Nanocomposite Materials for New Energy Conversion Device

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ABSTRACT

This thesis gives an approach how to develop new perovskite and nanocomposite cathode material for low temperature solid oxide fuel cells on the basis of nanocomposite approach to lower the operating temperature of SOFC. $Ba_xCa_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (BCCF) and BSCF perovskite or nanocomposite oxides have been synthesized and investigated as catalytically potential cathode materials for low temperature solid oxide fuel cells (LTSOFC). Some single component materials have been also synthesized for new energy conversion device or EFFC. These nanocomposite and perovskite electrical conductors were synthesized by wet chemical, sol gel, co-precipitation and solid state reaction methods. Comparison with that of commercial $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode material, BCCF and locally prepared BSCF exhibit higher electrical conductivities as compared to that of commercial BSCF at same setup and conditions. In particular, novel $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has shown the maximum conductivity of 143 S/cm in air and local BSCF with conductivity of 313 S/cm in air at 550°C were measured by DC 4 probe method. An additional positive aspect of BCCF is that it is cost effective and works at room temperature but with small output which will lead SOFC to operate at extremely low temperatures. XRD patterns of the samples reveal perovskite and nanocomposite structures of the said materials. Microstructure studies give the homogeneous structure and morphology of the nanoparticles by using High Resolution Scanning Electron Microscopy (SEM). Cell resistance has been determined by Electrochemical Impedance Spectroscopy (EIS). Devised materials have shown very good mechanical strength and stability proving their importance in advanced fuel cell technology. Power density of devices from 126 to 192 $mWcm^{-2}$has been achieved.

Keywords: Nanocomposite, perovskite oxides, room temperature, DC 4 probe method, XRD, SEM, EIS, morphology, mechanical strength.

‘‘He has subdued everything in the heavens and on earth for you, within the bounds of His Law. And herein are signs for those who think and reflect (about the fact that whoever acquires knowledge of the Laws which govern all activities in the universe, will be able to control these forces and beneficially utilize them).’’

The Holy Quran (45:13)

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I want to dedicate my research work in the name of my great mother.

NOMENCLATURE

AFC	Alkaline fuel cell
ASOFC	Advanced solid oxide fuel cell
BCCF	Barium calcium cobalt ferrite
BSCF	Barium strontium cobalt ferrite
CNG	Compressed natural gas
DC	Direct current
DMFC	Direct methanol fuel cell
EFFC	Electrolyte free fuel cell
EIS	Electrochemical impedance spectroscopy
FC	Fuel cell
GDC	Gadolinia doped ceria
HTSOFC	High temperature solid oxide fuel cell
ITSOFC	Intermediate-temperature solid oxide fuel cell
LSCF	Lanthanum strontium cobalt ferrite
LNO	Lithiated-nickel oxide
LSM	Strontium doped lanthanum manganite
LTSOFC	Low temperature solid oxide fuel cell
MCFC	Molten carbonate fuel cell
NANOCOFC	Nanocomposite materials for fuel cells
OCV	Open circuit voltage
PAFC	Phosphoric acid fuel cell
PEMFC	Polymer electrolyte membrane fuel cell
SDC	Samaria doped ceria
SEM	Scanning electron microscopy
SIC	Super-ionic conduction

SOFC	Solid oxide fuel cell
TPM	Two phase material
TSOFC	Tubular solid oxide fuel cell
YSZ	Yttria-stabilized zirconia

Symbols

ABO_3	Structure formula for perovskite material
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
Co	Cobalt
Cu	Copper
E	Open circuit voltage
F	Faraday constant
H_2	Hydrogen molecule
Ni	Nickel
N_2	Nitrogen molecule
O^{2-}	Oxide ion
ΔG	Change in Gibbs free energy
e^-	Free electron
n	Number of moles
ε	Efficiency
Q_{in}	Chemical energy in the fuel provided to the cell stack
W_e	Work done for an electron

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1 Introduction

1.1 Energy Crisis

World has focused its most of the attention to get rid of the energy crisis in rapidly increasing demands for its consumption. World's fuel reserves are going to its end point with a speed of leaps and bounds. Abundant, clean and economical energy sources are the major demands of the developing nations with modern civilizations. According to the entire energy consumption of the world's auto mobile and industrial usage in 2008, about 85% of the consumed energy was contributed from conventional fossil fuels (oil, coal and natural gas). It is very important to recognize that only 15 % of energy was obtained from nuclear, hydro, biomass, wind, solar power etc. It is very essential to get the attention of the research and development towards the critical situation of oil and natural gas, if production remains constant, these are enough only for coming few decades. Similarly coal is enough to last in next 130 years [1]. Because of the supply limits, these could be scares and expensive with the increasing demands and passage of time.

The price of oil and petrol will increase as their demand is increasing day by day till difficult to reach. As we know that few years ago natural gas and CNG was pretty cheaper than diesel oil and petrol. I have observed keenly in Pakistan that most of the vehicles were converted from Diesel and petrol to the CNG due to which all the load was put on CNG and the prices jumped several 100% within a decade and load shedding of CNG in half days of week has created a lot of problems. Same could happen in the other countries if we will convert our technology from one conventional fuel into another, relying only on nonrenewable energy resources would be alarming. So we have to think about the alternate energy sources to keep the world's progress to be continued. Besides the limitations of the oil and gas reserves, energy supply system based on the combustion of the fossil fuels cause environmental problems: acidifying emissions, air pollution and emission of gases creating greenhouse effect.

The energy crisis and emerging environmental problems require the efficient use of energy while keeping the space neat and clean. Since global energy demands are continuously increasing with rapid population growth, Scientists are facing the big challenge to develop the sustainable and environmentally friendly energy resources [2]. Solid state ionic devices such as lithium ion batteries, fuel cells and solar cells could be the alternate energy storage and conversion technologies being the possible solutions for environmental issues [3].

1.2 Fuel Cell

Fuel cell is very important electrochemical device which converts chemical energy of a fuel (hydrogen, methanol, ethanol, synthetic gas etc.) provided to the anode into electrical energy when air is supplied to the cathode of the cell, is a step leading transition towards hydrogen-based economy [4]. When ethanol is supplied on anode side and oxygen on cathode side as input, dc power, heat and water are the output as the result of the electrode's chemical reaction [5]. Generally in conventional FC, an electrolyte material is sandwiched between

anode and cathode. Both electrode materials are good conductors while electrolyte is an insulator for electrons and good conductor for ions. A stack cell by series combination of multiple fuel cells is being established to get the desired voltage and electrical power [6].

1.2.1 Anode

A component in the fuel cell configuration which helps the fuel electro-oxidation process and it conducts electrons through the external circuit provided.

Properties of a functional anode are given below [7]- [9].

i) Porous material with high catalytic activity for fuels

ii) Mixed conductivity (electronic and ionic)

iii) Compatible thermal expansion coefficient (TEC) with electrolyte

iv) Low polarization resistance

Some common anode materials for solid oxide fuel cells are Ni, Co and Cu. Oxides of these metals are mixed with compatible electrolyte material to use as mixed conductor for anode functionality, where anode part contributes electronic conductivity and electrolyte part is responsible for ionic conductivity in fuel cell operation [10].

1.2.2 Electrolyte

It is a solid material which is insulator for electronic conduction and conductor for ionic conduction in fuel cell operation. It is very critical material which is considered as the responsible for SOFC performance. YSZ is a conventional electrolyte for SOFC; it is an ionic conductor and is active at 700-800 °C to ensure an appropriate output power. Gadolinia doped ceria (GDC) [11], Samaria doped ceria (SDC) [12]are alternative electrolytes for ITSOFCs.

1.2.3 Cathode

It is the component of fuel cell for reduction of oxygen molecules. Oxide ions are transported from cathode to electrolyte; it is also responsible for the distribution of electronic current. Lithiated-nickel oxide (LiNiO) is used as conventional cathode material. BSCF, LSCF, LaSrMnO etc. are also some common materials developed as cathode materials for SOFCs.

It is very important to have the following characteristics for a good cathode material [7], [13].

i) Mixed conductor (electronic and ionic)
ii) Highly porous
iii) Physically and chemically stable under oxidizing atmosphere
iv) Compatible thermal expansion coefficient with electrolyte.

1.2.4 Interconnects

Metallic or ceramic layers are used as interconnects in order to get a series combination of fuel cells for high profile power generation. These are responsible for linkage of one cell to the other and so on.

1.3 Types of Fuel Cell

Various types of fuel cells, Phosphoric Acid (PAFC), Molten Carbonate (MCFC), Alkaline (AFC), Solid Oxide (SOFC) and Proton Exchange Membrane (PEMFC) fuel cells, characterized based on electrolyte materials are used for power generation [5], [14]. This classification is responsible for the type of the electrolytes used, chemical reaction occurs in the cell; type of useful catalysts, operating temperature for the cell, type of the fuel and many other factors involved in the fuel cell operation. All types of fuel cells show their own advantages, potential application and limitations [15].

1.3.1 Polymer Electrolyte Membrane Fuel Cells (PEMFC)

These cells are also known as proton exchange membrane fuel cells with high power density and are advantageous due to favorable power density as compared to other types of fuel cells [15]. Solid polymer is used as an electrolyte and porous carbon electrodes with platinum catalyst are fixed in PEMFC as shown in figure 1.1. They operate in a temperature range 50-100 $^{\circ}$C with 53-60% mobile efficiency and 25-35% stationary efficiency [5], [13], [16]-[18]. Due to low operational temperature, they start up quickly with better durability; they are useful for transport applications [6], [19]. However they require expensive platinum catalyst for the oxidation of hydrogen, this noble metal is very sensitive to carbon monoxide (CO) poisoning. An additional reactor is required to eliminate CO gas in the fuel if hydrogen is obtained from some alcohol or hydrocarbon due to which system will be expensive.

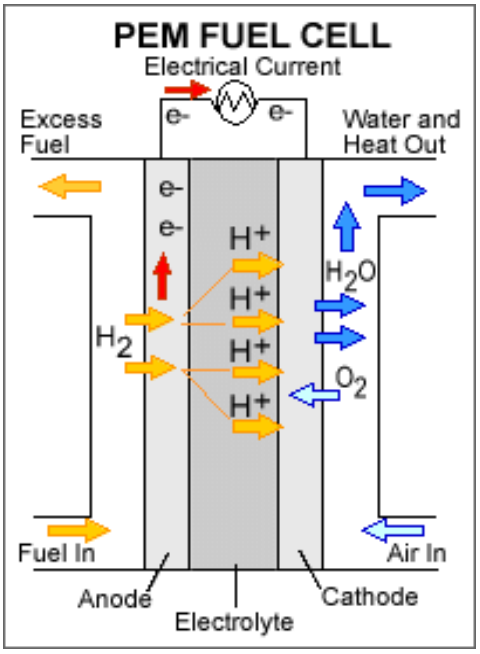

Figure 1.1: PEM Fuel Cell Working Principle [15]

Pure hydrogen storage is a significant barrier to use PEM fuel cells in vehicles. Because of low energy density of hydrogen it is quite difficult to store sufficient amount of hydrogen on-board to make sure the vehicle in order to travel the same distance of 300 to 400 miles, equivalent to gasoline fuel. Hydrogen can be obtained by reforming the high density fuels (methanol, ethanol, liquefied petroleum gas, gasoline and natural gas) but for this purpose we need an on-board fuel processor which will make the system more expensive [15].

1.3.2 Direct Methanol Fuel Cells (DMFCs)

As we know that most of the fuel cell types are powered by hydrogen as a fuel. DMFCs are powered by methanol instead of pure hydrogen. Steam enriched methanol is fed directly to the anode of the fuel cell. These fuel cells have no fuel storage problem as methanol has higher energy density as compared to that of hydrogen but less than petrol or diesel oil [15].

1.3.3 Alkaline Fuel Cells (AFCs)

In alkaline fuel cells, aqueous solution of potassium hydroxide is used as electrolyte and several non-precious metals can be used as catalyst for anode and cathode. Conventional alkaline fuel cells operate in temperature range 50-200 °C while modern AFCs are being operated from 23-70 °C with efficiency about 60% in space applications [13], [15]-[18]. These fuel cells are limited easily by carbon dioxide (CO_2) and CO poisoning; even small amount of CO_2 in air can affect the operation of the cell which also reduces the life time of the device [5], [15]. Working principle of AFC is shown in figure 1.2.

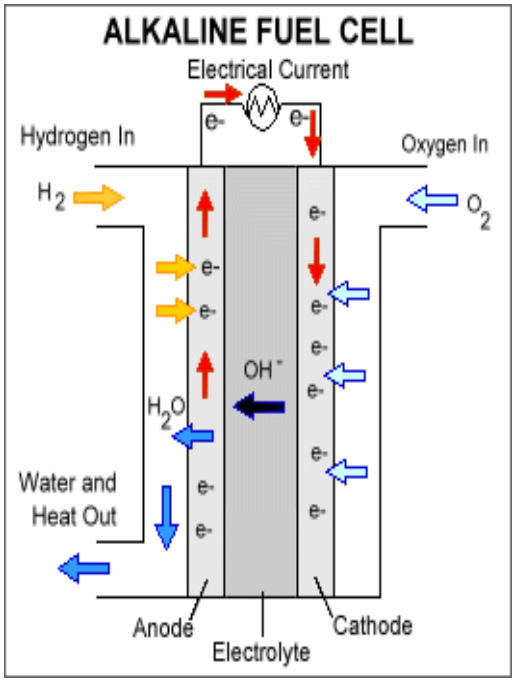

Figure 1.2: Alkaline Fuel Cell Working Principle [15]

To avoid from the poisoning, purification of hydrogen and oxygen is required before using in the cell which is much costly process [6], [19]-[20]. It is difficult to commercialize AFCs because of lower operating hours of 8000 hours for their stable operation, while more than 40000 operating hours are demanded for commercial use [15].

1.3.4 Phosphoric Acid Fuel Cells (PAFCs)

These cells use phosphoric acid as an electrolyte which is contained in Teflon-bonded silicon carbide matrix, platinum catalyst is also contained at porous carbon electrodes [15]. Schematic diagram for PAFC is show in figure 1.3. They operate at 200-250 °C with 40% efficiency [5], [13], [16]-[18]. PAFCs are more tolerant for impurities in fossil fuels than PEMFCs and are used usually for stationary power generation as well as some of them are also used in city buses. Their efficiency is 85% while being used for cogeneration of heat and electric power but for electricity production, they are efficient only 37-42% [15]. PAFCs with same weight and volume are weaker than other types of fuel cells. They are expensive fuel cells because they need expensive noble-platinum catalyst for electrodes [19]-[20].

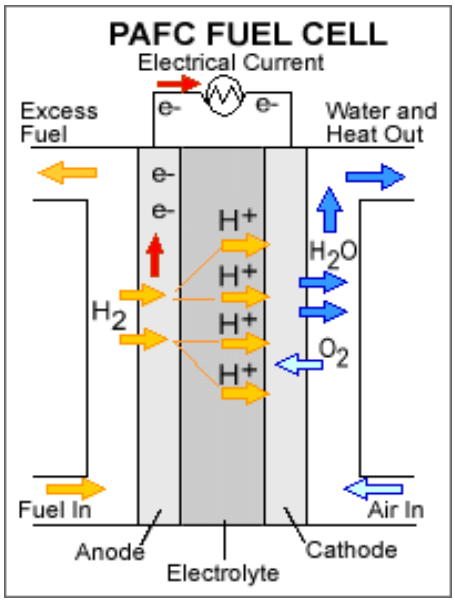

Figure 1.3: PAFC Working Principle [15]

1.3.5 Molten Carbonate Fuel Cells (MCFCs)

They are moderate-high temperature (600-700 °C) devices with molten carbonate salt mixture as an electrolyte in porous Lithium Aluminum oxide ($LiAlO_2$) matrix while at electrodes non precious catalysts can be used and have an efficiency of 45-47% [5], [13], [15]-[18]. Working principle is shown in figure 1.4. MCFCs by coupling with turbines give 65% efficiency which is considerably greater than PAFCs. If heat loss can be used then efficiency can reach up to 85% [5], [15]. They don't need any external reformer for conversion of fuel into hydrogen as this process is automatically done due to high temperature for its operation which is very useful to reduce the cost. These cells are not poisoned by CO and CO_2; instead they can operate with CO as a fuel. Durability is their major limitation, high operating temperatures and corrosive electrolyte cause component breakdown and corrosion [5], [15], [19]-[20].

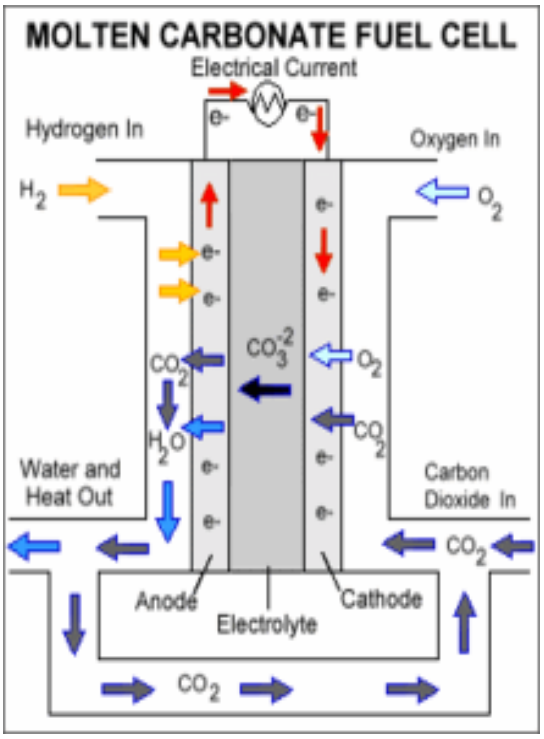

Figure 1.4: MCFC Working Principle [15]

1.3.6 Solid Oxide Fuel Cells (SOFCs)

SOFC using a solid oxide electrolyte is the dominant over rest of the fuel cell technologies, because of the ability to use currently available fossil fuels, low cost, long term stability, low emissions and fuel (including hydrogen, natural gas, gasoline, diesel and coal-derived synthetic gas) flexibility but still needed to reduce operating temperature [21]. It converts chemical energy of the fuel by combining fuel and oxidant gases electrochemically across an ionic conductor into electric power without combustion [3].

SOFC working principle is shown in figure 1.5. These fuel cells use a solid and non-porous ceramic material as an electrolyte. It has an efficiency of 60% by converting fuel into electricity but when using co-generation system to capture waste heat to convert into useful electric power, its efficiency approaches to 85% [15]. SOFCs are operated in three different ranges of temperature, conventional high temperature solid oxide fuel cell (HTSOFC) works from 800-1000 °C, intermediate temperature SOFC (ITSOFC) operates from 600-800 °C and low temperature SOFC (LTSOFC) which can operate below 600 °C. Yttria Stabilized Zirconia (YSZ) is used as an electrolyte in conventional HTSOFC with an average efficiency of 45-70% [13], [16]-[20].

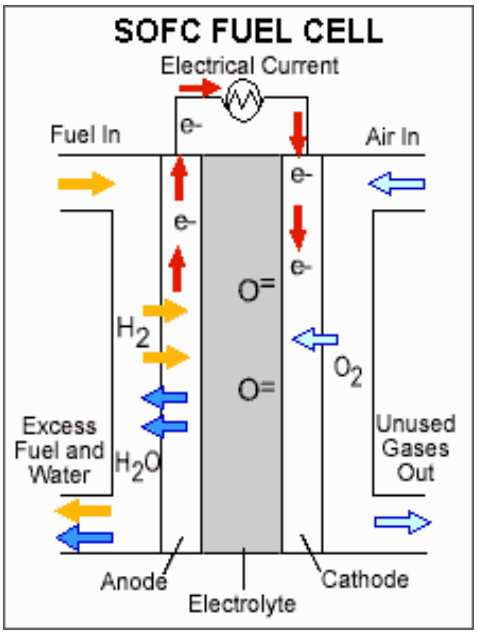

Figure 1.5: SOFC Working Principle [22]

SOFCs are not sticky only with precious metal catalyst and are responsible for reducing the cost. Due to high temperature, internal reformation of fuels is also accessible because of this reason, a variety of fuels are enable to be used in these fuel cells. SOFCs can tolerate sulfur, in addition they are not poisoned by CO and even this gas could also be used as a fuel for the device. This property of SOFC allows gases to be used generated from coal. I would like to suggest that SOFC can be very useful for producing electricity from Thar coal in Pakistan because of the existence of huge coal mines over there. Synthetic gas can be obtained from Thar coal due to which efficiency can be increased much more. Combustion engines can be operated directly from coal, deliver 30-35% efficiency whereas using SOFC, more than 60% electrical efficiency can be achieved. The best way to get higher efficiency from SOFC is to use syngas being best fuel from coal to generate electricity.

High temperature limits the durability of the cell and also causes material degradation and in order to maintain high temperature for the operation of the device, affects the cost of the system. Scientists are trying their best to make it possible to operate advanced SOFC at low temperatures from 300-600 °C [23]. In tubular solid oxide fuel cell (TSOFC), solid electrolyte based on nonporous metal oxide is used like YSZ, SDC or GDC. It operates at 1000 °C, oxygen ions are responsible for the ionic conduction in the tubular [19]-[20], [23].

1.3.6 Configuration of SOFC

Most recent advances technologies are updated, SOFCs can be classified into three sub-types on the basis of their structure.

i) 3-Layer device
ii) 2-Layer device
iii) Single layer device

In conventional 3-layer device, anode and cathode are separated by a thin layer of electrolyte to get an open circuit voltage (OCV) and an outer circuit is established between the electrodes to measure the short circuit current. Electrolyte research from many decades have been continued to improve the ionic conductivity of electrolyte because it is a key component in conventional fuel cell. Due to lack of expertise and financial supports, affordable and useful electrolytes were not introduced in past, so this technology could not be commercialized.

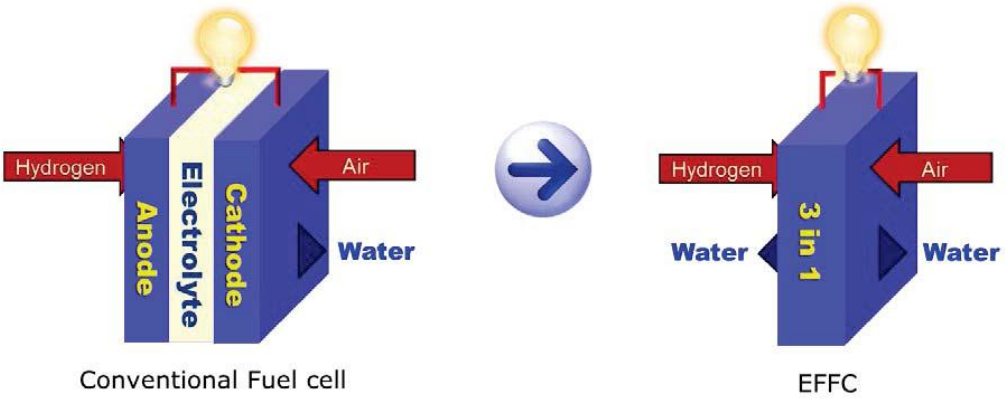

Figure 1.6: Comparison between Conventional FC and EFFC [10]

In very latest developments, a breakthrough technology/single and two layer electrolyte-free fuel cells were invented by Professor Bin Zhu's group at The Royal Institute of Technology (KTH) Stockholm, Sweden in 2010, was selected as a research highlight by Nature Nanotechnology, 2011. The electrolyte free fuel cell (EFFC) consists of only one layer is a mixture of all the conventional anode, electrolyte and cathode three components, or 2-layer based on only anode and cathode two components without the electrolyte layer is introduced and same OCV and current is achieved like conventional 3-layers device even better. Difference between 3 and single layer device is given in the figure above. EFFC is also called as single component FC which is very easy to handle and to be commercialized. Many scientific mechanisms are responsible for their better performance over 3-layer device which we are investigating with much care and responsibility in our ongoing research work. A comprehensive comparison between a conventional and electrolyte free fuel cell is shown in figure 1.6.

1.4 Perovskite Materials and Advance SOFC or Low Temperature SOFC

Tremendous efforts have been done to decrease the operational temperature of SOFC. A key issue in reducing the operating temperature of the cell is poor activity of cathode and reduction of oxygen ion conductivity at lower temperatures. Perovskite cathode materials with ABO_3 structure formula containing Cobaltite with high electronic and ionic mixed conductivities have been proven as better cathode material in ASOFCs at low temperature. Most common cathode material in SOFC is Strontium doped $LaMno_3$ (LSM). It is not a practical cathode material due to its poor catalytic activity as well as low ionic conductivity at low temperatures [24]. It was studied in literature that $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ was used as Perovskite cathode material in ASOFCs at low temperatures but they showed relatively low cell performance [25]. Another Perovskite cathode material with composition $Ba_xSr_{1-x}Co_yFe_{1-}$

$_yO_{3-\delta}$ (BSCF) has attracted much more attention because of its high conductivity as well as very good catalytic activity and oxygen transport for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [21], [26].

1.5 Thermodynamics of SOFC

SOFCs work on the principles of thermodynamics, hydrogen gas is fed as a fuel to the anode of the cell and air is supplied from the cathode side. Oxidation of hydrogen takes place at anode and Oxygen is reduced at cathode while electrolyte is used as transport medium for the oxide ions, during this process following chemical reactions take place in the cell [13].

Anode half-cell reaction; if the anode material is catalytically active, hydrogen molecule is oxidized by losing electrons and converts into protons, these protons latterly react with oxide ions to produce water:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (1.1)$$

Cathode half-cell reaction; oxygen is reduced into oxide ion by gaining two electrons for each atom at cathode:

$$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-} \quad (1.2)$$

Complete fuel cell reaction; the over cell reaction is given below:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad (1.3)$$

Open Circuit Voltage (OCV)

OCV, E of a SOFC is established between anode and cathode. The magnitude of OCV is determined by Gibbs free energy expression for ΔG [27],

$$\Delta G = - nFE \quad (1.4)$$

$$E = - \Delta G/nF \quad (1.5)$$

OCV depends on temperature, concentration gradient of hydrogen, oxygen, water at the anode and cathode of the cell.

Cell Efficiency

Efficiency of the fuel cell is determined by following relation [27],

$$\varepsilon = W_e/Q_{in} \quad (1.6)$$

1.6 Renewable and Nonrenewable Energy Resources for SOFC

Conventional or nonrenewable energy resources are fossil fuels and renewable energy resources such as biofuels, wind, solar etc. Both types of energy resources can be used for SOFCs. Usually hydrogen and hydrocarbon fuels (coal gas and natural gas) are favorable for the fuel cell devices, liquid fuels (methanol, ethanol, di-methyl ether, bio gas etc.) are also being used for operating fuel cells. SOFC is best over the other types of fuel cell due to its

fuel flexibility property [28]-[31]. Pyrolysis is a developed process for thermochemical conversion of solid biomass into gaseous fuels to use in the operation of SOFC [10]. Another process for the production of gaseous fuel (biogas) is gasification [32]-[35], it was developed in the laboratory of department of energy technology at KTH Stockholm, Sweden. CH_4, CO_2, CO, N_2 and H_2 are the constituents of the synthesized biogas in the lab.

1.7 NANOCOFC Science

A nanocomposite material for fuel cells (NANOCOFC) is a scientific approach to develop functional nanocomposite materials to operate the SOFCs at low temperatures (300-600 °C). The prepared nanocomposite materials can also be used in many other solid electrochemical devices for the production of electrical power [36]-[42]. A wide flexibility and feasibility are the key requirements for the development of the advanced fuel cell nano-architectures. These nanocomposite are two-phase materials (TPM) which reveal some unique characteristics and multiple functions are given below [37]-[42].

i) TPM materials contain an interface between two phases of their structure; this two-phase interfacial region (core-shell structure) is responsible for the material functionalities. Conventional structural limits are eliminated by the interfacial functionalities using TPM composites.
ii) The ionic transport process does not play any viable role in two-phase nanocomposite electrolytes and is different from conventional bulk structure. Interfacial super-ionic conduction (SIC) and mechanisms are fast enough through the interfaces in composite materials revealing the functionalities and electrical properties.
iii) Source ions (O^{2-}, H^{+}) and SIC share positively to enhance device performance at low temperatures 300-600°C.
iv) Interfacial-SIC and mechanisms help for the development of functional composite materials directly as well as from non-functional materials until functional interfaces can be active.
v) New opportunities for the advance development of functional nanocomposite for LTSOFCs can be created by interfacial as well as surface redox reactions.

1.8 Objectives

Main focus of the study was set to operate the ASOFCs in low temperature as well as to reduce the system cost by developing

i) New perovskite or nanocomposite cathode materials for ASOFCs.
ii) Treatment and optimization of nanocomposite materials for new energy conversion device.
iii) Preparation of active materials, determination of their conductivities and microstructures.

iv) Calibration of SOFC components and Fuel cells
v) Testing of different SOFC devices.

2. EXPERIMENTAL TECHNIQUES

2.1 Perovskite or nanocomposite materials-synthesis for ASOFC

In this section different synthesis routes e.g. solid state reaction, co-precipitation, wet chemical, sol gel etc., have been described, how they have been applied for the preparation of perovskite-type or nanocomposite materials for LTSOFCs or ASOFCs.

2.1.1 Synthesis of Perovskite-type or Nanocomposite electrodes

Different nanocomposite electrode materials were prepared by performing the experiments on different platforms (laboratories) provided by Fuel Cell Group at KTH. Some were used, as-prepared cathode, in fuel cell calibration.

2.1.1.1 Preparation of electrode $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)-perovskite

BSCF, an electrode material was synthesized by co-precipitation method. 0.5M of Barium Nitrate, $Ba(NO_3)_2.H_2O$ (Sigma-Aldrich, USA) named as solution A was mixed with Strontium Nitrate, $Sr(NO_3)_2.H_2O$ (Sigma-Aldrich, USA) in a bath, using 0.5:0.5 molar ratio of precursors of both compounds. This solution was then stirred on a magnetic stirrer for 1 hour at 70°C, meanwhile 0.5M of Cobalt Nitrate hexa-hydrate, $Co(NO_3)_2.6H_2O$ (Sigma-Aldrich) named as solution B was prepared with Iron Nitrate nona-hydrate, $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich) in a separate bath with molar ratio of 0.8:0.2 for the two compounds, this solution was also stirred for half an hour at 70°C. Solution B was mixed drop wise in solution A. Adding both of the solutions, resultant solution was named as solution C. The complete scheme for preparation of local BSCF is given in the flow chart in figure 2.1. Almost same scheme was adopted for most of the samples preparation.

An appropriate percentage of Ammonia, NH_3 (Sigma-Aldrich) was added to the composite solution C (mixture of solution A and B) for maintaining the pH value between 2-4 according to the literature and the solution was named as solution D, it was well stirred for 4 hours at 70°C. Then 0.047M of oxalic acid dehydrated solution was prepared and added drop wise in well stirred solution D. It was again stirred for half an hour till clear precipitates of the BSCF were observed in the beaker. Precipitates were washed in water and filtered properly. These resultant precipitates were then dried at 120 °C overnight. The dried precipitates were ground well homogeneously into powder form in mortar with pestle. This ground powder was then sintered at 1000 °C for 5 hours to get the perovskite structure. The sintered material was nicely ground again to get BSCF powder to use for different requirements. It is observed that BSCF shows perovskite structure with ABO_3 structure formula.

To prepare the nanocomposite cathode material, as-prepared BSCF powder and samarium doped Ceria, SDC (Sigma-Aldrich) were mixed with 1:1 volume ratio using standard solid state reaction method for synthesizing a mixed conductor. After ensuring a homogeneous ground material, its calcination was done at 700 °C for 4 hours. In this way BSCF-SDC a nanocomposite cathode with mixed conductivity was achieved for fuel cell fabrication.

Flow Chart for BSCF

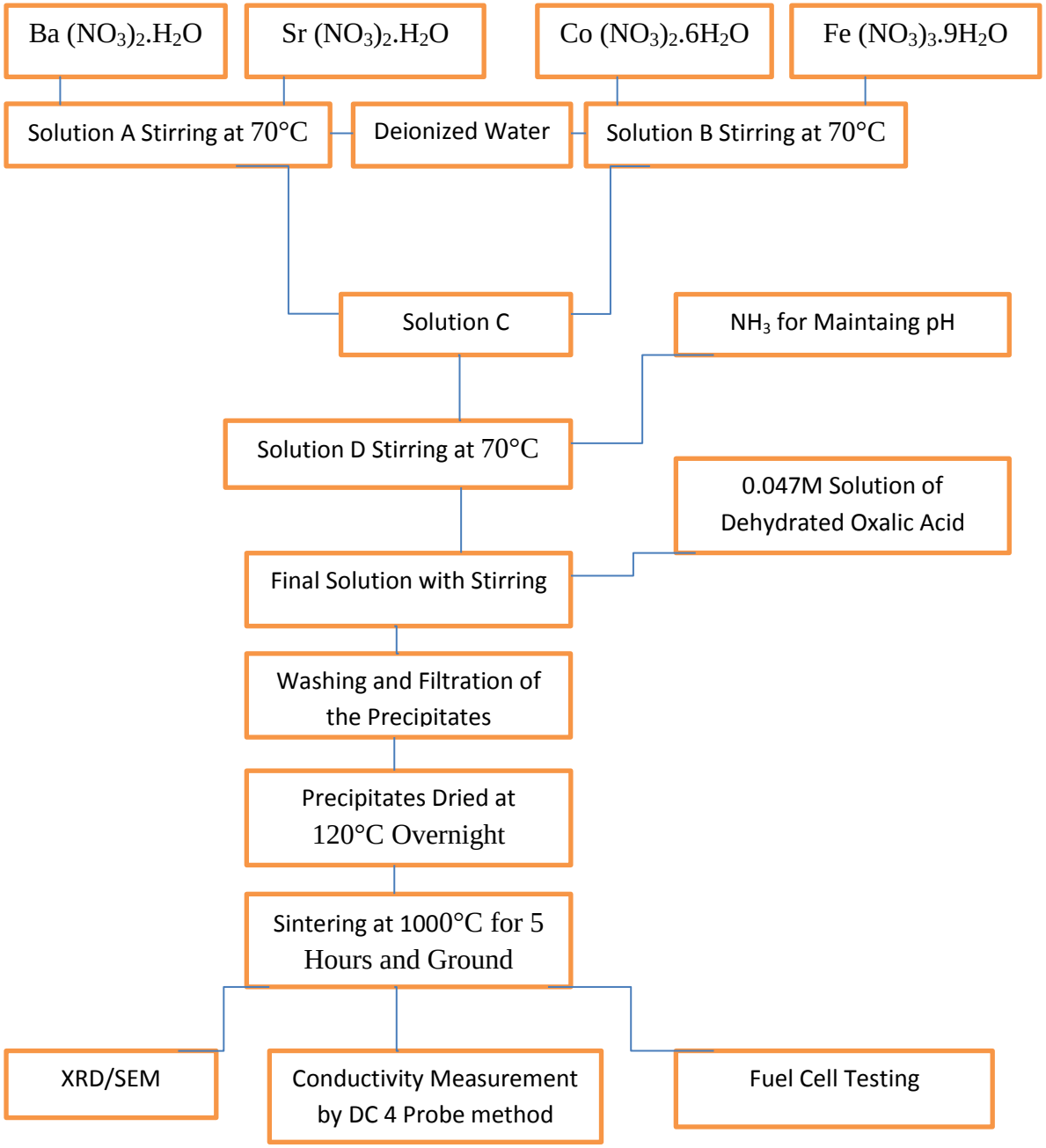

Figure2.1: Co-precipitation Synthesis Process for BSCF

2.1.1.2 Preparation of cathode $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

BCCF, a cathode material was prepared by wet-chemical method. Specified amounts of Barium Nitrate, $Ba(NO_3)_2.H_2O$ (Sigma-Aldrich, USA), Calcium Nitrate tetra-hydrate, $Ca(NO_3)_2.4H_2O$ (Sigma-Aldrich, USA), Cobalt Nitrate hexa-hydrate, $Co(NO_3)_2.6H_2O$ (Sigma-Aldrich) and Iron Nitrate nona-hydrate, $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich) were mixed all-together in a separate beaker with molar ratios 0.3:0.7: 0.8:0.2 respectively to make a 100

ml aqueous solution. This scheme was used to replace Strontium with Calcium at A-site in ABO_3 structure. It was aimed that resultant material should have the perovskite-type structure with ABO_3 form. The total mixture was continuously stirred for 30 minutes. An appropriate amount of citric acid was also added in the precursor's solution for auto-combustion of the material, and then the net solution was stirred again for 2 hours at 80 °C. After getting auto-combustion, the ash was ground well in mortar with pestle (conventional method) so that fine and homogeneous powder was obtained and sintered at 950 °C to get the proper structure of the material. It was ground again to get the fine powder form of the sintered BCCF.

As-prepared BCCF powder was mixed with SDC with a volume ratio of 1:1 by using solid state reaction method to use it as cathode material in 2, 3-layer SOFCs. The mixed conductor BCCF-SDC was calcined at 700 °C for 4 hours for its further use in cell performance. In this way, nanocomposite mixed-electronic and ionic conductor was prepared. This powder was further used for cell operation in the Fuel Cell Rig.

2.1.1.3 Preparation of cathode $Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

Another perovskite cathode material BCCF was also prepared by wet-chemical method. The stoichiometric amounts of $Ba(NO_3)_2.H_2O$, $Ca(NO_3)_2.4H_2O$, $Co(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ were mixed as it is, were obtained from the supplier without any further purification all-together in a separate beaker with molar ratios 0.9: 0.1: 0.8: 0.2 respectively in order to get 100 ml aqueous solution. The mixture was stirred on magnetic stirrer accompanied with a heating system for 30 minutes. A prescribed amount of citric acid was also added in the solution for auto-combustion, and was stirred again for 2 hours at 70-80 °C. Magnetic bead is responsible for homogeneous mixing during the stirring process. As a result of auto-combustion, the ash was obtained which was ground well in mortar with pestle (a conventional method) to get a fine and homogeneous powder. Powder was sintered at 950 °C in the furnace to get the expected structure of the cathode material. It was ground again to get the fine powder form of the BCCF structure. It was expected according to theoretical background that BCCF would be perovskite material with ABO_3 general formula.

As-prepared BCCF powder was mixed with SDC with a volume ratio of 1:1 by using conventional method by mortar and pestle for its future use as cathode material in the form of mixed conductor to use in 2 and 3-layer SOFCs. The mixed conductor, BCCF-SDC was calcined at 700 °C for 4 hours for its further use in cell performance. So nanocomposite mixed-electronic and ionic conductor was prepared. This powder was then used for cell fabrication and tested in the Fuel Cell testing Rig. These (BCCF) prepared materials were used in Fuel cell Laboratory at Aalto University Helsinki, Finland.

2.1.1.4 Preparation of cathode $Ba_{0.5}Sr_{0.5}Cu_{0.7}Fe_{0.3}O_{3-\delta}$ (BSCF)

Another electrode perovskite material BSCF was prepared by wet-chemical method with the same strategy. Pure precursors of Ba $(NO_3)_2.H_2O$, Sr $(NO_3)_2.H_2O$, Copper Nitrate tri-hydrate Cu $(NO_3)_2.3H_2O$ (Sigma-Aldrich, USA) and Fe $(NO_3)_3.9H_2O$ was mixed as it is, they used as obtained from the supplier without any further purification in a beaker with molar ratios 0.5: 0.5: 0.7: 0.3 respectively in a 100 ml aqueous solution. The mixture was stirred by electronic

magnetic stirrer accompanied with a heating system for 30 minutes. Temperature of the stirring solution of the mixed precursors was controlled by an internal temperature sensor system.

A supporting amount of citric acid was then added in the solution for auto-combustion, and was stirred again for 1.5 hours at 80 °C. Material obtained from auto-combustion, was ground well in mortar with pestle using conventional method to get a uniform powder. The powder was sintered at 950 °C in the furnace to get the expected structure of the cathode material. It was ground again to get the fine powder of the copper supported BSCF structure. This attempt was made to replace Cobalt with Copper at B-site in ABO_3 structure. And it was assumed that obtained material would have the perovskite structure.

As-prepared Copper supported BSCF powder was simply mixed with SDC with a standard volume ratio of 1:1 by using conventional method of mixing by mortar and pestle for its future use as cathode material as a mixed conductor in 2 and 3-layer devices. The mixed conductor, BSCF-SDC was calcined at 700 °C for 4 hours for its further use in fuel cell testing. So in this way nanocomposite mixed (electronic, ionic) conductor was obtained. The NANOCOFC approach was applied in order to obtain mix-conductor powder. Conductivity was measured by the tubular furnace at the Fuel Cell Rig at KTH.

2.2 Nanocomposite materials-synthesis for new energy conversion device

Zhu. Bin., et al revealed a breakthrough when they invented single component fuel cell or new energy conversion device by applying NANOCOFC approach and they introduced nanocomposite (two phase) materials with mix conductivities [10]. This part contains synthesis of nanocomposite materials for new energy conversion device. These materials are also referred as single component materials. These materials are very important for fuel cell power generation.

2.2.1 Composite material (LNCZ) synthesis for new energy conversion device

A nanocomposite material (LNCZ) was prepared by standard solid state reaction method. Lithium carbonate, Li_2CO_3, Nickel carbonate basic, $NiCO_3.2Ni(OH)_2.4H_2O$, Copper carbonate basic, $CuCO_3.Cu(OH)_2$ and Zinc carbonate basic, $2ZnCO_3.3Zn(OH)_2$ were obtained from Sigma Aldrich and were used without further purification. Precursors of all compounds were ground with a molar ratio of 1.5:7:2.5:7. Well mixed homogeneous mixture of the precursors was sintered at 800 °C for 4 hours in a furnace. As-prepared composite LNCZ oxide was ground for 10 minutes to get homogeneous fine powder. This electrode material was then mixed and ground with electrolyte powder of SDC in an appropriate volume ratio of 1:1 to prepare single component material. Finally, this composition was sintered at 700 °C for 4 hours. The sintered material was well ground for more than 15 minutes and was converted into fine powder form to use as single component fuel cell or new energy conversion device.

2.2.2 Preparation of composite (LiNiO) for new energy conversion device

A nanocomposite material for multipurpose functionalities was prepared by solid state reaction method. The stoichiometric amounts of Li_2CO_3 (Sigma Aldrich), $NiCO_3.2Ni(OH)_2.4H_2O$ (Sigma Aldrich) were mixed with molar ratio 1:1 respectively and were ground in mortar with pestle for better homogeneity of the mixture. Once the uniform mixture was prepared then it was sintered in a furnace at 800 °C for 4 hours. After cooling down at room temperature, as-prepared material was ground for 10 minutes and uniform grains of nano-powder were achieved in this process applying NANOCOFC approach. Afterward, as-prepared LiNiO was mixed with electrolyte powder of SDC with a volume ratio of 1:1 to prepare a composite material to be used as single component material. For this purpose, mixture of both powders was ground for more than 15 minutes so that uniform mixture could be achieved. This composite powder was sintered again at 700 °C for 3 hours to get well-structured single component material. The resultant material was ground again for 10 minutes and used in new energy conversion device.

2.3 Dry press method for conductivity measurement

Homogeneous ground powder was compacted in the form of pellets for transport purposes to measure the conductivity and other properties evaluation, respective powders were pressed by dry press method. Powder of electrode materials was pressed in a die of 13 mm diameter to shape the thick pellets with diameter of size of the die. It was observed that the active area of the prepared pellet was 0.64 cm^2 when used in sample holder for conductivity measurements. The thickness of the pellets was about 2-3 mm for its testing and in some cases up to 5 mm. Powder for manufacturing the pellet, in the die was provided a stress under the pressure of 50 MPa for 5 minutes. When the pellets were made, they were put in the furnace at 650 °C for heat treatment for 1 hour. The pellets were pasted with silver paste on both sides for better electrical contact before testing them at Fuel Cell Testing Rig. For testing, tubular furnace was used, where sample holder was put and shielded with heat blocking material.

2.4 Fuel Cell Fabrication

A number of SOFCs were fabricated for testing the performance. For this purpose, fuel cells were prepared with different configurations.

2.4.1 Conventional fuel cell or 3-layers device (anode/electrolyte/cathode)

Conventional fuel cells consist of two different electrode configurations as given below.

a. Asymmetrical fuel cell (with different materials for anode and cathode)
b. Symmetrical fuel cell (anode and cathode of same materials)

2.4.1.1 Asymmetrical fuel cell

An asymmetric fuel cell of standard 13 mm diameter for testing was compacted. Fine powder of anode material was laid on nickel foam substrate as a first layer in a stainless steel die; a thin layer of electrolyte was spread over the anode as second layer and finally cathode powder (different from anode) was layered next to the electrolyte forming a complete assembly which can work as conventional energy conversion device. Mostly, NiO was used as anode, SDC as electrolyte and synthesized material (BSCF, BCCF, copper supported BSCF or LiNiO) as cathode. In some cases, LiNiO was also used as anode and NiO or BSCF as cathode. This fundamental configuration was pressed in a dry molding press. Stress was applied by exerting a pressure of 200 MPa.

The designed sample was put under the same load for 5 minutes. After this, fuel cell was extracted safely from the die and saved for later usage. Samples of different thickness were prepared and then sintered at 650 °C for one hour only. In few cases, sintering was done to make the bared device active and mechanically strong but most of the time, devices were used as un-sintered. In every case of the sample of all pellets, the active area of the fuel cell was measured as 0.64 cm^2. For fuel cell's performance measurements, both of the electrode surfaces were painted with silver paste for efficient current collectors. The cells were tested at different temperatures.

2.4.1.2 Symmetrical fuel cell

In this type, fuel cell was fabricated in similar way as asymmetrical fuel cell with same components and their structure. The only difference in this type was that anode and cathode were of same nanostructured material. Device was pressed under the applied load of 200 MPa for 10 minutes. In symmetrical case, LNO was used as anode and cathode of the fuel cell while SDC was fixed as an electrolyte. Pellets were fabricated of 13 mm diameter and an active area of 0.64 cm^2. On both sides of the cell, silver paste was painted and performance was measured at different temperatures. In either of the type, electrolyte was sandwiched between anode and cathode. In every case, when I measured the performance of the non-sintered cell immediately after fabrication, metal support was given by using nickel foam to the anode side. I have not used nickel foam in all of my sintered cells.

2.4.2 Two layers fuel cell (anode/cathode) (Electrolyte free fuel cell)

Two layers fuel cell device was designed by just removing the electrolyte layer and compacting rest of the two layers (anode and cathode). 2-layers devices were fabricated of 13 mm diameter with an active area of 0.64 cm^2. Most of the times LNO or NO was used as anode and BSCF or LNO respectively were used as cathode materials. Pellets were pressed under an external load of 200 MPa for 10 minutes. Metal support was provided by nickel foam on anode side of the device. Pellets were coated by silver paste on cathode sides before testing them. 2-layer devices were tested in a tubular furnace between 400-600°C temperatures.

2.5 New energy conversion device (Single component fuel cell)

New energy conversion device was made by two kinds of single component materials separately. In this type of fuel cell only single homogeneous nanocomposite layer is pressed to make the system for energy conversion. The single component fuel cell is also known as electrolyte free fuel cell because of the removal of electrolyte layer which is being considered as responsible to avoid short circuit but in case of single layer device, we get the same performance without electrolyte layer as it was with electrolyte layer in conventional 3-layer device. In this fuel cell, homogeneous mixture of electrode and electrolyte is prepared and pressed in the form of pellets.

2.5.1 Single component fuel cell based on LNCZ

To prepare this type of fuel cell, first of all LNCZ was mixed with SDC in a volume ratio of 1:1. A homogeneous mixture was prepared and sintered at 700 °C for 4 hours, after cooling; it was ground and pressed in the form of pellets of size about 1 mm. Nickel foam was provided as a substrate for support as well as a current collector. Single layer devices were fabricated by applying a stress of 250 MPa for 30 minutes. Diameter of the fuel cell was 13 mm and active area of the device was 0.64 cm^2. Before testing in the tubular furnace, air providing side of the electrolyte free fuel cell were painted by silver paste. Performance of the cell was measured at 550 °C, hydrogen was provided from nickel foam side and the other layer was exposed to air.

2.5.2 Single component fuel cell based on LiNiO

First of all single component nanocomposite material by homogeneous mixture of LiNiO and SDC was prepared in a volume ratio of 1:1. Then this mixture was sintered at 700 °C, after cooling this sample, was ground for 10 minutes to make it fine powder for new energy conversion device. This powder with mixed conductivity was compacted by dry press method under the load of 250 MPa. To get this fuel cell of thickness about 1 mm, only one layer of single component material was spread over nickel foam and obtained the pellets with uniform density. Pellets of 13 mm diameter and active area 0.64 cm^2 were fabricated. The pellets without Ni foam were sintered at 600 °C for testing. Then these pellets were painted with silver paste on both sides for efficient current collectors. Performance was measured without any further heat treatment of the device.

3 Results and Discussion

3.1 Electrode Material-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)

3.1.1 XRD Pattern for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)

The crystalline phase of the locally synthesized BSCF material was examined by XRD. XRD pattern was determined by using a Philips X'pert pro super diffractometer with Cu-Kα radiation of wavelength (λ=1.5418 Å) working at 45 kV voltage, 35 mA current, shown in figure 3.1. As-prepared powder material was sintered at 1000°C for 8 hours to get proper perovskite structure with ABO_3 formula. XRD peaks of the locally prepared BSCF were matched with the peaks of BSCF and BPCF ($BaPrCoFeO_3$) [26], [43]. Comparison of XRD pattern shows that as-prepared material has perovskite structure with peaks at particular positions.

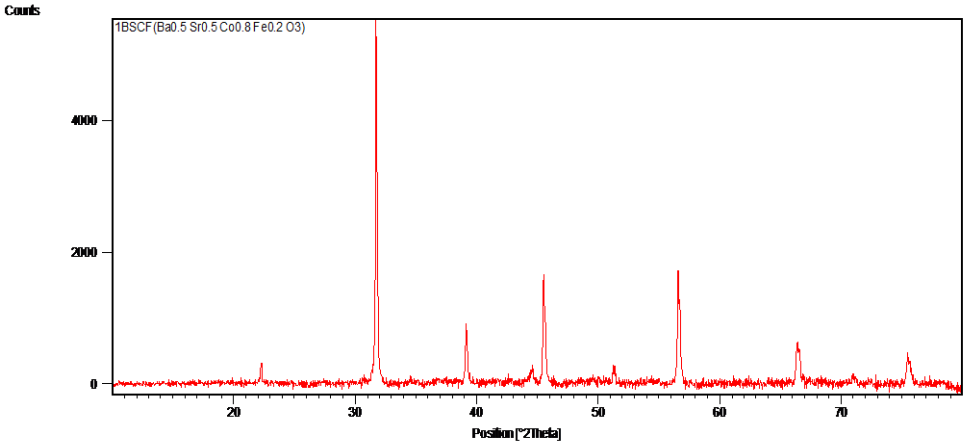

Figure 3.1: XRD Pattern for Locally Prepared BSCF

3.1.2 Electrical Conductivity Measurements for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)

Thickness of pellet = 2.0 mm = 0.2 cm, Effective area = 0.64 cm^2

Table 3.1 BSCF Conductivity dependence on temperature

S. No	Temperature (°C)	1000/T (K^{-1})	Resistance (Ω)	Resistivity (Ωcm)	Conductivity (Scm^{-1})
1	550	1.22	0.001	0.0032	313
2	500	1.29	0.003	0.0096	104.17
3	450	1.38	0.009	0.0288	34.72
4	400	1.49	0.020	0.064	15.63
5	350	1.61	0.039	0.1248	8.01
6	300	1.75	0.074	0.2368	4.22
7	250	1.91	0.128	0.4096	2.44
8	200	2.11	0.277	0.8864	1.13

Locally prepared BSCF cathode material is a mixed conductor with both ionic and electronic conductivity but electronic conductivity is two orders higher than ionic conductivity so we can say that the measured DC-conductivity refers to electronic conductivity only. DC-conductivity measurement was performed by dc 4 probe method, for this purpose, thick pellets of 13 mm diameter were pressed under a heavy load of 250 MPa. The results obtained in the presence of air are plotted by using MATLAB in the figure 3.2; values of 1000/T means are inversely proportional to the absolute values of temperature. It is quite clear from the graph that conductivity is inversely proportional to 1000/T therefore it should be proportional to the temperature and was increased more and more with rise in temperature. The maximum conductivity, more than 300 S/cm was achieved around 550°C as shown in table 3.1 and it remained stable with passage of time as long as was measure which confirms its potential use in fuel cell field. Any material degradation with aging was not seen, it means that material is thermally and mechanically enough stable to be used.

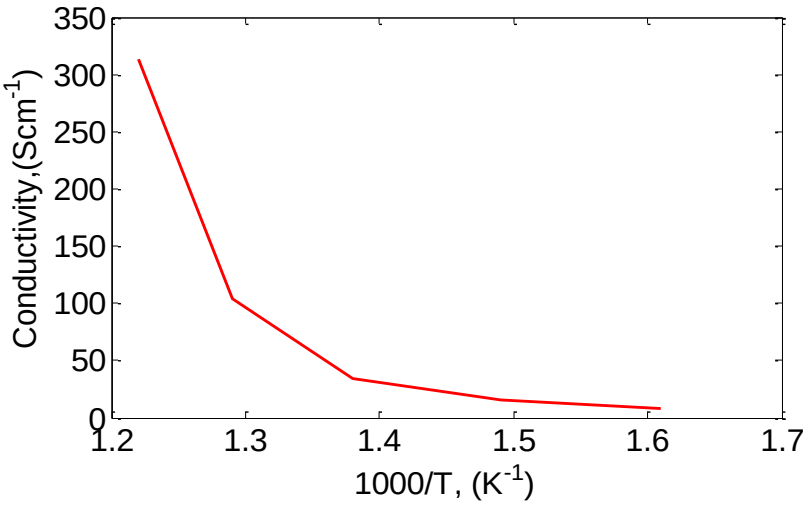

Figure 3.2: Plot between Conductivity and Absolute Temperature for Local BSCF

As perovskite BSCF has mixed conductivity so the total conductivity is sum of the high electronic and low ionic conductivities because of the presence of electronic holes and oxygen vacancies, where the electronic conductivity is almost two orders of magnitude higher than that of ionic conductivity [26]. Since electronic conductivity is dominant in this case so we can consider that our measured conductivity refers to the electronic conductivity of the material.

3.2 Electrode Material- $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

3.2.1 XRD peaks for $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

XRD pattern of the synthesized BCCF cathode nanocomposite material was examined by X-ray diffractometer with Cu-Kα radiation, with 45 kV applied voltage and 35 mA current, shown in figure 3.3. An internal wavelengths used from anode material were obtained by Copper (Cu). As-prepared nanocomposite material was sintered at 900°C for 10 hours to get

proper structure. The XRD pattern of the novel material was determined. It is observed that BCCF has nanocomposite structure. This pattern shows that prepared material has nanocomposite effect additional to the perovskite structure because while preparing this material, NANOCOFC approach was used to get more effective performance of the fuel cell. If we compare this pattern with the perovskite material peaks, we come to know that perovskite peaks are also there in this pattern.

It was assumed that Calcium atoms should be doped properly at A-sites in ABO_3 formula structure. It is estimated that Calcium is doped but with some dislocations in the resultant structure. Its nanocomposite characteristics have shown awesome conductivity of the resultant powder. The conductivity was expected to be 50 S/cm at 600°C but it was proven more than 100 S/cm even at 550°C. Our prepared material has mixed conductivity (both electronic and ionic). But the measured conductivity is referred to as electronic being dominant on ionic conductivity.

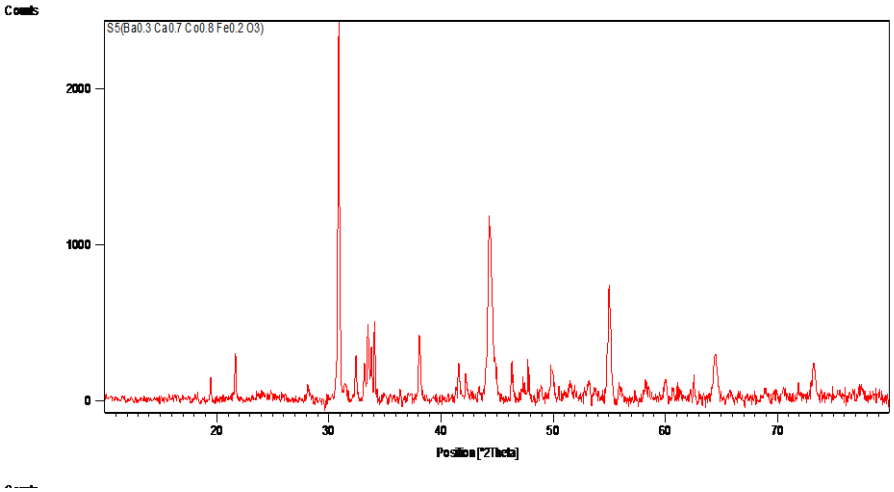

Figure 3.3: XRD Pattern for Locally Prepared S5 (BCCF)

3.2.2 Conductivity Measurements for $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

Thickness of pellet = 2.4 mm = 0.24 cm, Effective area = 0.64 cm^2

Table 3.2 BCCF (a) Conductivity dependence on temperature

S. No	Temperature (°C)	1000/T (K^{-1})	Resistance (Ω)	Resistivity (Ωcm)	Conductivity (Scm^{-1})
1	550	1.22	0.003	0.007	143
2	500	1.29	0.010	0.026	38.46
3	450	1.38	0.021	0.055	18.18
4	400	1.49	0.059	0.157	6.37
5	350	1.61	0.110	0.293	3.41
6	300	1.75	0.185	0.493	2.03
7	250	1.91	0.285	0.759	1.32

The conductivity measurement was done by dc 4 probe method and is manipulated in table 3.2. Thick Pellets of 13 mm diameter were pressed under a load of 250 MPa. The conductivity results versus 1000/T were plotted using MATLAB in the figure 3.4. The graph represents that conductivity increases rapidly with rise in temperature. At 550°C maximum conductivity of about 130 S/cm was measured in the presence of air. This is a novel material and we hope that conductivity will be improved by co-precipitation method or by using NANOCOFC approach on this material. It has been observed that it has no any material degradation and BCCF is mechanical and electrically stable for long time spam. It exhibits its potential use in the field due to low cast and low emissions.

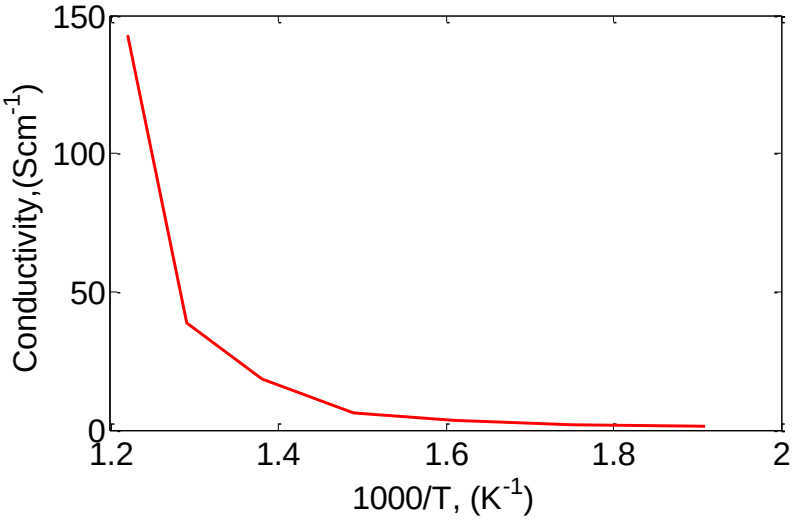

Figure 3.4: Plot between Conductivity and Absolute Temperature for S5 (BCCF)

3.3 Electrode Material- $Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

3.3.1 XRD peaks for $Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

The phase structure of the synthesized BCCF cathode nanocomposite was determined by X-ray diffractometer with Cu-Kα radiation, with 45 kV applied voltage and 35 mA current, shown in figure 3.5. An internal wavelengths used from anode material were obtained by Copper (Cu). As-prepared nanocomposite material was sintered at 900°C for 10 hours to get proper structure.

The XRD pattern of this cathode material was determined as nanocomposite structure. This pattern shows that as-prepared material has nanocomposite effect additional to the perovskite peaks, as NANOCOFC approach was used to get more effective performance of the fuel cell while using this material as cathode. If we compare this pattern with the perovskite peaks, we come to know that the perovskite peaks also exist in this pattern. It was assumed that Calcium atoms should be doped properly at A-sites in ABO_3 formula structure. As-prepared material has mixed conductivity (both electronic and ionic). But the measured conductivity is referred to as electronic being dominant on ionic conductivity.

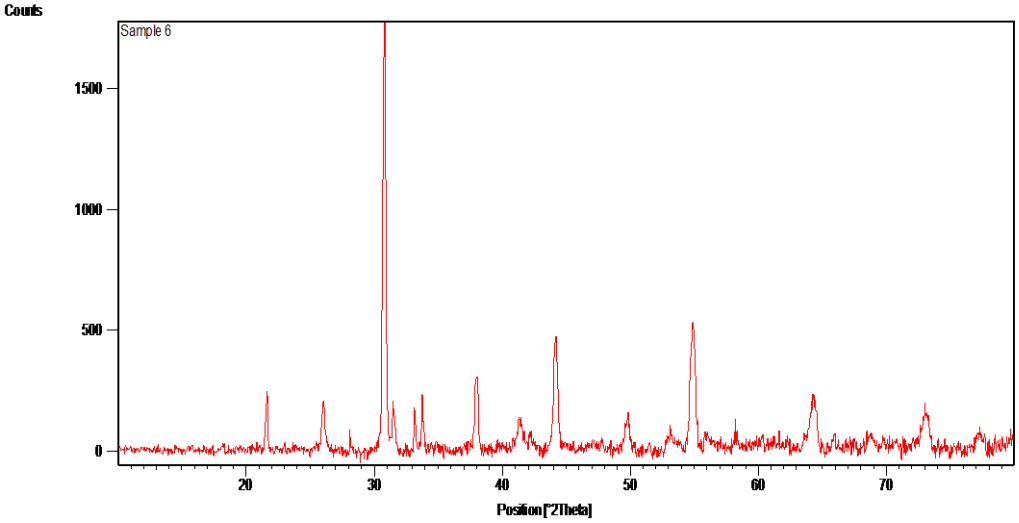

Figure 3.5: XRD Pattern for Locally Prepared Sample 6 (BCCF)

3.3.2 Conductivity Measurements for $Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

Thickness of pellet = 1.6 mm

Effective area = 0.64 cm^2

Table 3.3 BCCF (b) Conductivity dependence on temperature

S. No	Temperature (°C)	1000/T (K^{-1})	Resistance (Ω)	Resistivity (Ωcm)	Conductivity (Scm^{-1})
1	550	1.22	0.010	0.04	25
2	500	1.29	0.025	0.1	10
3	450	1.38	0.052	0.208	4.81
4	400	1.49	0.090	0.36	2.78
5	350	1.61	0.150	0.6	1.67
6	300	1.75	0.243	0.972	1.03

Another useful composition of BCCF has been observed with suitable conductivity results measured by DC 4 probe method in the presence of air and mentioned in table 3.3. For this purpose, powder material was compacted in the form of pellets using 13 mm diameter die and pressed under a load of 250 MPa. The results obtained in air are plotted by using MATLAB in figure 3.6. Graph shows maximum conductivity of 25 S/cm at 550°C. Material was found thermally, electrically and mechanically stable with aging.

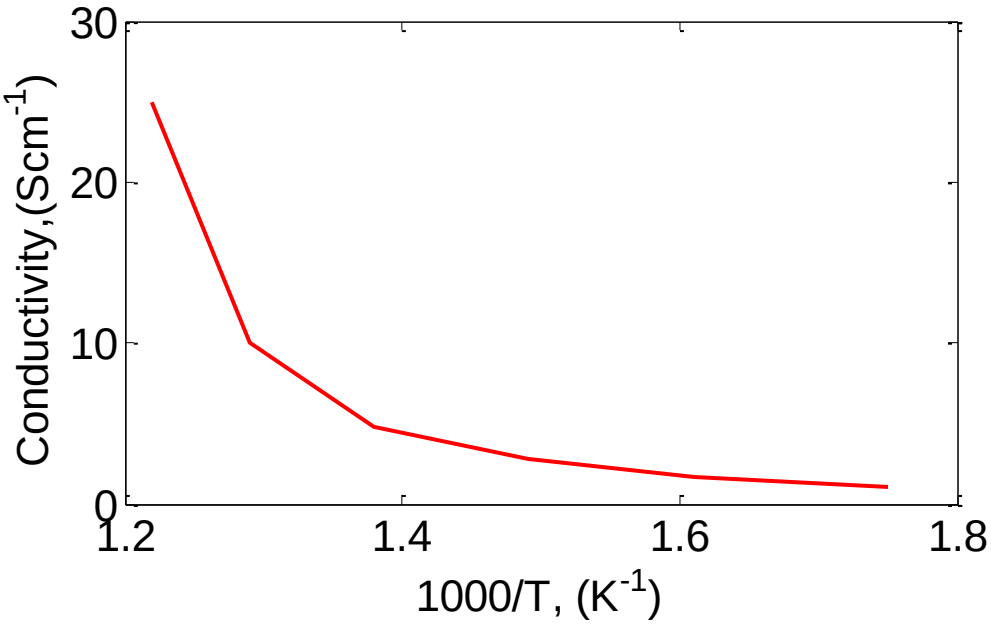

Figure 3.6: Plot between Conductivity and Absolute Temperature for Sample 6 (BCCF)

3.4 Electrode Material- $Ba_{0.5}Sr_{0.5}Cu_{0.7}Fe_{0.3}O_{3-\delta}$ (Copper supported BSCF)

3.4.1 XRD Peaks for $Ba_{0.5}Sr_{0.5}Cu_{0.7}Fe_{0.3}O_{3-\delta}$ (Copper supported BSCF)

The phase of the synthesized Copper supported BSCF material was examined by X-ray diffractometer with Cu-Kα radiation, with 45 kV applied voltage and 35 mA current, shown in figure 3.7. Actually internal wavelengths used from anode material were obtained by Copper (Cu). As-prepared nanocomposite material was sintered at 980°C for 9 hours to get proper perovskite structure. The XRD peaks of the locally prepared copper supported BSCF were matched with the peaks of BSCF and BPCF [26], [43].

Comparison of the peaks shows that as-prepared material has perovskite structure. This structure has showed that Copper atoms are doped at B-site along with iron atoms of the ABO_3 formula structure. It was assumed initially before starting this research work that Cu should be doped at B-site in perovskite structure and after complete doping XRD pattern should be obtained as proved. Our prepared material has mixed conductivity (both electronic and ionic). But our measured conductivity is referred as electronic one being dominant.

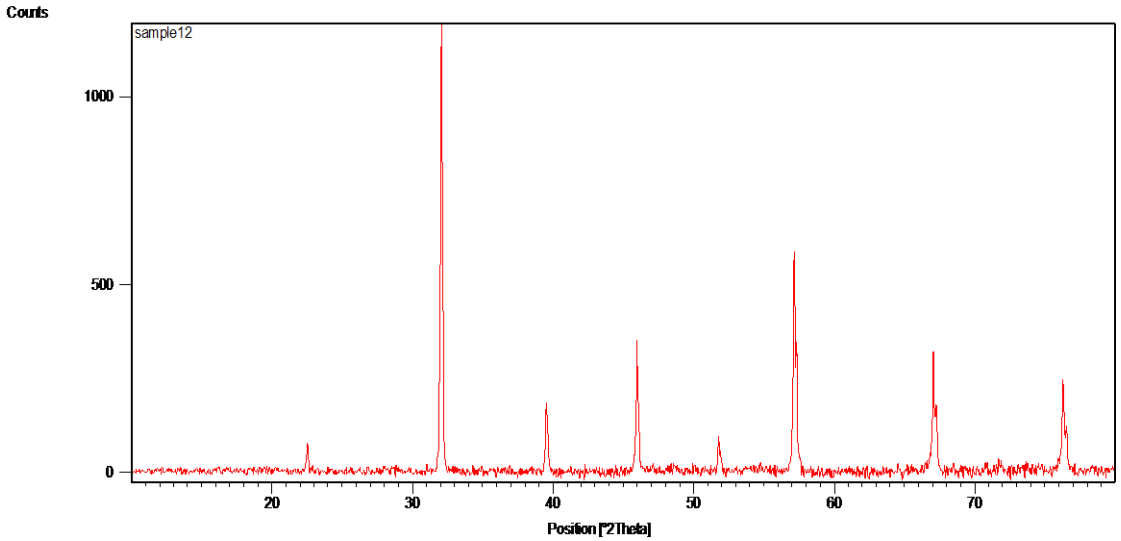

Figure 3.7: XRD Pattern for Copper Supported BSCF

3.4.2 Conductivity Measurement for $Ba_{0.5}Sr_{0.5}Cu_{0.7}Fe_{0.3}O_{3-\delta}$ (BSCF)

Thickness of pellet = 3.3 mm = 0.33 cm

Effective area = 0.64 cm^2

Table 3.4 BSCF (C=Cu) Conductivity dependence on temperature

S. No	Temperature (°C)	1000/T (K^{-1})	Resistance (Ω)	Resistivity (Ωcm)	Conductivity (Scm^{-1})
1	550	1.22	0.020	0.038	26.32
2	500	1.29	0.040	0.077	13
3	450	1.38	0.075	0.144	6.94
4	400	1.49	0.122	0.235	4.26
5	350	1.61	0.198	0.382	2.62
6	300	1.75	0.284	0.548	1.82

BSCF material with a replacement of cobalt with copper has shown a suitable conductivity as interpreted in table 3.4. DC conductivity was measured by DC 4 probe method in air; thick pellets of 13 mm diameter were pressed by dry method under a heavy load of 250 MPa. Pellet was pasted with silver for current collection and was tested in tubular furnace. It was observed that a conductivity of 26 S/cm measured at 550°C, the measured results were plotted using MATLAB as shown in the figure 3.8. It has been seen that conductivity increases with increase in temperature. With aging, no material degradation is occurred. Material showed stable conductivity with aging. As it is a novel material so it is expected that its conductivity might improve by using other synthesis roots due to which size of the particle will change and grain boundary will improve which can positively affect the performance.

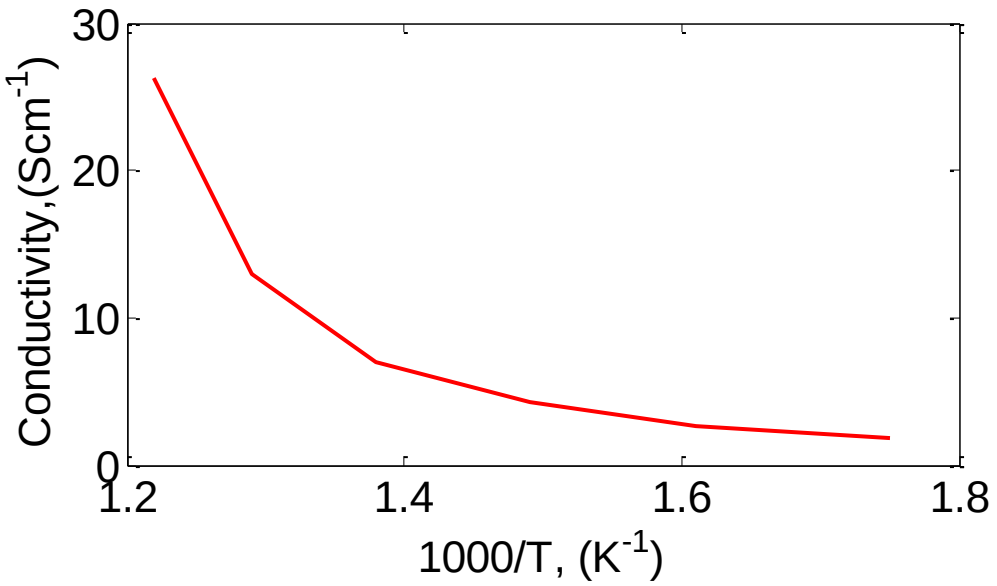

Figure 3.8: Plot between Conductivity and Absolute Temperature for Copper Supported BSCF

3.5 Microstructure of As-prepared Materials

3.5.1 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)

Figure 3.9 shows the morphology and nanostructure of the locally prepared BSCF cathode by SEM: field emission scanning electron microscope (FESEM, JEOL 7000F, operating at 20 kV). Same SEM machine was used for microstructure analysis of all samples. This BSCF can be used for ASOFC and LTSOFC. A range of particle sizes from 80 nm to 120 nm has been observed in figure 3.9. This shows that nanoparticles are well prepared by using co-precipitation synthesizing method.

The locally prepared BSCF perovskite cathode is a porous material with chemical formula ABO_3, Ba and Sr establish A cation while Co and Fe construct B cation in the formula. Both cations are almost of same size and they occupy octahedral site. The nanoparticles have been observed by SEM with very high resolving power. Due to smaller particle size of the material, the conductivity obtained is enough high, might be due to the high grain boundary effect reducing the contact resistance between the particles, cause more and more transport of electrons and ions through the interfaces established by the grain boundary. This is already considered that the interfaces based on particle sizes are of high importance.

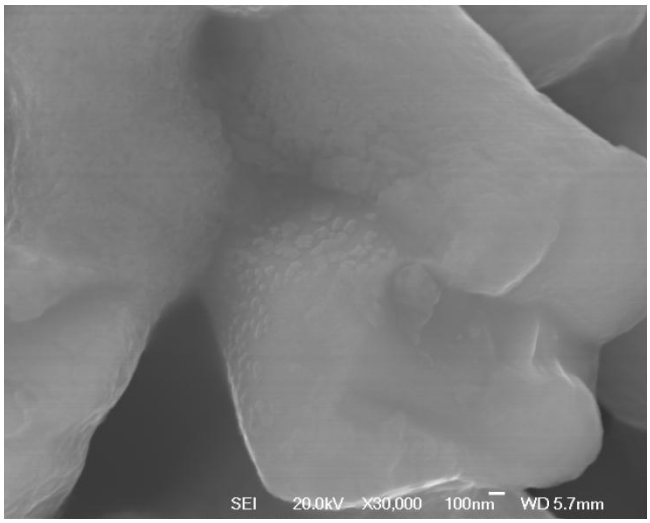

Figure 3.9: SEM Image for Local BSCF

3.5.2 $Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

A sintered novel mixed conductor BCCF cathode material was examined by SEM to investigate microstructure as shown in figure 3.10. Particle size varies from 500 nm to 1 µm. The morphology of the particles is octahedral with a quite large scale. The particles are observed in the form of clusters, it is also possible that particles have changed their microstructure due to high sintering temperature. This material has been developed first time therefore many studies including its melting point is needed to be investigated. The material is enough porous that it can be used as a good electronic conductor cathode in ASOFC. The bigger size of the particles is might be due to wet chemical method, it could be improved by using NANOCOFC approach to get better grain boundary. It is also expected that conductivity will be improved more by decreasing the size of the particles by using more appropriate synthesizing method. Sintering time and treatment time may also affect the size of the particles. I sintered this material at high temperature (1000°C) for a long time (8 hours), due to which might be microstructure changed and could be its conductivity also affected.

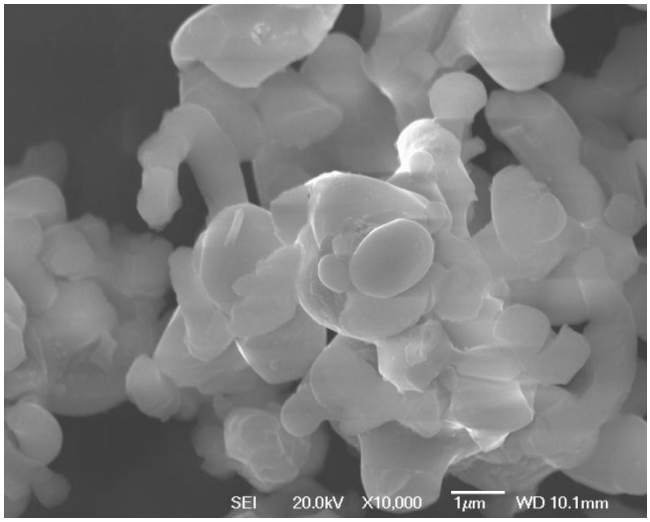

Figure 3.10: SEM Image for S5 (BCCF)

3.5.3 $Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BCCF)

Figure 3.11 shows the SEM image of the BCCF with another composition where we got the conductivity above the acceptance level of cathode materials for fuel cell. Topography of the material shows that particle size varies in a range of 100-300 nm, particles distribution is uniform only in a certain region. Nanostructured material has high porosity and is useful for improvement in the electrochemical performance of the fuel cell.

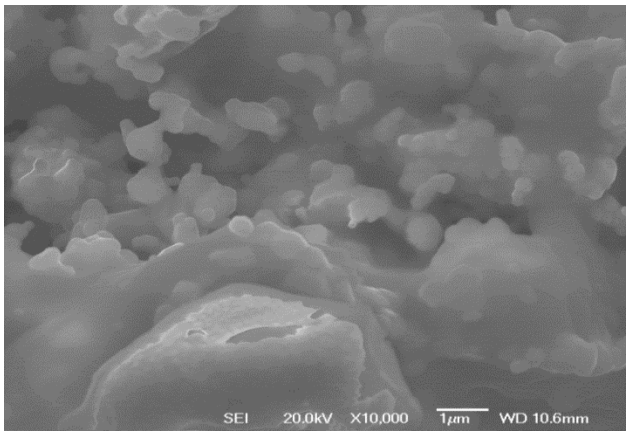

Figure 3.11: SEM Image for Sample 6 (BCCF)

3.5.4 $Ba_{0.5}Sr_{0.5}Cu_{0.7}Fe_{0.3}O_{3-\delta}$ Copper Supported (BSCF)

Topography of nanostructured material by replacing cobalt with copper in perovskite material (BSCF) has been investigated by scanning electron microscopy as shown in the figure 3.12. The image exhibits that size of the particles vary from 100 nm to several hundred nanometers. At some places in the image particles can be identified clearly but at some other places particles look stuck in the form of clusters. We can also see at the bottom of the image that grains of quite bigger size contain particles of the material which might be melted due to high temperature sintering. XRD pattern for this material shows that it has perovskite structure with perfect doping of copper replacing cobalt atoms in ABO_3 chemical formula.

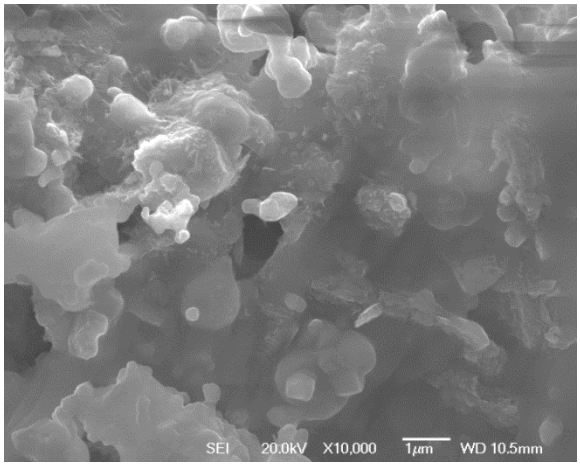

Figure 3.12: SEM Image for Copper Supported BSCF

3.6 Microstructure of Single Component Material

3.6.1 LNCZ

Morphology and microstructure of the conventional single component electrode material was analyzes by HRSEM. The image exhibits the size of the particles varying from 500 nm to 1 µm. Particles distribution almost show the homogeneity in micrometer range. An additional property in the topography observed is material structure in the form of nanowires as shown in figure 3.13. The diameter of the nanowire observed is about 100 nm and length of the wires is up till several micrometers. These nanowires might be responsible for improved results of the single component device.

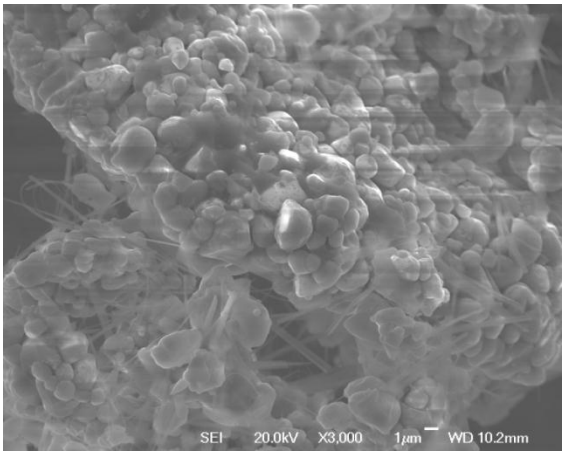

Figure 3.13: SEM Image for LNCZ

3.6.2 LiNiO-SDC single component

Scanning electron microscopy was used to investigate the microstructure of the single component material mixed LiNiO.SDC. Morphology shows that particle size is varying between 50 to 100 nm; it is obvious from the SEM image in figure 3.14. Particle distribution is uniform and particle size is homogeneous in the range. This single component material is locally prepared which shows some good results.

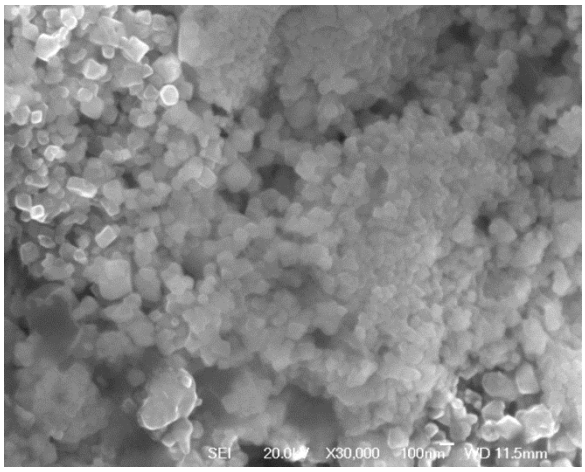

Figure 3.14: SEM Image for LiNiO.SDC

3.7 Cell Performances

3.7.1 Conventional Fuel Cell (3-layers device)

Most of the materials prepared were used in fuel cell fabrication in two ways.

i) **Asymmetrical fuel cell**

a) Anode = NO.SDC, electrolyte = SDC, cathode = BSCF.SDC

NO.SDC/ SDC/ BSCF.SDC Fuel Cell Performance

Hydrogen was provided to anode and air to cathode. Hydrogen was oxidized on anode and oxygen was reduced on cathode due materials being chemically catalytic for corresponding gases. On cathode, all other gases in the air are bounced back from the outlet. The ceramic materials are useful to use air to accept only oxygen [44]. The output results are given below.

OCV = 0.87V I = 0.45A

Cell resistance is about 8 ohms as plotted by EIS in figure 3.15 given below.

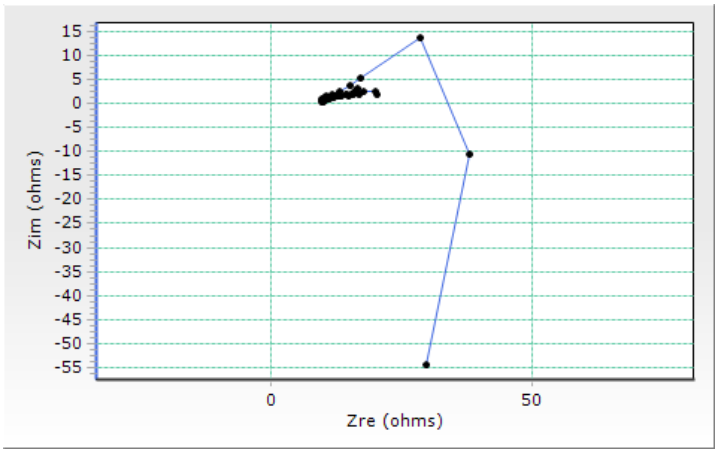

Figure 3.15: EIS Plot for Impedance for Asymmetric 3-Layer Device

b) NiO.SDC/SDC/BCCF.SDC Fuel Cell Performance

3-layer device was fabricated when thin layer of SDC electrolyte was sandwiched between anode and cathode. Hydrogen was supplied on NiO.SDC side and air was given to the BCCF.SDC side. Performance was tested at 550°C and the results are plotted in figure 3.16, given below. By changing more composition of mixed anode and cathode results can be improved much more.

OCV = 0.96 V I = 0.37 A

Plot shows that maximum power density of 126 $mWcm^{-2}$ is obtained.

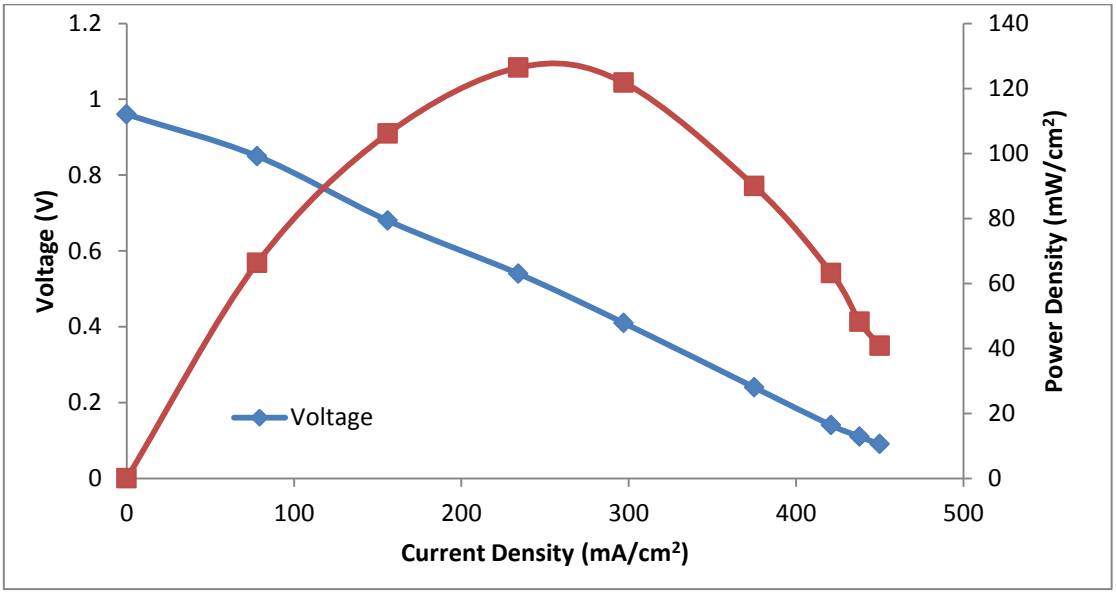

Figure 3.16: Single Cell Performance with Hydrogen

ii) **symmetrical fuel cell**

a) Anode and cathode = LiNiO.SDC , Electrolyte= SDC

This device of 13 mm diameter was mounted in a sample holder and tested in tubular furnace at 550°C, Hydrogen gas was used as a fuel and air was used as an oxidant, OCV and close circuit current was measured given below.

OCV= 1.05 V I = 0.52 A

Device was also tested by electrochemical impedance spectroscopy and plot obtained is given below in figure 3.17, where Zre is real impedance and Zim is imaginary impedance. By EIS analysis cell resistance was determined of about 10 ohms as can be seen in the plot.

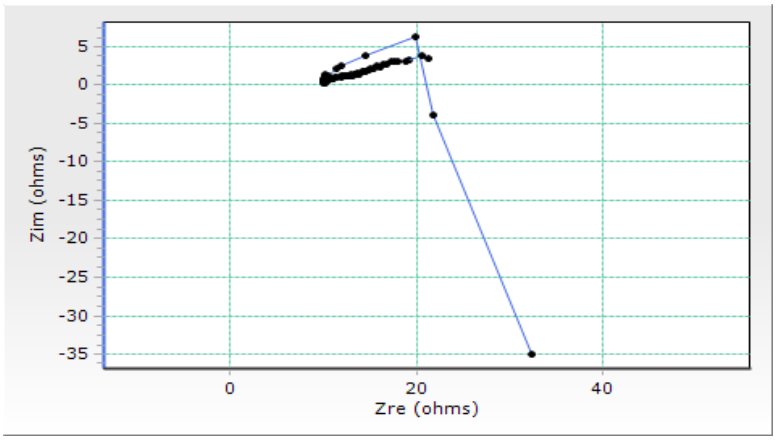

Figure 3.17: EIS Plot for Impedance for Symmetric 3-Layer Device

3.7.2 2-layers device Performance with H_2

a) NiO.SDC/ LiNiO.SDC

NiO.SDC was used as an anode to supply hydrogen gas and LiNiO.SDC was used as cathode. The device was fabricated being anode supported and electrolyte layer was removed. The results obtained by this configuration are given below in figure 3.18.

OCV = 0.95 V I = 0.48 A

Cell resistance determined from EIS analysis is about 15 ohms can be seen in the plot.

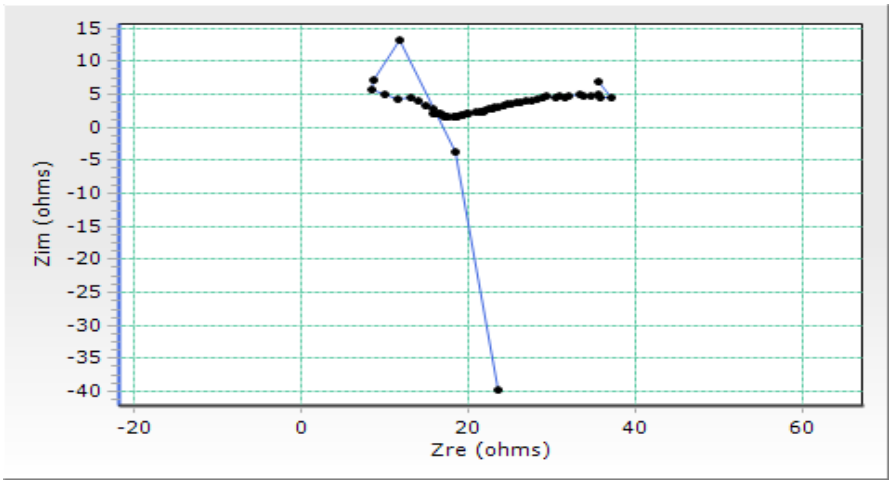

Figure 3.18: EIS Plot for Impedance for 2-Layer Device

b) LiNiO.SDC/ BSCF.SDC Fuel Cell Performance

LNO.SDC was used as an anode layer and hydrogen was supplied on this side during the cell testing while BSCF.SDC used as cathode layer, air supply was provided on this layer during cell performance at 550°C. OCV, close circuit current and EIS impedance plot in figure 3.19 given below.

OCV = 1.05V I = 0.54A

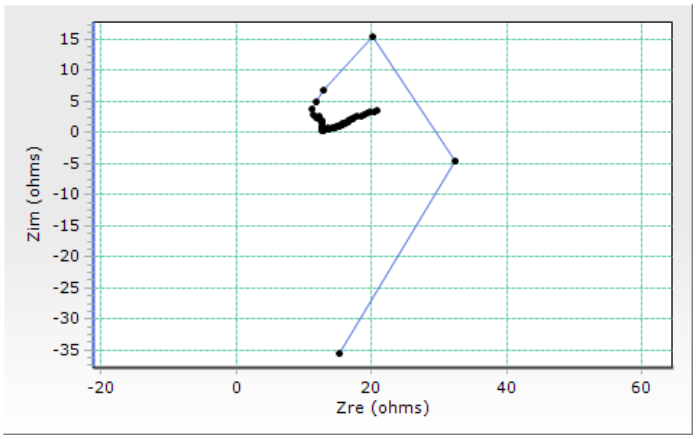

Figure 3.19: EIS Plot for Impedance for 2-Layer Device with BSCF

Plot shows that cell resistance is approximately 12 ohm.

c) NiO.SDC/BSCF.SDC

Results obtained with this configuration are given below.

OCV = 0.72 V, I = 0.32 A at 550°C

3.7.3 Single layer device (single component or EFFC)

a) LiNiO.SDC Fuel Cell Performance

A simple mixture of LiNiO and SDC was ground well and used as single component to fabricate EFFC. The following results show that single component has almost the same performance at 550°C as that of 3-layer device at same temperature. Both OCVs and close circuit currents are quite comparable.

OCV= 0.97 V I = 0.53 A

Impedance plot in figure 3.20 also shows that the cell resistance is comparable with plot of 3-layer device.

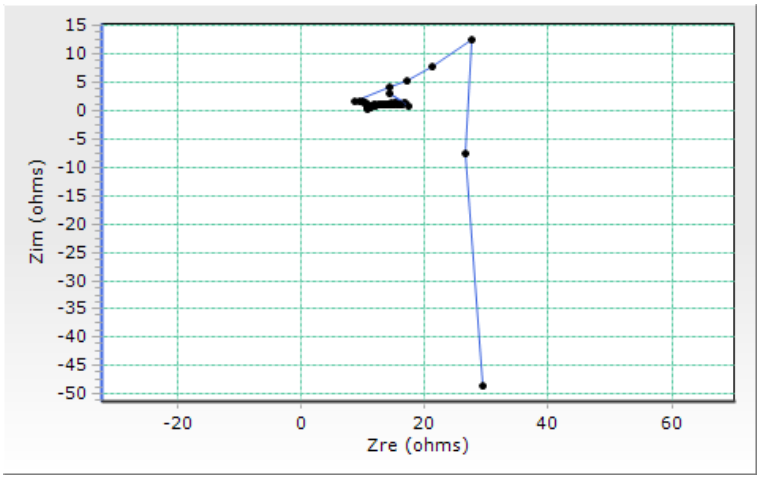

Figure 3.20: EIS Plot for Impedance for Single Layer Device with LiNiO

b) Single Component NiO.SDC.BSCF

Sides of the pellet were painted by silver paste as current collector, hydrogen gas was used as a fuel and air was provided by opposite side.

OCV= 0.67 V, I = 0.32 A. At 550°C

c) LNCZ.SDC Cell performance

Both sides of the EFFC device were painted by silver paste as current collector and were tested at 550°C. Hydrogen and oxygen were supplied from the opposite sides, effective area was 0.64 cm^2 and the thickness of the pellet was kept about 1 mm. Following results were obtained by testing the above sample.

OCV = 0.88 V, I = 0.53 A

Maximum power density of 192 $mWcm^{-2}$ has been achieved as shown in the graph in figure 3.21.

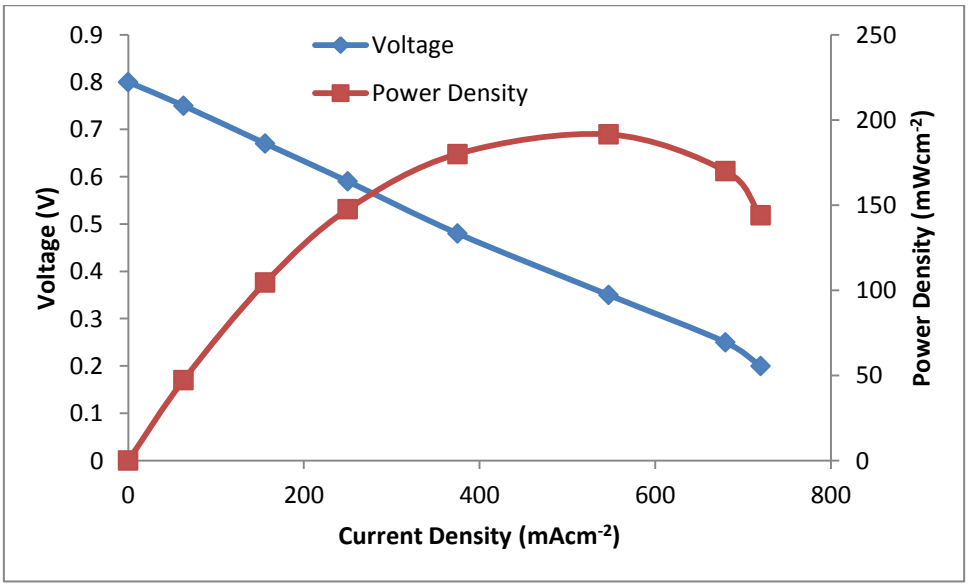

Figure 3.21: Single Cell Performance with H_2

4 Conclusions

In this work, new perovskite and nanocomposite cathode materials have been successfully synthesized for ASOFCs or LTSOFCs. Low temperature SOFC and EFFC have been developed based on locally prepared nanocomposite and perovskite materials. Following conclusions have been drawn from the results obtained through this research work conducted for master thesis.

1. It is concluded that synthesis techniques for the preparation of nanocomposite material plays an important role in higher results as compared to the other available methods. Best methods have been found as co-precipitation technique and best method for the treatment of the materials for improvement and creating more nano sized particle is NANOCOFC approach with which higher results have been obtained.

2. It has been observed that the best material prepared with perovskite structure is BSCF with highest conductivity of 313 Scm^{-1} which is higher than commercially available BSCF. Also best nanocomposite material prepared is BCCF with high conductivity of 143Scm^{-1} at 550°C. Treatment of nanocomposite materials for new energy conversion device using NANOCOFC approach has proved the improvement in the results distinctly [45]. DC 4 probe technique has been used for the measurement of conductivity. Microstructures were determined by SEM which showed good characteristics of the as-prepared materials at nanoscale level.

3. Cell components were calibrated for the fabrication of LTSOFC or ASOFC and were tested at low temperature range 300-600°C and found potential materials for power generation. Power density of 126 $mWcm^{-2}$have been achieved. Single component materials were also used for new energy conversion device. LNCZ.NSDC with maximum power density of 191$mWcm^{-2}$at 500°C and LiNiO.SDC have been proved with reasonable results and were found as potential materials for EFFC which can be used for commercial purpose. A number of SOFC devices were fabricated and tested extensively.

4. XRD pattern investigate whether under observation material is either perovskite or nanocomposite [46]. Studying these patterns, it is concluded that few of as-prepared materials are perovskite while others have nanocomposite phase structure, whereas both types of materials show comparable results in cell performance.

5. EIS results for devices have also confirmed the as-prepared materials useful for R&D. At the beginning of this scientific research level, production of novel and conventional materials have been done and investigated catalytically which were found to be very promising for environmentally friendly energy conversion technology. If these materials could be prepared with more precautions and then should be used in different combinations of cell components in conventional fuel cell as well as single

component materials, it is expected that cells with highest performance can be optimized. In future, this technology can be optimized by making it commercially available product.

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