CHARACTERISTICS OF BSCF5582 POWDER AND FUEL CELL PERFORMANCE UNDER SINGLE CHAMBER CONDITIONS EVALUATION

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Abstract

The $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF5582) powder is synthesized as the cathode material for Single Chamber Solid Oxide Fuel Cell (SC-SOFC) $La_{1.8}Dy_{0.2}Mo_2O_9$ (LDM) based electrolyte. The crystal size, which was calculated from the XRD result, is around 48.59 nm by taken the (110) plane. The morphology of cell cross-section is good adhesion without any reaction between layers. The single cell NiO+GDC/LDM/i-GDC/GDC-BSCF5582 consisting 26µm-thick cathode generates peak power density of 200 mW/cm² at 650°C under flowing mixture of CH₄/air in temperature range of 575-675°C. The BSCF5582 can be used for SC-SOFC using LDM electrolyte under single chamber conditions.

Keywords: BSCF5582, Fuel cell, SC-SOFC

Introduction

Solid Oxide Fuel Cell (SOFC) is an electrochemical energy conversion system with high efficiency in energy conversion, high power density, fuel flexibility and inexpensive electrode materials [1, 2]. Beside many advantages, the conventional SOFC has many drawbacks due to high temperature operating. Therefore, it's needed to reduce the operation temperatures from ~ 700 – 1000 °C to intermediate temperatures (IT) range, of 500 – 800 °C [3] for chemical stability, reducing thermal expansion coefficient difference between electrodes and electrolyte layers and extend the range of acceptable material selection, etc.

Generally, when operating in the IT range, the power density is suppressed because of low activity for the electro-chemical reduction of oxygen. Thus, various perovskite oxides investigated for **IT-SOFC** have been as cathode materials such as $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ (LSCF6482), $Sm_0 Sr_0 Sr_0 CoO_3$ (SSC) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3}$ (BSCF5582) [4, 5]. BSCF5582 is discovered as prospective candidate cathode material for IT-SOFCs [6, 7, 8] due to its high rate of oxygen diffusion [1, 8, 9] and low polarization resistance [10]. Moreover, oxygen-reduction in BSCF not only is produced on the triple-phase boundary, but also on the surface of the electrode [11], that lead to improve the diffusion of the oxygen ions from the cathode surface to the cathode/ electrolyte interface.

Unfortunately, BSCF still remains some drawbacks. One of the challenges is the reaction between strontium in A site of perovskite with molybdenum in $La_{1.8}Dy_{0.2}Mo_2O_9$ (LDM) electrolyte material during heating treatment. The undesired reactions produce an interfacial-insulating layer of SrMoO₄ and Sr₃MoO₆ [6] leads to high polarization resistance at the cathode/electrolyte interface and reduce the catalytic activity. Thus, it is necessary to apply a barrier layer of Gd_{0.1}Ce_{0.9}O_{1.95} (GDC) between electrolyte and cathode layers.

Due to a promising material as cathode for IT-SOFC, BSCF5582 powder were synthesized and characterized using XRD and SEM techniques. The NiO+GDC/LDM/i-GDC/GDC-BSCF5582 cells were fabricated and evaluated under single chamber conditions using mixtures of methane and air.

Experimental

Synthesis of Powders

The $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) powders was synthesized via the citrate acid gel route [11] and the LDM powder was synthesized via solid state reaction [6, 12] as described in detail in our previous publications. To get the fine powder, GDC and LDM powder were ball milled in ethanol media using 5mm diameter zirconia balls.

BSCF5582 powder was prepared by citrate–EDTA complexing method [13] using stoichiometric amount of Ba(NO₃)₂ (>99.9%), Sr(NO₃)₂ (>99%), Co(NO₃)₂.6H₂O (>99%), and Fe(NO₃)₃.9H₂O (>99%). To obtain final powder, the gel was burned at 140°C for overnight in an electric oven, then the ash was calcined at 500°C for 2 h to obtain intermediate powder, finally this powder was re-calcined at 975°C for 2h. The crystalline phases of the BSCF5582 powder were examined by using an A D/Max-RC X-ray diffractometer (Rigaku Co., Tokyo, Japan), equipped with a CuK α radiation source. The

crystalline size was calculated by Scherrer equation [13], $D = \frac{0.9\lambda}{B\cos\Theta}$ (1)

where D is the crystalline size, λ is the wavelength of the radiation, B is the corrected peak width at half-maximum intensity and θ is the peak position.

Fabrication of the Single Cell

The porous anode supported cell was fabricated as following steps. The mixture of 1000oC calcined GDC powder, commercial NiO powder (>99.5%) and graphite flash in weight ratio of 0.34:0.51:0.15 was uniaxial pressed and sintered at 1175°C for 2 h to form porous anode in ~0.5mm thickness and ~13 .5 mm in diameter.

The LDM paste and GDC paste were described in previous publication [12]. The fine LDM powder was mixed with α -terpineol and ethyl cellulose by ball milling to get LDM paste. The LDM paste was applied on the polished porous NiO+GDC anode pellet using spin coating. The spin coating was repeated 6 times to reach the desired electrolyte thickness of ~60 m. In each time, the wet layer of LDM on anode pellet was dried in an electric oven at temperature of 500°C for 30 min. After drying, the last layer of LDM, the barrier layer of GDC was applied on the LDM layer for 1 time to form NiO +GDC/LDM/i-GDC disk. The NiO+GDC/LDM/i-GDC disk was co-sintered at 1225°C for 5h with heating and cooling rate of 2°C min-1.

To fabricate the final cell of NiO+GDC/LDM/i-GDC/GDC+BSCF5582, the paste of GDC+BSCF5582 mixture with different weight ratio was screen printing on the surface of i-GDC layer and then sintered in air at 975°C for 2h. The GDC+BSCF5582 paste were prepared in the same manner with LDM paste. Cathode is including four GDC+BSCF5582 layers in weight ratios of 7-3, 5-5, 3-7 and 1-9, in which the GDC+BSCF5582 (1-9) layer exposed in gas stream as shown in Figure 1.

The morphology of anode surface, cathode surface and the cell cross-section were examined by using a field-emission scanning electron microscope SEM (JSM6500F, JEOL, Tokyo, Japan), equipped with an energy-dispersive spectrometer for elemental analysis (INCA, Oxford, U.K.).

To evaluate performance of the cell, the chamber and the cell were set up as described in the literature [12]. Mixture of methane and oxygen was feed in the chamber with flow rate of 800sccm and CH_4/O_2 ratio of 2:1. The I–V, I–P data were collected with a Keithley 238 source-measure unit (Keithley Instruments, Cleveland, OH) after the desired furnace temperature was reached at least 10 min. The power density (P) was calculated based on the geometric area of the cathode, 0.636 cm².



Figure 1. Schematic of the NiO+GDC/LDM/i-GDC/GDC+BSCF5582 cell

Results and Discussion

XRD and Crystalline Characteristics

The X-ray diffraction patterns of the calcined BSCF5582 powder at 975°C for 2h are shown in Figure 2 These results represent that all peaks of the calcined BSCF5582 (Fig.2b) are well indexed on a cubic lattice model of $Sr(Co_{0.81}Fe_{0.19})O_{2.78}$, JCPDS No. 82-2445 [14] and well crystallized. However, all peaks shift to a lower two theta caused by partial substitution of smaller ion of Sr2+ (r=112ppm) by larger Ba2+(r=134ppm) ion. The substitution leads to larger lattice constant of a = 3.978 Å compared to un-substitution materials of a=3.849Å [14]. Moreover, the crystalline size of BSCF5582 is calculated from XRD data with the value of 48.59 nm by using the (110) plane data.

Figure 3 represents the results of scanning electron microscope SEM of calcined BSCF 5582 powder. It is seen in the SEM images that approximate particle size is between 100 and 200 nm. However, these particles are aggregate.



Figure 2. XRD pattern of 975°C calcined BSCF5582



Figure 3. SEM micrographs of the 950°C calcined BSCF 5582 for 2h

Micro Structure of Fuel Cell Base on BSCF5582

The morphology of cathode, anode surface and adhesions between layers are shown in Figure 4. Cathode, i-GDC and electrolyte thickness were measured of $26\mu m$, $5.6\mu m$ and $50\mu m$, respectively. The SEM result (Figure 4a) shows that the porous are homogeneous distributed on the anode surface. The pore size ranges from 3 to 5 μm with their shape from the plate-like graphite particles. In addition, the anode piece of 15 wt% graphite is hard enough for fuel cell fabrication, such as for screen printing.

Also shown in Figure 4b, the porous are homogeneous distributed on the cathode surface but insufficient porosity, comparing to previous sturdy [12].



Figure 4. Microstructure of the single cell NiO+GDC/LDM/i-GDC/GDC+BSCF5582

The reason of this phenomenon can be explained as the small particle size of cathode material due to the long cathode paste ball milling time of 2h. Fine powders are easily aggregate resulting less room for oxygen diffusion inside the cathode bulk for electrochemical reactions. However, microstructure of cross-section in Figure 4c shows a good adhesion between layers that promote the transportation of the oxygen ions from the cathode side to the cathode/electrolyte interface. The more oxygen ions at the interface on the cathode side, the more oxygen ions can be transferred to anode site through electrolyte layer that promote more electricity generation via the following reaction:

$$H_2 + O^2 \rightarrow H_2 O + 2e^-$$
 (2)

Fuel Cell Performance

The NiO+GDC/LDM/i-GDC/GDC-BSCF5582 cell performance using methane and air mixture is represented in Figure 5. I-V and I-P characteristics of the cell, in the flowing CH₄/air mixture, are plotted at 575, 600, 625, 650 and 675°C. The power density increases with the increasing temperature from 575 to 650°C, and then decrease as temperature above 650°C. The highest peak power density was recorded 200 mW/cm² at 650°C. The cell temperature, in the parentheses, was always higher than the furnace temperature by 31–38°C, because oxidation of methane is exothermic [12]. The peak power density value of the NiO+GDC/LDM/i-GDC/GDC+BSCF5582 cell is higher than that of the Ni-YSZ/YSZ/GDC/BSCF-GDC cell, reported by Kao et al., 191.3 mW/cm² at 750°C [15]. The peak power density value is higher than that of Kao's cell due to ionic conductivity of GDC higher than that of YSZ [16] at reduced temperatures. However, the peak power density value is still smaller than that of the Ni+GDC/LDM/ Fe-GDC/LSCF6482 cell, 220 mW/cm² at 700°C [12]. The lower power of our cell could result from the less-ideal porous cathode due to using a fine powder, that leads to densified easily. Less porous is against rate of oxygen diffusion throughout the cathode layer. Thus, oxygen concentration is not sufficient for cathode reaction lead to low electricity generated at anode side.



Figure 5. The I–V and I–P characteristics of the NiO+GDC/LDM/i-GDC/GDC+BSCF5582 cell in the flowing CH₄/air mixture at various temperatures

Conclusions

The application of BSCF5582 as cathode materials for SC-SOFC using LAMOX as electrolyte material was investigated. The cell NiO+GDC/LDM/i-GDC/GDC+BSCF5582 was operated under flowing mixture of CH₄/air in temperature range of 575-675°C. The peak power density of 200mW/cm² is not sufficient high compared to other publications. It is necessary to improve by studying the effect of cell configuration and operation conditions.

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