$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Perovskite Anode for Solid Oxide Electrolysis Cells

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Abstract

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) anode is synthesized by citrate-EDTA complexing method. Metal nitrate with required molar ratios is used as a precursor while the solution of EDTA and citric acid are used as complexing agents. 25%vol of ammonia solution is used to adjust the solution pH value. Aqueous precursor solutions are dried at 110°C and subsequently calcined at 950°C for 4 h. The crystallinity, morphology, specific surface area and structural stability were investigated by X-ray diffraction (XRD), Scanning electron microscope (SEM), Nitrogen adsorption and Thermogravimetric analysis (TGA), respectively. The synthesized BSCF is fabricated as an oxygen electrode in cathode-supported solid oxide electrolysis cells (SOEC). The electrochemical performance measurement is carried out when the operating temperature is controlled between 600 to 900 °C with the feed containing humidified hydrogen at cathode chamber using varied steam to hydrogen ratio (60:40, 70:30 and 90:10). Furthermore, comparing between the electrochemical performance of commercial and synthesized $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is discussed.

Keywords: Solid oxide electrolysis cell**,** Perovskite oxide, Barium strontium cobalt ferrite, BSCF, anode

1. Introduction

Nowadays renewable and green energy has been worldwide interest. Solid oxide electrolysis cell (SOEC) is a promising technology for hydrogen production through steam electrolysis since it can produce pure hydrogen without purification unit. However, SOEC performance is still limited by poor electrocatalytic activity at the anode, leading to a lower oxygen permeation reaction. Perovskite anode offers fast kinetics and high efficiency with the formula of ABO_3. The crystal perovskite structure consists of A and B site, where A site is either rare earth or alkaline earth and B site can be transition metals, allowing oxygen ion and electron conductivity - mixed ionic and electronic conductivity property. Goldschmidt tolerance factor (t) indicates the distortion and stability of the crystal structures. It is the relationship between the radii of the various ions. In general, the tolerance factor can deviate from the ideal perovskite structure which can calculate from the equation (1)

$$t = \frac{(r_A + r_O)}{\sqrt{2}\,(r_B + r_O)} \qquad (1)$$

where r_A, r_B and r_O are the ionic radii of the A, B cations and oxygen anion, respectively. The structure with the tolerance close to 1.0 at high temperature is the ideal perovskite. The cubic perovskite structure is stable in the range $0.8< t < 1.0$, while $t >1.0$ preferred for the hexagonal structure (Egorova et al, 2015). For the conventional perovskite materials used as anode in SOEC, the A site usually La, Ba and Sr, while the B site is the transition metal such as Mn, Co and Fe (Jiang et al, 2014). Our previous work compared Sr-doped $LaMnO_3$ (LSM) mixed with 8% mol yttria-stabilized zirconia (YSZ) with BSCF. It was found that BSCF exhibited higher activity, but lower stability (Kim-Lohsoontorn and Bae, 2011). Moreover, cobalt based perovskite oxide has gained much attention, especially $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$(SCF). The SCF shows high performance on the oxygen permeability at intermediate temperature, but has rather limited structural stability in reducing temperature. To improve this material, the SCF can be developed by partial substituting Sr with Ba in perovskite structure. It was reported that partial substitution of Sr with Ba helps improving BSCF in terms of phase stability and oxygen permeation because the Ba^{2+} cation has a much greater covalent bond on the perovskite structure (Shao et. Al, 2000). Hence, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is a potential candidate for SOEC anode. In this study, $Ba_{0.5}Sr_{0.5}$ $Co_{0.8}Fe_{0.2}$ (BSCF) perovskite was synthesized using citrate-EDTA complexing method. The synthesized BSCF was compared with commercial BSCF under the same conditions. The electrochemical performance of the SOECs having synthesized and commercial BSCF was investigated.

2. Experimental

2.1 Materials synthesis and characterization

The BSCF powder was synthesized by citrate-EDTA complexing method. Perovskite material with the formula $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) was synthesized using the salts of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$. Firstly, ethylenediaminetetraacetic acid (EDTA) was mixed with NH_4OH solution to make a NH_3-EDTA solution. Then, the desired molar ratio of metal nitrate was added in combined solution which was heated and stirred. After that, the amount of anhydrous citric acid was added with 0.06 mol. The mole ratios of EDTA: total metal ions: anhydrous citric acid were 1: 1: 1.5. The pH of the mixture was adjusted to 6 by 25%vol ammonia solution. After continuously stirred for 24 h. and heated at 120°C, the sticky gel was formed. For heat treatment, the gelled BSCF precursors were drying in oven at 110°C for 24 h. Finally, the samples were calcined at 950°C for 4 h. to obtain the BSCF powder. The crystallinity, morphology, specific surface area and structural stability were investigated by X-ray diffraction (XRD), Scanning electron microscope (SEM), Nitrogen adsorption and Thermogravimetric analysis (TGA), respectively.

2.2 Solid oxide electrolysis cell fabrication

The SOECs with the configuration of Ni-YSZ/ YSZ/ BSCF were used in this investigation. NiO powder and 8% mol yttria-stabilized zirconia (YSZ) were mixed in a weight ratio of 60:40 and ball-milled for 24 h using ethanol as the media. The mixed powder was pressed into pellets for 30s, then sintered at 1100°C for 2 h to obtain a button-type cathode-supported cell. Then, the YSZ electrolyte slurry was coated on one side of the cathode by dip coating technique. The YSZ dipped cathode was sintered at 1450°C for 4 h. Then, the BSCF ink was painted onto YSZ electrolyte with the circular area of 0.19 cm^2, followed by sintered at 1000°C for 2 h. The electrical

connection was made to the both electrodes of the SOEC via platinum wires and paste. Finally, the cell was placed in the reactor and sealed with the glass sealant (Ultra-Temp 552, Aramco, USA).

3. Results and discussion

The XRD patterns of the BSCF synthesized by citrate-EDTA complexing method and commercial BSCF are shown in Fig.1. Both of the BSCF samples exhibited identical peak positions. The synthesized BSCF showed single phase and cubic structure as same as commercial BSCF. Sharp peaks were observed from both samples, indicating highly crystallinity. It can be seen that synthesized BSCF exhibited higher intensity XRD peaks when compared with commercial BSCF, indicating higher crystallinity and larger average crystallite size (58 and 25 nm for synthesized BSCF and commercial BSCF, respectively)

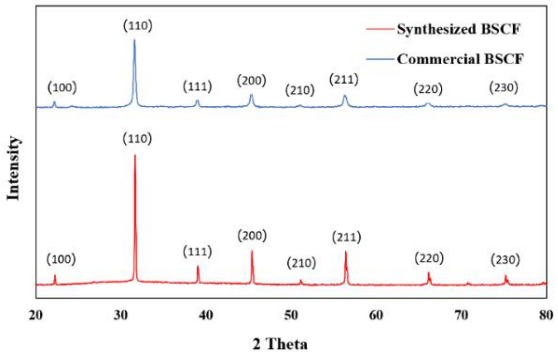

Fig.1 XRD patterns of synthesized BSCF after calcined at 950°C for 4 h. compared with commercial BSCF

Typical SEM images of synthesized BSCF and commercial powder are shown in Fig.2 and Fig.3, respectively. After calcining at 950°C for 4 h, the BSCF powder agglomerated, corresponding to the relatively larger crystallite size in synthesized BSCF. It also should be noted that particle sizes of the synthesized and commercial BSCF was rather irregular and particle size distribution was rather large. BET surface area of the commercial BSCF and synthesized BSCF were 4.32 m^2/g and 5.58 m^2/g, respectively.

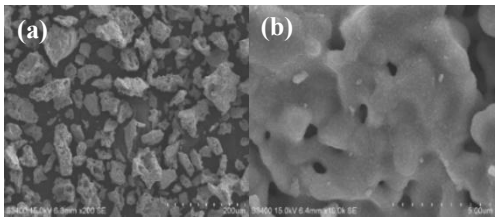

Fig.2 SEM photographs of (a) synthesized BSCF which calcined at 950°C for 4 h. And (b) magnified scale

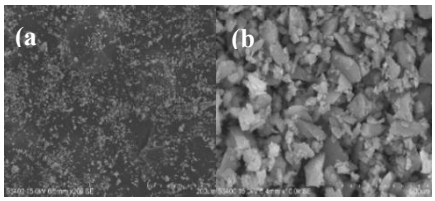

Fig.3 SEM photographs of (a) commercial BSCF which calcined at 950°C for 4 h. And (b) magnified scale

The thermal behaviour of synthesized BSCF and commercial BSCF were measured using TGA and are shown in Fig.4. The sample weight loss was measured in air and N_2 atmosphere between room temperature to 800°C to compare the thermal stability of the samples. Both samples showed weight loss during the TGA measurement. This weight loss can be affected from the reduction of metal ions Co^{4+} and Fe^{4+} to their lower valence state (Co^{3+} and Fe^{3+}) as well as the loss of lattice oxygen due to high ionic radius (Patra et. al, 2011). Commercial BSCF showed much higher weight loss in the TGA profile than the synthesized BSCF in both atmospheres (air and N_2). Weight loss in the air and N_2 of commercial BSCF was 5.81% and 4.87%, respectively, while it was 1.34% and 2.26% for the synthesized BSCF, respectively. It can indicate that synthesized BSCF using citrate-EDTA method can provide relatively high thermally stable perovskite structure even at high temperature. It was reported that BSCF exhibits stability even in low O_2 partial pressure and stability of BSCF depends on cobalt content (Ovenstone et. al, 2008). Increasing cobalt content can increase oxygen permeation but decrease thermal stability of the material.

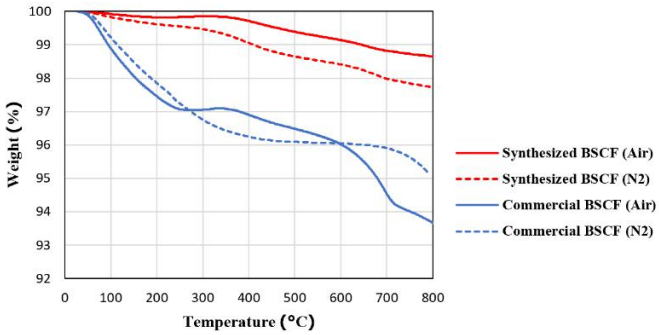

Fig.4 TGA profile of synthesized BSCF and commercial BSCF in air and N_2 at temperature between room temperature and 800 °C

Electrochemical performance of the cathode supported SOEC was measured. The I/V response of the SOEC having commercial BSCF and synthesized BSCF anode is presented in Fig.5(a) and Fig.6(a), respectively. The cell was measured between applied voltage of 0.5 to 1.8V, operating temperature range between 600 to 900 °C and steam to H_2 ratio at 70/30 (53.84% H_2O, 23.07% H_2, 23.07% N_2). The electrochemical performance is similar for both commercial BSCF and synthesized BSCF cells. The current density increased with the increasing of operating temperature. As the temperature increased from 600 to 900°C, the current density of Ni-YSZ/ YSZ/ Commercial BSCF increased from 0.038 to 0.415 A cm^{-2} at 1.5V.

Similarly, Ni-YSZ/ YSZ/ Synthesized BSCF, at 1.5V the current density increased from 0.034 to 0.433 A cm^{-2}. Variables of steam content on the electrochemical performance for both commercial BSCF and synthesized BSCF cells are shown in Fig.5(b)and Fig.6(b), respectively. At operating temperature 800 °C with steam to H_2 ratio was varied at 60/40, 70/30 and 90/10, respectively. It was observed that the open circuit voltage (OCV) decreased with increasing steam content, in accordance with the Nernst equation. According to the Nernst equation, OCV decreases from 0.97 to 0.86 when the temperature increased from 600 to 900°C (53.84%H_2O, 23.07%H_2, 23.07%N_2 at the cathode and air at the anode). However, measure OCV of Ni-YSZ/ YSZ/ Commercial BSCF was 0.76, 0.75, 0.72, 0.74, 0.77, 0.74, and 0.67 for temperature of 600, 650, 700, 750, 800, 850, and 900°C, respectively. Similarly, OCV of Ni-YSZ/ YSZ/ Synthesized BSCF was 0.63, 0.63, 0.52, 0.59, 0.57, 0.53 and 0.5. Lower measure OCV can indicate leakage in sealing around the cell.

As presented in Fig.5(b), steam content insignificantly affected the electrochemical performance of the cell. Electrochemical performance of the cell with commercial BSCF at 90/10 H_2O/H_2 ratio was slightly lower, representing by the slope of I/V graph. Mass transport limitation was observed in both cells as can be seen from the increasing slope of the I/V graph at higher current density.

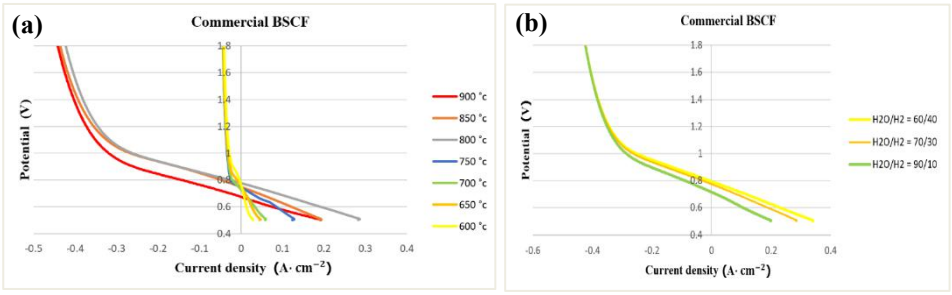

Fig.5 Cathode-supported SOEC having commercial BSCF anode
(a) effect of operating temperature (steam/H_2 = 70/30) (b) effect of steam to H_2 ratio (operating temperature at 800°C)

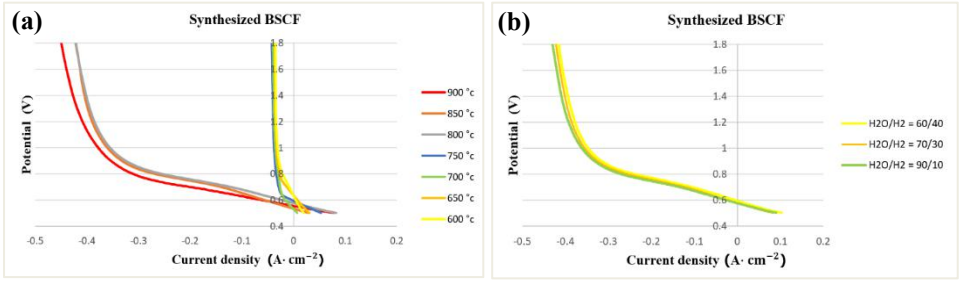

Fig.6 Cathode-supported SOEC having synthesized BSCF anode
(a) effect of operating temperature (steam/H_2 = 70/30) (b) effect of steam to H_2 ratio (operating temperature at 800°C)

4. Conclusions

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was successfully synthesized by citrate-EDTA method. Single phase perovskite was obtained by calcining the gelled BSCF precursor at temperature 950°C for 4 h. Although synthesized BSCF showed larger crystallite size comparing with commercial BSCF, the sample exhibited relatively better thermal stability. The electrochemical performance of commercial BSCF and synthesized BSCF cells were studied under different operating temperature and steam to H_2 ratio. The current density increased with the increasing of operating temperature. Steam content insignificantly affected the electrochemical performance of the cell while mass transport limitation was observed in the SOEC. The synthesized BSCF showed the performance close to the commercial BSCF.

5. References

Egorova YV, Scherb T, Schumacher G, Bouwmeester HJM, Filatova EO. Soft X-ray absorption spectroscopy study of (Ba0.5Sr0.5) (Co0.8Fe0.2)1−xNbxO3−δ with different content of Nb (5%–20%). Journal of Alloys and Compounds. 2015;650:848-52.

Jiang B, Cheng H, Luo L, Lu X, Zhang N, Liu J. Oxygen permeation and phase structure properties of partially A-site substituted BaCo0.7Fe0.225Ta0.075O3-δ perovskites. Journal of Energy Chemistry. 2014;23(2):164-70.

Kim-Lohsoontorn P, Bae J. Electrochemical performance of solid oxide electrolysis cell electrodes under high-temperature coelectrolysis of steam and carbon dioxide. Journal of Power Sources. 2011;196(17):7161-8.

Ovenstone J, Jung J-I, White JS, Edwards DD, Misture ST. Phase stability of BSCF in low oxygen partial pressures. Journal of Solid State Chemistry. 2008;181(3):576-86.

Patra H, Rout SK, Pratihar SK, Bhattacharya S. Thermal, electrical and electrochemical characteristics of Ba1−xSrxCo0.8Fe0.2O3−δ cathode material for intermediate temperature solid oxide fuel cells. International Journal of Hydrogen Energy. 2011;36(18):11904-13.

Shao Z, Yang W, Cong Y, Dong H, Tong J, Xiong G. Investigation of the permeation behavior and stability of a Ba0.5Sr0.5Co0.8Fe0.2O3−δ oxygen membrane. Journal of Membrane Science. 2000;172(1):177-88.