INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–8

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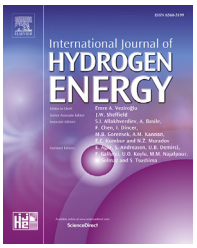

Synthesis and electrochemical properties of layered perovskite substituted with heterogeneous lanthanides for intermediate temperature-operating solid oxide fuel cell

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ARTICLE INFO

Article history:
Received 27 November 2017
Received in revised form
1 April 2018
Accepted 2 April 2018
Available online xxx

Keywords:
Intermediate temperature-operating solid oxide fuel cell (IT-SOFC)
Phase synthesis
Cathode
Electrical conductivity
Area specific resistance (ASR)

ABSTRACT

In this study, phase synthesis and electrochemical properties of $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ ($x = 0–0.9$) oxide systems where neodymium and samarium were replaced at the A-site of $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ layered perovskite are investigated for use as cathode materials in Intermediate Temperature-operating Solid Oxide Fuel Cells (IT-SOFCs).

The structure of $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ ($x = 0–0.9$) oxide systems can exist in either an orthorhombic ($x = 0–0.4$) or tetragonal ($x = 0.5–0.9$) form. The maximum electrical conductivities in $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ ($x = 0–0.9$) oxide systems were obtained from $Sm_{0.2}Nd_{0.8}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SNBSCO8) and their values are 1280 and 280 Scm^{-1} at 50 °C and 900 °C, respectively. The area specific resistances (ASRs) of SBSCO are 3.019, 0.611, and 0.092 Ωcm^2 at 500, 600, and 700 °C, respectively. However, SNBSCO8 single phase gives the lowest ASRs of 1.751, 0.244 and 0.044 Ωcm^2 at the same temperatures tested. SNBSCO8 is thus a promising candidate cathode material for IT-SOFC applications.

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https://doi.org/10.1016/j.ijhydene.2018.04.011
0360-3199/

Introduction

Solid Oxide Fuel Cells (SOFCs) are energy devices that converts chemical energies of oxygen and hydrogen to electrical energy directly through the electrochemical reaction between hydrogen and oxygen at high temperature ranges. They are more efficient than thermal power generation and are attracting attention as environmentally friendly renewable energy devices because H_2O is produced as a byproduct [1,2].

The high temperature operating conditions of SOFCs, for example from 700 °C to 1000 °C, afford the advantages of increasing/enhancing the activities of the electrode and the electrolyte. However, high temperature stability problems in electrodes, chromium poisoning, a durability issue of the metal material constituting the SOFC, and oxidation problems have been arisen [3–5].

One of the strategies to solve these problems of SOFCs is to reduce the operating temperature to an intermediate temperature range. However, the relatively lower temperature condition can decrease the activity of the electrode, including cathode and anode, as well as increase the ohmic resistance of the electrolyte. The major source of voltage loss caused by polarization of intermediate temperature solid oxide fuel cell (IT-SOFC) operation is mainly related to cathode materials. Therefore, new cathode materials showing highly advanced electrochemical catalytic properties have been studied by researchers focused on IT-SOFCs [5–7].

Recently, layered perovskite oxides showing chemical compositions of $A'A''B_2O_{5+d}$ have been investigated and applied to the cathodes of IT-SOFCs based on their superior oxide ionic diffusivity, excellent oxygen surface exchange coefficients, high oxygen transport properties and higher electronic conductivity for layered perovskite oxide systems [8–10].

In the case of layered perovskites, lanthanides such as La, Pr, Nd and Sm can be replaced with A′-site and Ba or Sr can also substituted into the A″-site of layered perovskites [8–10]. In order to enhance electrocatalytic properties of layered perovskites, transition elements of Co, Fe, Mn, Ni, and Cu can be substituted into the B-site of layered perovskites [11–13]. IT-SOFC cathodes using $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO) were synthesized by replacing La with Sm in an oxide system of $LnBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ and excellent electrochemical properties of the SBSCO single phase and 50 wt% SBSCO and 50 wt% CGO91 (10 mol% gadolinia-doped ceria) (SBSCO:50) were reported by our groups [14]. For example, for the area specific resistances (ASRs) of SBSCO:50, the lowest values were 0.10 Ωcm^2 at 600 °C and 0.013 Ωcm^2 at 700 °C.

In addition, the electrochemical properties and the long-term performance of an in-situ SBSCO:50 cathode were also characterized for metal supported solid oxide fuel cell (MS-SOFC) application. From these measurements, the ASRs of an in-situ SBSCO:50 were 0.031 Ωcm^2 in the first stage of measurement at 700 °C and 0.046 Ωcm^2 after 1000 h. Significantly, the difference in the ASR of in-situ SBSCO:50 cathode was only 0.015 Ωcm^2 for a 1000 h operation period [15].

In the synthesis of $LnBa_{0.5}Sr_{0.5}Co_2O_{5+d}$, single lanthanide element is generally substituted into the A′-site of a layered perovskite. On the other hand, no case where two or more kinds of lanthanide are substituted at the A-site and applied to the cathode of a SOFC has not been reported thus far. In this light, the aim of this study is to investigate phase synthesis characteristics of $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0–0.9) oxide systems where neodymium (Nd) and samarium (Sm) elements were stepwise replaced at the A-site of a $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ layered perovskite by using the glycine nitrate process (GNP). Significantly, electrochemical properties of $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0–0.9) were also analyzed to determine its suitability as a cathode material for direct application to IT-SOFCs.

Experimental

Sample preparation and X-ray diffraction measurement

Samarium nitrate ($Sm(NO_3)_3$–$6H_2O$), neodymium nitrate ($Nd(NO_3)_3$–$6H_2O$), barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), and cobalt nitrate ($Co(NO_3)_2$–$6H_2O$) were used for the synthesis of $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0–0.9) in which neodymium (Nd) was stepwise replaced at the A-site of a $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO) layered perovskite. The chemical compositions and their abbreviations in the oxide system of these cathodes are summarized in Table 1.

Using the glycine nitrate process (GNP), the starting materials described above were weighed in a stoichiometric mole ratio. The mole ratio of glycine for combustion was three times the moles of $(NO_3)_3$ and $(NO_3)_2$ nitrates. These raw materials were dissolved completely with nitrates and glycine in deionized water. The solution for GNP was evaporated at 300 °C under stirring on a hot plate and then the ashes were calcinated at various temperatures for 3 h at a heating rate of 5 °C/min to thermally decompose the remaining nitrate-glycine mixture and to convert these mixtures to single phases of $Sm_{1-x}Nd_xBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (x = 0–0.9). In order to confirm the single phases of oxide systems, X-ray diffraction (XRD, Model D/MAX 2500 H, RIGAKU) measurements were carried out using Co Ka radiation operated at 40 kV and 45 mA. The obtained data were matched with the results in previously reported studies [14,16].

Chemical reactivity

For the reactivity of $Sm_{0.2}Nd_{0.8}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SNBSCO8) and electrolyte materials, two electrolytes, commercial 10 mol % gadolinia-doped ceria ($Ce_{0.9}Gd_{0.1}O_2$, CGO91, Rhodia) and

Table 1 – Abbreviations of layered perovskite materials.

Chemical composition	Abbreviations
$Sm_{0.9}Nd_{0.1}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO1
$Sm_{0.8}Nd_{0.2}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO2
$Sm_{0.7}Nd_{0.3}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO3
$Sm_{0.6}Nd_{0.4}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO4
$Sm_{0.5}Nd_{0.5}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO5
$Sm_{0.4}Nd_{0.6}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO6
$Sm_{0.3}Nd_{0.7}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO7
$Sm_{0.2}Nd_{0.8}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO8
$Sm_{0.1}Nd_{0.9}Ba_{0.5}Sr_{0.5}Co_2O_{5+d}$	SNBSCO9
$SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$	SBSCO
$Ce_{0.9}Gd_{0.1}O_{2+d}$	CGO91

Please cite this article in press as: Song SW, et al., Synthesis and electrochemical properties of layered perovskite substituted with heterogeneous lanthanides for intermediate temperature-operating solid oxide fuel cell, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.011