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Electrochemical behavior of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2-x}\text{Zn}_x\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($x = 0-0.2$) perovskite oxides for the cathode of solid oxide fuel cells

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ARTICLE INFO

Article history:

Received 1 January 2011
 Received in revised form
 26 January 2011
 Accepted 26 January 2011
 Available online 15 March 2011

Keywords:

Solid oxide fuel cell (SOFC)
 Barium strontium cobalt zinc ferrite (BSCZF)
 Zinc doping

ABSTRACT

Zinc-doped barium strontium cobalt ferrite ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2-x}\text{Zn}_x\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCZF), $x = 0, 0.05, 0.1, 0.15, 0.2$) powders with various proportions of zinc were prepared using the ethylenediamine tetraacetic acid (EDTA)-citrate method with repeated ball-milling and calcining. They were then evaluated as cathode materials for solid oxide fuel cells at intermediate temperatures (IT-SOFCs) using XRD, H_2 -TPR, SEM, and electrochemical tests. By varying the zinc doping (x) from zero to 0.2 (as a substitution for cobalt which ranged from zero to 100%), it was found that the lowest doping of 0.05 (BSCZF05) resulted in the highest electrical conductivity of 30.7 S cm^{-1} at $500 \text{ }^\circ\text{C}$. The polarization resistances of BSCZF05 sintered at $950 \text{ }^\circ\text{C}$ were $0.15 \text{ } \Omega \text{ cm}^2$, $0.28 \text{ } \Omega \text{ cm}^2$ and $0.59 \text{ } \Omega \text{ cm}^2$ at $700 \text{ }^\circ\text{C}$, $650 \text{ }^\circ\text{C}$ and $600 \text{ }^\circ\text{C}$, respectively. The resistance decreased further by about 30% when $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (SDC) electrolyte particles were incorporated and the sintering temperature was increased to $1000 \text{ }^\circ\text{C}$. Compared to BSCF without zinc, BSCZF experienced the lowest decrease in electrochemical properties when the sintering temperature was increased from $950 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$. This decrease was due to an increase in thermal stability and a minimization in the loss of some cobalt cations without a decrease in the electrical conductivity. Using a composite cathode of BSCZF05 and 30 wt.% of SDC, button cells composed of an Ni-SDC support with a $30 \text{ } \mu\text{m}$ dense SDC membrane exhibited a maximum power density of 605 mW cm^{-2} at $700 \text{ }^\circ\text{C}$.

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1. Introduction

Solid oxide fuel cells (SOFCs) have been the focus of a growing amount of research in several fields because of their high electricity conversion efficiency. One of the main current issues is a focus on reducing their operating temperature. SOFCs that can be operated at intermediate temperatures ($500-800 \text{ }^\circ\text{C}$) (IT-SOFC) may have many benefits in terms of

fabrication-operating cost, cell material selection and a life span that is only limited by a mismatch in thermal expansion rates or a side reaction between cell parts [1]. Various transition metals have been investigated on the B-site of perovskite-type oxides as replacements for traditional high temperature cathode materials like LSM ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$). Among these, cobalt-based materials such as $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$, $\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, and $\text{Pr}_{1-x}\text{Ba}_x\text{Co}_2\text{O}_{5-\delta}$ have

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been actively reported as candidate materials for IT-SOFC cathodes [2–5]. It is known that cobalt-based materials exhibit excellent mixed ionic and electronic conductor (MIEC) performance in the intermediate temperature range. For example, the area specific resistance of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ is $0.01 \Omega \text{ cm}^2$ at 700°C [6].

However, cobalt-based materials have some problems associated with easy evaporation and reduction of cobalt elements or a high thermal expansion coefficient [7]. Thus, instead of cobalt, zinc has recently received attention as an attractive doping element as the cathode material of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ [8–11]. This development occurred after Wang et al. reported that as an oxygen permeable membrane in air, zinc doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ maintained chemical stability during changes in temperature and conditions of low oxygen partial pressure because of its constant oxidation state (Zn^{2+}) [12]. For example, the cathode material of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSZF) exhibits a remarkable cathode polarization resistance of $0.13 \Omega \text{ cm}^2$ at 700°C [9]. However, because zinc is in a constant oxidation state (Zn^{2+}), it can serve to block electronic conduction. This is because electron conduction in perovskite requires an overlap of oxygen's 2p orbital with the 3d of B-site metal having a variable oxidation state, also known as the Zerner double exchange process [13,14]. Therefore, an optimum doping composition for zinc must exist so that it can be used as an alternative element to cobalt.

In this study, zinc doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCF) perovskites were synthesized to be used as cathode materials for IT-SOFCs using ethylenediamine tetraacetic acid (EDTA) and citric acid as chelating agents. The level of zinc substitution for cobalt in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2-x}\text{Zn}_x\text{Fe}_{0.8}\text{O}_{3-\delta}$ (BSCZF) was varied ($x = 0, 0.05, 0.1, 0.15, 0.2$) to find the optimum value that increased chemical stability without sacrificing electronic conductivity and reactivity in the oxygen reduction reaction.

2. Experimental

2.1. Synthesis of BSCZF powders

Perovskite-type oxide powders of BSCZF ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2-x}\text{Zn}_x\text{Fe}_{0.8}\text{O}_{3-\delta}$, $x = 0, 0.05, 0.1, 0.15, 0.2$) were synthesized using the modified EDTA-citrate method [10]. Stoichiometric ratios of $\text{Ba}(\text{NO}_3)_2$ (Junsei, 99%), $\text{Sr}(\text{NO}_3)_2$ (Junsei, 97%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 99.9%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Samchun, Korea, 99%) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Samchun, 98.5%) were dissolved in an EDTA-ammonia solution (pH = 6–7). The mole ratio of EDTA to total metal cations was kept at 1.0. Under constant stirring, 1.5 mol of citric acid were added to the solution for every mole of total metal cations. To dissolve the citric acid, the solution pH was kept at 6 by adding the ammonia solution. After the dissolution was complete, the solution temperature was raised to 80°C . After a few hours, the solution turned a dark-red colored gel. After being dried in oven at 150°C overnight, the gel turned into a black powder. To increase the homogeneity of the powder, it was subjected to pre-calcination at 700°C for 1 h, and followed by ball-milling for 1 day. The ball-milled powder was sintered at 950°C for 5 h, and followed again by ball-milling for 1 day to obtain the final powder.

2.2. Preparation of cells and bars

Pellets of $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (SDC, Fuel Cell Materials, USA), having a diameter of 17 mm and thickness of 1.1 mm, were prepared by pressing the powder uniaxially and sintering at 1400°C for 3 h. A cathode slurry was prepared by mixing cathode powder with an organic vehicle (6 wt% ethyl cellulose in terpineol solution). A symmetric cell was manufactured by coating the cathode slurry on both sides of an SDC pellet using a screen printer. Cells with two different cathodes were obtained by sintering at 950°C for 4 h or at 1000°C for 3 h. The cathode area in the cell was kept at 0.28 cm^2 . Silver paste and platinum wire were attached to the electrode surface to act as a current collector.

A button cell was fabricated using an anode support that was manufactured by pressing a mixture of NiO-SDC (weight ratio of 55:45) with 35 vol% graphite (Sigma Aldrich) at 200 MPa and sintering at 1200°C for 3 h. The anode support was dipped into a slurry solution containing an anode functional layer (AFL) composed of NiO-SDC (weight ratio of 60:40). After being dried, it was sintered at 1200°C for 3 h. The electrolyte layer of SDC was then formed on the AFL layer by dipping into a slurry solution containing SDC powder and pre-sintering it at 1200°C for 2 h. After repeating the coating and pre-sintering steps several times to achieve a desired thickness, it was finally sintered at 1500°C for 3 h to form a dense layer. A cathode slurry was prepared by grinding BSCZF-SDC composite (weight ratio of 70:30) powder with an organic vehicle in an agate mortar. The slurry was then coated onto the dense SDC layer using a screen printer. Finally, a slurry of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF, Fuel Cell Materials, USA) was coated onto the cathode layer as a current collecting layer using a screen printer. The two layers of the cathode side were sintered at 950°C for 4 h, and their areas were kept at 0.28 cm^2 .

To measure the electrical conductivity, a black bar of BSCZF powder with a relative density of about 97% was obtained by pressing 1 g of BSCZF powder at 200 MPa and sintering at 1170°C for 10 h with a ramping and cooling rate of 2°C min^{-1} [10].

2.3. Characterization of powders

Phase identification of the BSCZF powder was determined by means of X-ray diffraction (X-PERT PRO with $\text{Cu K}\alpha$ radiation) analysis. Morphology of the sintered cathode layer was observed with a scanning electron microscope (JSM-7401F, JEOL). The electrochemical behavior of the symmetric cell with two electrodes was evaluated with electrochemical impedance spectroscopy (EIS) (CLB-500, BioLogic Science Instruments, France). Impedance spectra were measured at six points per decade in the range of 100 kHz to 100 mHz and at a signal amplitude of 5 mV at 50°C temperature intervals from 550°C to 800°C under an open-circuit state. EC-Lab software V9.98 was used to analyze the impedance spectra. Electrical conductivity of prepared bars was measured using the DC four-probe method at 20°C temperature intervals from 300°C to 800°C using the galvanostatic mode of the CLB-500 in air. Temperature-programmed reduction (TPR) was carried out using a fixed-bed reactor with 0.2 g BSCZF powder in 5 vol.% H_2 in argon (flowing at 30 mL min^{-1}) from 0 to 900°C with

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