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Preparation and performance of $La_{1-x}Sr_xCuO_{3-\delta}$ as cathode material in IT-SOFCs

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Abstract

The cathode material $La_{1-x}Sr_xCuO_{3-\delta}$ ($x = 0.15$, 0.2, 0.3, 0.4) was synthesized by a sol–gel method. X-ray diffraction revealed it to form a single phase of perovskite. The investigation of the electrical properties suggested that $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ has the highest electrical conductivity. $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ has better electrochemical properties than $La_{0.6}Sr_{0.4}CoO_{3-\delta}$. When using $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ as cathode based on SDC electrolyte one can obtain higher current density and power density at intermediate temperatures.

Keywords: SOFC; Cathode; $La_{1-x}Sr_xCuO_{3-\delta}$

1. Introduction

Because of lower operating temperature, the intermediate temperature solid oxide electrolyte fuel cells (IT-SOFCs) extends the range of material selection for electrodes, reduces the cost of production and application, and improves the stability and reliability when the SOFCs system has to work for a long-period of time. Recently, reduction of operating temperature can be achieved either by thinning the electrolyte, or by using highly conductive electrolyte, such as doped cerias [1–3]. At the same time, it is important to develop a cathode material that can adapted to the intermediate temperature electrolyte and has high conductivity and low cathodic polarization at intermediate temperature so that it can reduce the power loss by ohmic resistance and cathodic polarization [4].

$La_{1-x}Sr_xMnO_3$ perovskite (LSM) is regarded as one of the most promising cathode materials for SOFCs because of its high thermal and chemical stability [5]. While LSM has shown promising performance for SOFCs operating at temperatures above 800 °C, its performance decreases rapidly as the operating temperature decreases. Considerable research interest is, therefore, currently directed towards cobalt-containing perovskite oxides, which tend to exhibit higher ionic conductivities than LSM due to a greater concentration of oxygen vacancies [6–8].

Investigation suggested that lanthanum copper oxide with the addition of divalent Sr ions is a oxygen deficient perovskite. However, all investigations relating to this material were concentrated on its superconducting behavior and found it has excellent electrical conductivity [9–11]. Recently, it was reported that this material also has the capability of catalytic oxidation [12]. Above all, this material is considered to be a possible cathode adapted to IT-SOFCs [13]. In this paper, the cathode materials $La_{1-x}Sr_xCuO_{3-\delta}$ ($x = 0.15$, 0.2, 0.3, 0.4) were synthesized by a sol–gel method, and the high temperature electrical conductivity was measured. The cathodic overpotential with SDC ($Sm_{0.15}Ce_{0.85}O_{1.925}$) electrolyte and the single cell performance based on SDC electrolyte and a 65% NiO/SDC anode was also measured.

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2. Experiment

2.1. Preparation of the samples

$La_{1-x}Sr_xCuO_{3-\delta}$ ($x = 0.15, 0.2, 0.3, 0.4$) was prepared by a sol–gel method. Stoichiometric amounts of La_2O_3 (99.99%, heated at 800 °C for 6 h), $Sr(NO_3)_2$ (99.5%) and CuO (99.0%) were dissolved in concentrated nitric acid (65–68%), then citric acid (99.8%) was added as solid in a molar ratio 1:1.2 with the metallic ions; distilled water was added. Then the solution was stirred, heated slowly to form a glutinous colloid. The colloid was then dried, ground and sintered at 600 °C for 12 h. The sintered powders were subsequently cold-pressed at 250 MPa, as discs about 13 mm in diameter and 1.5 mm thick, and sintered in air at the desired temperature for 12 h. Electrical conductivity was measured by using these samples.

Using starting materials of CeO_2 and Sm_2O_3, the preparation of the electrolyte $Sm_{0.15}Ce_{0.85}O_{1.925}$ (SDC) powders was also made by the sol–gel method. Powders prepared by the same process as above were sintered in air at 1400 °C for 10 h, and subsequently cold-pressed at 250 MPa, as discs about 13 mm in diameter and 1 mm thick, and sintered in air at 1400 °C for 10 h, resulting in the electrolyte substrate. The cathode powders mixed with binders of glycerine were painted on the SDC substrate, sintered in air at 850 °C for 6 h, used to measure the cathodic overpotential.

The anode material NiO/SDC was prepared using the glycin-nitrate method. $Ni(NO_3)_2{\cdot}6H_2O$ (98.0%) was dissolved in distilled water to form an aqueous solution, to which glycin (99%, 1.2 mol glycin per mol Ni^{2+}) was added in the solid state. Then, the solution was slowly heated until self-combustion of the precipitates. Homogeneous powders were obtained and mixed with SDC (35 wt.%). The NiO/SDC powders were mixed with binders of glycerine and painted on the SDC substrate and sintered in air at 1350 °C for 6 h. The cathode material was painted on the other side of the SDC substrate and sintered in air at 850 °C for 6 h. At last, a single cell was made by connecting the materials. Using H_2 as fuel gas and air as oxidant, the single cell performance was tested.

2.2. Properties measures of the samples

The crystal structure and phase purity were measured by X-ray diffraction (XRD) (Rigaku-D-Max Ra system, with Cu Kα radiation operated at 12 kW). Electrical conductivity was measured by using the four-point dc technique. Cathodic overpotential was measured in a Solartron SI 1287 electrochemical interface measuring apparatus using a current-interruption technique. The single cell performance was tested in a Solartron SI 1287 electrochemical interface measuring apparatus too.

3. Results and discussion

3.1. Results of XRD

Fig. 1 shows the XRD patterns of $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ sintered in air at different temperatures for 12 h. When sintered at 700 °C, the $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ perovskite structure was observed, but some impurity phases also existed. When the sample was sintered at 900 °C, $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ was formed as a single phase perovskite structure.

3.2. Electrical conductivity

In Fig. 2, the electrical conductivity of Sr-doped lanthanum copper oxide, $La_{1-x}Sr_xCuO_{3-\delta}$ ($x = 0.15, 0.2, 0.3, 0.4$) is plotted as a function of Sr addition, the electrical conductivity of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ is also shown as compared to $La_{1-x}Sr_xCuO_{3-\delta}$ ($x = 0.15, 0.2, 0.3, 0.4$), the samples were all sintered in air at 900 °C for 12 h. In the composition range $x = 0.15$–0.3, the electrical conductivity increased with increasing Sr addition. $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ shows the highest electrical conductivity, $\sigma = 850$ S/cm at 800 °C. It is higher than the electrical conductivity of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ at the same temperature. The increment of the electric conductivity of the Sr-doped lanthanum copper oxide can be explained by the small polaron conduction mechanism [14]. However, for $x = 0.4$, the electrical conductivity is lower than in $La_{0.7}Sr_{0.3}CuO_{3-\delta}$, the reason may be that the amount of Sr is larger than the limit of the solid solution.

3.3. Cathodic polarization

Selecting $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ which has the highest electrical conductivity, its electrochemical properties were researched further. With SDC as electrolyte and $La_{0.7}Sr_{0.3}CuO_{3-\delta}$ as cathode, the cathodic overpotential was measured by a three-electrode current-interruption

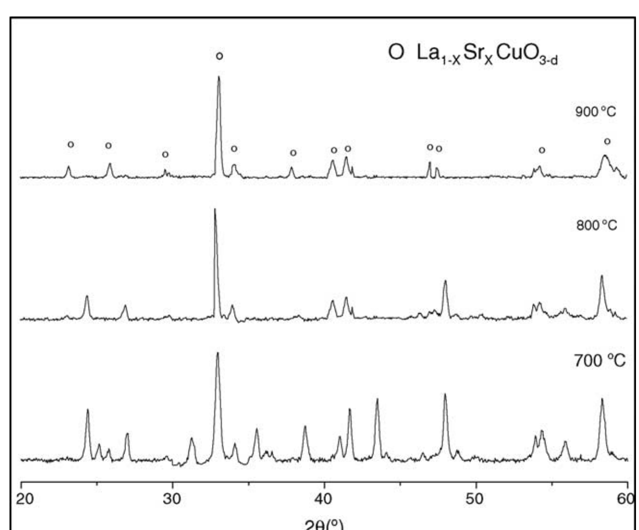

Fig. 1. X-ray diffraction patterns of $La_{0.7}Sr_{0.3}CuO_{3-\delta}$.