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Behavior of strontium- and magnesium-doped gallate electrolyte in direct carbon solid oxide fuel cells

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ABSTRACT

Perovskite-type $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) is synthesized by conventional solid state reaction. Its phase composition, microstructure, relative density, and oxygen-ionic conductivity are investigated. Tubular electrolyte-supported solid oxide fuel cells (SOFCs) are prepared with the LSGM as electrolyte and gadolinia doped ceria (GDC) mixed with silver as anode. The SOFCs are operated with Fe-loaded activated carbon as fuel and ambient air as oxidant. A typical single cell gives a maximum power density of 383 mW cm^{-2} at 850 °C, which is nearly 1.3 times higher than that of the similar cell with YSZ as electrolyte. A stability test of 72 min is carried out at a constant current density of 210 mA cm^{-2}, with a fuel utilization of 60%, indicating that $LaGaO_3$-based electrolyte is promising to be applied in direct carbon SOFCs (DC-SOFCs).

1. Introduction

Nowadays, fossil fuels are dominating the worldwide energy consumption market, resulting in serious problems of resource depletion and environmental pollution. Thus, renewable energies, such as solar and wind energies, are attracting more and more attention. However, in the foreseeable future, the renewable energies are still far from meeting the energy demand of the world. Developing innovated energy conversion technologies with high efficiency and low emission of pollutants (including CO_2) is a practical choice to use the limited fossil energy carriers cleanly and effectively. The direct carbon fuel cell (DCFC) is such a technology which directly converts the chemical energy of carbon to electric power with high conversion efficiency and low emission [1]. The carbon-rich fuels of DCFCs, such as the petroleum, coal coke, as well as biomass carbon and so on, are quite abundant and ready to available. Regarding to DCFCs, most researchers have made much effort to explore the fuel cells based on liquid electrolyte such as molten hydroxides and carbonates [2–4]. However, the operation of DCFC with liquid electrolyte is rather dangerous at high temperature due to the risk of liquid leakage and corrosion [3]. The direct carbon solid oxide fuel cell (DC-SOFC) is a completely solid state energy conversion device that can avoid the above problem [5,6]. The DC-SOFC can be defined as a SOFC with solid carbon as fuel without feeding gas [7–10]. With high energy capacity and safe operation with solid carbon fuel, DC-SOFC has been regarded as a prior option for potential high performance battery [11].

A whole solid state DCFC was first proposed by Nakagawa and Ishida [5] and Gür and Huggins [6]. Later on, Gür proposed a fluidized bed DCFC using carbon fuel [12] by carrying gas (He and CO_2). There have been some reports about the superiority of DC-SOFCs [9–11]. Wang et al. [13] and Shao et al. [14] separately reported a Ni-ScSZ anode-supported DC-SOFC. Maximum power densities of 75 and 104 mW cm^{-2} were obtained at 800 °C by the two groups, respectively. Tang [9] fabricated and operated tubular YSZ electrolyte-supported SOFCs with activated carbon as fuel, with silver as both of the anode and cathode. The cell showed a maximum power of 16 mW at 800 °C and was successfully operated for 37 h at a constant current density of 12 mA cm^{-2}. Bai et al. [11] has prepared a cone-shaped anode-supported SOFC, with YSZ electrolyte, Ag-GDC anode, and LSM cathode. The single cell

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with Fe loaded activated carbon as fuel revealed a maximum power density of 424 mW cm^{-2} at 850 °C.

So far, the conventional electrolyte, yttria-stabilized-zirconia (YSZ), has been used in DC-SOFCs. Lanthanum gallate doped with Sr and Mg (LSGM), with oxygen ion conductivity higher than that of YSZ, has been regarded as a promising alternative to YSZ electrolyte [15–19]. There have been demonstrations of operating LSGM electrolyte SOFCs on hydrogen, but there are few reports on using LSGM in DC-SOFCs. It is worthwhile to investigate the feasibility of using LSGM as the electrolyte SOFCs operated directly on carbon so that more options could be provided for choosing component materials of DC-SOFCs.

In this paper, we report our work on preparing the LSGM material, investigating its properties, and applying it in DC-SOFCs. The output performances, AC impedance of the SOFCs with solid carbon as fuel are tested. The factors affecting the electrochemical and degradation performance of LSGM-supported DC-SOFC are discussed.

2. Experimental

2.1. Samples preparation

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ powder was prepared using conventional solid state reaction. La_2O_3 (99.99% purity), $SrCO_3$ (99% purity), Ga_2O_3 (99.99% purity), MgO (98% purity) were used as starting materials. Before weighing, the raw material of La_2O_3 was calcined at 950 °C for 4 h and MgO was calcined at 1000 °C for 2 h. Then stoichiometric amount of La_2O_3, $SrCO_3$, Ga_2O_3, MgO were mixed with zirconia ceramic medium balls (weight ratio of ball to powder is 3:1) in an agate jar using ethanol as solvent and ball-milled for 24 h. The mixture was thoroughly dried and pre-calcined at 1000 °C for 4 h, then pressed into pellets and sintered at 1250 °C for 30 h. Finally the pellets were ground thoroughly in an agate mortar to get the LSGM powder.

The LSGM powders were mixed and ground with ethanol and 6 wt.% polyvinyl butyral (PVB), then uniaxially pressed into pellets using a stainless steel mold (13 mm in diameter) under a pressure about 373 MPa. Finally, the pellets were sintered at 1400 °C for 4 h in air to obtain dense electrolyte pellets with diameter of 11.4 mm and thickness of about 1 mm.

2.2. Preparation of electrolyte tube

Tubular LSGM electrolyte was fabricated by dip-coating technique [20,21]. Twenty-five grams (25 g) LSGM powder, 0.5 g trithanolamine (TEA) as dispersant, 1.0 g polyethylene glycol (PEG) as plasticizer, 1.0 g dioctyl phthalate (DOP) as plasticizer and 20 g ethanol as solvent, were mixed and ball-milled for 1 h using an agate jar and zirconia ball medium. Polyvinyl butyral (PVB) was dissolved in the ethanol at 60 °C. Then it was added to the slurry and the slurry was ball-milled for 2 h to get homogeneous slurry. The slurry was poured into a container and a test tube (as a forming mould), with clean and smooth outside surface, was vertically inserted into the slurry. After a few seconds, the test tube was taken out and dried in open air. Then a layer of LSGM was formed on the test tube. The dip coating process was repeated for several times to get the required thickness. After drying, the green tube-shaped electrolyte was removed off from the test tube. The thickness of the electrolyte wall was 0.15 mm after sintering at 1400 °C for 4 h. Tubular YSZ electrolyte with thickness of 0.15 mm was also fabricated by dip-coating technique in a similar way.

2.3. Preparation of anode and cathode

GDC powder was mixed with silver paste (DAD-87, Shanghai Institute of Synthesized Resins) with a weight ratio of GDC:Ag as 55:45 through grinding the mixture in an agate mortar for 2 h. Then the obtained homogeneous slurry was respectively painted on inside and outside of each of the LSGM electrolyte tube as anode and cathode, then dried at 120 °C. Finally, the tubes were annealed at 880 °C for 4 h. The cathode area for all the single cells was the same (1.9 cm^2). A silver mesh was drawn on the cathode surface of each cell as the current collector.

2.4. Preparation of the Fe-loaded catalyst on activated carbon powder

Activated carbon was mixed with $Fe(NO_3)_3 \cdot 9H_2O$ solution (98.5% purity) with the mass ratio of C:Fe = 95:5. The mixture was vigorously stirred at 80 °C for 12 h to get a colloid. Then the colloid was dried at 120 °C for 2 h and heat-treated at 800 °C for 30 min under flowing Ar to decompose the nitrate. Finally, 5 wt.% Fe was loaded on the activated carbon as catalyst in the form of Fe_mO_n [8].

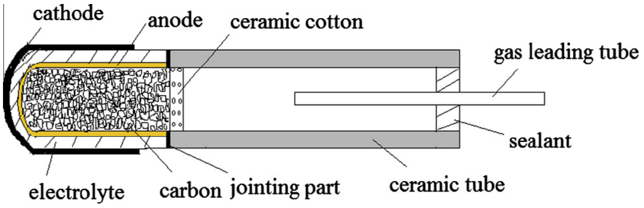

Fig. 1. Schematic illustrations of tube-shaped single SOFC with carbon fuel.

2.5. Cell assembling and testing

Each tubular single cell was attached to an Al_2O_3 ceramic tube with silver paste as sealing and jointing materials [22,23]. The cells were heated and tested with humidified hydrogen (50 mL min^{-1}) as fuel and ambient air as oxidant in the temperature range of 750–850 °C, with an interval of 50 °C. Then, the tested cells were treated in two different ways. The first way is to cool down the cells to room temperature and then to fill each of the cells with 0.17 g 5 wt.% Fe-loaded activated carbon, as shown in Fig. 1. The carbon was fed into the anode of the cell through the ceramic tube. Then, some ceramic cotton was introduced into the tube to fix the carbon powder. A gas-guide tube was fixed and sealed at the open end of the ceramic tube to make the produced gas getting away conveniently. The second way is to reduce the operating temperature to 750 °C and switch the fuel to dry CO (50 mL min^{-1}) to test the cell in the temperature range of 750–850 °C.

2.6. Characterization

Phase identification of the as prepared powders was carried out by X-ray diffraction (XRD, D8 ADVANCE, Bruker, Cu Kα radiation, operated at 40 kV, 40 mA; λ = 0.15418 nm). The selected 2θ range was from 20° to 80° and the scanning step was set as 0.02°.

The microstructures of the samples were examined by a scanning electron microscope (SEM, Hitachi S-4300, Japan). And EDX measurement was also taken for some of the cells.

The density of the sintered LSGM pellets sintered at 1400 °C was measured using Archimedes method. The ionic conductivity of the dense electrolyte pellets were calculated by measuring the impedance spectra data with four-probe method using Iviumstat electrochemical analyzer. To prepare samples for the conductivity measurement, silver paste was painted on both surfaces of LSGM electrolyte pellets as symmetrical electrodes, each with an area of 0.25 cm^2. The painted silver was dried and annealed at 800 °C for 2 h to evaporate the organic materials in the silver paste. The measuring temperature was 600–850 °C, the frequency ranged from 0.1 Hz to 100 kHz. The measurements were carried out at a voltage amplitude of 10 mV.

All the electrochemical performances of the cells were tested by four-probe setup using Iviumstat electrochemical analyzer. Finally, the stability measurement for the cell was taken at 800 °C under a constant current density of 210 mA cm^{-2}.

3. Results and discussions

3.1. XRD analysis

The XRD pattern of the LSGM powder prepared by solid state reaction is shown in Fig. 2. It shows that the main phase of perovskite is formed at a synthesizing temperature of 1250 °C, however, accompanied with trace amount of second phase $LaSrGaO_4$. It is difficult for the starting materials to mix thoroughly in atomic level in solid state reaction. So it is quite hard to avoid the existence of impurity using the solid state reaction to synthesize LSGM powder. It is necessary to improve the sintering temperature to decrease the impurities.

3.2. Microstructure of the samples

Fig. 3 shows typical microstructures of the LSGM samples. Fig. 3(a) shows the microstructure of the LSGM powder sintered at 1250 °C. As shown in the picture, the particles stack closely which is beneficial to make the electrolyte dense. Fig. 3(b) shows the cross-sectional image of tri-layer structure of single cell after stability testing. The LSGM layer, which has been sintered at 1400 °C, is relatively dense with some ignorable closed pores. The