Crystal Structure and Ionic Conductivity Study of Ni- Doped BSCF Cathode for Low Temperature SOFCS

Suman Kumar Burnwal and P. Kistaiah

Abstract--- Nickel doped BSCF ($Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_{0.6}Ni_xO_{3-\delta}$ (BSCF_{Ni}); $x=0.05, 0.1, 0.15$, and 0.2) cathode materials were synthesized using sol-gel citrate method for low temperature ($300-500^\circ\text{C}$) Solid Oxide Fuel Cell (SOFC) application. The nanopowders of BSCF_{Ni} were then calcinated at various temperatures in the range of $600-1000^\circ\text{C}$. The nanopowders were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM) and differential scanning calorimeter (DSC). A cubic perovskite structure was observed in the X-ray diffraction measurements. The average crystallite size of the nanopowder obtained varies between $40-60\text{ nm}$. DSC result, measured in the temperature range of $200-600^\circ\text{C}$, shows no phase transition. Ionic conductivity of the BSCF_{Ni} for varying concentration of nickel was measured in the temperature range of 200°C to 500°C . An emphasis is made on the effect of Ni doping on these properties.

Keywords--- SOFC, Nanopowders, Cathode, Ionic Conductivity

I. INTRODUCTION

THE use of Solid Oxide Fuel Cells (SOFCs), which represent the cleanest, most efficient and versatile technologies for chemical-to-electrical energy conversion, could significantly reduce the production of greenhouse gases while minimizing pollutant emission. SOFC technology faces major problems, on the way to commercialization, such as long term stability, production cost and high operating temperature. On the one hand, high temperatures limit the choice of materials and complicate the production process, degradation phenomena on the other hand, which restrict the life time of SOFC, are more problematic at higher temperatures. One important goal in SOFC research is therefore the search for cathode materials which offer a sufficient electrochemical performance already at intermediate temperatures ($873-1073\text{ K}$). Design requirements for cathode are: high electronic conductivity and ionic conductivity, moderate thermal expansion coefficient with stability similar to other SOFC materials (usually the electrolyte), large triple phase boundary, low area specific resistance (ASR), catalyze the dissociation of

oxygen and low electrode resistance [1, 2]. Most of these characteristics are possessed by the MIEC and its composite materials.

Reduction of the operation temperature in SOFC system has a vital importance in reducing the cost of the system, which is an inevitable path for the commercialization of this technology. A key obstacle to reduced temperature operation of SOFC is the poor catalytic activity of traditional cathode materials like Lanthanum Strontium Manganites (LSM) for electrochemical reduction of oxygen in the temperature range of $300-500^\circ\text{C}$. However, mixed electronic and ionic conductors (MIEC), such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) and $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (BSCF), attract much attention as cathodes due to their unique ability to improve SOFC performance which depends on the oxygen incorporation reaction.

MIEC perovskite oxide (ABO_3) is widely considered as an ideal cathode material for low and intermediate temperature solid oxide fuel cell. BSCF perovskite is a new material with high catalytic activity, which means that oxygen atoms can be oxidized as ions as efficient as possible i.e., good oxygen permeability, and it shows an excellent performance as cathode on ceria electrolyte in low temperature range from $400-600^\circ\text{C}$ [3]. According to E. Bucher BSCF is well known to transport a significant amount of oxygen anions via oxygen vacancies, the ionic conductivity value found is 0.018 S/cm at 700°C [4].

In the present work, the emphasis is put on Ni doped BSCF perovskite i.e., $Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_{0.6}Ni_xO_{3-\delta}$ (BSCF_{Ni}) for low temperature ($200-500^\circ\text{C}$) application as cathode of SOFC. The paper presents the effect of porosity, low sintering temperature results in high porosity, on the ionic conductivity of the samples. From the study it is found that BSCF_{Ni} with Ni concentration $x=0.15$ shows the highest ionic conductivity.

II. EXPERIMENTAL WORK

Citrate method is used for the preparation of the samples of $Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3-\delta}$ (BSCF_{Ni}) powder in the present work. Initially, the nitrate salts of Barium [$Ba(NO_3)_2$]; Strontium [$Sr(NO_3)_2$]; Cobalt [$Co(NO_3)_2 \cdot 6H_2O$]; Iron [$Fe(NO_3)_3 \cdot 9H_2O$]; and Nickel [$Ni(NO_3)_2 \cdot 6H_2O$] are mixed in their stoichiometric ratio in double distilled water and stirred it for hours till the complete salts gets dissolved. To this solution citric acid is added in the ratio of 1:1 and again stirred for hours till homogeneous solution is obtained. The pH of the above solution is adjusted to 7 by adding ammonia solution

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and heated for hours at 85 °C and the sol is changed into gel. The gel formed is heated at 120 °C for 8 hrs, resulting in the formation of the black precursor powder of BSCFNi.

To increase the homogeneity of the powder, it is subjected to calcination at 1000 °C for 4 hrs, followed by grinding in an agate mortar for hours. Pellets of BSCFNi, having a diameter of 13 mm and thickness of 2 – 3 mm, are prepared by pressing the powder uniaxially at a pressure of 10 kg m⁻¹sec⁻². The pellets are then dried at 100 °C for 2 hours in a closed container.

The crystal structures and lattice parameters of the BSCFNi perovskite are determined by means of X-ray diffraction (X-PERT PRO with Cu-K α radiation) analysis. Morphology of the calcined powder is observed with a scanning electron microscope. Differential Scanning Calorimeter (DSC) measurement, carried out in the temperature range of 300-600 °C, shows no phase transition. The electrochemical behaviour of the Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3- δ} for varying composition of Ni was evaluated with electrochemical impedance spectroscopy (EIS) in the frequency range of 1 Hz to 1 MHz and at signal amplitude of 5 mV at 50 °C temperature intervals from 200 °C to 500 °C under an open circuit state.

III. RESULTS AND DISCUSSION

A. Structural Study

BSCFNi calcined powders with various levels of Ni doping exhibit well-crystallised XRD patterns measured in the Bragg angle range of 20° ≤ 2 θ ≤ 80° as shown in figure-1. With increase in the Ni concentration, the pattern peak shifts towards high angle direction which corresponds to the lattice shrinkage. The peaks are indexed on the basis of a cubic perovskite phase with the space group Pm3m (221) [5]. It has been reported that the synthesis of the sample through citric route forms undesired secondary phases of Barium and Strontium due to the poor distribution of the alkaline-earth metal (for example, Sr²⁺) in the solution caused by the relatively weak chelation between Sr²⁺ and carboxylate ligands [6-8]. However, these undesired secondary phases can be removed by calcining at 1000 °C. Thus the synthesised powders are calcined at 1000°C to increase the homogeneity of the powder that could be observed from the X-ray diffraction pattern showed in figure-1.

Figure-1: XRD Patterns of Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3- δ} (0.05 ≤ x ≤ 0.2) Samples

Table 1: Room Temperature XRD Data for Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3- δ} samples

Ni- dopant (x)	Lattice Constant (Å)	X-ray density (gm/cm ³)	% Porosity
0.05	3.9551	5.838	30.41
0.10	3.9471	5.873	29.97
0.15	3.9407	5.901	29.63
0.20	3.9368	5.919	29.26

The lattice parameters of BSCFNi are calculated by least square programme using the whole pattern matching. The calculated lattice parameters, X-ray density and porosity (%) are shown in Table-1. It is observed from the table that the lattice parameter decreases with increase in Ni concentration. It is expected that the the substitution of the smaller Ni³⁺ (0.74 Å) cation for Co³⁺ (0.75 Å) cation of the B-site with Fe in 4+ state (Fe⁴⁺ ionic radii=0.73 Å) caused a little shrinkage in the lattice and results in the formation of oxygen vacancies [9]. The average crystallite size of BSCFNi powders as calculated by Debye-Scherrer's equation was 50 nm. Also the high porosity of the BSCFNi pellets obtained is due to low sintering tempertaure.

Scanning Electron Micrographs of Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3- δ} powder calcined at 1000 °C for 4 hrs are shown in figure-2. The presence of highly porous spherical particles with a nano-metric grain size, varying between 1 to 2 μm, is observed in the morphology of powders obtained in this work, which resembled the typical cathode structure for SOFC.

Figure 2: SEM Images of the Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3- δ} (0.05 ≤ x ≤ 0.2) Powder

The result of a DSC experiment is a curve of heat flux versus temperature measured for Ni-0.15 and Ni-0.2 concentration, shown in figure-(3). The sample undergoes exothermic processes, such as Crystallisation, shows less heat required to raise the sample temperature. This may be due to the increase in the relative density of the Ba_{0.5}Sr_{0.5}Co_xFe_{0.6}Ni_{1-x}O_{3- δ} with increase in the nickel concentration. It was also observed from the figure-3 that no phase transition takes place measured for the calcined powders (calcinations temperature 1000 °C) of BSCFNi in the temperature range of 200 to 600 °C.

Figure 3: DSC Curve of BSCFNi Nanopowders for $x=0.15$ and $x=0.2$ Concentration

B. Ionic Conductivity Measurement

The ionic conductivity of the cathode electrode is calculated as a characteristic measure for the MIEC cathode performance. Figure-4 shows the variation of ionic conductivity of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{0.6}\text{Ni}_{1-x}\text{O}_{3-\delta}$ ($0.05 \leq x \leq 0.2$) measured in the temperature range of 200-500 °C for the pellets of area 1.327 cm^2 .

The ionic conductivity (σ_{ion}) in the cathode takes place at low frequencies and it increases with increase in the temperature as expected. The ionic conductivity values of the BSCFNi measured for $0.05 \leq x \leq 0.2$ is shown in table- 2. It is observed from the table that the ionic conductivity (σ_{ion}) value increases for $x=0.05$ to 0.15 except for $x=0.2$. The ionic conductivity (σ_{ion}) value is higher for Ni concentration $x=0.15$ compared to other Ni dopant concentration. The high ionic conductivity is due to the better catalytic behaviour of BSCFNi and the significant open porosity which enable oxygen reduction not only on the surface but also in the entire volume of the electrode.

Figure 4: Ionic Conductivity for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{0.6}\text{Ni}_{1-x}\text{O}_{3-\delta}$ ($0.05 \leq x \leq 0.2$)

Table 2: Ionic Conductivity Data for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{0.6}\text{Ni}_{1-x}\text{O}_{3-\delta}$ Samples ($0.05 \leq x \leq 0.20$) Measured at 400 and 500 °C

Ni-Concentration (x)	Ionic Conductivity ($\text{S}\cdot\text{cm}^{-1}$)	
	400 °C	500 °C
0.05	0.0013	0.0086
0.10	0.0199	0.0784
0.15	0.1014	0.5257
0.20	0.0209	0.0343

The oxygen reduction behaviour could be explained in terms of the lattice shrinkage. The lattice shrinkage in the samples of BSCFNi increases with increase in the nickel concentration as the smaller Ni^{3+} ($0.74 \text{ \AA}$) cation replaces the Co^{3+} ($0.75 \text{ \AA}$) cation at the B-site (Fe is in +4 state) of ABO_3 perovskite structure. The average oxidation state of the B-site is 3.333 which lead to the formation of oxygen vacancies in the lattice to maintain the electrical neutrality of the perovskite on account of the charge compensation. The formation of oxygen vacancies increases with increase in the Ni concentration in BSCFNi. It is known that the oxygen vacancies on the electrode surface or in the electrode provide the reaction site for the reduction of molecular oxygen and the pass way for the diffusion of reduced oxygen ions [10-12]. Therefore, the oxygen vacancies concentration of the cathode material should play an important role on the change of the ionic conductivity due to the oxygen adsorption or desorption and the oxygen ions diffusion in the electrode.

According to Kharton, the high ionic conductivity of BSCFNi perovskite with increase in the Ni content, substituted in place of Co, could be attributed to the weaker Ni-O bond strength compared to Co-O bond [13]. The decrease in the σ_{ion} for Ni-0.20 may be due to the Ni dopant concentration exceeding a certain value called percolation limit, at which electronic conduction becomes predominant [14].

In this work, BSCFNi with Ni concentration of $x=0.15$ has the highest ionic conductivity value of 0.5257 S/cm at 500 °C compared to the reported σ_{ion} values of BSCF which were obtained to be 0.006 S/cm at 600 °C and 0.018 S/cm at 700 °C [15]. Other reported ionic conductivity results are $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ [16, 17], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ [18, 19] and $\text{Sr}_{0.9}\text{Ce}_{0.1}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ [16] whose σ_{ion} values are 0.22 S/cm , 0.058 S/cm and 0.04 S/cm obtained at 800 °C respectively.

IV. CONCLUSION

BSCF with varying Nickel contents ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{0.6}\text{Ni}_{1-x}\text{O}_{3-\delta}$, $x=0.05, 0.1, 0.15$ and 0.2) are prepared using sol-gel citrate method. The samples are calcined at 1000 °C to remove any secondary phases to yield well crystallized BSCFNi powders. The effect of Nickel doping (Ni substitution for Cobalt in BSCF) on the microstructure, heat flux (obtained from DSC) and the ionic conductivity (σ_{ion}) was investigated and it was found that Ni doping with $x=0.15$ showed the better result. Thus the BSCFNi with optimum Nickel doping level can be a good candidate as cathodes for low temperature SOFCs application.

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REFERENCES

- [1] E. Maguire, B. Gharbage, F.M.B. Marques and J.A. Labrincha; Solid State Ionics, 127, 329-335, 2000.
- [2] S.C. Singhal; Solid State Ionics 135, 305-313, 2000.
- [3] S.J Skinner; Fuel Cells Bull; 33, 2001.

- [4] E. Bucher, A. Egger, P. Ried, W. Sitte and P. Holtappels, *Solid State Ionics* 179, 1032, 2008.
- [5] H. Koster and F H B Mertins, *Powder Diffraction* 18, 56-59, 2003.
- [6] J. Pena-Martinez, D. Marrero-Lopez, J.C. Ruiz- Morales, P. Nunez, C. Sanchez-Bautista and Dos Santos-Garcia, *International Journal of Hydrogen Energy* 34, 9486-95, 2009.
- [7] J. Pena-Martinez, D. Marrero-Lopez, J.C. Ruiz-Morales, B.E. Buerger, P. Nunez and L.J. Gauckler, *Solid State Ionics* 177, 2143-7, 2006.
- [8] K. Huang, J. Wan and J.B. Goodenough, *Journal of Material Science*, 36, 1093-8, 2001.
- [9] Wei Zhou, Ran Ran, Zongping Shao, *Journal of Power Sources* 192, 231-246, 2009.
- [10] T. Ishihara, T. Kudo, H. Matsuda and Y. Takita, *J. of Electrochemical Society*, 142, 1519, 1995.
- [11] S. Kim, S. Wang, X. Chen, Y.L. Yang, N. Wu, A. Ignatiev, A.J. Jacobson and B. Abeles, *J. of Electrochemical Society*, 147, 2398, 2000.
- [12] T. Horita, K. Yamaji, N. Sakai, H. Yokokawa, T. Kawada and T. Kato, *Solid State Ionics* 127, 55, 2000.
- [13] V.V. Kharton et. al., *Solid State Ionics* 132, 119-130, 2000.
- [14] V.V. Kharton, A.A. Yaremchenko and E.N. Naumovich, *J. Solid State Electrochem.* 3, 303, 1999.
- [15] Zhou Wei, Ran Ran and Zongping Shao, *Journal of Power Sources* 192, 231-246, 2009.
- [16] H. Ullmann, N. Trofimenko, F. Tietz, D. Stöver and A. Ahmad-Khanlou, *Solid State Ionics* 138, 79, 2000.
- [17] Y. Teraoka, H.M. Zhang, K. Okamoto and N. Yamazoe, *Mater Res Bull* 23, 51, 1988.
- [18] A. Petric, P. Huang and F. Tietz, *Solid State Ionics* 135, 719, 2000.
- [19] Y. Teraoka, T. Nobunaga, K. Okamoto, N. Miura and N. Yamazoe, *Solid State Ionics* 48, 207, 1991.