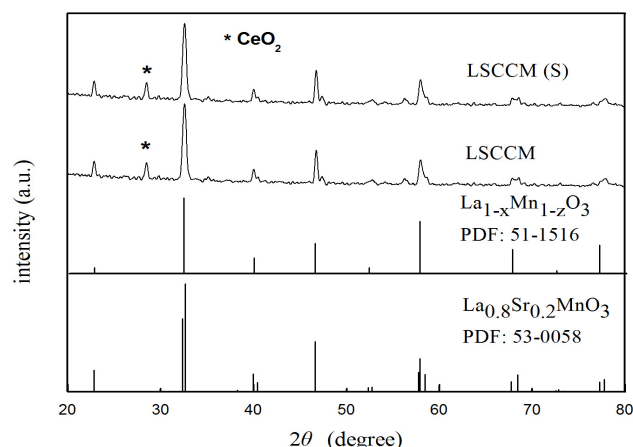


Fig. 1. XRD patterns of La_{0.75}Sr_{0.15}Ce_{0.1}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCCM) before and after exposure to 5%H₂S-5% wet H₂ at 900 °C for 4h and the standard

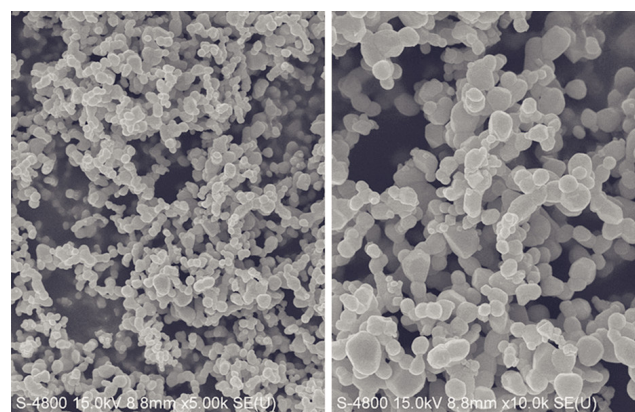


Fig. 2. SEM images of La_{0.75}Sr_{0.15}Ce_{0.1}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCCM) microstructure calcined at 1100 °C and the standard

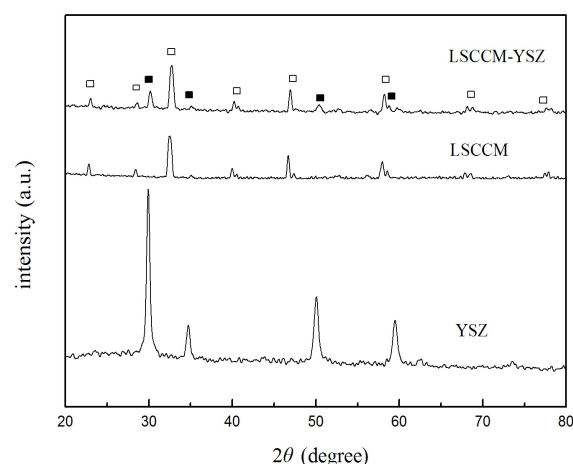


Fig. 3. XRD patterns of YSZ, LSCCM and LSCCM-YSZ after being calcined at 900 °C in air for 4h

C. Structural Compatibility with Electrolyte YSZ

Yttria-stabilized zirconia (YSZ), which we selected, has been a state-of-the-art electrolyte material. Because it exhibits good thermal and chemical stability, high oxide-ion conductivity and adequate mechanical strength at elevated

temperatures. LSCCM-YSZ was prepared by physically mixing the pure LSCCM and YSZ with an equal molar ratio, and then calcined at 900 °C for 4 h. As the XRD pattern (Fig. 3) shows, the middle curve stands for symmetric electrode LSCCM, and electrolyte YSZ is the below profile. The XRD pattern of LSCCM-YSZ (the above one) is consistent with the combination of LSCCM and YSZ phases, without any other new peak. Hence, LSCCM has good structural compatibility with electrolyte YSZ.

D. Cell Testing

Here the electro-catalytic properties, such as, the catalytic activities towards fuel were studied on YSZ electrolyte-supported cells consisting of $\text{La}_{0.75}\text{Sr}_{0.15}\text{Ce}_{0.1}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ symmetric electrode. 5%.vol% H_2S -5%.vol% wet H_2 was the fuel, while another electrode was exposed to the ambient atmosphere. Fig. 4 shows typical plots of voltage and power density versus current density at different temperatures. When the temperature rises from 600 °C to 900 °C, the cell OCV descends from 0.55 V to 0.92 V. And when the temperature reached 800 °C, the cell OCV reached up to 0.92. Moreover, the temperature is around 0.90 V. From the slope of current density versus voltage curve, we know that the apparent cell resistance decreases with increasing temperature, as is typical for SFCs. Moreover, the values of both the maximal power density (P max) and the maximal current density (I max) have increasing trends as a function of the temperature. Peak of power density showed 16.03 mW/cm^2 at 900 °C.

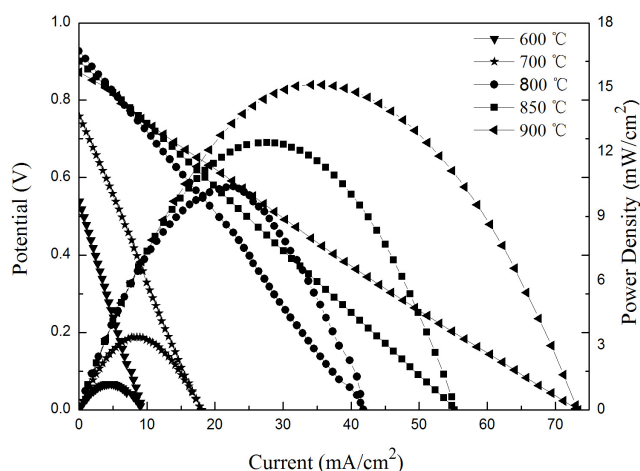


Fig. 4. I-V and I-P curves of single cell with LSCCM/YSZ/LSCCM in 5% H_2S -5% wet H_2 at different temperatures

IV. CONCLUSION

LSCCM powders were prepared by the sol-gel combustion method and characterized as a potential anode material for symmetric solid oxide fuel cells under H_2S -containing atmosphere. LSCCM maintains good chemical stability under redox conditions through XRD analysis and also exhibited good chemical compatibility with YSZ in H_2S -containing atmosphere. Best sulfur tolerance of LSCCM was studied by XRD test after exposure to 5% H_2S -5% wet H_2 at 900 °C, and best porosity of LSCCM was studied by SEM. For the cell with the configuration of LSCCM|YSZ|LSCCM, the maximum open circuit voltage is 0.92 V and the maximum power density is 16.03 mW/cm^2 .

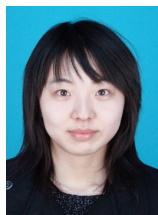
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