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Reduced-temperature redox-stable LSM as a novel symmetrical electrode material for SOFCs

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ABSTRACT

Based on its reduced-temperature redox-stable phenomenon, the state-of-the-art perovskite oxide $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) is proposed as a novel symmetrical electrode material for solid oxide fuel cells (SOFCs) at intermediate temperatures. LSM exhibits redox instability at high temperatures ($\geq$850 °C) in agreement with the literature, whereas LSM is stable in both fuel and air conditions at intermediate temperatures ($\leq$800 °C). The electrical conductivity of LSM in both air and humidified H_2 (3% H_2O) exhibit a semiconductor behavior, and the maximum values are 123.8 S cm^{-1} and 2.01 S cm^{-1} at 800 °C, respectively. LSM-$Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (LSM-GDC) composite electrode was used to improve the electrochemical performance. The area specific resistance of LSM-based electrode decrease from 3.03 Ω cm^2 to 1.44 Ω cm^2 in air and from 10.49 Ω cm^2 to 5.19 Ω cm^2 in H_2 at 800 °C by adding mixed ionic-electronic conducting GDC, respectively. The electrochemical performance of symmetrical SOFCs with LSM-based electrodes are dramatically enhanced by more than 120 percent at 800 °C. The LSM-GDC composite electrode delivered optimum electrochemical properties with 140 h long-term stability, demonstrating its potential as both anode and cathode for symmetrical SOFCs at intermediate temperatures.

1. Introduction

Solid oxide fuel cells (SOFCs) have been regarded as the replacement of the conventional combustion technology for its high conversion efficiency and low pollution to overcome the situation of fossil fuels and environment [1,2]. Typical SOFCs based upon yttria-stabilized zirconia (YSZ) have been available in the market and demonstrate a good performance with the component of Ni-YSZ cermet anode, YSZ electrolyte and $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) cathode [3,4]. The state-of-the-art Ni-YSZ anode shows a high ionic and electronic conductivity, good compatibility with other components and high catalytic activity for hydrogen oxidation [5,6]. However, it is sensitive to sulfur poisoning and carbon deposition during the operation when using hydrocarbon as fuel, resulting in the degradation of anode performance [7]. To avoid the corresponding degradation of this cermet anode, mixed ionic and electronic conductors (MIEC) with robust structure under fuel atmosphere as well as good coking and sulfur poisoning tolerence have been evaluated as potential anode materials, such as $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ [8–11], $La_{0.5}Sr_{0.2}TiO_{3-\delta}$ [12], $Sr_2MgMoO_{6-\delta}$ [13–15] et al.

Another effective way to enhance the tolerance of coking and sulfur poisoning is the employment of same material as both anode and cathode for SOFCs, which was defined as symmetrical solid oxide fuel cells (SSOFCs) [16–18]. In this configuration, the deposited carbon particles and sulfide can be removed by changing anode to cathode successively. Furthermore, The fabrication process can be simplified by one step co-fired technology owing to the same electrode [19]. However, the development of proper electrode material is a significant challenge for SSOFCs. Because the symmetrical electrode material needs to operate at both oxidizing and reducing environment, that means it should have robust structure stability under both oxidizing and reducing environment [20,21]. Moreover, the electrode material should provide sufficient electrocatalytic activity for both oxygen reduction reaction (ORR) and

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fuel oxidation reaction. Over the past decade, several perovskite materials have been evaluated as symmetrical electrode for SSOFC, including $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ [16], $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [22], $Pr_{0.6}Sr_{0.4}Fe_{0.7}Ni_{0.2}Mo_{0.1}O_{3-\delta}$ [23], $La_{0.5}Sr_{0.5}Co_{0.5}Ti_{0.5}O_{3-\delta}$ [24] and $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ [25], etc. However, these symmetrical electrode materials only show valuable performance at high temperatures. So, in order to make SSOFCs economically competitive with traditional SOFCs, some new materials with high performance at intermediate temperatures need to be investigated.

$La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) is a commercial cathode material and exhibit an excellent performance at high temperatures owing to its remarkable catalytic activity for ORR [26,27]. However, LSM exhibits redox instability at high temperatures (≥850 °C), and the cell performance decreased obviously as the operating temperature reduced because of its extremely low ionic conductivity and the rapid decline of the electrocatalytic activity [28]. Introducing an ionic conductor (YSZ or $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (GDC)) to LSM cathode can improve the cell performance visibly at intermediate temperatures due to the enlarged active sites at triple-phase boundary [29]. In this works, LSM-GDC was evaluated as both cathode and anode for symmetrical solid oxide fuel cells at intermediate temperatures. The phase structure, electrical conductivity and electrochemical performance under both oxidizing and reducing atmospheres were investigated systematically.

2. Experimental

2.1. Synthesis

$La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) and $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (GDC) powders were prepared by a modified Pechini method. $La(NO_3)_3\cdot nH_2O$, $Sr(NO_3)_2$, $Mn(NO_3)_2$, $Gd(NO_3)_3\cdot 6H_2O$, $Ce(NO_3)_3\cdot 6H_2O$ were used as raw materials. The stoichiometric amounts of the raw materials were dissolved in distilled water, and followed by adding 10 ml nitric acid and citric acid with the molar ration of 1.5:1 to metal ions. pH value of the solution was set to 7–8 by adding ammonium hydroxide. A uniform aqueous solution was obtained and then heated on a 2 kW electric furnace under stirring until combusted. The precursors were calcined at 900 °C and 700 °C for 3 h in air to get LSM and GDC powders, respectively.

2.2. Sample preparation

LSM powder was pressed at a pressure of 220 MPa to form black bars with the dimension of 40 mm × 5 mm × 2 mm, followed by sintering at 1350 °C for 5 h in air for conductivity measurements. The primary YSZ powder (Commercial, Ningbo) was ball-milled for 24 h using acetone as media and Hypermer KD-1 as dispersant. The ball-milled powder was then pressed into pellets with the diameter of 15 mm at 200 MPa, and sintered at 1450 °C for 10 h in air to form YSZ pellets with 400 μm in thickness. The symmetrical and single cells were conducted on an electrolyte supported configuration. The composite electrode was prepared by mixing thoroughly the LSM powder and the GDC powder (70:30 wt%). LSM and LSM-GDC powders were mixed with 10 wt% ethyl cellulose in terpineol adequately using as electrode slurry and then brushed onto both surfaces of YSZ electrolyte, followed by heated at 1200 °C for 3 h. The area of single cell cathode was 0.2 cm^2 and Ag paste was applied as the current collector for both anode and cathode.

2.3. Characterization

The phase structure of synthesized samples and redox stability were characterized by X-ray diffraction (XRD) with a DX-2800 diffractometer with Cu Kα radiation at 40 kV and 30 mA. The XRD data were refined with the Rietveld method using GSAS. X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo, USA) with Al-Ka radiation source was used to analyze the LSM electrode powder before and after reduction in humidified H_2 at 750 °C. The electrical conductivity of the LSM was measured in the temperature range of 350–800 °C in air and humidified H_2 with a four-probe dc method using a van der Pauw configuration. The polarization resistance values (R_p) of LSM and LSM-GDC electrodes on the YSZ pellets were measured with symmetric cells in the temperature range of 650–800 °C in air and humidified hydrogen by IM6 Electrochemical Workstation (ZAHNER, Germany). The testing frequency range of impedance spectra was from 1 MHz to 0.01 Hz with an alternating voltage of 5 mV. I-V and I-P curves of YSZ-supported single cells were evaluated by a DC Electronic Load (IT8511) using ambient air as oxidant and humidified hydrogen (3%H_2O) as fuel. The long-term durability of single cell was evaluated with LSM-GDC single symmetrical cell exposed in 3%H_2O-97%H_2 atmosphere. The cross-section microstructure and morphology of the single symmetrical cell after long-term stability test was observed by Scanning Electron Microscope (SEM, EM-3200).

3. Results and discussion

Fig. 1(a) shows the XRD pattern of as-prepared LSM powder calcined at 950 °C for 3 h. All peaks for LSM exhibit a characteristic of hexagonal crystal structure without any impurity, which can be indexed to JCPDS 53–0058. In addition, the prepared LSM powder was reduced at 850 °C,800 °C and 750 °C for 5 h in humidified H_2 (3%H_2O) to investigate the redox stability under anodic environment as shown in Fig. 1(b–d). It can be clearly seen that LSM reduced at 850 °C has broken its crystal structure, indicating the redox instability at high temperatures, which is in agreement with the reports by Shao [30]. When reduced at 800 °C, the intensity of XRD pattern cut down and exist some small phase, but the Hexagonal structure is still remained. Furthermore, the XRD pattern of LSM reduced at 750 °C keeps the Hexagonal crystal structure obviously. LSM exhibits redox instability at high temperatures (≥850 °C), whereas LSM is stable in both fuel and air conditions at intermediate temperatures (≤800 °C).

In addition, the Rietveld refinement patterns and results for LSM calcined in air and reduced in H_2 are shown in Fig. 2. The samples

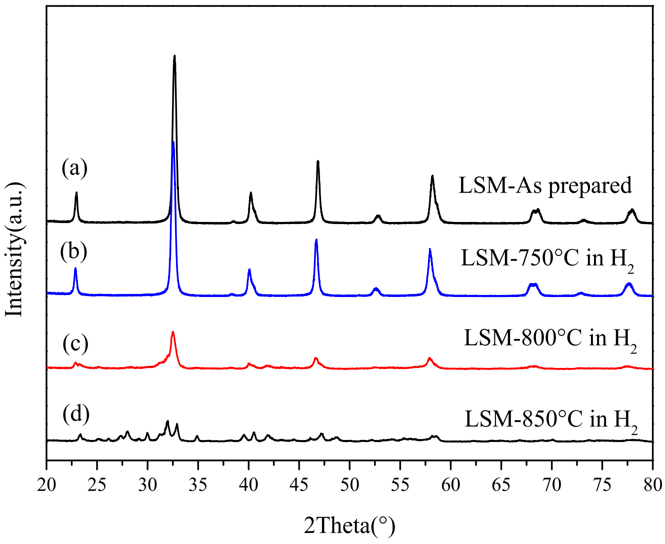

Fig. 1. XRD patterns of as-synthesized LSM powder calcined at 900 °C in air (a) and reduced at different temperature in humidified H_2 (b–d).