

Influence of Preparative Techniques on Microstructure and Electrochemical Properties of $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (BSCF3764) Cathode for IT-SOFC*

B. S. Nagrare and S. P. S. Shaikh

Department of Physics, R. T. M. Nagpur University

Nagpur – 440 033 Maharashtra, India

Email: bhagi.nagarare@gmail.com, shree3rare@gmail.com

(Received June 14, 2011)

Abstract: $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (BSCF3764) was synthesized via three different methods; solid state reaction (SSR), glycine nitrate process (GNP), and EDTA-citric acid complexing sol-gel method (SG). Effect of preparation techniques on XRD, microstructure, 4-probe DC conductivity and transport properties using EIS were studied. Both, phase formation temperature and time of BSCF3764 synthesized by SG was found to be low as compared to other two methods. Grain size of around 0.2-0.3 μm in case of SSR and grown grains with size of approximately 0.1-0.2 μm along with pinholes. Composition synthesized by SG showed highest electrical conductivity at around 700 $^{\circ}\text{C}$. The performance of BSCF3764 cathode on GDC (8020) electrolyte was dependent on the synthesis technique. The ASR values of BSCF3764 prepared by SSR, GNP and Sol-gel were found to be 1.567, 0.931 and 0.548 Ωcm^2 at 700 $^{\circ}\text{C}$. The cathode polarization resistance and activation energy was found to be minimum in BSCF3764 prepared by SG. The polarization resistance was found to be linearly dependent on oxygen partial pressure; E_a for variation of ASR with Po_2 was lowest, 0.0028 eV, in composition synthesized via SG.

Keywords: MIEC; BSCF; Scanning electron microscopy; EIS; Oxygen partial pressure.

1. Introduction

Solid oxide fuel cells (SOFCs) are currently attracting considerable interest as stationary power generators due to the high efficiency and low emission levels of pollution that they promise. SOFCs offer flexibility in planning and establishment of power generation capacity as a result of their modular nature¹. Fuel cells have been commonly accepted as a kind of clean, safe and convenient power source with high energy efficiency and are on the

*Paper presented in CONIAPS XIII at UPES, Dehradun during June 14-16, 2011.

verge of revolutionizing the electric power industry by offering better ways to produce electricity and to deliver it to the consumers^{2,3}. High temperature SOFC (HT-SOFC) has disadvantages like high cost, degradation and fabrication. Hence, with the need to decrease the operating temperature and commercialize it; intermediate-temperature SOFC (IT-SOFC) with high functional cathode materials providing mixed ionic and electronic conductivity along with low polarization resistance has been developed.

During the past two decades, mixed ionic-electronic conducting (MIEC) materials have received great interest because of their potential applications in separation of oxygen from air, as electrodes for solid oxide fuel cells (SOFCs)^{4,5}, construction of membrane reactors for partial oxidation of methane to syngas^{6,7} and oxidative coupling of hydrocarbon to value-added products⁸. The main advantage of the MIEC membrane reactor is that air instead of oxygen can be used as the oxygen source, which avoids the expensive separation of the nitrogen either before or after the reaction. Furthermore, the gradual introduction of oxygen reduces the contact with the partially oxidized products, which enhances the yield of the desired products. For a promising oxygen separating membrane material, it must possess high oxygen permeability as well as stable lattice structure under changes in oxygen partial pressure. The structure of the porous electrodes is critical for the performance of a solid oxide fuel cell (SOFC). Recently, Shao *et al.*⁹ have reported $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) as a high performance cathode material for next generation solid oxide fuel cell. The high power output of BSCF cathodes has been resulted from the high rate of oxygen diffusion through the material. In recent years, perovskite type mixed conducting oxides $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF5582) composite showed great potential as a cathode material and has received considerable attentions. MIEC offers reduced cathode polarization at operating temperatures by extending the active oxygen reduction site from the typical electrolyte-electrode gas TPB through the disclosed cathode surface¹⁰⁻¹⁴.

Additionally, $\text{Ln}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Sm}$), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) compound have been also evaluated and achieved excellent results in both dual-chamber and single chamber configurations¹⁵. Bo Wei et al. reported the crystal structure, thermal expansion and electrical conductivity of the perovskite oxide $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($0.3 < x < 0.7$) for $x < 0.6$. They found that the composition lattice constant increase with increase in Ba content¹⁶. Recently effect of a reducing agent for silver modified $\text{Ag}/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ electrode on the electrochemical activity prepared by electroless deposition technique has been studied. The anode-supported single cell with the N_2H_4 -reduced

Ag/BSCF cathode showed improved performance and reached peak power densities of 826, 562 and 428 mWcm⁻² at 600, 550 and 500 °C, respectively¹⁷. The influence of iron content on the area-specific resistance (ASR) for Ba_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_{3-δ} using LSGM as electrolyte material has been investigated¹⁸. The increase of iron content in BSCF materials results in an increase of area-specific resistance (ASR), e.g. 0.04, 0.08 and 0.13 Ω.cm² for compositions with y = 0.2, 0.4 and 0.6, respectively, at 800 °C.

The conventional method for the preparation of hetero-metallic oxides or carbonates, such as perovskite, has been the solid state reaction at high temperatures of the corresponding binary metal oxides or carbonates¹⁹. The development of innovative processing methods through chemistry permits one to lower the preparation temperature and to improve homogeneity and reproducibility of the ceramic products. Furthermore, it facilitates synthesis of porous, ultrafine and chemically pure powders of mixed metal oxides at lower temperatures. In present work, Ba_{0.3}Sr_{0.7}Co_{0.6}Fe_{0.4}O_{3-δ} abbreviated as BSCF3764; is synthesized by three different methods. The emphasis is put on the effect of preparative technique on microstructure, dc conductivity and electrochemical impedance with varying oxygen partial pressure of BSCF3764 cathode on GDC (8020) electrolyte.

2. Experimental

In present investigation, the perovskite BSCF3764 were prepared by three different methods; designated by the abbreviations solid state reaction (SSR), glycine nitrate process (GNP) and EDTA-citric acid complexing sol-gel method (SG).

2.1 Methods of synthesis

2.1.1 Solid state reaction (SSR)

The perovskite type Ba_{0.3}Sr_{0.7}Co_{0.6}Fe_{0.4}O_{3-δ} was synthesized by conventional solid state reaction method which has been reported earlier²⁰. The starting compounds were SrCO₃, BaCO₃, Co₃O₄ and Fe₃O₄, procured from Sigma Aldrich were 99.99 % pure. Initially, these starting reagents were heated at 200 °C in an electric oven for more than 12 hour, before weighting, in order to remove water content, if any. The dried reagents were weighed, using Mettler balance AE 163 with an accuracy of 0.00001 g, according to the stoichiometry of Ba_{0.3}Sr_{0.7}Co_{0.6}Fe_{0.4}O_{3-δ}; and ground in an agate mortar under acetone as a medium. The homogeneous powder was later compacted in the form of circular discs of dimension 9×1-2 mm, diameter and thickness, using Specac (UK) hydraulic press and dia at 5

ton/cm² and allowed to react at 1,000 °C in air for 10 h a temperature required for perovskite phase formation, followed by cooling the products down to room temperature with a rate of 5 K/min. The ceramic pellets produced were again crushed, pelletized followed by sintering in air at a temperature of 50 to 100 °C higher than the temperature of powder annealing.

2.1.2 Glycine nitrate process (GNP)

Ba(NO₃)₂, Sr(NO₃)₂, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O and glycine (H₂NCH₂COOH), all of which were procured from sigma Aldrich, were used as starting materials. These starting materials with the required molar ratios were mixed in deionized water to obtain transparent solutions. The solutions were heated to obtain viscous liquids on a hot plate at about 80 °C. Then the viscous liquids were transferred into a baker which was heated to 200-300 °C. The water was evaporated quickly and the solutions got swelled and ignited resulting in porous, foamy and fragile materials. The as prepared materials were calcined at 1,000 °C for 5 h in air to obtain pure, well-crystallized powders²¹.

2.1.3 EDTA-Citric acid complexing sol-gel process (SG)

BSCF3764 powders were synthesized by a combined EDTA–citrate complexing sol–gel process. The detailed procedure for this process has been reported in Ref. [22]. In brief, required amounts of metal nitrates were prepared into a mixed solution followed by the addition of EDTA and citric acid, at a pH of ~6 with the help of NH₄OH at a mole ratio of total metal ions:EDTA: citric acid of 1:1:1.5. The water was evaporated at 90 °C, resulting in transparent gels which were first pre-fired at 250 °C and then further calcined at 1,000°C for 5 h in air to produce the final products.

2.2 Cell fabrication

For electrochemical investigations, the initial slurry/ink of the Ba_{0.3}Sr_{0.7}Co_{0.6}Fe_{0.4}O_{3-δ} cathode was obtained as follows. A gram of BSCF3764 powder was mixed with 3 wt.% polyvinyl buteral binder, ¼% sodium free corn oil, and ethyl methyl ketone (2-3ml). The mixture was then ball-milled using a Pulverisette-6 (Fritsch Germany) for 3 h with 300 revolutions per minute (optimised). Fifteen tungsten carbide balls of diameter 10mm and 80-ml bowl of the same material were used. Gadolinium-doped ceria (GDC8020), nano-powder (GDC8020, 99.99% pure, Sigma Aldrich, USA), was fired at 900 °C for 2 h. Subsequently, GDC electrolyte pellets of 9 and 1–2 mm diameter and thickness, respectively

were prepared followed by sintering at 1,400 °C for 6 h. The density of GDC pellet was about 96% of the theoretical value. The slurry/ink of cathode material was then spin coated at 1000 rpm for 60 s and 1500 rpm for 60s, during stage 1 and stage 2 respectively; on both the flat surfaces of the sintered GDC electrolyte to obtain the symmetric cells of following configuration, BSCF3764/GDC/BSCF3764, for all the three methods. The symmetric cells were initially baked in microwave oven at P-HI (90% power) for 10 m so as to burn out the organic binders. Finally, they were sintered at 1,000 °C for 3 h so as to study the effect of synthesis method on microstructure and electrochemical performance of the BSCF3764 cathode.

2.3 Characterizations

The phase identification of the BSCF powders prepared by three different methods was performed by X-ray powder diffraction (XRD) with a PANalytical X'pert PRO (Philips, the Netherlands) instrument that employed Cu K α radiation. A curved graphite crystal was used as a monochromator. The X-ray diffraction measurements were carried out in a 2θ range from 20 to 80° with a step size and time per step of 0.020 ° and 5 s, respectively. The sintered densities of all the samples were determined using Archimedes' principle using Mettler Toledo balance with density kit. The microstructures of the sintered samples were examined with a JEOL JSM-6380A scanning electron microscope (SEM) to evaluate the morphologies of the as-synthesized powders and grain size of the compound. Microhardness was measured by the Vickers indentation technique (HMV-2 microhardness tester, Shimadzu, Japan). Spin coating was done with the help of Millman spin coater. A thin platinum film on both flat surfaces of sintered samples was obtained by d.c. sputtering and resulted in good ohmic contacts for d.c. electrical conductivity measurements. Prior to the conductivity measurements, the sample was spring-loaded in a ceramic cell holder (Amel, Italy) and heated to 700 °C for 1 h to homogenize the charge carriers. The resistance during the cooling cycle was measured as a function of temperature using the four-probe method with a computer-controlled Keithley 6221 current source and a 2182A nanovoltmeter in delta mode. The temperature of the sample during the measurement was controlled with an accuracy of ± 1 °C with a Eurotherm 2216e temperature controller.

The electrochemical impedance spectroscopy (EIS) measurements on all the sintered cells were carried out using computer-controlled Solartron 1255B FRA in combination with Solartron SI 1287 potentiostat. Prior to the impedance measurement, the spring-loaded cells were heated to 700 °C.

During the cooling cycle, at each set temperature, a dwell time of 30 m was given to ensure thermal equilibrium in the cell. Real and imaginary parts of impedance were measured as a parametric function of frequency and temperature in the range of 0.01 to 1×10^6 Hz and 500 to 700 °C, respectively. The ac signal amplitude was 50 mV. The desired oxygen partial pressure (P_{O_2}) around the cell, during impedance measurements, was achieved by mixing appropriate quantity of high purity grade oxygen gas with nitrogen using electronic mass-flow-meters-cum-controllers (Teledyne-Hastings, USA). The dc polarization potential was applied across cell during the EIS measurements with Solartron SI 1287 electrochemical interface. The EIS data were collected and fitted using the complex non-linear least square (CNLS) fitting program from the Scribner advanced Zview 3.3a software for electrochemical research and development.

3. Results and Discussion

3.1 XRD

The XRD patterns of calcined $Ba_{0.3}Sr_{0.7}Co_{0.6}Fe_{0.4}O_{3-\delta}$ (BSCF3764) prepared by three different methods are shown fig.1. The results obtained by XRD show only the presence of cubic perovskite phase BSCF (JCPDS-00-039-1083) for all the samples [already published in previous work, ref 23]. It can be seen that the cubic perovskite phase has been formed after calcinations. Some amount of impurity phases is present which becomes almost negligible after sintering. Fig. 2 shows XRD patterns of sintered samples at temperatures required by respective methods. In case of BSCF3764 prepared by SSR the impurity phases are more as compared to the other two. In GNP and SG techniques the sintering temperature should be 950 °C in order to obtain the single phase. In contrast, a sintering temperature of 1150 °C and a processing time at least 10 h are usually required by the conventional solid-state reaction method to obtain the pure perovskite structure oxides. Compared to that, the samples prepared by GNP and SG method shows a substantial decrease of the sintering temperature and the processing time for the formation of the desired single-phase perovskite structure, the reason could be that the energy required in there two methods for phase transformation is less. The crystallite size of samples prepared by GNP and SG were smaller then that prepared by SSR. The crystallite size, lattice parameter, sintered density and cell volume of BSCF3764 prepared by three different methods along with the microhardness of the perovskite structure are listed in table 1.

3.2 SEM

In ceramic materials the microstructure, particle size, the connection between the particles and the porosity is certainly influenced by the synthesis method. Methods like GNP and SG favor obtaining of porous particles, because the reactions produce homogeneous material composed of small and uniform particles. The sample prepared by SSR showed lower surface area and larger particle size than the other two. Aggregates of fine particles and irregularly shaped patches consisting of larger aggregates are found. As seen from fig.3 (b) and (c) the sample prepared by GNP and SG has pinhole like structure which could be associated with the fast gas release and combustion behavior. Clear grain boundaries are found on the surface with the grain size of around 0.2-0.3 μm in case of SSR. Well necked grown grains with size of approximately 0.1-0.2 μm along with some pinholes; resulting form of completely fused together particle and no grain boundary; were observed in sample prepared by GNP and SG. The SEM images of symmetric cell BSCG/GDC/BSCF shown in fig. 4 were sufficiently porous with good interfacial contact with the electrolyte with no sign of delamination. In samples synthesized by SSR well densified and enclosed pores were observed. No visible cracks were found across the electrolyte when SEM images of symmetric cell were examined. Scanning electron microscopy reveals the formation of porous material consists of aggregates of fine particles and irregularly shaped patches in case of composition synthesized by SSR. A well-bonded pinholes network is obtained in samples prepared by GNP and SG method.

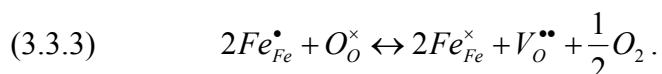
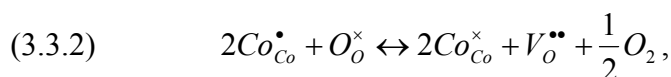
3.3 Electrical conductivity

The plots of $\ln \sigma T$ versus $10^3/T$ for BSCF3764 synthesized by three methods is depicted in fig 5. It is evident from the fig. 5 that the electrical conductivity of the sample prepared by three methods increases with increase in temperature. The conductivity of the sample prepared by SG shows a steady increase. There is a sudden increase at 580 $^{\circ}\text{C}$ in the conductivity of the sample prepared by SSR and GNP, which could be attributed to the phase transition. With increase in temperature, the proportion between the number of triple and tetravalent state cation reaches the optimum value to give highest concentration of electron holes, which results in higher conductivity. Below and above the transition temperature all the samples obey Arrhenius law

$$(3.3.1) \quad \sigma = \sigma_0 \exp(-E_a / kT),$$

where, σ_0 and E_a are pre-exponential factor and activation energy respectively.

Apparently activation energy (E_a) can be calculated from the slopes of linear correlations. The values of E_a for BSCF3764 prepared by SSR, GNP and SG were 0.048, 0.045 and 0.046 eV, respectively. The decrease in electrical conductivity at high temperature (above 700 °C) observed in BSCF3764 (SG) was attributed to the decrease of carrier mobility. The reduction in carrier mobility is believed to be resultant due to the high oxygen vacancy concentration present in high temperature region which may act as scattering centre's or as random traps for electrons. Furthermore, along with the thermally induced lattice oxygen losses, more oxygen are formed, which in turn causes the thermal reduction of Co^n/Fe^n to lower valence site i.e. $\text{Co}^{n-1}/\text{Fe}^{n-1}$, respectively [24-29]. These can be described according to the defect reaction (in the Kroger-Vink notation).



The valence changes are also associated with an increase of the ionic radius, as can be seen in Table 2, especially for the reduction of Co^{4+} to Co^{3+} . Accordingly, the reductions cause a decrease in the B-O bond according to Pauling's second rule, and hence the size of BO_6 octahedra increases, thus enhancing the lattice expansion³⁰. This, in turn, decreases the concentration of charge carriers and the covalent interaction, and may cause the observed change in the conductivity³¹.

3.4 Electrochemical impedance studies

Figs. 6, 7 and 8 shows the impedance spectra for BSCF 3764 /GDC /BSCF 3764 symmetric cell prepared by three methods at 600, 650 and 700 °C, respectively. The impedance spectra consisted of two separable depressed arcs. This indicated that there were at least two electrode processes corresponding to the two arcs during molecular oxygen reduction. The impedance spectra are successfully fitted by equivalent circuit as shown in fig.9. Here, L represents the inductance which might be the consequence of current/voltage probe or the high frequency phase shift of the electrochemical device. The overall ohmic resistance, R_Ω , includes the electrolyte resistance, the electrode ohmic resistance, and the lead resistance. The resistance at the high frequency is probably associated with the charge

transfer processes (R_{E1}), which include the ion-transfer process occurring at the electrode/electrolyte interfaces and the electron-transfer process accompanying with the oxygen reduction reaction. The low-frequency arc can be attributed to the diffusion processes (R_{E2}), which include the adsorption–desorption of oxygen, oxygen diffusion at the gas-cathode interface and surface diffusion of intermediate oxygen species^[32-40]. The difference between real axes intercepts of the impedance plot is considered to be the electrode polarization resistance ($R_p = R_{E1} + R_{E2}$). The fitting results of the three parts resistances obtained from the 3.3a Zview program (Scribner Associates, Inc.) Parameters Q1 and Q2 are constant phase elements. The cathode area specific resistance was deduced by the relation.

$$(3.4.1) \quad \text{ASR} = R_{\text{interface}} * \text{Surface area}/2.$$

Fig.10 shows ASR of BSCF3764 prepared by the methods as a function of temperature. The tail present in the fourth quadrant may be attributed to the inductance of the circuit. The area specific resistance was found to be decreased with increase in temperature. The area specific resistance was 1.567, 0.931 and 0.548 $\Omega\cdot\text{cm}^2$ at 700 °C and 2.89, 2.01 and 1.642 $\Omega\cdot\text{cm}^2$ at 600 °C, for BSCF3764 prepared by SSR, GNP and SG, respectively. Also there was decrease in the activation energy from SSR, GNP to SG. These values are low as compared to other cathode material; e.g. BSCF5546, BSCF5564 and BSCF5582 with approximate ASR values 20.88, 26.205 and 29.558 $\Omega\cdot\text{cm}^2$ at 600 °C^[41]. Fig.11 shows the effect of variation in the dc potential on ASR of the BSCF3764 prepared by SSR and SG, but the change in the dc potential overloaded the voltage across the cell above 0.3V in case of BSCF3764 prepared by GNP. In general, the ASR reduces with an increased biasing potential. The dependence of polarization resistance on oxygen partial pressure is depicted in fig. 12. ASR and P_{O_2} are found to be linearly dependent. For BSCF3764 composition synthesized by SG, E_a was found to be 0.0028 eV at 700 °C; lowest within the three methods used; in presence of oxygen partial pressure. Since the slope of ASR with variation in P_{O_2} is almost straight, also the activation energy is found to be less in BSCF3764 synthesized by SG, it could be concluded that it has stable lattice structure under different oxygen partial pressures.

Conclusion

$\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ was synthesized using three different methods. Single phase perovskite can be obtained by calcining the gelled BSCF (SG) at 1000 °C for 5h. BSCF3764 prepared by SSR show well necked

consolidated particles and hence the coalescence between neighboring particles while pinhole were observed in case GNP and SG. Electrochemical performance of BSCF/GDC/BSCF was evaluated with respect to change in temperature, dc potential and oxygen partial pressures. The cell prepared by SG showed a promising electrochemical performance with lowest ASR value of $0.5486 \Omega \cdot \text{cm}^2$ at 700°C . Furthermore, BSCF3764 prepared by SG depicted lowest activation energy in EIS in presence of Po_2 , i.e. $E_a = 0.0028 \text{ eV}$. Amongst the three methods used to synthesize BSCF3764, SG was found to be the best performing method and BSCF3764 as a potential candidate for IT-SOFC.

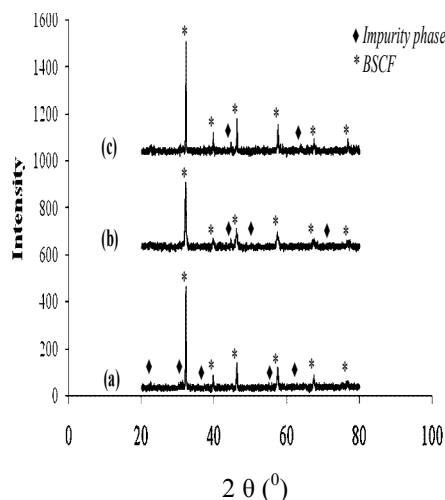


Fig. 1: XRD patterns of BSCF3764 after calcination (a) SSR [1000 $^\circ\text{C}$ for 10h], (b) GNP [1000 $^\circ\text{C}$ for 5h], (c) SG [1000 $^\circ\text{C}$ for 5h]

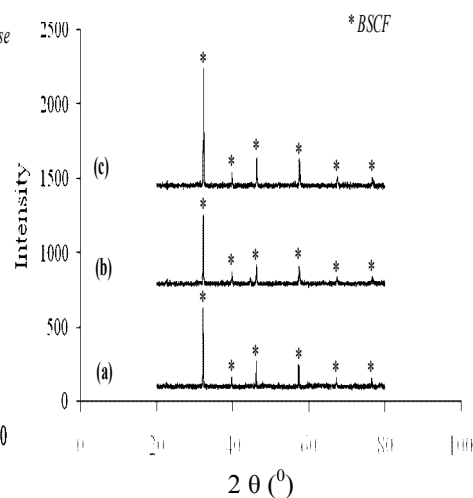


Fig. 2: XRD patterns of BSCF3764 after sintering (a) SSR [1050 $^\circ\text{C}$ for 10h], (b) GNP [950 $^\circ\text{C}$ for 5h], (c) SG [900 $^\circ\text{C}$ for 3h]

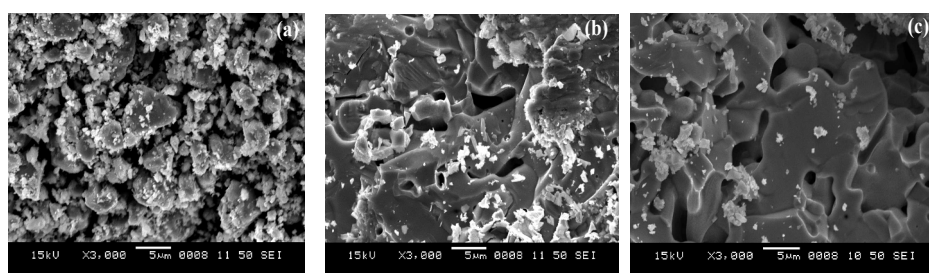


Fig. 3: SEM images of BSCF3764 surface (a) SSR, (b) GNP, (c) Sol-gel

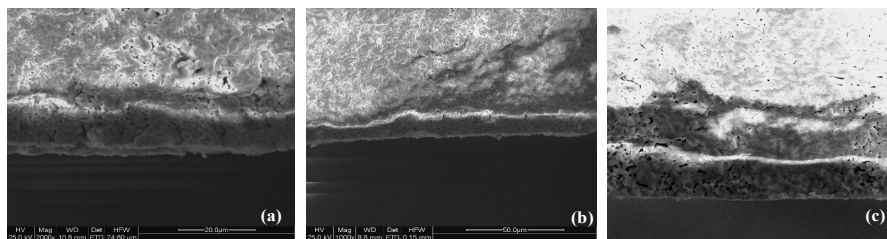


Fig. 4: SEM images of cross section of BSCF/GDC/BSCF (a) SSR, (b) GNP, (c) Sol-gel

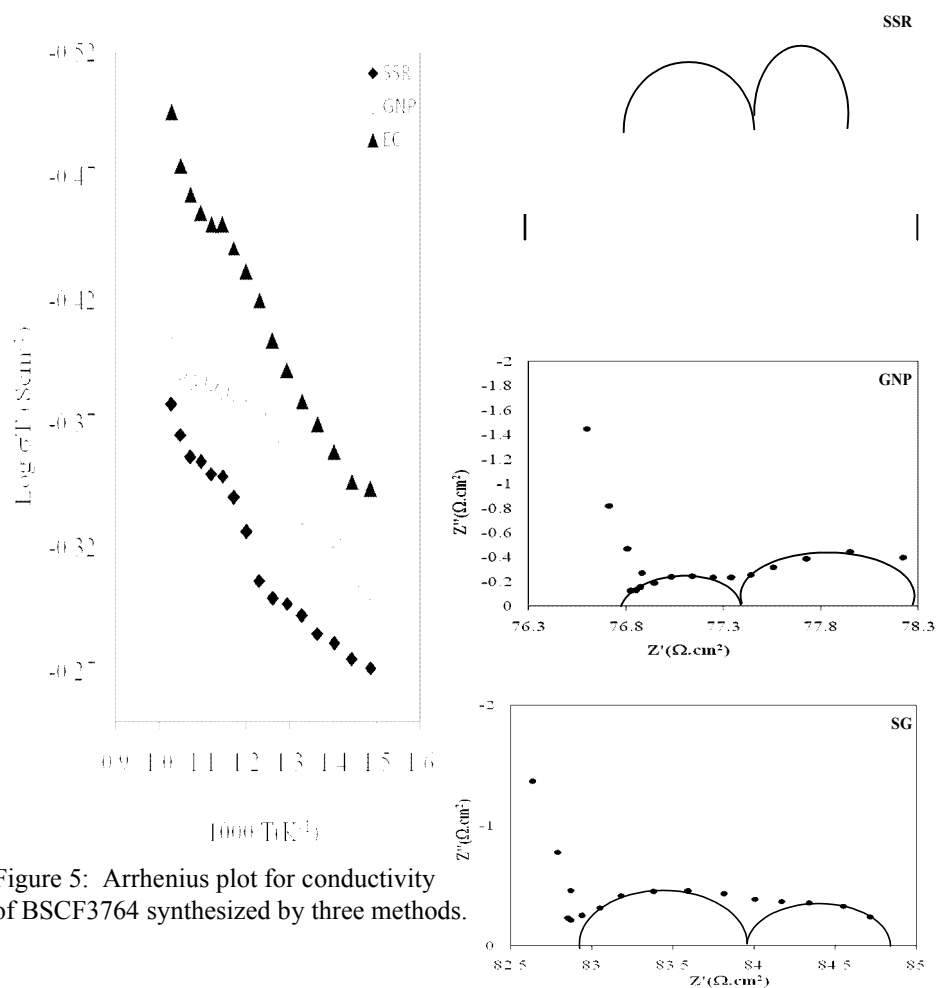


Figure 5: Arrhenius plot for conductivity of BSCF3764 synthesized by three methods.

Figure 6: AC impedance spectra of BSCF3764 at 600 °C synthesized by three methods.

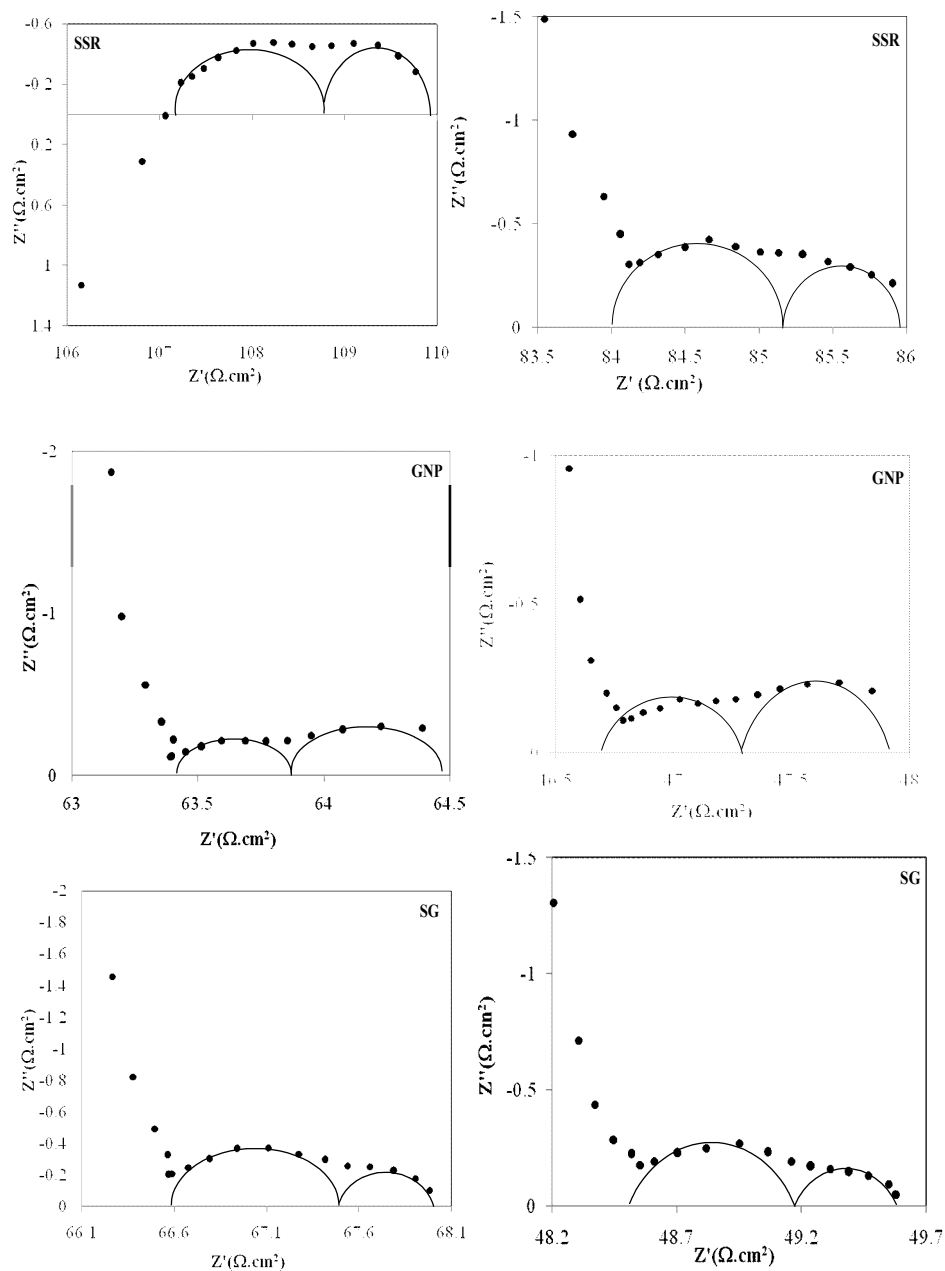


Figure 7: AC impedance spectra of BSCF3764 at 650 °C synthesized by three methods.

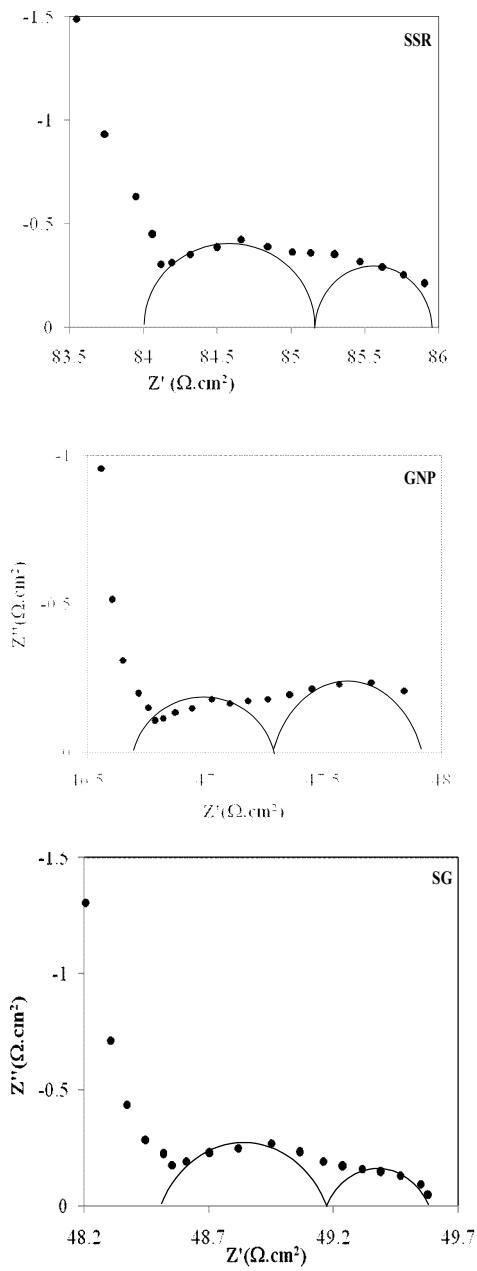


Figure 8: AC impedance spectra of BSCF3764 at 700 °C synthesized by three methods.

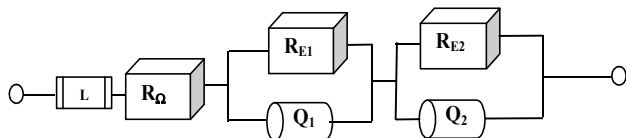


Figure 9: Electrical equivalent circuit for symmetric cell

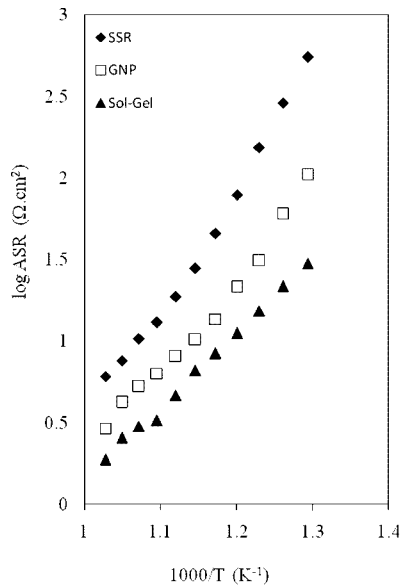


Figure 10: Variation of ASR as a function of temperature

Figure 11: Variation of ASR of BSCF3764 synthesized by SSR and SG as a function of DC potential

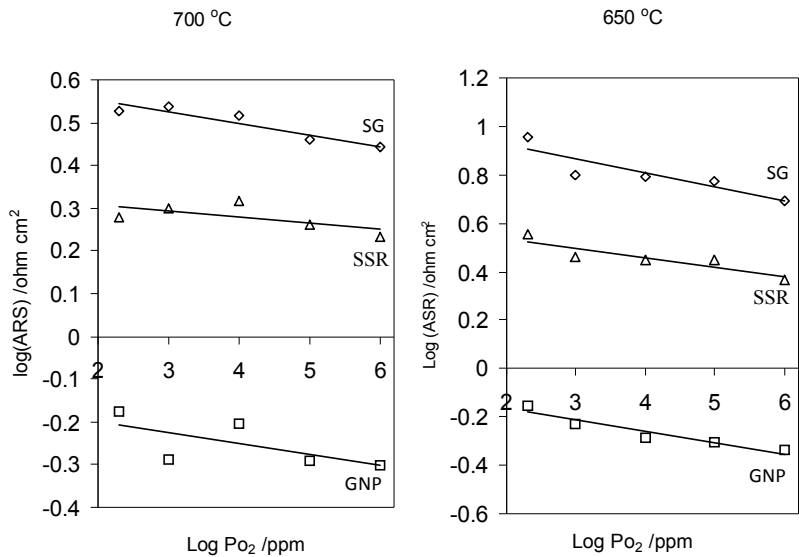


Figure 12: Variation of ASR as a function of pO_2

Table 1: A comparison of crystallite size (C_s), lattice parameter (a), sintered density (ρ_{Sint}), cell volume and microhardness (μ -hardness) of BSCF3764 synthesized by three methods

Methods	C_s (nm)	a (Å)	ρ_{Sint} (g/cm ³)	V (Å)	μ -hardness (HV)
SSR	258.8	3.822	3.706	55.87	359.24
GNP	193.7	3.922	4.353	60.36	456.93
SG	203.6	3.963	4.714	62.24	426.32

Table 2: Effective ionic radii and oxidation states of cations in the perovskite lattice [26]

Element	Oxidation states	Effective ionic radius(nm)
Oxygen	O ²⁻	0.126 (CN=6) ^a
Barium	Ba ²⁺	0.175 (CN=12)
Strontium	Sr ²⁺	0.158 (CN=12)
Cobalt	Co ²⁺	0.0885 (CN=6)HS ^b
	Co ³⁺	0.075 (CN=6)HS
	Co ⁴⁺	0.067 (CN=6)HS
Iron	Fe ³⁺	0.0785 (CN=6)HS
	Fe ⁴⁺	0.0725 (CN=6)

a- CN, co-ordination number, b – HS, high spin

Table 3: A comparison of activation energies of BSCF3764 synthesized by the methods

Methods of synthesis	E_a (eV) (log σT Vs $10^3/T$)	E_a (eV) (ASR Vs temp.)	E_a (eV) (ASR Vs dc pot.) at 700 °C	E_a (eV) (ASR Vs P_{O_2})	
				700 °C	650 °C
SSR	0.048	2.951	0.1339	0.0053	0.0111
GNP	0.045	2.190	----	0.0052	0.009
SG	0.040	1.7925	0.129	0.0028	0.0079

Acknowledgments

Author is thankful to UGC, for awarding MANF fellowship for financial support. Also, special thanks to Materials Science Research Laboratory, Department of physics, RTM, Nagpur University, Nagpur, Maharashtra.

References

1. S. Lee, S. K. Woo, K. S. Lee and D. K. Kim, Mechanical properties and structural stability of perovskite-type, oxygen-permeable dense membranes, *Desalination*, **193** (2006) 236-243.
2. M. Arnold, H. Wang and A. Feldhoff, Influence of CO₂ on the oxygen permeation performance and the microstructure of perovskite-type (Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3- δ} membranes, *J. Membr. Sci.*, **293** (2007) 44-52.
3. J. W. Stevenson, T. R. Armstrong, R. D. Carneim, L. R. Pederson and W. J. Weber, Electrochemical properties of mixed conducting perovskites La_(1-x)M_(x)Co(1-y)Fe(y)O(3-delta) (M=Sr,Ba,Ca), *J. Electrochem. Soc.*, **143** (1996) 2722-2729.

4. N. Q. Minh, Ceramic fuel cells, *J. Am. Ceram. Soc.*, **76** (1993) 563-588.
5. Y. H. Huang, R. I. Dass, Z. L. Xing and J. B. Goodenough, Double perovskites as anode materials for SOFC, *Science*, **312** (2006) 254-257.
6. U. Balachandran, J. T. Dusek, R. L. Mieville, R. B. Poeppel, M. S. Kleefisch, S. Pei, T. P. Kobylinski, C. A. Udovich and A. C. Bose, Material and fabrication challenges in the development of monolithic solid oxide fuel cells, *Appl. Catal. A: Gen.*, **133** (1995) 19-29.
7. T. Kadowaki, T. Shiomitsu, E. Matsuda, H. Nakagawa, T. Maruyama, Applicability of heat resisting alloys to separator of planar-type SOFC, *Solid State Ionics*, **67** (1993) 65-69.
8. F. T. Akin and Y. S. Lin, Oxidative Coupling of Methane in a Dense Tubular Membrane with High Yields, *AIChE J.*, **48** (2002) 2298-2307.
9. Z. P. Shao, S. M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, *Nature*, **49** (2004) 170-173.
10. Y. P. Lu, A. G. Dixon, W. R. Moser, Y. H. Ma and U. Balachandran, *Catal. Today*, **56** (2000).
11. S. Lee, Y. Lim, E. A. Lee, H. J. Hwang and J. W. Moon, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LBCF) cathodes prepared by combined citrate-EDTA method for IT-SOFCs, *J. Power Sources*, **157** (2006) 848-854.
12. Z. Duan, M. Yang, A. Yan, Z. Hou, Y. Dong, Y. Chong, M. Cheng and W. Yang, *J. Power Sources*, **160** (2006) 57-64.
13. J. Pena-Martínez, D. Marrero-López, J. C. Ruiz-Morales, B. E. Buegler, P. Núñez, L. J. Gauckler, SOFC test using $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as cathode on LSGM electrolyte *Solid State Ionics*, **177** (2006) 2143-2147.
14. Q. L. Liu, K. A. Khor, S. H. Chan, High-performance low-temperature solid oxide fuel cell with novel BSCF cathode, *J. Power Sources*, **161** (2006) 123-128.
15. L. W. Tai, M. M. Nasrallah, H. U. Anderson, D. M. Sparlin, S. R. Sehlin, Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 2. The system $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, *Solid State Ionics*, **76** (1995) 273-283.
16. B. Wei, W. Su, Z. Lü, X. Huang, S. Li, G. Ai, Z. Liu, Electrochemical characteristics of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ - $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite materials for low-temperature solid oxide fuel cell cathodes, *Mater. Lett.*, **60** (2006) 3642-3646.
17. Wei Zhou, Ran Ran, Rui Cai, Zongping Shao, Wanqin Jin, Nanping Xu, On $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0.1-0.9$) oxides as cathode materials for $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ based IT-SOFCs, *J. of Power Sources*, **186** (2009) 244-251.
18. J. Pena-Martínez, D. Marrero-López, J. C. Ruiz-Morales, P. Núñez, C. Sánchez-Bautista, J. Canales-Vázquez, *Intrnl J. of hydrogen energy*, **34** (2009) 9486-9495.
19. C. Y. Tsai, A. G. Dixon, W. R. Moser and Y. H. Ma, Dense perovskite membrane reactors for partial oxidation of methane to syngas, *AIChE J.*, **43** (1997) 2741-2751.
20. Egle Girdauskaite, Helmut Ullmann, Mahmoud Al Daroukh, Vladimir Vashook, M. Bülow and Ulrich Guth, Oxygen stoichiometry, unit cell volume, and thermodynamic quantities of perovskite-type oxides, *J. Solid State Electrochem*, **11** (2007) 469-477.
21. Y. H. Lim, J. Lee, J. S. Yoon, and C. E. Kim, *J. Power sources*, **171** (2007) 79-85.
22. W. Zhou, Z. P. Shao, W. Q. Jin, *J. Alloys Compd.*, **426** (2006) 368-374.
23. B. S. Nagrare, S. S. Bhoga, Investigation on Structure and Electrical Property of Perovskite Type $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ ($x = 0.2-0.8$) Oxides, *Integrated Ferroelectrics*, **116** (2010) 101-112.

24. Z. Shao, G. Xiong, J. Tong, H. Dong, and W. Yang, Ba effect in doped $\text{Sr}(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ on the phase structure and oxygen permeation properties of the dense ceramic membranes, *Sep. Purif. Technol.*, **25** (2001) 419-429.
25. D.Li, W.Liu, H.Zhang, G.Jiang, and C.Chen, Fabrication microstructure, mechanical and oxygen permeation of $\text{Ba}(\text{Sr})\text{Zr}(\text{CoFe})\text{O}_{3-\delta}$ dispersed $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ mixed-conducting composites, *Mater. Lett.*, **58** (2004) 1561-1564.
26. A. C. Van Veen, M. Rebeilleau, D. Farrusseng, and C. Mirodatos, Studies on the performance stability of mixed conducting BSCFO membranes in medium temperature oxygen permeation, *Chem. Commun.*, (2003) 32-33.
27. R. D.Shannon, Revised values of effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Cryst. A*, **32** (1976) 751-753.
28. Y.Teraoka, M.Yoshimatsu, N.Yamazoe and T.Seiyama, Oxygensorptive properties and defect structure of perovskite-type oxides. *Chem. Lett.*, (1984) 893-896.
29. L.W.Tai, M.M.Nasrallah, H.V.Anderson, D.M.Sparlin and S.R.Sehlin, Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 1: The system $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$, *Solid State Ionics*, **76** (1995) 259-271.
30. G.V. Kostogloudis, P.S. Fertis, and C. Ftikos, The perovskite oxide system $\text{Pr}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$: crystal structure and thermal expansion, *J. Eur. Ceram. Soc.*, **18** (1998) 2209-2215
31. K. T. Lee, A. Manthiram, Synthesis and Characterization of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ ($0 < y < 1.0$) Cathodes for IT-SOFC, *J. Power Sources*, **158** (2006) 1202-1208.
32. F. H. Heuveln, H. J. M. Bouwmeester, Electrode properties of Sr-doped LaMnO_3 on YSZ. II. Electrode kinetics, *J. Electrochem. Soc.*, **144** (1997) 134-140.
33. Y. J. Leng, S. H. Chan, K. A. Khor, S. P. Jiang, Performance evaluation of anode-supported solid oxide fuel cells with thin) lm YSZ electrolyte, *Int. J. Hydrogen Energy*, **29** (2004) 1025-1033.
34. S.B.Adler, J.A.Lane, B.C.H.Steele, Electrode Kinetics of Porous Mixed-Conducting Oxygen Electrodes, *J. Electrochem Soc.*, **143** (1996) 3554-3565.
35. X.J.Chen, S.H.Chan, K.A.Khor, Simulation of composite cathode in SOFC, *Electrochem Acta* , **49** (2004) 1851-1861.
36. F.Qiang, K.N.Sun, N.Q. Zhang, X.D.Zhu, S.R.Le, D.R.Zhou, Characterization of electrical properties of GDC doped A-site deficient LSCF based composite cathode using impedance spectroscopy, *J. Power Sources*, **168** (2007) 338-345.
37. S.B.Adler, Mechanism and kinetics of oxygen reduction on porous LaSrCoO electrodes, *Solid State Ionics*, **111** (1998) 125-134.
38. M.J.Jørgensen, M.Mogenssen, Impedance of solid oxide fuel cell LSM/YSZ composite cathodes, *J. Electrochem Soc.*, **148** (2001) A 433-A442.
39. S.P.Jiang, W.Wang, Fabrication and performance of GDC-impregnated LSM cathodes for IT-SOFC, *J. Electrochem. Soc.*, **152** (2005) A1398-A1408.
40. W. Zhou, R. Ran, Z. Shao, W. Jin and N. Xu, Evaluation of A-site cation deficient $(\text{Ba}_{0.5}\text{Sr}_{0.5})_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($x>0$) perovskite as a solid-oxide fuel cell cathode, *J. power sources*, **182** (2008) 24-31.
41. Y. H. Lim, J. Lee, J. S. Yoon, C. E. Kim and H. J. Hwang, *Journal of power sources*, **171** (2007) 79-85.