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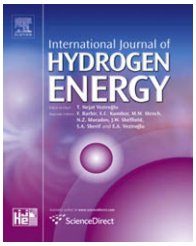

Evaluation of Sr substituted Nd_2CuO_4 as a potential cathode material for intermediate-temperature solid oxide fuel cells

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ABSTRACT

The $Nd_{1.7}Sr_{0.3}CuO_4$ (NSCu) material with perovsikite-related structure was synthesized and evaluated as a new cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The crystal structure, thermal expansion, electrical conductivity and electrochemical performance of NSCu have been investigated by X-ray diffraction, a dilatometer, DC four-probe method, AC impedance and cyclic voltammetry (CV) techniques. The polarization resistances of NSCu cathode on Sm-doped ceria (SDC) electrolyte in air were $0.07\ \Omega\ cm^2$, $0.24\ \Omega\ cm^2$ and $1.60\ \Omega\ cm^2$ at 800 °C, 700 °C and 600 °C, respectively. The results demonstrated that both impedance and CV methods are consistent with high exchange current density i_0 (390.7 mA/cm^2 and 76.1 mA/cm^2 at 800 °C and 700 °C.), making NSCu a promising cathode material for the IT-SOFCs based on doped ceria electrolytes.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical power generation devices which are attracting more and more attention due to their high efficiency, low emission, and excellent fuel flexibility. Typical SOFCs operate at high temperature (~1000 °C), which introduces a series of problems such as high reactivity between cell components, material compatibility and fabrication cost [1–3]. Therefore, there is an increasing interest in intermediate-temperature solid oxide fuel cells (IT-SOFCs) operated in the range of 500–800 °C [4–6].

As the operating temperature of SOFCs is lowered, the cathode–electrolyte interface begins to limit the cell performance [7]. The development of new cathode materials with low polarization resistance is therefore of great importance. Significant mixed ionic–electronic conductivity has been reported in materials of the K_2NiF_4 structure type, primarily on the La_2NiO_4 and La_2CuO_4 systems [8–13]. From the preliminary studies it is evident that the K_2NiF_4 type materials show considerable promise as potential cathode for IT-SOFCs.

Many of the layered cuprate compositions have previously been investigated with respect to their superior electrical properties at low temperatures, and evaluated the potentials as cathode materials. Li et al. [12] have investigated $La_{2-x}Sr_xCuO_{4-\delta}$ ($x = 0.1, 0.3, 0.5$) series oxides as prospective cathode for IT-SOFCs based on ceria electrolytes, and $La_{1.7}Sr_{0.3}CuO_{4-\delta}$ electrode exhibited the highest performance with an area specific resistance (ASR) of $0.16\ \Omega\ cm^2$ at 700 °C in air among $La_{2-x}Sr_xCuO_{4-\delta}$ materials. Aguadero et al. [14] evaluated $La_2Ni_{1-x}Cu_xO_{4+\delta}$ as possible cathode materials and found that the total conductivity and the matching of the thermal expansion coefficient (TEC) values were fairly satisfactory while the area specific resistance (ASR) is rather high (ASR $\sim 1\ \Omega\ cm^2$ at 850 °C).

Up to now, the researches based on A_2BO_4 type oxides as cathode materials are mainly focused on La at A-site. Little attention has been paid to other rare earths like Nd or Pr

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[10,13,15,16]. Soorie and Skinner [13] have investigated $Nd_{2-x}Ce_xCuO_4$ ($0 < x \leq 0.2$) type oxides as possible cathode on both $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) electrolytes. From area specific resistance (ASR) measurements it was established that the best cathode/electrolyte combination was $Nd_{1.8}Ce_{0.2}CuO_4$ on an LSGM electrolyte. However, the investigated Ce substituted Nd_2CuO_4 exhibited relatively large ASR (two orders of magnitude worse than the existing materials).

In this study, we evaluated Sr substituted Nd_2CuO_4 as a potential cathode material for IT-SOFCs. The phase structure, thermal expansion property, electrical conductivity and electrochemical properties were investigated.

2. Experimental

2.1. Synthesis of $Nd_{1.7}Sr_{0.3}CuO_4$ powder

The $Nd_{1.7}Sr_{0.3}CuO_4$ (NSCu) powders were synthesized via a combined EDTA–citrate complexing method. EDTA (0.04 mol) was dissolved in 40 ml of 1 M $NH_3{\cdot}H_2O$ solution to prepare $NH_3{\cdot}H_2O$–EDTA buffer solution. Nd_2O_3 powder was prepared in an aqueous solution by dissolving it in diluted nitric acid with heating and magnetic stirring before applying the complexing synthesis. Then, the calculated amount of metal nitrates $Sr(NO_3)_2$, $Cu(NO_3)_3{\cdot}3H_2O$ were prepared separately as an aqueous solution and then dissolved in the above EDTA–$NH_3{\cdot}H_2O$ solution under heating and stirring. After stirring for certain time, proper amount of citric acid was added. The mole ratio of EDTA, citric acid and total metal ions was controlled around 1:1.05:1. $NH_3{\cdot}H_2O$ was then added to adjust pH values to ~6 to avoid the precipitation occurrence after citric acid addition. The solution was kept stirring and heating at 80 °C. With the evaporation of water, a dark purple polymeric resin was obtained. The samples were then baked in a drying oven at 120 °C for 48 h. Finally, the dried polymeric resin was calcined at 800 °C for 2 h under an air atmosphere. The as-synthesized powders were ball-milled by zirconia balls for 30 min to break up any agglomerations which were formed during the calcination.

2.2. Preparation of cathode

Three-electrode electrochemical cells consisting of porous NSCu working electrode (WE), silver counter electrode (CE) and reference electrode (RE) and SDC electrolyte were fabricated to test the electrochemical characteristics of the porous NSCu–SDC interface. Uniaxially pressed SDC electrolyte disks were sintered at 1550 °C for 2 h in air with the resulting dimension about 12 mm in diameter and 1 mm in thickness. The electrode pastes were prepared by mixing the calcined NSCu powder with ethylcellulose at a weight ratio of 10:1, and then mixed with terpilenol as a solvent. Then, the NSCu pastes with an area of 0.25 cm^2 were printed twice by a brush on one side of the SDC disks and then calcined at 950 °C for 2 h in air. Silver paste was brushed onto the SDC disk about 4 mm away from NSCu electrode with a ring shape and onto the other side of SDC disk as counter electrode with the same area of NSCu electrode, and sintered at 700 °C for 30 min. The Pt grids and leads were stuck with Ag current collector for the electrochemical property measurements.

2.3. Characterization

X-ray diffraction was carried out with an ARL X-ray powder diffractometer using Cu Kα radiation. For thermal expansion and conductivity measurements, the as-synthesized powders were granulated with 5 wt.% PVA and pressed into rectangular bars with nominal dimensions of $64 \times 5 \times 5$ mm^3 under 50 MPa. Then the bars were sintered at 1200 °C for 2 h. The thermal expansion of the rectangular specimens was measured from room temperature to 1073 K in air, using a dilatometer (RPZ-01, Luoyang, China), with a heating rate of 5 K/min. The electrical conductivity of sintered rectangular bars was measured in open air from 373 K to 1073 K using DC four-terminal method. Electrochemical impedance spectroscopy (EIS) measurements of the electrode materials on the SDC electrolyte were carried out with excitation potentials of 10 mV over a frequency range from 100 KHz to 0.1 Hz generated by an impedance analyzer (CHI 660C electrochemical workstation, Chenhua, China) in the temperature range from 500 to 800 °C. Cyclic voltammetry (CV) measurements (5 mV/S) were performed using CHI 660C. The IR drop originating from the electrolyte resistance was compensated by a postfactum correction of the CVs, using the series resistance obtained from the EIS data, in order to establish the resistance-free *i–E* characteristics.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents XRD pattern of NSCu powder after calcination at 800 °C for 2 h in air. All the peaks can be well indexed as Nd_2CuO_4 perovskite-related structure with the space group of *I4/mmm*. The lattice parameters and the cell volume of NSCu are calculated to be $a = 0.3942$ nm $c = 1.213$ nm and $V = 0.1893$ nm^3, respectively.

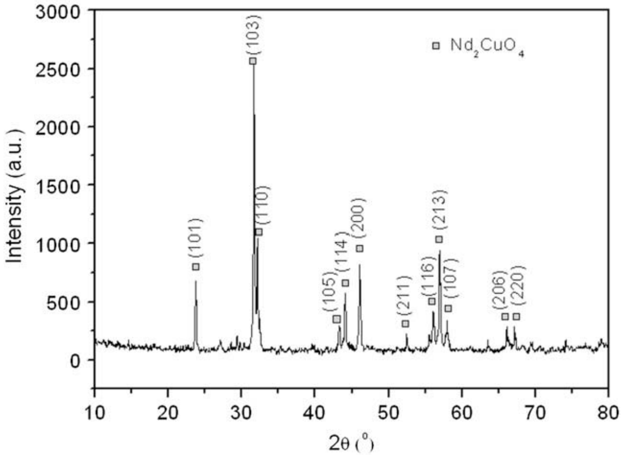

Fig. 1 – XRD pattern of $Nd_{1.7}Sr_{0.3}CuO_4$ powder calcined at 800 °C for 2 h in air.