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Electrochemical performances of BSCF cathode materials for ceria-composite electrolyte low temperature solid oxide fuel cells

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The $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ (BSCF) cathode material was synthesized and evaluated for cathode in low temperature solid oxide fuel cells (LTSOFCs). Using Ni as anode, $Sm_{0.2}Ce_{0.8}O_2$(SDC)-carbonate composites as electrolyte and the BSCF as cathode to construct the fuel cell (LTSOFC), maximum power output of 860 mW/cm^2 has been achieved at 500 °C. The LTSOFC at a large area, 14 cm^2, has delivered 5 W corresponding to a power density of 358 mW/cm^2 at 510 °C. These results have been the first recorded for the best performance of SOFCs at low temperatures.

Keywords: BSCF; cathode; SDC-carbonate composite electrolyte; LTSOFC

1. INTRODUCTION

Low temperature (LT: 300-600 °C) solid oxide fuel cell (SOFC) is a new trend in SOFC R&D [1-3]. The high operating temperature (HT: about 1000 °C) of the conventional SOFC technology puts very high demands on the materials and technology resulting in too expensive technologies to match marketability. On the other hand, LTSOFCs can still maintain the SOFC advantages at an extremely low cost level, exhibiting great market potentials. The LTSOFC is new, having not been developed for such a long historical period due to lack of the materials. Recent developments on the ceria-based composites, e.g. SDC (samarium doped ceria)-carbonate composites have demonstrated excellent performances for LTSOFCs, showing a new generation fuel cell technology [1-4]. Continuous R & D request the compatible cathode materials that play an important role in developing advanced LTSOFCs.

Conventional SOFC cathode materials, such as perovskite oxides, e.g. $La_{1-x}Sr_xMnO_3$ (LSM), possess high stability and similar thermal expansion coefficient (TEC) with Y_2O_3 stablized ZrO_2 (YSZ) electrolyte in excellent compatibility [5-8]. However, their cathodic overpotential for oxygen reduction at temperature below 700 °C is not acceptable. Thus, developments of new cathode materials are necessary for LTSOFC.

Perovskite oxides have interesting properties, such as ionic conductivity, superconductivity, magnetorresistance and ferroelectricity. $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF) is one of the most promising cathode materials for intermediate temperature (600-800 °C) SOFCs [9, 10]. Latest developments using the Ba replacing La to obtain the $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ (BSCF) as the cathode is attractive in term of its high conductivity, excellent oxygen transport and catalytic activity. It was reported by Shao et al in Nature [11] using the BSFC as the cathode in the samarium-doped ceria (SDC) electrolyte fuel cells excellent performance of 1010 $mWcm^2$ was achieved at 600 °C, and 200 mW/cm^2 at 450 °C for a fuel cell with two chambers' construction. We further explored such BSCF cathode material for the ceria-composite electrolyte LTSOFCs to develop high performances at lower temperatures, e.g. 400-500 °C. We used the new electrolyte of the SDC-carbonate composites which have much higher conductivity than the SDC electrolyte used by Shao et al, thus, much better fuel cell performances can be expected.

2. EXPERIMENTAL PART

BSCF precursor powder was prepared by sol-gel method. To enhance the complex ability of polyacrylicaced (PAA), we adjusted the pH of the PAA solution to 3-5 with ammonia. $Ba(NO_3)_2$,$Sr(NO_3)_3.6H_2O$,$Co(NO_3)_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$ in molar ratio 0.5:0.5:0.8:0.2 were used for preparation. First, dissolving $Ba(NO_3)_2$ and $Sr(NO_3)_3.6H_2O$ into distilled water to get a mixture solution , then dripped this solution into overdosed the mixture 1.5 times PAA solution, stirring for 6h. Meanwhile another mixed solution of $Co(NO_3)_3.6H_2O$ and $Fe(NO_3)_3.9H_2O$ was prepared and, dropped into the former solution slowly, keeping on stirring for 12h to form a sol. Heated at 80 °C overnight, sol changed into gel. The obtained gel was dried at 120 °C for 12h to get a gel precursor. The Precursor powder was calcined at 1100 °C for 2h.

The crystal structure of the powder was analyzed by D/MAX-3A X-RAY diffractometer with Co Ka radiation, 35kv voltage and 30mA current. The morphology of the powder was examined in a Philips 330 scanning electron microscope (SEM).

The fuel cell MEA (membrane electrode assembly) was constructed using a composite anode-supported technique. The composite electrolyte was prepared by mixing the SDC carbonate composite electrolyte according to the weight ratio of 80% SDC : 20w% binary carbonates (67mol% Li_2CO_3:33 mol% $NaCO_3$). The mixtures were ground following a sintering at 650 °C for 0.5-1.0 h in air. The resulted material was ground again used for fuel cell electrolytes. The anode powder was composed of NiO with the as-prepared composite electrolyte (50 vol%:50 vol%) and the cathode was made in the same way by using the BSFC to replace the NiO. The fuel cell disk was made by directly pressing the composite electrolyte and composite anode and cathodes. In this construction, the fuel cell MEA had the electrolyte layer 0.2-0.3 mm thick and the electrode layers 0.7-0.8 mm in thickness, respectively. The fuel cell MEA was then heat-treated at 600 °C for 0.5h. The silver paste was covered on the cathode as current collector. Stainless steel was adopted for fuel cell device holder. The total cell size had 13 mm in diameter with an active electrode area about 0.7 cm^2 and around 1 mm in thickness. Meanwhile, a fuel cell device with a large active area of 14 cm^2 in a 4×4 cm^2 electrode is also constructed by hot pressing process. The fuel cell device was constructed with two chambers for anode and cathode, respectively. The gas flow was controlled in around 40ml/min hydrogen under 1 atm pressure, and in 80ml/min air for the 0.7 cm^2 active area fuel cell and 800ml/min hydrogen with 1 atm pressure and 1500ml/min air for the 14 cm^2 large active area fuel cell. The measurements were carried out between 400 °C and 510 °C.

3. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the powder BSCF calcined at different temperature were shown in Fig.1. It can seen from Fig.1 that a cubic perovskite structure could be formed after calcined at 800 °C, but its diffraction peaks were very weak and broad, indicating the BSCF powder was not crystallized completely. In addition, some additional unknown phases were found which may be indexed as Fe_3O_4, Co_3O_4 and SrO (or BaO). By increasing the sintering temperature, the additional phase diffractions disappear and the dominating phase peaks are strengthened, see Fig. 1.

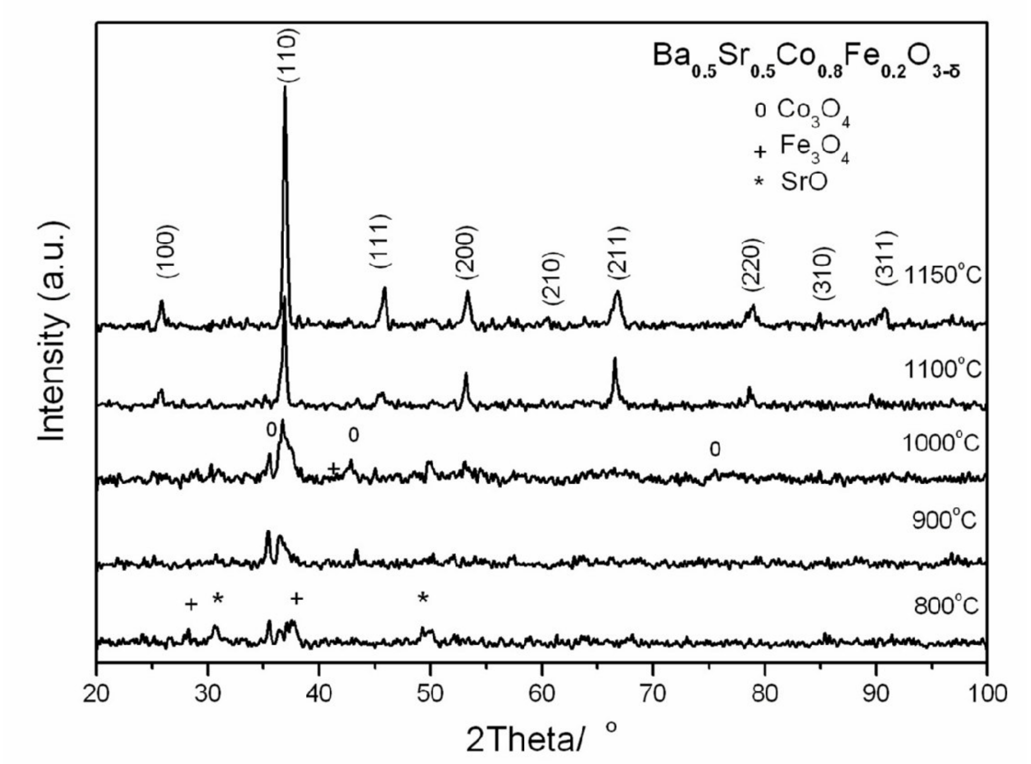

Figure 1. The XRD patterns of samples at different calcination temperatures

The single cubic perovskite structure of the BSFC was obtained after calcined at 1100 °C. After sintered at 1150 °C, the BSCF phase diffraction peaks turn to stronger and sharper. These results showed that the BSCF may be well crystallized after sintered at 1150 °C. The lattice constant a =

0.3948 nm is obtain by an average value calculating with 2θ for (211), (310), (311) peaks in the XRD pattern. It is also consistent with that reported by Shao et al [11]. The morphology of the BSFC powder analyzed by SEM showed the particle size of the powder being about 1~2μm.

Structure stability of the BSCF is concerned as an issue, especially in a deoxidized environment. BSCF is resulted from the substitution of Sr^{2+} partially by Ba^{2+} for the $SrCo_{0.8}Fe_{0.2}O_{3-d}$ (SCF). For SCF material its perovskite phase structure is thermodynamically stable only at higher temperature (>790) [12] and Ba^{2+} substituted BSCF does not undergo such a phase transition. It is expected that the suppression of oxygen vacancy ordering and phase transition thus result in significant ion conductivities at lower temperatures suitable for LTSOFC cathode applications with good performance due to its high conductivity.

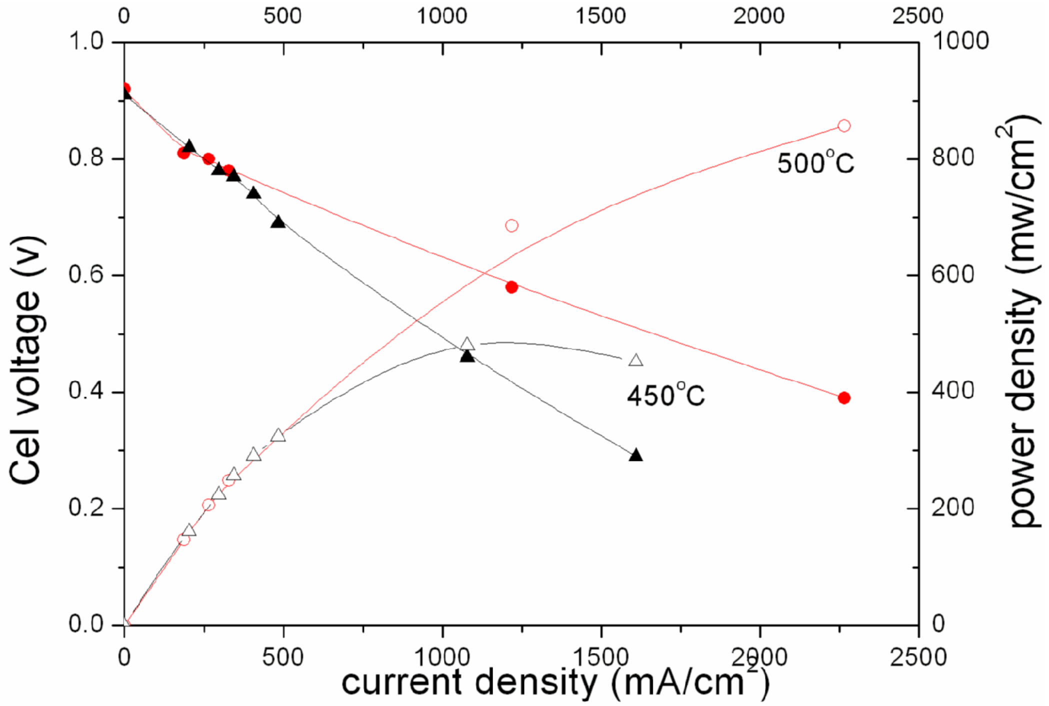

Figure 2. I-V and I-P curves of the cell at different temperatures 450 °C and 500 °C

Using the BSCF cathode for the SDC-carbonate composite electrolyte LTSOFCs, we found that the open circuit voltage (OCV) reached at a relatively stable value until the temperature increasing to a certain high value, e.g., 450 °C. Below this temperature, the as-prepared BSCF did not possess sufficient catalyst function, resulting thus in much lower fuel cell voltages. This could be improved by further optimizing and adjusting the composite cathode pore and microstructures in order to enhance the three-phase reaction area and catalyst functions. Figure 2 shows the characteristics of the fuel cell characteristics for voltage (V), current density (I) and power density (P) at 450 and 500 °C. It can be seen clearly from Fig. 2 that the maximum power density of 860 mW/cm^2 and 540.1mW/cm^2 with the short circuit currents of 2300 mA/cm^2 and 1604mA/cm^2 were obtained at 450 °C and 500 °C, respectively. In this case of using the SDC-carbonate composite as the electrolyte, the cell OCVs, power density, and current density were much higher than those obtained from the pure SDC electrolyte because the SDC-composite electrolytes improve ionic conductivity and chemical stability of the SDC [1-3]. The SDC-carbonate composite electrolytes have been reported possessing superionic conduction [13] and dual oxygen ion and proton conductivity [2, 14]. In addition, the SDC-carbonate composite is stable in the fuel environment by suppressing effectively the electronic conductivity [1-3]. The conductivity of 10^{-1} Scm^{-1} level was reported at 500 ^{o}C for the SDC-carbonate [2] which is comparable to the conductivity of the pure SDC at 800 ^{o}C and YSZ at 1000 ^{o}C. High conductive SDC-carbonate composite electrolytes can thus guarantee high performance fuel cells at low temperatures. Considering the thickness of the electrolyte in 0.2-0.3 mm, it can be commented that the power density of the fuel cell using the BSCF cathode was satisfactorily high for operating at low temperatures, and still have large potential to improve the fuel cell performances in case of the thinner electrolyte used.

On the other hand, the Ag paste used as the current collector in our case may also influence the results, especially at high current outputs due to the Ag particles scattered on the surface of the cathode. The formation of the Ag particle network on the cathode surface affects the current collecting effect then the power outputs. The Ag particles, about 10-nm size on average, are distributed on the surface of the BSCF and SDC-carbonate composite cathode. The pores formed by BSCF and SDC-carbonate may not be completely filled with Ag, because the coagulation of Ag and its non-uniformed distribution on the surface of the cathode. If we take Ag particles as hemispheres and the surface of the BSCF–SDC-carbonate layer as flat, we can estimate the surface area of Ag, the length of the cathode/Ag three-phase boundary and the covered area of the composite cathode BSCF–electrolyte (SDC-carbonate) surface by Ag particles, which can directly influence the current thus power outputs.

The long stability for the SDC-carbonate electrolyte fuel cells have been evaluated by Huang et al at larger areas, 3.14 cm^2 [15]. The similar results were also reported in our previous work [2, 3]. Several hundreds of hour operations and several-months life operation without significant degradation were reported to demonstrate the long-term stability of the investigated fuel cell system. However, the FC demonstrations have been reported so far in literature usually in the laboratory level with small areas, e.g. 0.7 - 3.2 cm^2 [1-3, 11, 15]. These sizes are still far away from applications. From the laboratory to applications needs tremendous efforts to scale up the fabrication technologies for large area cells. We have made successful fabrication on the large area cells, e.g. 4 x 4 cm^2 with an active electrode area of 14 cm^2. Figure 3 shows the I-V and I-P characteristics for this 14 cm^2 fuel cell operated at various temperatures between 400-510 ^{o}C. It can be seen for such a large area cell that the BSCF cathode material demonstrate again the excellent fuel cell performance. At 510 ^{o}C it can deliver around 5 W, corresponding an output power density above 358 mW/cm^2, meeting successfully commercial requests. It is well known in the scaling up process, critical technical efforts and requirements are needed to maintain the high performance obtained for the small size cells. It is general true the cell size scaling up process can cause significant performance loss. For example, the 3.14 cm^2 (active electrode area) FC reached only 490 mW/cm^2 at 550 ^{o}C compared to the smaller size 0.7 cm^2 reaching 860 mW/cm^2, but 358 mW/cm^2 for 14 cm^2 reported in this work. It can be sure that more technical efforts will certainly improve the cell performances at large areas. Therefore, there is still large potential to improve the performance by optimizing the fabrication techniques and protocols based on more skilled efforts. It should be stated that these results reported in this work are the best

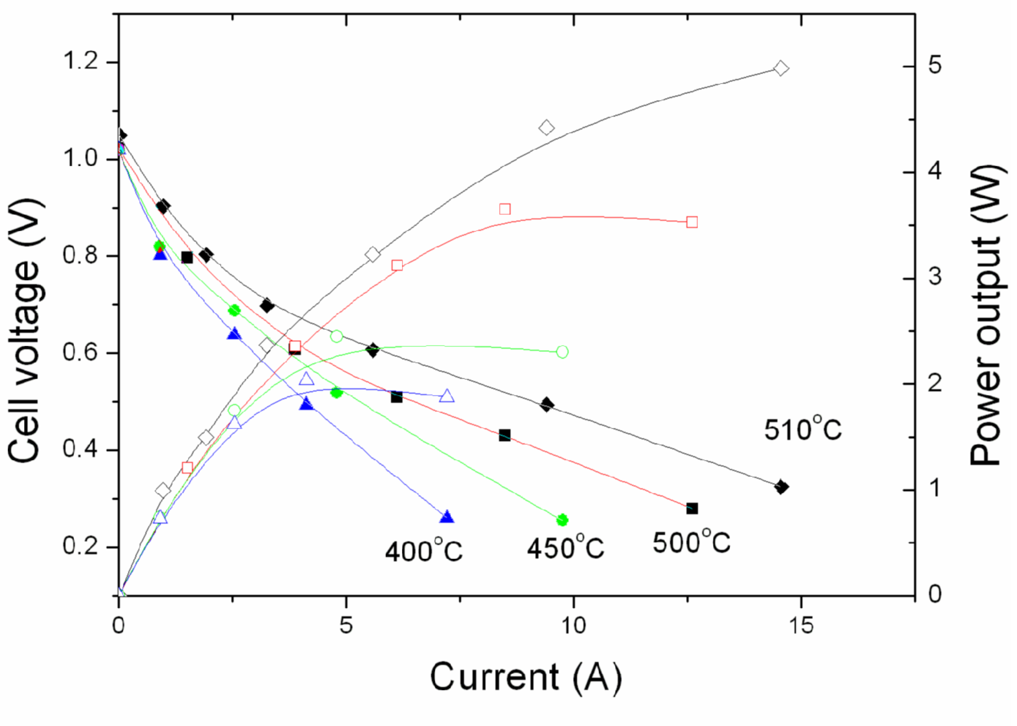

Figure 3. I-V and I-P curves of the 14cm^2 single fuel cell unit at different temperatures 400°C to 510°C

SOFC performance first recorded for both small and large areas with the BSFC cathode at such low temperatures. These results have also demonstrated again the excellence of the BSFC cathode properties for LTSOFCs.

4. CONCLUSIONS

The sol-gel method was used to prepare the BSCF cathode material. Complete crystalline structure of the proveskite oxide was formed after sintering at 1100 °C with the average particle size was between 1-2 um. The electrochemical behaviors of the BSCF material used as the cathode for the SDC-carbonate composite electrolyte fuel cell have been examined with excellent power outputs of the maximum power density of 860 mW/cm^2 and 540.1mW/cm^2 at 450 °C and 500 °C, respectively. Even at large area (14 cm^2) the BSCF cathode FC can still deliver 358 mW/cm^2 and 5 W at 510 °C. The present work has exhibited the BSCF as a type of the favorable cathodes for the ceria-composite electrolyte fuel cells operating at low temperatures to achieve excellent performances.

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