

Synthesis of Nanocomposites Anode Materials for  
Fuel Flexible Low Temperature Solid Oxide Fuel  
Cell



*By*

Muhammad Shakeel

CIIT/FA17-RPH-061/LHR

MS Thesis

In

MS(Physics)

COMSATS University Islamabad, Lahore Campus

Pakistan

Spring, 2019



**COMSATS University Islamabad, Lahore Campus**

**Synthesis of Nanocomposites Anode Materials for  
Fuel Flexible Low Temperature Solid Oxide Fuel  
Cell**

A Thesis Presented to

**COMSATS University Islamabad, Lahore Campus**

In partial fulfillment  
of the requirement for the degree of

**MS (Physics)**

By

**Muhammad Shakeel  
CIIT/FA17-RPH-061/LHR**

**Spring, 2019**

# Synthesis of Nanocomposites Anode Materials for Fuel Flexible Low Temperature Solid Oxide Fuel Cell

---

A Post-Graduate Thesis submitted to the Department of Physics as partial fulfillment of the requirement for the award of Degree of MS (Physics)

Name	Registration Number
Muhammad Shakeel	CIIT/FA17-RPH-061/LHR

## **Supervisor**

Dr. Ghazanfar Abbas

Assistant Professor, Department of Physics

COMSATS University Islamabad (CUI), Lahore Campus

July 2019

# Final Approval

---

This thesis titled

Synthesis of Nanocomposites anode materials for  
fuel flexible low temperature solid oxide fuel cell

By

*Muhammad Shakeel*

*CIIT/FA17-RPH-061/LHR*

Has been approved

For the COMSATS University Islamabad, Lahore Campus

External Examiner: \_\_\_\_\_

Prof. Dr. Riaz Ahmad

Chairman physics, GCU, Lahore

Supervisor: \_\_\_\_\_

Dr. Ghazanfar Abbas

Assistant Professor, Department of Physics, CUI, La

## Declaration

I Muhammad Shakeel CIIT/FA17-RPH-061/LHR hereby declare that I have produced the work presented in this thesis, during the scheduled period of study. I also declare that I have not taken any material from any source except referred to wherever due. If a violation of HEC rules on research has occurred in this thesis, I shall be liable to punishable action under the plagiarism rules of the HEC.

Signature of the student:

Dated: \_\_\_\_\_

\_\_\_\_\_  
Muhammad Shakeel  
CIIT/FA17-RPH-061/LHR

## Certificate

It is certified that Muhammad Shakeel CIIT/FA17-RPH-061/LHR has carried out all the research work related to this thesis under my supervision at the Department of Physics, COMSATS university Islamabad, Lahore campus.

Date: \_\_\_\_\_

Supervisor:

---

Dr. Ghazanfar Abbas  
Assistant Professor

Head of Department:

---

Dr. Muhammad Ashfaq Ahmad  
Associate Professor  
Department of Physics  
CUI, Lahore

Oh, Allah Almighty open our eyes,  
To see what is beautiful,  
Our minds to know what is true,  
Our hearts to love what is Allah

### **Dedicated To**

I dedicate this project to my beloved parents, respected teachers, my best friends and all those who prayed for my success.

## ACKNOWLEDGEMENT

All praises and thanks to **Almighty Allah**, the most beneficent and merciful, the creator of the universe, who enable us to complete our work successfully. All blessing to His prophet (P.B.U.H), who is the source of guidance and knowledge for humanity.

Any significant milestone in one's life is made possible by the contribution of many other along the way and my project supervisor, **Dr. Ghazanfar Abbas**, COMSATS university Islamabad, Lahore campus, his encouragement unequivocal guidance, and patience provided us the opportunity to complete this work. I am very thankful to my Co-supervisor, **Dr. M. Ashfaq Ahmed** who guide and encourage me at every step. As a mentor, his desire and ability to support me in whatever i need was crucial to finish this task.

Words are lacking to express my humble obligation to my affectionate, *Father, Mother*, and my sisters for their love, good wishes, inspirations and unceasing prayers for me, without which the present destination would have been mere a dream.

A very special thanks to my dear friend Zohaib-Ur Rehman who supported and guided me in every thick and thin me faced during my 2 years MS program.

**Muhammad Shakeel (CIIT/FA17-RPH-061/LHR)**



## ABSTRACT

### Synthesis of Nanocomposites Anode Materials for Fuel Flexible Low Temperature Solid Oxide Fuel Cell

Broad efforts have been made to create multi-fuel-based low temperature solid oxide fuel cell that will directly utilize hydrocarbons to produce electric power. It is very difficult to work because of the C-H bond activation and its immensely slow oxidation reduction in the low temperature range from 300 to 600 °C. The structural and electrochemical properties of prepared anode materials  $\text{Ba}_{0.15}\text{Zn}_{0.60}\text{Mn}_{0.15}\text{-Ag}_{0.10}$ ,  $\text{Ba}_{0.15}\text{Zn}_{0.60}\text{Mn}_{0.15}\text{-Cu}_{0.10}$ ,  $\text{Ba}_{0.15}\text{Zn}_{0.60}\text{Mn}_{0.15}\text{-Fe}_{0.10}$ , have been investigated within the sight of hydrogen, natural gas and ethanol at a low temperature of 650 °C. Through sol gel process prepared anode materials are synthesized. The average crystallite size has been found in the range of 19-90nm by XRD. Conductivity is measured by four probe method. Maximum conductivity of 4.8 S/cm, 4.3 S/cm and 4.4 S/cm have been found by using silver, copper, and iron as a catalyst at a temperature of 600 °C, 550 °C and 580 °C respectively. The impact of prepared nanocomposite materials on the performance of solid oxide fuel cell is investigated. The power density of the cell at different fuels has been checked and measurements demonstrate it varies from 100 to 500 mW/cm<sup>2</sup> at 650 °C among different fuels at the anode side. The present examination reveals that proposed anodes are promising multi-fuel material for low-temperature solid oxide fuel cell, and it doesn't have to change hydrocarbon fills to completely use the benefit of these cells.

## Table of Contents

<b>1. Introduction.....</b>	<b>1</b>
1.1. Introduction of energy.....	2
1.2. Fuel Cell.....	6
1.3. Reactions in fuel cell.....	8
1.4. Types of Fuel Cell.....	8
1.5. Solid Oxide Fuel Cell.....	9
1.6. Working of SOFC.....	10
1.7. Advantages of SOFC.....	11
1.8. Catalysts.....	11
1.9. Role of Catalyst in fuel cell.....	12
1.10. Fuels used in cell.....	12
1.11. Statement of problem.....	12
1.12. Choice of materials and their properties.....	13
<b>2. Literature Survey.....</b>	<b>15</b>
2.1. Literature survey.....	16
<b>3. Experimental Procedure.....</b>	<b>19</b>
3.1. Synthesis of Nanocomposites Material.....	20
3.2. Preparation of sample.....	20
3.2.1. Synthesis of material.....	20
3.2.2. Advantages of Sol Gel method.....	20
3.2.3. Sol Gel method.....	21
3.3. Cell Fabrication.....	24

3.4. Characterization Techniques.....	24
3.4.1. X-Ray Diffraction.....	25
3.4.2. Conductivity Measurement.....	27
3.4.3. Fuel Cell Testing.....	30
<b>4. Results and Discussion.....</b>	<b>33</b>
4.1. Characterization of Nanocomposites Materials.....	34
4.2. X-Ray Diffraction Analysis.....	34
4.2.1. Analysis of BaZnMn-Ag.....	34
4.2.2. Analysis of BaZnMn-Cu.....	35
4.2.3. Analysis of BaZnMn-Fe.....	36
4.3. Conductivity Analysis.....	37
4.4. Fuel Cell Performance Analysis.....	40
4.4.1. Analysis of BaZnMn-Ag.....	40
4.4.2. Analysis of BaZnMn-Cu.....	41
4.4.3. Analysis of BaZnMn-Fe.....	42
<b>5. Conclusion.....</b>	<b>44</b>
<b>6. References.....</b>	<b>45</b>

## TABLE OF FIGURE

---

Figure 1.1 Source of energy generation in Pakistan.....	3
Figure 1.2 Predication of Energy demand of Pakistan.....	4
Figure 1.3 Energy Resources.....	5
Figure 1.4 Schematic Diagram of Fuel Cell.....	7
Figure 1.5 Schematic Diagram of SOFC.....	10
Figure 3.1 Flow Chart of Sol Gel Method of Sample 1.....	22
Figure 3.2 Flow Chart of Sol Gel Method of Sample 2.....	23
Figure 3.3 Flow Chart of Sol Gel Method of Sample 3.....	24
Figure 3.4 Pallets of Prepared Materials.....	24
Figure 3.5 X-Ray diffraction pattern.....	26
Figure 3.6 Schematic diagram of 2 probe and 4 probes.....	28
Figure 3.7 Fuel Cell diagram of Testing.....	31
Figure 4.1 XRD result of Sample 1.....	35
Figure 4.2 XRD result of Sample 2.....	36
Figure 4.3 XRD result of Sample 3.....	37
Figure 4.4 Conductivity result of prepared samples.....	39
Figure 4.5 Performance result of sample 1.....	41
Figure 4.6 Performance result of sample 2.....	42
Figure 4.7 Performance result of sample 3.....	43

## **TABLES**

---

Table 1.1 Comparison between Fuel Cell Technologies

9

## LIST OF ABBREVIATIONS

---

SOFC	Solid Oxide Fuel Cell
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
PEM	Proton Exchange Membrane
PAFC	Phosphoric Acid Fuel Cell
AFC	Alkaline Fuel Cell
DMFC	Direct Methanol Fuel Cell
MCFC	Molten Carbonate Fuel Cell

# **Chapter 1**

## **Introduction**

## **1.1 Introduction of Energy:**

Energy is every country's backbone. It considers a fundamental for the development of any country. A constant supply of power is necessary for financial improvement of any country[1-3]. As the population is increasing the use of power supply is likewise expanding step by step. Now a day world is meeting most noticeably bad vitality emergency and it will be increasingly extreme with the progression of time because of remarkable power request in the nation. It is assessed that the interest will increment half in 2035.

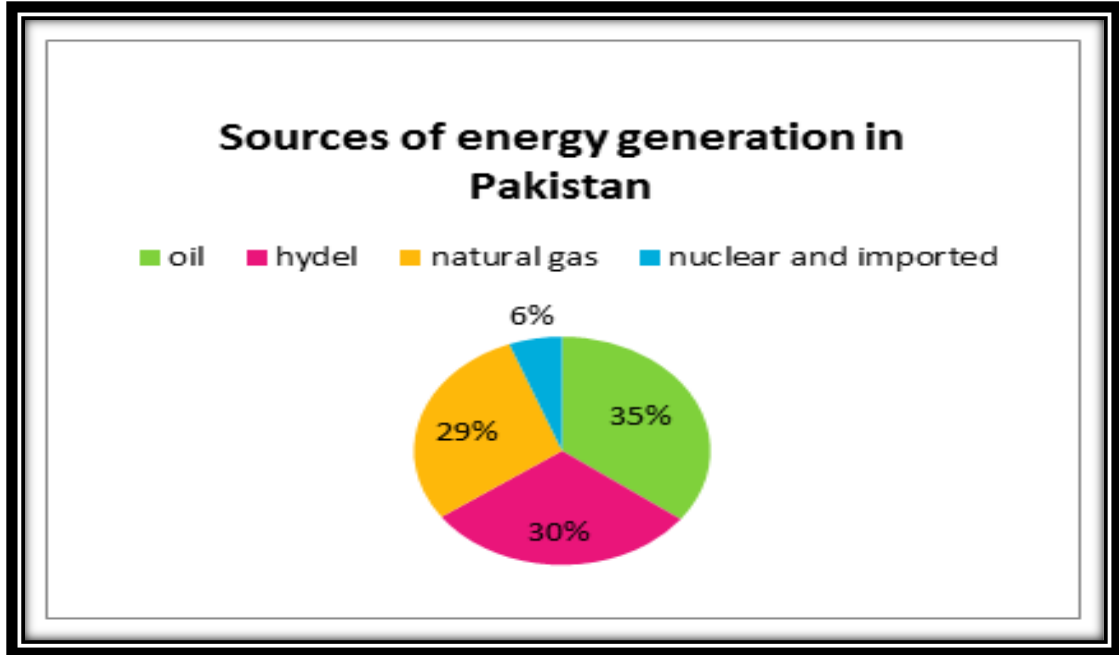
Now renewable products are the fundamental energy supplier of the world, but our environment is badly affected by these sources. Because of this, a worldwide temperature conversion is expanding step by step. This is the reason; it is assuming that worlds need to move their energy products into environmentally friendly products[4-9].

Pakistan is regarded as one of the worlds developing country. It is also presently facing serious energy crises because of population development and the fundamental needs of the general population. Round about 70 of Pakistan population is linked with agriculture directly or indirectly, so we can say that Pakistan is mostly depended on agriculture [1].

As we know that the canal system of Pakistan is the best in the world yet the power generation for the nation is not enough. Energy is also produced by thermal plants by using of fossil fuels, but it is exotic to Pakistan, however, it is over the top expensive for the nation and because of this, the expense per unit is high so it is considered as costly for our nation [4].

The important energy sources of Pakistan are given in figure 1.1.

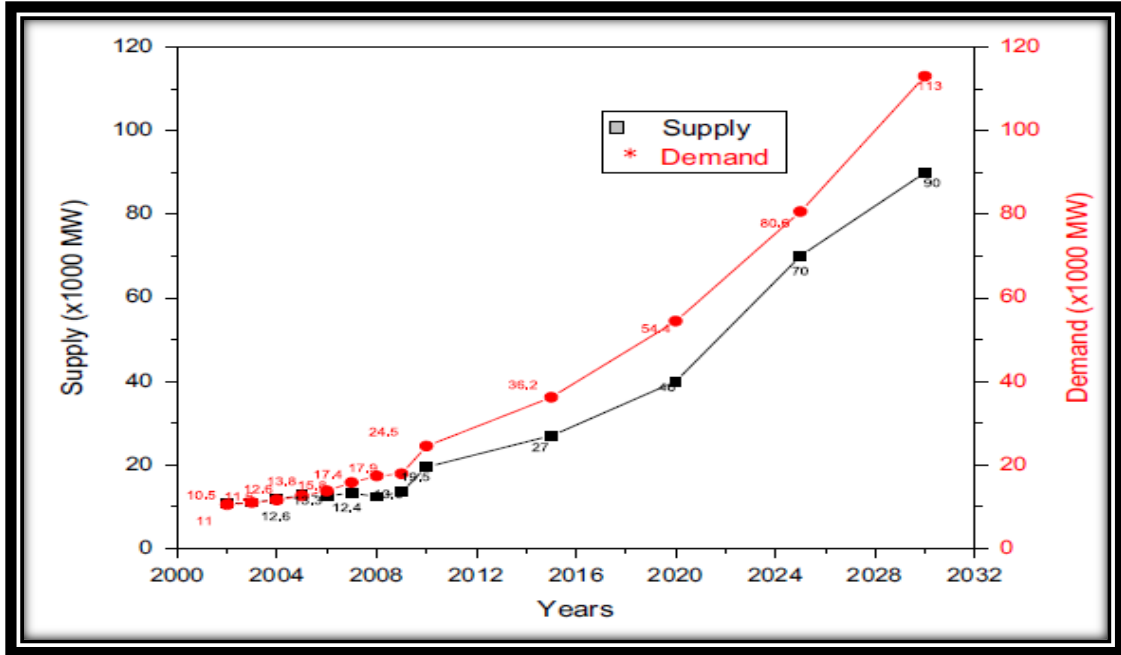




**Figure 1.1** Source of energy generation in Pakistan [3]

As Pakistan is the developing country, therefore the needs of energy are expanding quick but unfortunately, the energy production is not so enough to meet our demands. Generally, the need for energy for the country is about 17000MW and the normal deficiency is 5000 MW [10-12].

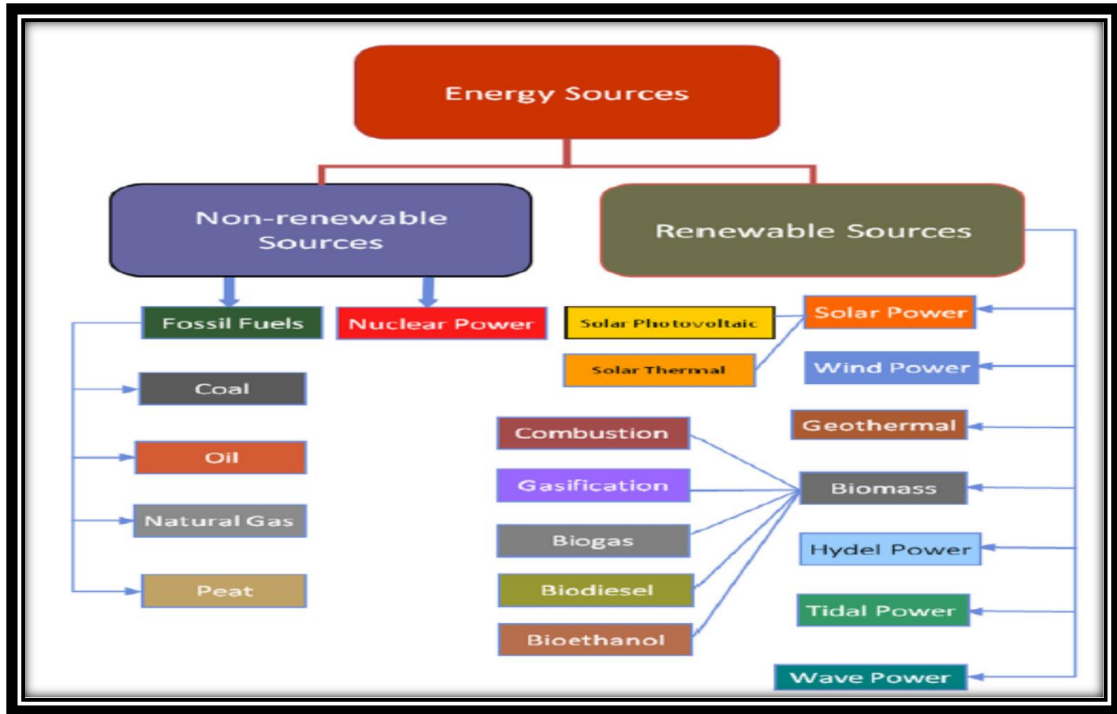
The expansion in vitality request of the nation up to 2030 is anticipated as in figure 1.2.



**Figure 1.2:** Prediction of the energy demand of Pakistan up to 2030 [3]

Pakistan is the nation which is honored with numerous vitality assets as sun powered, hydel, petroleum derivatives and geothermal biomass. The legislature of Pakistan is looking into a request to investigate sustainable power source assets and have made the approach to include 5% offer of it in all out a generation of vitality till 2030 [6, 13-15].

So as to deliver the energy at more amount the legislature and few other establishments and Research and development institutions underscoring on energy component innovation i.e Fuel Cell. It is demonstrated that the power device (fuel cell) is a vitality generator, will help significantly and it will diminish the nursery impact. To accomplish green power, individuals can utilize this spotless vitality creating framework as an energy component, which will be a suitable potential arrangement towards the vitality emergency. The fundamental fields of investigates are on the elements for high temperature power device FC, low temperature power device FC, etc. The Energy assets can be classified in various classes as appeared in figure 1.3.



**Figure 1.3:** Energy resources [3]

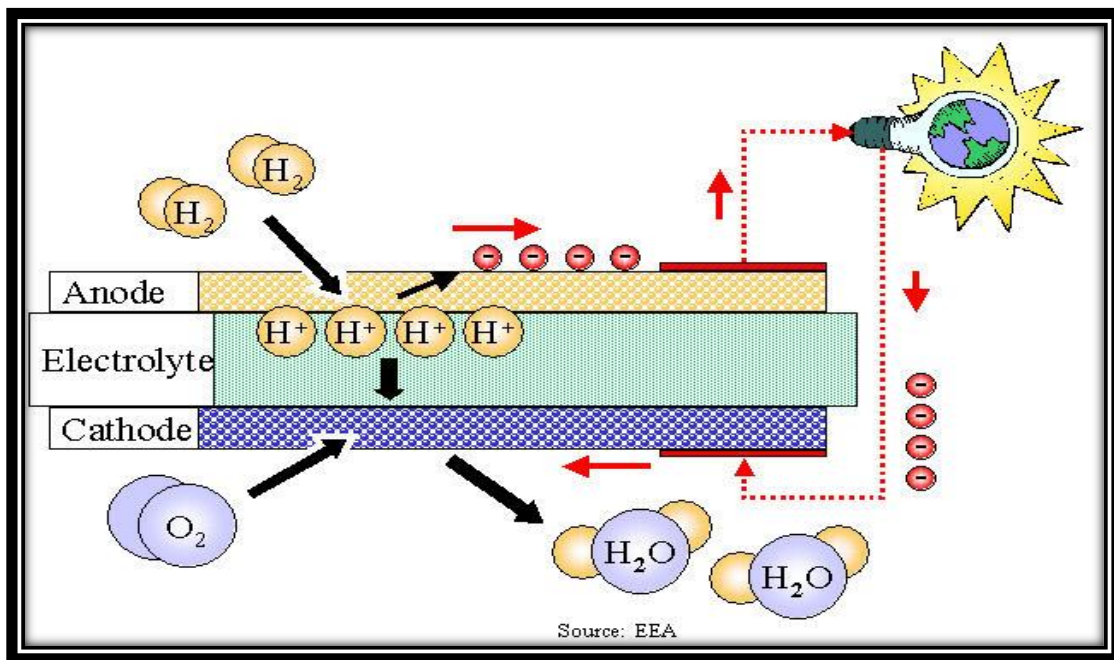
Countries like Japan, Sweden, USA, UK, and China have propelled Fuel Cell innovation effectively. The USA built up a Fuel Cell framework which can be utilized with hydrocarbon fills like diesel and gas as a result of the operational temperature run is higher for example 500-800°C. Different types of Fuel Cells can use a variety of fuels like bio gas, natural gas, hydrogen or air, etc [16]. Power device innovation has an incredible potential to deliver high vitality at less expensive rates and it is the best elective vitality source [3, 17-18].

## 1.2 Fuel Cell:

A fuel cell is an energy change gadget which changes over synthetic energy into electrical in an effective way without ignition. Power is created by utilizing diverse sorts of outside measure of fuel at the anode and oxidizing operators at the cathode side. The response happens in the presence of an electrolyte. Amid response, the reactants go in and the items stream out of the cell yet the electrolyte rests at a similar spot in the cell. Power modules keep on working till the important streams are kept up.

Aside from the definition, energy component is the same as that of battery, yet the fundamental distinction is available in the working of the two gadgets. The fuel in the power devices is ceaselessly sustained from the source or reactants which can be topped off once more, though the batteries utilize the synthetic substances store electrical vitality, which is available in it and can be revived with the assistance of outer vitality sources.

At the point when the battery is charged and released the terminals of the battery respond and change while the anodes of the power modules are synergist and moderately stable [19]. Sustainable power source assets are utilized as a fuel in the energy units as these are richly present in nature. Oxygen and hydrogen are utilized as a fuel in energy components to create power, warmth and water vapors [20, 21, 22, 23]. Basic diagram of the fuel cell is given below 1.4”



**Figure 1.4:** Schematic diagram of fuel cell

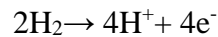
Basically, the cell comprises of dual electrodes which are permeable and are confined by thick electrolyte or layer. Platinum is utilized as an impetus to accelerate the procedure. Hydrogen is presented at the anode where oxidation occurs and hydrogen breaks into

electron and proton within the existence of impetus. Oxygen is presented at the cathode where it responds with the joined protons and electrons to create water and warmth as results. The expression "energy unit" is first utilized via Carl Langer and Ludwig Mond in 1889 [24]. Reactions that occur in the power device are express in the following equations [20, 25].

### **1.3 Reactions in fuel cell:**

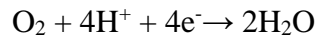
#### **At Anode**

Oxidation happens and the proton and electrons are created from hydrogen within the sight of catalyst as

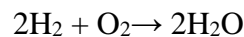


#### **At Cathode:**

Water is produced when electron and proton react with oxygen, chemical reaction are given below



#### **Net Reaction**



### **1.4 Types of Fuel Cell:**

Fuel cells can be divided into the following category depend upon their working guideline and electrolyte utilized in them. The use of solid electrolyte has advantages as compared to the liquid because it can be easily operated and avoid rusting. [26,27].

1. Alkaline Fuel Cell (AFC)
2. Direct Methanol Fuel Cell (DMFC)
3. Phosphoric Acid Fuel Cell (PAFC)
4. Proton/polymer Exchange Membrane Full Cell (PEMFC)
5. Molten Carbonate Fuel Cell (MCFC)

## 6. Solid Oxide Fuel Cell (SOFC)

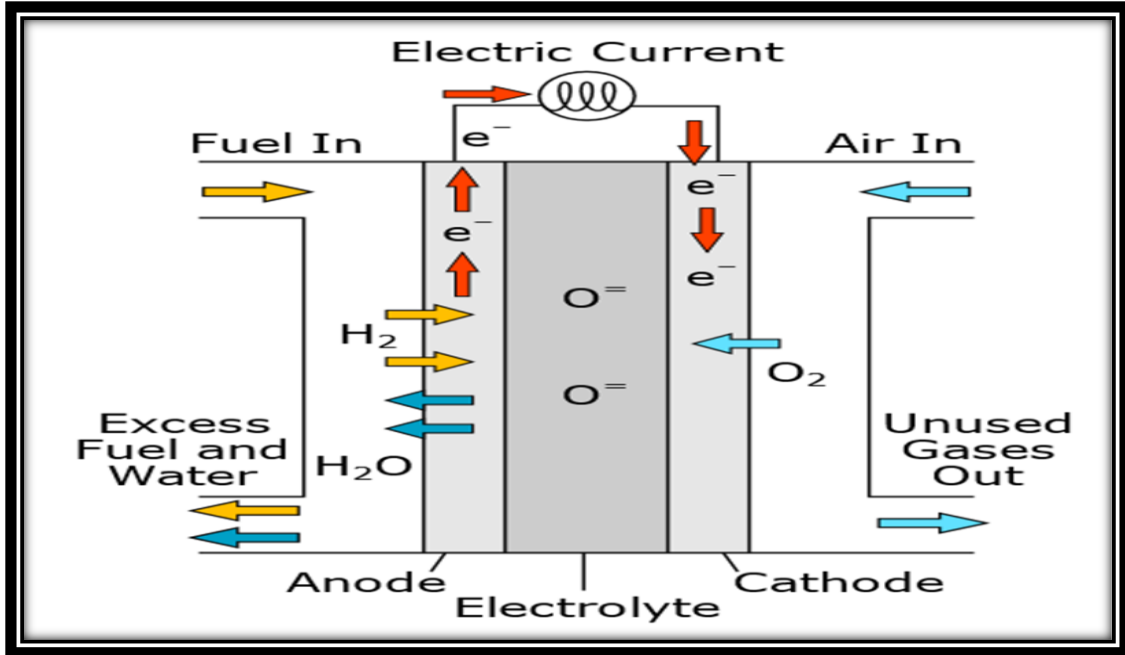
### 1.4.1 Comparison between different types of Full Cell:

	PAFC	PEM	MCFC	SOFC
<b>Electrolyte</b>	It has Ortho phosphoric acid	It has Sulfonic acid in polymer (NAFION)	It has Mixture of carbonates (Li and K)	It has Yttrium stabilized zirconia
<b>Operating Temperature</b>	Its temp is about 180 – 210 °C	Its temp is about 80 – 100 °C	Its temp is about 600 – 700 °C	Its temp is about 650-1,000° C
<b>Fuel</b>	Hydrogen use as a fuel	Hydrogen use as a fuel	Hydrogen/ CO both are used as fuel	Hydrogen/ Natural gas/ Synthetic gas use as a fuel
<b>Efficiency</b>	40%	30 – 40 %	43 – 44%	50 – 60%
<b>Applications</b>	Used in Stationary Power etc.	Used in Transportation Stationary Power etc.	Used in Stationary Power etc.	Used in Stationary Power etc.
<b>Outlook</b>	It has Specialty markets due to high cost	It has Getting the most attention due to its potential in vehicles, portable power and small stationary power (<200KW).	Its Product focused on commercial, industrial, institutional and specialty power markets.	It has High efficiency and low manufacturing cost per KW.

**Table 1.1:** Comparison of fuel cell technologies [26,27]

### 1.5 Solid oxide fuel cell (SOFC):

Solid oxide fuel cell is considered as the most promising kind of cell. Solid-Ceramic electrolytes are used in Solid Oxide Fuel cells. It works at higher temperature ranges from 600-1000°C. Traditional SOFC consist of basic three parts, which have a permeable anode, a permeable cathode, and electrolyte. The formal diagram of entire SOFC is demonstrated in figure 1.5.



**Figure 1.5:** Schematic diagram of Solid Oxide Fuel Cell

### 1.6 Working of SOFC:

The capacity of working with a generally wide scope of fuels such as ethanol, methanol, natural gas, and hydrogen. A broad ceramic layer of electrolyte is set between permeable terminals. Air is presented at the cathode where oxygen divides into ions in triple phase boundary (TPB).

The thick electrolyte doesn't enable the gas particles to pass and vaporous redox responses of the two terminals are isolated out. Any way the oxygen particles figure out how to diffuse to the anode through the electrolyte. Oxygen particles delivered in TPB area react with hydrogen within the sight of impetus and produce water and create ns [28]. These electrons make electrical energy on moving from anode to the outer circuit. The ideal power can be accomplished by organizing various cells in such an approach to interconnect each other [3,20,29, 30, 31].

## **1.7 Advantages of SOFC:**

SOFC have numerous advantages over different kinds, of fuel cell for example,”

- Environmentally supportive
- Fuel adaptable power age
- Efficient creating control more than many super watts high effectiveness
- Low clamor
- Long term security
- Low expenses of support

The demand for fuel cell energy is increased rapidly because of its practicality to create energy in a better manner. Essentially in Pakistan energy requests are additionally on peak and energy component innovation has extraordinary potential in the nation. As explained above sustainable power sources can be utilized as fuel rather than non-renewable energy sources and does not affect the environment. SOFCs can be utilized as mixture frameworks with sustainable power sources, for example, SOFC-biomass crossover framework, SOFC-wind hybrid framework, SOFC-coal half breed framework and SOFC-poly generation-based frameworks [3].

## **1.8 Catalysts:**

It is essentially a substance that rise the rate of response yet does not participate in the response. A little measure of catalyst is abundant to build the rate of response [32]

## **1.9 Role of catalyst in fuel cell:**

Catalysts are utilized to accelerate the response in this way, in fuel cell catalyst are used to raise the rate of change of fuel into energy. A catalyst is helpful in a fuel cell for two sorts of responses.



- 1- As input, we must catalyze the part of hydrogen into proton and electron.
- 2- As a product, CO is formed that can affect the electrode performance. In this way, we must catalyze the joining response of CO and H<sub>2</sub>O to deliver CO<sub>2</sub> and H<sub>2</sub>.  
The fuel cell performance can be enhanced by quickening the responses as mentioned above [33].

### **1.10 Fuels used in the cell:**

The main advantage of SOFC is fuel flexibility. SOFC's cell is probably the most fuel flexible of different fuel cell type, it can work with a large variety of hydrocarbon fuels such as hydrogen, natural gas, ethanol, methanol, etc. The adaptability of fuel is particularly very important because it avoids the problem of cost and safety etc. I can use hydrogen, ethanol, and methane as a fuel for testing the anode. Methane is likely the most considered elective fuel for SOFCs since it is enough and the primary constituent of both common and biogas. Ethanol is a fluid fuel that has high energy thickness that can be effectively put away and transported and has a high potential for hydrogen generation with high efficiencies and zero net carbon emission [34].

### **1.11 Statement of the Problem:**

The Ni-Yttria-stabilized Zirconia cermet anode in existing SOFC's are not developed for hydrocarbon fuel. In direct utilization of hydrocarbon fuel, Ni-ceria or Cu-ceria anodes have been used, but these anodes have limitations [10]. Like Ni content support coking and can only use with methane at relatively low temperature and Cu is not good electrolyte as Ni, also has low melting point metal which is not suitable for high temperature SOFC's. These are the problems with the Ni-YSZ SOFC's, so we want to prepare the anode that will minimize these problems. We use metallic components in place of electronically conducting ceramics that will not support coking. In our work, we try to prepare anode that directly utilizes hydrocarbons with propane and butane as well.

## **1.12 Choice of Materials and their Properties:**

Nanocomposite materials can be prepared from a collection of materials for SOFC such as samarium, cerium, gadolinium, zinc, cadmium, nickel, copper and lanthanum, barium and so on. The determination of the materials is commonly depending on different factors that include:

- Stability at high temperature
- Should be electronically directing
- Should be ionically directing and so forth.

In this work nitrite of Zinc (Zn), barium (Ba), manganese (Mn), silver (Ag), Copper (Cu) and iron (Fe) have been used because these are the metals and are stable at high temperature.

### **1.12.1 Advantages of Barium:**

Barium is used to avoid corrosion during the working of the SOFC.

- Retains water and encourage water emanated carbon expulsion response.
- Gives consumption and substance protection from arranged material.

### **1.12.2 Advantages of copper:**

- Copper opposes coke development during the working of SOFC.
- Electronic conductivity can be increased by adding this.
- It is good against the deposition of the carbon during the working.

### **1.12.3 Advantages of Manganese:**

- It can be used to enhance the sintering ability during working.
- It can also be used to as electron acceptor from zinc.

#### **1.12.4 Advantages of Zinc:**

- To minimize the polarization losses and to stabilize the material during working.
- Also used to enhance electrical conduction.

#### **1.12.5 Advantages of silver:**

- Silver gives a decent electrical conductivity in both oxidizing and reducing condition with insignificant increment in contact resistance up to 800 °C.
- Silver is a good electronical conductor and used as an electrocatalyst.
- Rather than nickel, silver has much little solubility of carbon so it will not be damage by carbon deposition and can be used as an anode material for that SOFC which were using hydrocarbons as a fuel.

**Chapter 2**  
**literature survey**

## 2.1 Literature Survey:

- **Yapeng Z.et al. - (2017)** investigated the anode materials of GDC and cermet of silver for SOFC. Hydrogen and dry propane are used as fuel. Their performance was tested and then compared with the Ni-GDC. SOFC performance of Ni-GDC and Ag-GDC are the same when testing is done with hydrogen but with propane performance is quite different. The open circuit voltage (OCV) of a SOFC with Ag-GDC anode is steady at ~1 V but with Ni-GDC anode consistently drops from the underlying 1.2V -0.85 V in 140 minutes [35].
- **San Ping J.et al. (2009)** Investigated the anode materials of Pd impregnated LSCM/YSZ by direct applying the methane and ethanol as a fuel for SOFC. The electrocatalytic activity of LSCM/YSZ increases by impregnation of Pd nanoparticles. When methane and ethanol are used as fuel then power density is increased by 2 to 8 times at a temperature of 800 °C. When methane and ethanol are used as a fuel than no carbon formation are noticed. So, this anode material is more effective when methane and ethanol are used as fuel [36].
- **Bing H.et.al (2016)** A titanium-doped  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  composite is created as an anode segment of low temperature solid oxide modules working on methane fuel. Crystallographic parameters of  $(\text{Ce}_{0.8-x}\text{Ti}_x)\text{Sm}_{0.2}\text{O}_{2-x}$  ( $0.00 < x < 0.10$ ) are researched as for the measure of titanium. The composites demonstrate a cubic state with the titanium sum being in the range of 0.00-0.07, while the cross-section parameters decline when the amount of titanium content increases. Cell with Ni- $(\text{Ce}_{0.73}\text{Ti}_{0.07})\text{Sm}_{0.2}\text{O}_{2-d}$  ( $x=0.07$ ) anode shows a low polarization opposition and power density ( $679 \text{ mW cm}^{-2}$  at  $600 \text{ }^\circ\text{C}$ ). The cell performance shows that the cell display low degradation rate with the dry methane [37].
- **Manoj R.P.et.al (2008)** Investigated that SOFC with  $\text{Sr}_{0.8}\text{La}_{0.2}\text{TiO}_3$  anode-side backings, Ni- Sm-doped ceria bond layer,  $\text{NiY}_2\text{O}_3$ -settled  $\text{ZrO}_2$  (YSZ) anode layer, YSZ electrolyte, and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM)– YSZ cathode is represented. These cells are steady when natural gas is used as a fuel at current densities of  $0.2 \text{ Acm}^{-2}$ .

This shows good strength against coking in petroleum gas, contrasted and traditional Ni-YSZ anode of SOFCs which quickly coke, even that when current densities are higher [38].

- **Raza.R.et.al (2010)** They built up another without nickel anode for a low-temperature solid oxide cell (LTSOFC) that showed an extraordinary electrochemical yield of  $1000\text{mW cm}^{-2}$  at  $550\text{ }^{\circ}\text{C}$ . The nanostructure anode had great conductivity and was good with cerium oxide-based electrolytes. The presentation of a single cell was similar as well as superior to those utilizing standard Ni-YSZ and Ni-SDC terminals (anode). The developed anode may have application for the hydrocarbon supported fuels which avoid the deposition of carbon [39].
- **G.Abbas.et.al(2012)** Investigated that composite terminals of  $\text{Cu}_{0.16}\text{Ni}_{0.27}\text{Zn}_{0.37}\text{Ce}_{0.16}\text{Gd}_{0.04}$  (CNZGC) oxides have been effectively synthesis by solid state response technique as anode material for (LTSOFC). These terminals are characterized by XRD which are sintered at different temperature and times. Molecule size of enhanced synthesis was determined  $40\text{--}85\text{ nm}$  and sintered at  $800\text{ }^{\circ}\text{C}$  for 4 hours. The conductivity of  $4.14\text{ S/cm}$  was achieved by using 4 prob DC technique at a temperature of  $550\text{ }^{\circ}\text{C}$ . Hydrogen was utilized as fuel and air as oxidant at anode terminal and cathode terminal separately. At a temperature of  $550\text{ }^{\circ}\text{C}$  the highest power density was obtained are  $570\text{ mW/cm}^2$  [40].
- **Rida B.et.al (2018)** Investigated that  $\text{Ba}_{0.15}\text{Cu}_{0.15}\text{Ni}_{0.10}\text{Zn}_{0.60}$  oxide is used as anode material and arranged by means of a sol-gel method. The basic examination and surface morphology are investigated through X-Ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM), individually. The normal molecule size was determined to be  $231\text{ nm}$ . Then three-layer cell was made for absorbing the fuel cell performance. The cell was tested by using hydrogen as a fuel at a temperature range of from  $450\text{ }^{\circ}\text{C}$  and  $650\text{ }^{\circ}\text{C}$ . Maximum conductivity and power density were obtained  $10.4\text{ Scm}^{-1}$  and  $350\text{mWcm}^{-2}$ , individually. Above mentioned material showed a reasonably good power density at a low temperature so it will be a good applicant for LT-SOFC anode [41].

- **Fida H.et.al (2019)** The basic and electrochemical properties of anode material  $\text{Ni}_{0.6}(\text{Ba}_{0.3}\text{Ce}_{0.2}\text{Zn}_{0.5})_{0.4}$  have been examined within the sight of hydrogen, flammable gas, ethanol, glucose, and sugar-cane at a low temperature of 600 °C. The normal crystalline size has been discovered 25–90 nm by both checking electron microscopy and X ray beam diffraction strategies. The power density of the cell at different fuels has been watched and analysis shows that it differs from 57 to 315  $\text{mWcm}^{-2}$  at a temperature of 600 °C when using various fuels at the anode side. The present investigation shows that the above mention anode material is promising multi-fuel anode material for low-temperature SOFC, and it doesn't have to change hydrocarbon fills so as to completely use the benefit of these cells [42].
- **Imran, SK.et.al (2011)** Investigated the fuel cell working with various metal-oxide based terminals. The power densities of 584  $\text{mW cm}^{-2}$  and 514  $\text{mW cm}^{-2}$  at a temperature of 520 °C and 570 °C individually were found. The impact of terminal catalyst work, ethanol fixation on the electrical performance was examined at various temperature starting from 300 °C to 600 °C. The impact of kept carbon on the anode was examined by X-beam spectroscopy and scanning electron microscope in the wake of testing the cell with bioethanol [43].
- **J Liu et.al (2002)** Results are displayed on a SOFC anode material intended for use with C-containing fuels, a composite of an electronically directing ceramic,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.8}\text{Mn}_{0.2}\text{O}_{3-x}$ , an ionically conducting  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{0.19}$  GDC and a little portion Ni. The above mention anode materials show the comparable performance to that of Ni-GDC when hydrogen and methane are used as a fuel. This anode also gives good results with propane and butane and, not at all like Ni-GDC, there was practically zero coking. The 4 wt % Ni content in the anode was important to get good performance, showing that a little measure of Ni gives a considerable electrocatalytic impact while not causing coking [44].

## **Chapter 3**

### **Experimental Procedure**



### **3.1 Synthesis of Nanocomposites Materials:**

There are several strategies utilized for the planning of the nanocomposite material; the generally utilized techniques are wet substance strategy, co-precipitation strategy, sol-gel technique, and solid-state response technique. In my research project, materials were combined by utilizing sol-gel technique since it has higher efficiency and lower cost and is a very easy approach to synthesizes the nanocomposites. After making the composites materials, the prepared composites materials were squeezed into pellets to measure the conductivity.

### **3.2 Preparation of sample:**

In this part, the sample preparation method has been discussed.

#### **3.2.1 Synthesis of materials:**

Different techniques have been used for preparing the nanocomposites materials but here I utilized sol-gel strategy because it has a number of advantages. In my thesis, I can use a catalyst with some metal precursors. The effect of catalyst can be checked on the properties of the sample.

#### **3.2.2 Advantages of Sol-Gel method:**

- Improved homogeneity because of the blending at the atomic dimension.
- Lower energy utilization because the structure can be gotten at moderately low temperatures.
- No requirement for unique or costly apparatus.
- It permits the manufacture of any oxide composition, yet in addition some non-oxides, just as the generation of new hybrid organic and inorganic materials.

### 3.2.3 Sol-Gel Method:

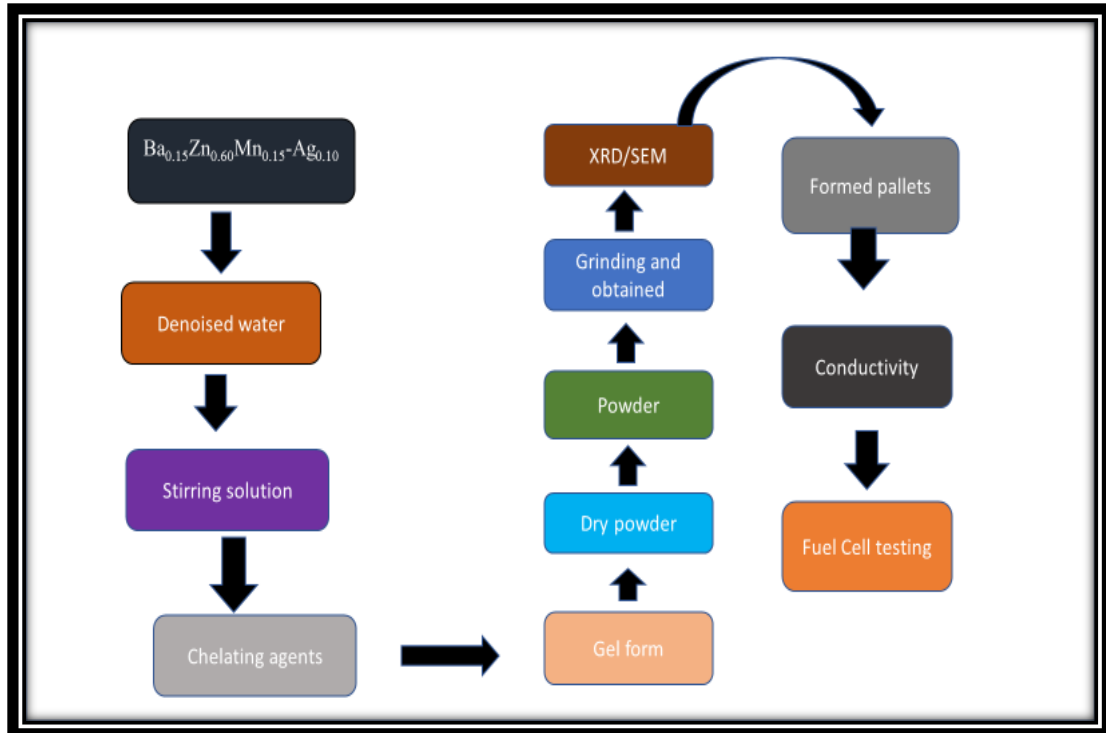
#### Sample Preparation Methodology:

First, metal precursors are taken, then dissolve these in di-ionized water and place it in the hot magnetic stirrer plate for stirring. Then take the chelating agent and dissolve in another beaker. After that dissolve the chelating agent in the metal precursors beaker drop by drop to form the gel. To get the dry powder placed the gel solution in the oven for some time. To obtain the homogeneity of the powder placed this in the furnace at a specific temperature. After sintered to get the homogenous particles the material is grind in mortar and pestle. Further, the material is used for characterization.

#### Sample 1:

- The metal precursors used for preparing the anode materials are zinc nitrate, manganese nitrate, barium nitrate respectively.
- Silver nitrate is used as a catalyst in this sample.
- Take the compositions of (zinc nitrate, manganese nitrate, barium nitrate and silver nitrate) to make a proposed  $\text{Ba}_{0.15}\text{Zn}_{0.60}\text{Mn}_{0.15}\text{-Ag}_{0.10}$ .
- All these nitrate materials were dissolved in 100ml denoised water.
- Citric acid was used as a chelating agent and then mixed with the solution at a temperature of  $80\text{ }^{\circ}\text{C}$  for 7 hours at a magnetic stirrer plate to form a gel.
- To get the dry powder, the gel was put in the oven at a temperature of  $250\text{ }^{\circ}\text{C}$  for 3 hours.
- After that to obtain the homogeneity and structure development put the sample in the furnace at a temperature of  $700\text{ }^{\circ}\text{C}$  for 6 hours.
- After sintering, the material grind in mortar and pestle for homogeneous particle.

The flow chart of prepared anode for samples 1 was shown in figure 3.1.

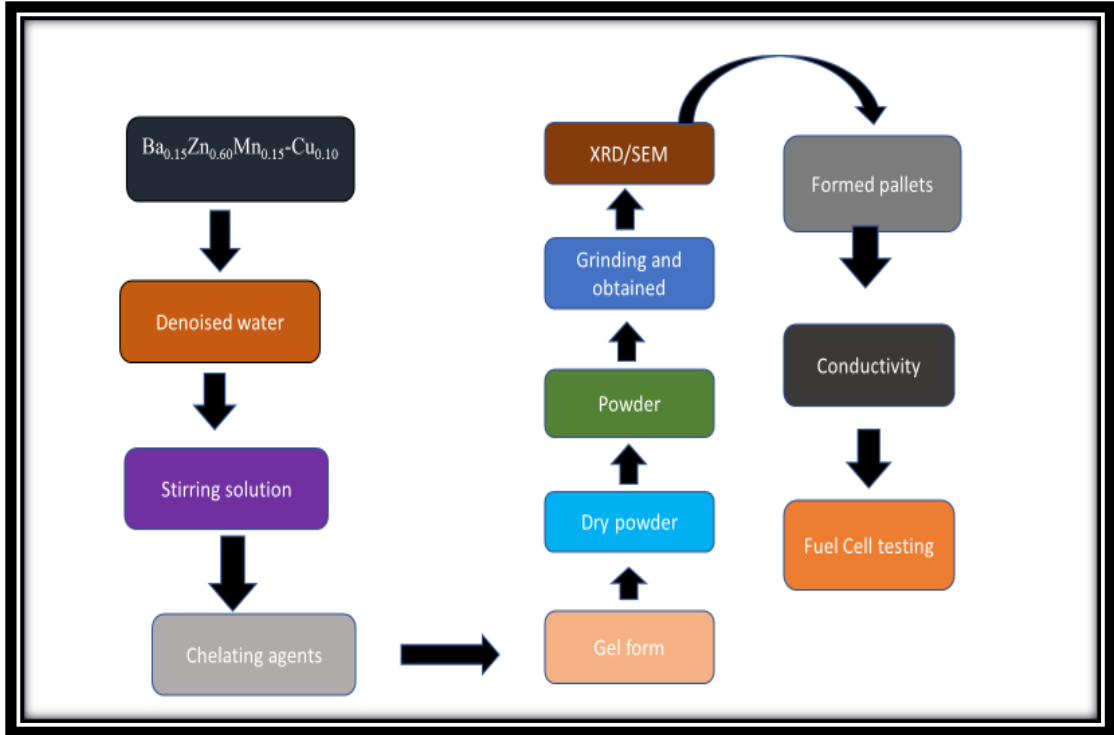


**Figure 3.1:** Flow chart of the sol-gel method of sample 1.

**Sample 2:**

- For sample 2 similar metal precursors are taken.
- Copper nitrate is used as a catalyst in this sample.
- The proposed material in this sample is  $\text{Ba}_{0.15}\text{Zn}_{0.60}\text{Mn}_{0.15}\text{-Cu}_{0.10}$ .
- For further above mention, steps are taken.

The flow chart of prepared anode for samples 2 was shown in figure 3.2.

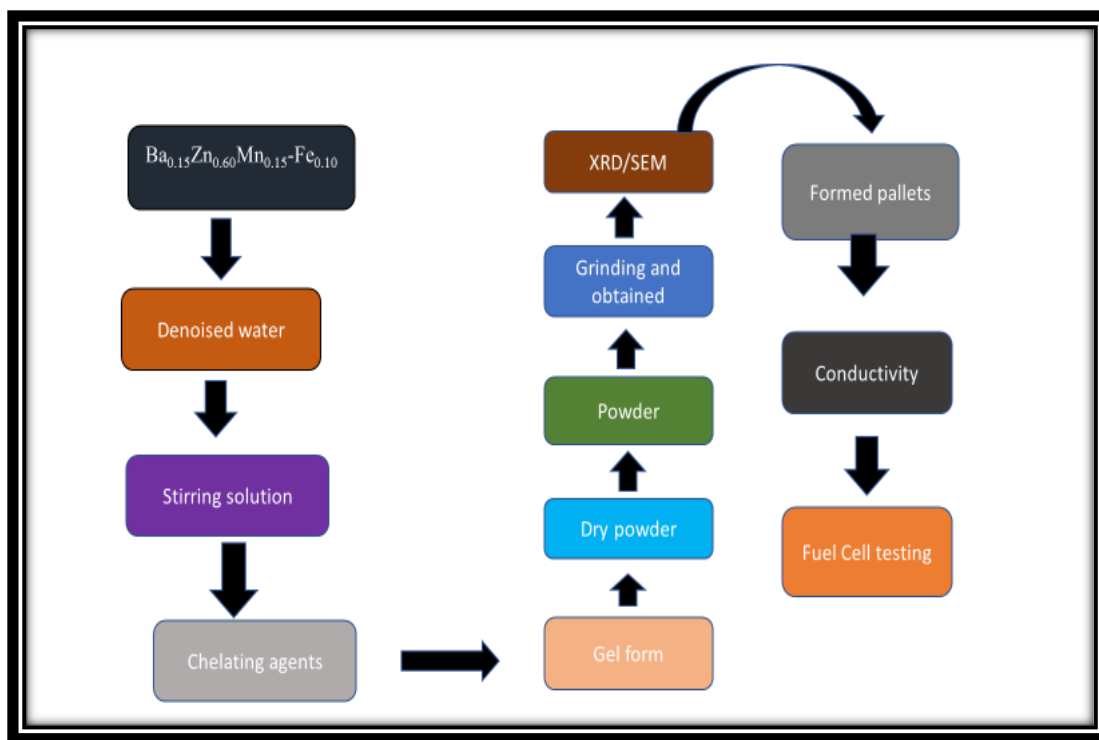


**Figure 3.2:** Flow chart of the sol-gel method of sample 2

**Sample 3:**

- For sample 3 similar metal precursors are taken.
- Iron nitrate is used as a catalyst in this sample.
- The proposed material in this sample is  $\text{Ba}_{0.15}\text{Zn}_{0.60}\text{Mn}_{0.15}\text{-Fe}_{0.10}$ .
- For further above mention, steps are taken.

The flow chart of prepared anode for samples 3 was shown in figure 3.3



**Figure 3.3:** Flow Chart of the sol-gel method of sample 3

### 3.3 Cell Fabrication:

After making the materials, the prepared materials were squeezed by a hydraulic press to make the pallets which were sintered at 700 °C for 1 hour. The prepared pallets are used for measuring the conductivity. For fuel cell performance a complete cell is made in which the electrolyte is in the center, Anode and cathode is on the other sides.



**Figure 3.4:** Pallets of prepared samples

### **3.4 Characterization Techniques:**

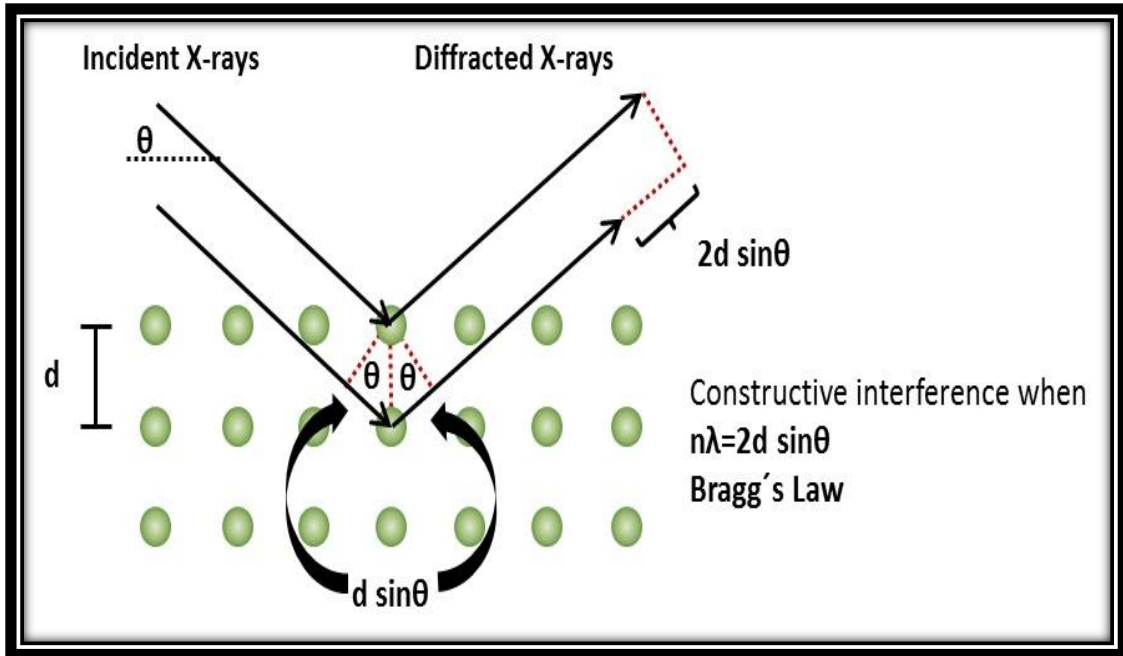
After making the sample, then different techniques were used to find out the morphology of the material, the arrangement, and electrical and other properties. The precise knowledge about the structure of the material can be found from the X-Ray diffraction technique. DC conductivity can be found through four probe method. Fuel cell testing is done in approach to a solid oxide fuel cell to decide cell execution. In this part, we will shortly explain every one of these techniques. We have utilized the below mention characterization tools to know about the material.

- X-ray diffraction
  
- Scanning electron microscopy
  
- Conductivity measurements
  
- Fuel cell testing

#### **3.4.1 X-Ray Diffraction:**

X-beam diffraction is considered as one of the characterization methods of the material which is utilized to locate the crystalline structure, crystallite size, and material's substance composition. X-beams are created when the electrons of a few keV energy are quickened at a metal target which emits out the center electrons from the metal target by stimulated electrons.

At the point when the electrons compare to higher shell fall into the lower shell then x-beams are produced. Most basic metal targets are the copper source. These radiated x-beams are called characteristic x-beams as they have well-characterized wavelengths which compare to energy contrast between the upper and lower shells in the metal target [45]. The x-ray beams are fall on the material which dissipates the x-beams (figure 3.5).



**Figure 3.5:** X-Ray Diffraction pattern

X-ray beams wavelength (1-100 Å) are comparative in size to the between atomic spacing (dhkl) of material, this reason the diffraction and dissipating of the waves, gathering data about material's individual particles and their course of action. Bragg's law tells at which wavelengths and edge approaching x-ray beam will cause the constructive interference of dispersed waves:

$$n\lambda = 2d\sin\theta \dots\dots\dots(3.1)$$

Where,

n = Integer

$\lambda$  = X-Ray wavelength

d = Atomic spacing

$\theta$  = Angle between incident x-ray and atomic layer

Full width half maximum (FWHM) can be calculated by the XRD that is utilized to determine the crystalline nature of the material. If the value of FWHM is large than Bragg's

peak which is broad and expansive indicates that the size of crystallite is small, and crystallinity is not good [46].

The crystallite size can be calculated by the Scherrer's formula:

$$D = \frac{K \lambda}{\beta \cos \theta} \dots \dots \dots (3.2)$$

Where,

D = Diameter of the grain

$\beta$  = full width at half of the maximum value of the diffraction peak (FWHM)

$\lambda$  = X-ray wavelength (for Cu-K $\alpha$ ,  $\lambda=1.54060 \text{ \AA}$ )

$\theta$  = diffraction angle

K = Scherer's constant (K = 0.94)

### 3.4.2 Conductivity Measurement:

Conductivity is the capacity of a metal or a gas - in short, all materials - to pass an electric flow. In solutions, the current is conveyed by cations and anions though in metals it is conveyed by electrons. Electricity conduction of the solution depends on many factors;

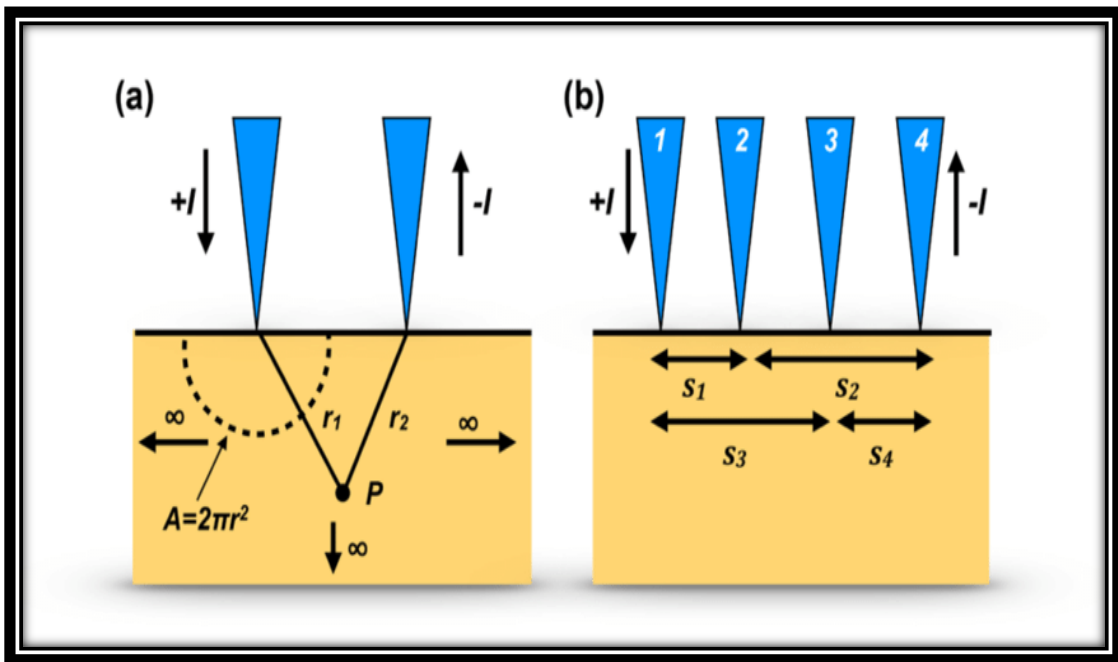
- Concentration
- Mobility of particles
- Valence of particles
- Temperature

To decide the proton as well as electron conduction in a material conductivity estimation is significant. Conductivity is estimated in S/cm<sup>2</sup>. Two contact techniques are utilized to measure the DC conductivity of the pellets of the sample.



- 2-point probe method
- 4-point probe method

In a 2-point test, known current or is connected to the pellets. Utilization of voltage or current and estimation of the other yield the resistance of pellet, that measured resistance can be utilized to find out the resistivity (or conductivity) of the pellet. Figure 3.6 (A) represents the apparatus of the 2-point probe. Current is kept running along the length of the sample,  $I$ , and current and voltages are estimated with similar terminals at the two ends. Figure 3.6 (B) represents the apparatus of a 4-point probe. experiment [47]. In a 4-point test strategy, 4 terminals were utilized rather than two terminals to measure current and voltage. Voltage is measured from the internal 2 terminals and a consistent current is connected to other external 2 terminals.



**Figure 3.6:** Schematic diagram of 2 probes and 4 probes

We use the 4-probe method to measure the conductivity of our prepared samples at different temperatures for each sample. The conductivity was measured by using the formula:

We can use 4 probe method to measure the conductivity of anode material. First of all, pellets were made of three samples by the hydraulic press under a pressure of 4000Pa. The diameter of the pallets is 13mm and 2mm is thickness. Prepared pallets were sintered at 700 °C for 1 hour. Silver paste is coated on both sides of the pallets for good conduction of the current. The electrical conductivities of the prepared pellets were calculated between the temperature of 350 °C to 650 °C.

Conductivity can be finding out by using the following equation.

$$\sigma = L/RA \dots\dots\dots(3.4)$$

Where,

- L= Thickness of the pellet
- R= Resistance
- A= Active area of the pallets

For our sample, the active area of the pallet is 0.64 cm<sup>2</sup>.

The electrical band gap is calculated from conductivity measurements by using the Arrhenius equation:

$$K= A \exp (-E_a/RT)\dots\dots\dots (3.5)$$

Where K is the rate constant, A is a pre-exponential factor, E<sub>a</sub> is activation energy, R is general gas constant, and T is the temperature in degree Kelvin.

Taking the logarithm of two sides of equation 3.5, hence we can get a straight-line equation. It is given as follows:

$$\ln(k) = \ln(A)-E_a/R (1/T)$$

$$\text{Slope} = -E_a/R$$

The electrical bandgap for sometimes is approximately double the activation energy [38-39].

$$E_{eg} = 2 E_a$$

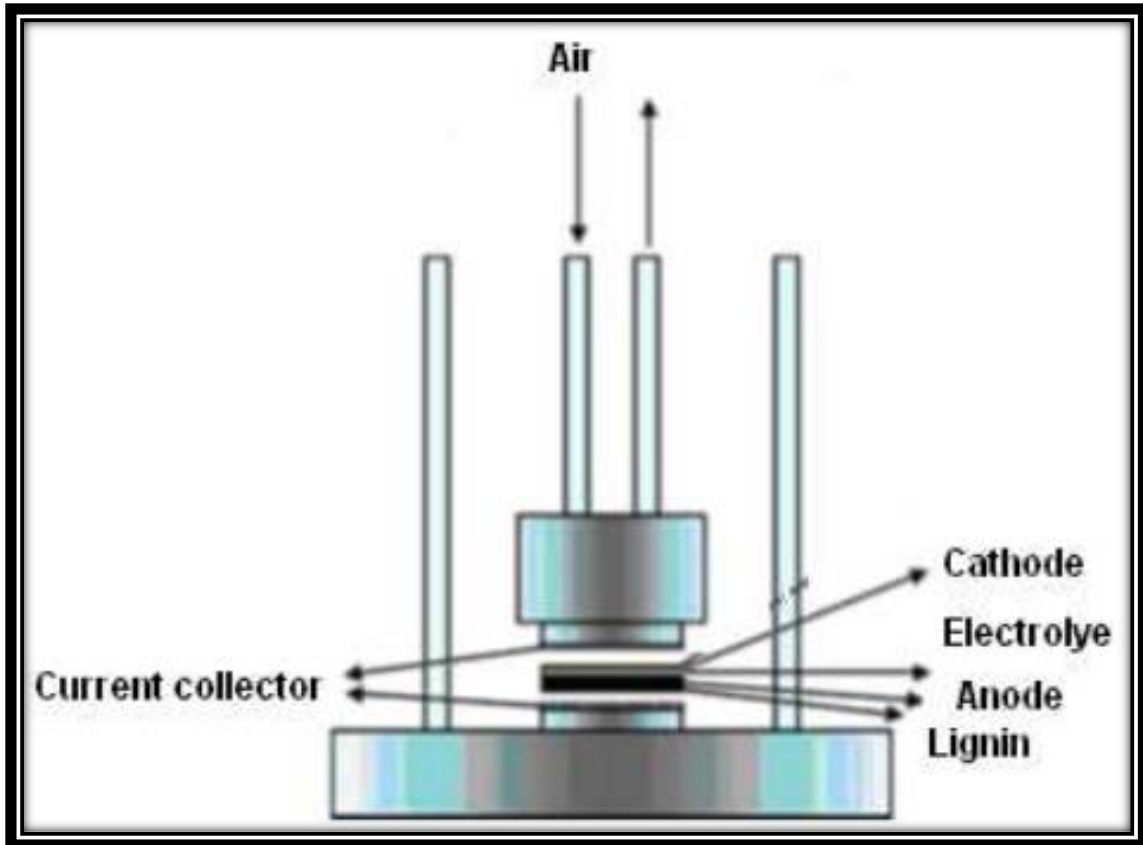
Where,

$$E_{eg} = \text{Electrical band gap}$$

The electrical bandgap is sometimes larger than optical bandgap due to coulombs repulsion energy.

### **3.4.3 Fuel Cell Testing:**

Fuel cell testing technique comprises of two u- shaped like terminals. The prepared cell was fixed in the device, two terminals at the center were used for the transfer of air to the cathode. The fuel is applied in the cathode side. To finding the performance, the dye was placed in the furnace and start heating to the temperature at which we want to take readings. When the temperature reached to the limit than values of the voltage and current was measured. Then from the reading draw the curves of current density and power density. The figure for fuel cell testing is shown below.



**Figure 3.7:** fuel cell diagram of the testing

- Three layers of the electrode were prepared for making the cell for fuel cell performance.
- We can take 0.4g of anode material and take 0.3g of already prepared samarium doped ceria (SDC) of electrolyte material from the lab. Similarly, we can take 0.3g of (LNCZ) of cathode material from the lab.
- Then we can make the pallet of 1g by the hydraulic press and sinter for 1 hour at a temperature of 700 °C
- Then the cell was placed in the furnace and activated temperature for the cell was measured.
- We can use three different fuels such as hydrogen, natural gas, and ethanol for testing the cell.

- At that point, the temperature was well ordered expanded and execution was examined by computing the Open Circuit Voltage (OCV), at that point load was given to measure the current gradually load is expanded and current determined.
- Then current density will be calculated by the formula  $I_d = I/A$  where A is the active area of the pallet and I am the current.
- Similarly, the performance of the three cells is obtained by using different fuels.

## **Chapter 4**

### **Results and Discussion**

## **4.1 Characterization of Nanocomposites Material:**

This part is consisting of the outcomes which will be obtained by utilizing distinctive characterization procedures e.g., XRD, Conductivity and Fuel cell testing to think about the crystalline structure, conductivity, and fuel cell performance and so on.

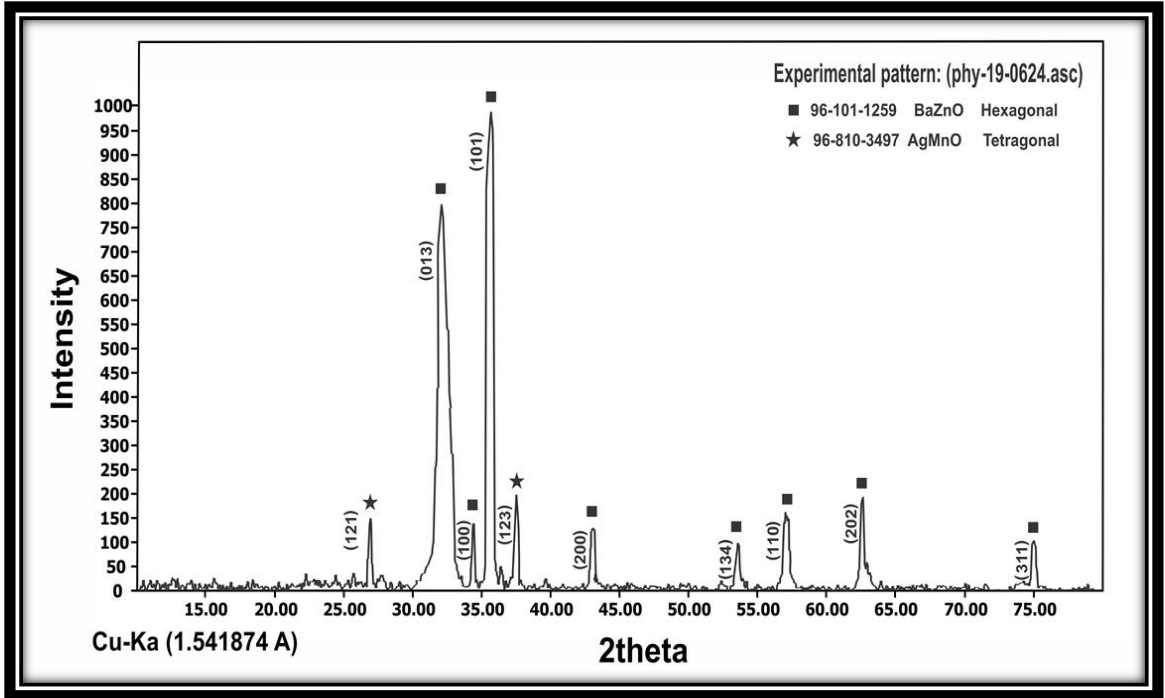
## **4.2 X-Ray diffraction analysis:**

In this part analysis of the three samples has been discussing. The effect of a catalyst on anode materials is also explained.

### **4.2.1 Analysis of BaZnMn-Ag:**

Figure 4.1 represents the pattern of XRD of sample BaZnMn-Ag, which was examined by Match and Diamond software, which was sintered at 700 °C for 4 hours. XRD pattern demonstrates that the got composite material is crystalline and has two phases structure one is hexagonal and other is tetragonal.

Diffraction peaks of the XRD arrangement of AgMnO with (COD card no. 96-810-3497) are recorded to be a tetragonal structure, where as peaks correspond to BaZnO shows the hexagonal structure since all the diffraction peaks are good matching with that of ZnO crystalline structure with ( COD Card No. 96-101-1259). A few noises have been finding which might be because of instrument adjustment issues or water vapors. Double phase determined for nanocomposite prepared material in which one phase attributed to the catalytic phase and second phase provide the channel for electron execution from anode side to cade side during cell performance. The average crystallite size was calculated to be 19 nm. Which gives evidence the material have a large surface area. In energy nanocomposite materials large surface area enhance the conduction of electron as well as ions of oxide and hydrogen. Miller indices values associated with each peak given the information of plan present in determined structured.



**Figure 4.1:** XRD result of BaZnMn-Ag

#### 4.2.2 Analysis of BaZnMn-Cu:

The nanostructure and crystallographic investigation of BaZnMn-Cu anode were shown in Fig. 4.2. The consequences of XRD results represent that the prepared BaZnMn-Cu anode has good crystalline nanostructure. XRD pattern demonstrates in this sample that the prepared BaZnMn-Cu anode material has two phases structure one is hexagonal and other is cubic.

Diffraction peaks of the XRD arrangement of CuMnZnO with (COD card no. 96-152-4535) are recorded to be a cubic structure, which is the catalytic part. Where as the peaks correspond to BaZnO shows the hexagonal structure since all the diffraction peaks are good matching with that of ZnO crystalline structure with ( COD Card No. 96-900-4179). The average crystallite size was calculated is 21 nm. In this sample, the increase in the crystallite size is due to a decrease in the FWHM. There are 12 diffraction peaks in this sample of which (100), (002), (101), (012), (110), (013), (200), (112), (201) corresponds to BaZno where (100), (101), (211) represent the CuMnZnO, and out of all these peaks the most prominent intensity peaks òare (101) peak for hexagonal phase.



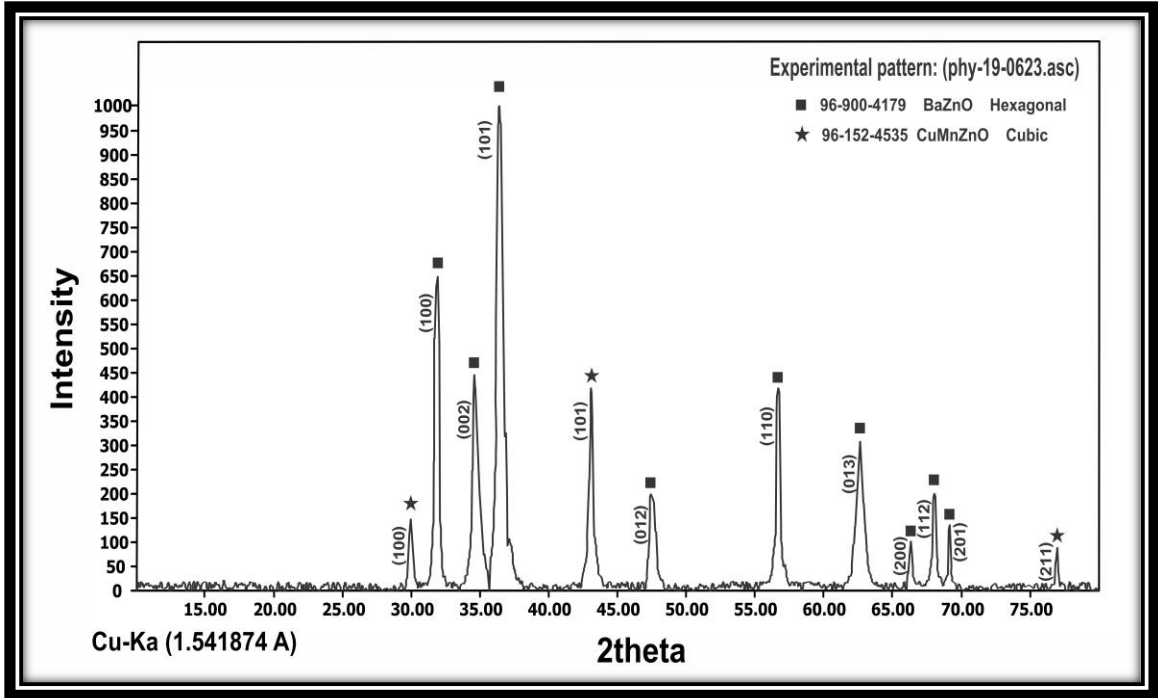
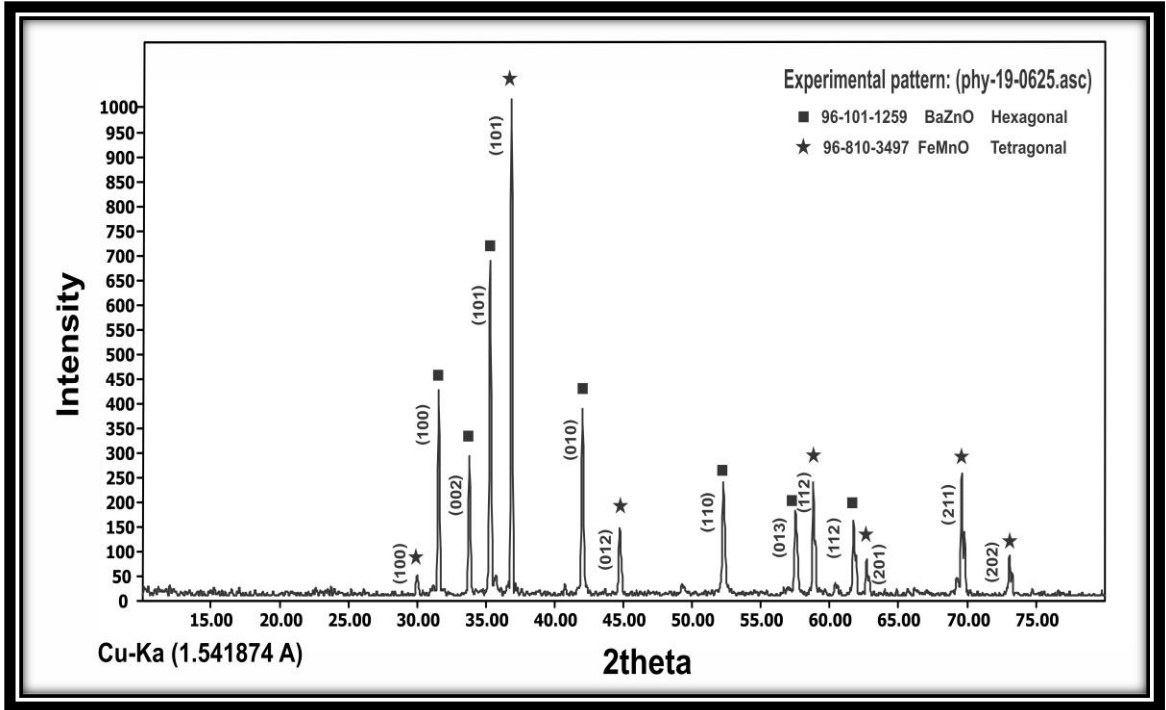


Figure 4.2: XRD result of BaZnMn-Cu

#### 4.2.3 Analysis of BaZnMn-Fe:

Diffraction pattern of BaZnMn-Fe anode material is given in figure 4.3. The outcomes display that the sample, which was sintered at 700 °C for four hours execute crystalline Nanostructure. From the figure we can see that there is two phase structure one is hexagonal shown by BaZnO with (COD card no. 96-101-1259) and second is tetragonal shown by a catalytic part of FeMnO with (COD card no. 96-810-3497).

The crystallite size of the BaZnMn-Fe anode material was determined from the XRD data by applying Scherer's formula and observed to be 64 nm. It has been analyzed from the XRD study that materials which are sintered at a temperature of 700°C are good to make nanostructure crystalline structure. In this sample, we can see from the figure that most of the detective peaks are sharp, so the crystallite size is large as compared to the other two samples.



**Figure 4.3:** XRD result of BaZnMn-Fe

### 4.3 Conductivity analysis:

Convenient electrical conductivity is the main parameter to get better execution performance of the anode materials. Four-probe DC estimation technique was used to get results of electrical conductivity of prepared samples BaZnMn-Ag, BaZnMn-Cu and BaZnMn-Fe of nanocomposites materials between the temperature range of 300 °C to 650 °C at the air environment independently. The results of these prepared samples are shown in the figure of 4.4. From the graph, we can see that the electrical conductivity of each sample increases with the rise in temperature. Nonetheless, the most electrical conductivity was attaining at temperature 600 °C of the sample with a silver catalyst. From the three prepared samples, the maximum conductivity was found to be 4.8 S/cm at a temperature of 600 °C with a silver catalyst. Silver at a lower temperature is thermally active so it gives maximum conductivity at a temperature of 600 °C as compared to the other sample. Also, silver is the good conductor because its electrons are free to move as compared to that of

other elements. The second curve (black) represents the sample of the copper catalyst which gives the lower conductivity as compared to the silver. The conductivity of copper increase linearly with the increase in temperature. So, we can say that copper is less conductive than silver. So, it gives a maximum conductivity of 4 S/cm at a temperature of 550 °C. After 550 °C the conductivity starts to decrease because it will be unstable at that temperature, we can say that the effect of degradation happens. Third cure represents the effect of iron catalyst, from the curve we see that iron at low temperature is not thermally active, so it needs a high temperature for activation as compared to that of other samples. So, its maximum conductivity was found to be 4 S/cm. So, we can conclude that Ag behavior shows good conductivity because most of the SOFC works in this range of temperature. The genuinely great conductivity at even lower temperature makes it a possibly a great possibility for low temperature SOFC.

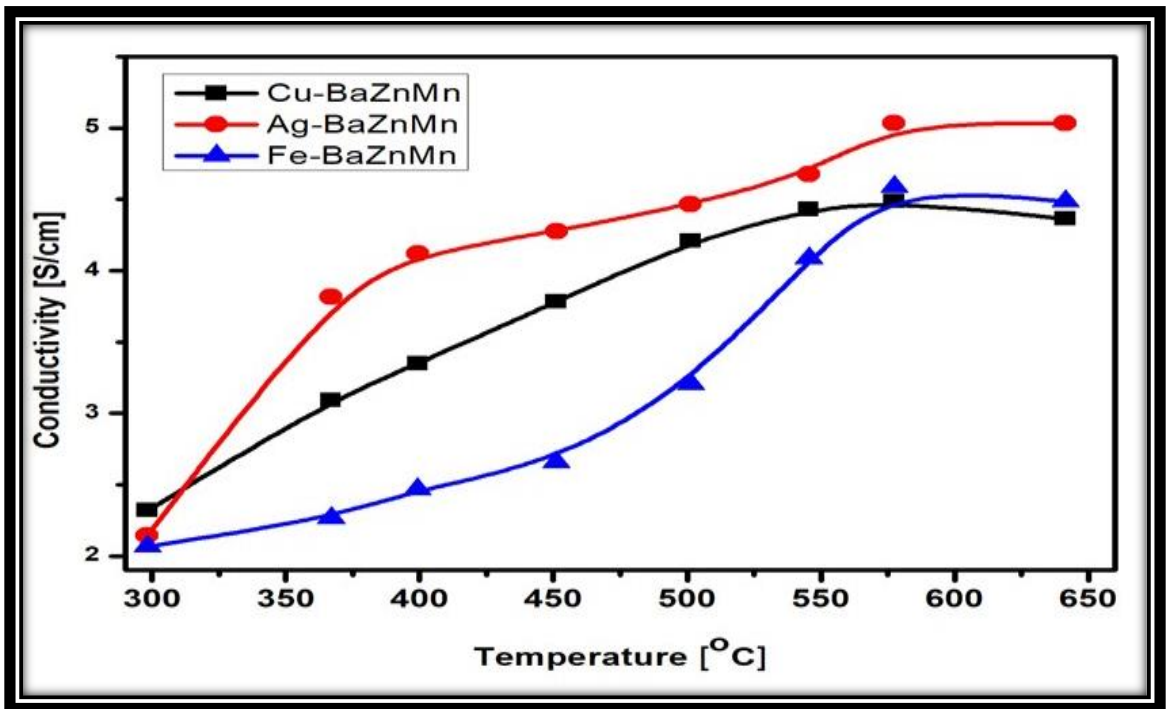


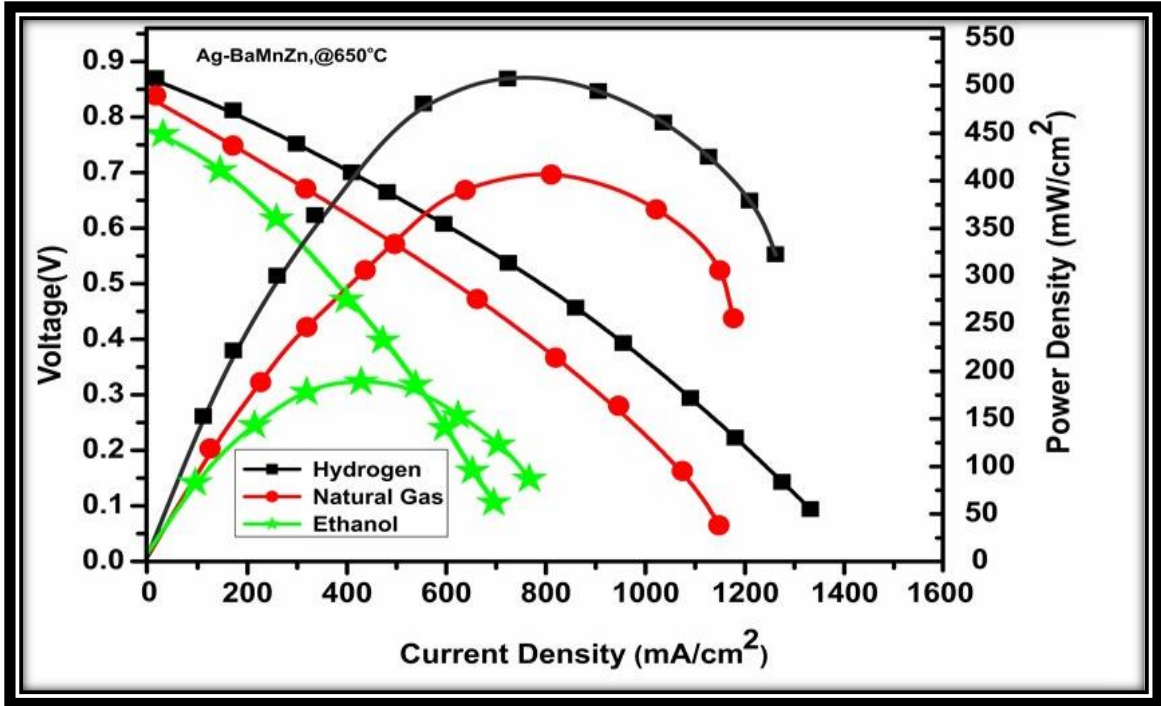
Figure 4.4: Conductivity result of prepared samples

#### **4.4 Fuel cell Performance analysis:**

In this part, fuel cell performance can be calculated. For this, we analyze three samples with different catalyst.

##### **4.4.1 Analysis of sample BaZnMn-Ag:**

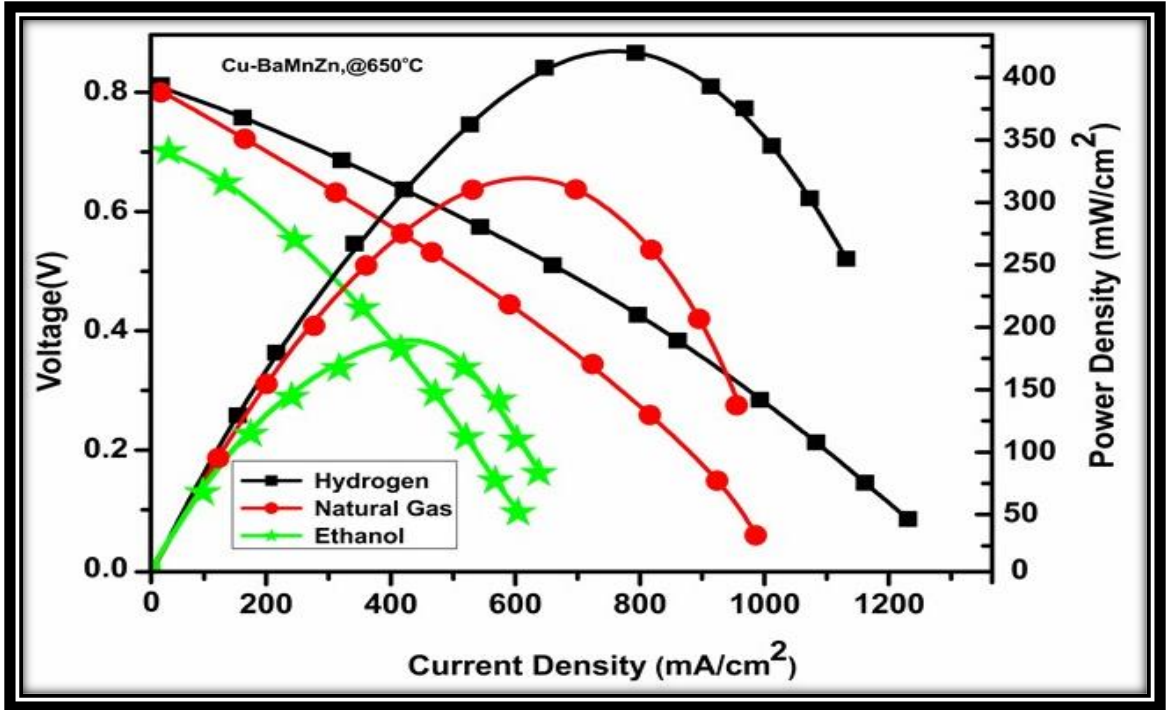
This graph represents the fuel cell performance of above mention anode sample with silver as a catalyst. Cell performance can be measured by using three different fuels such as hydrogen, natural gas, and ethanol at a temperature of 650 °C. Within the sight of these fuels, testing was done in order to check the open circuit voltage and its relating current at different resistances. First, the cell was prepared by using NSDC and LNCZ as an electrolyte and cathode respectively. We can find good results of performance when we used hydrogen as a fuel. We find the maximum power density of 500 mW/cm<sup>2</sup> with hydrogen. From the graph, we see that the power density of the sample is low when we used natural gas and methanol as a fuel. The measured power density with these fuels is 400 mW/cm<sup>2</sup> and 150 mW/cm<sup>2</sup> respectively. The open circuit voltage measured with these fuels is 0.9V, 0.85V and 0.78V respectively. And the maximum current density was found to be a 1300 mA/cm<sup>2</sup>.



**Figure4.5:** Performance result of BaZnMn-Ag with different fuels

#### 4.4.2 Analysis of sample BaZnMn-Cu:

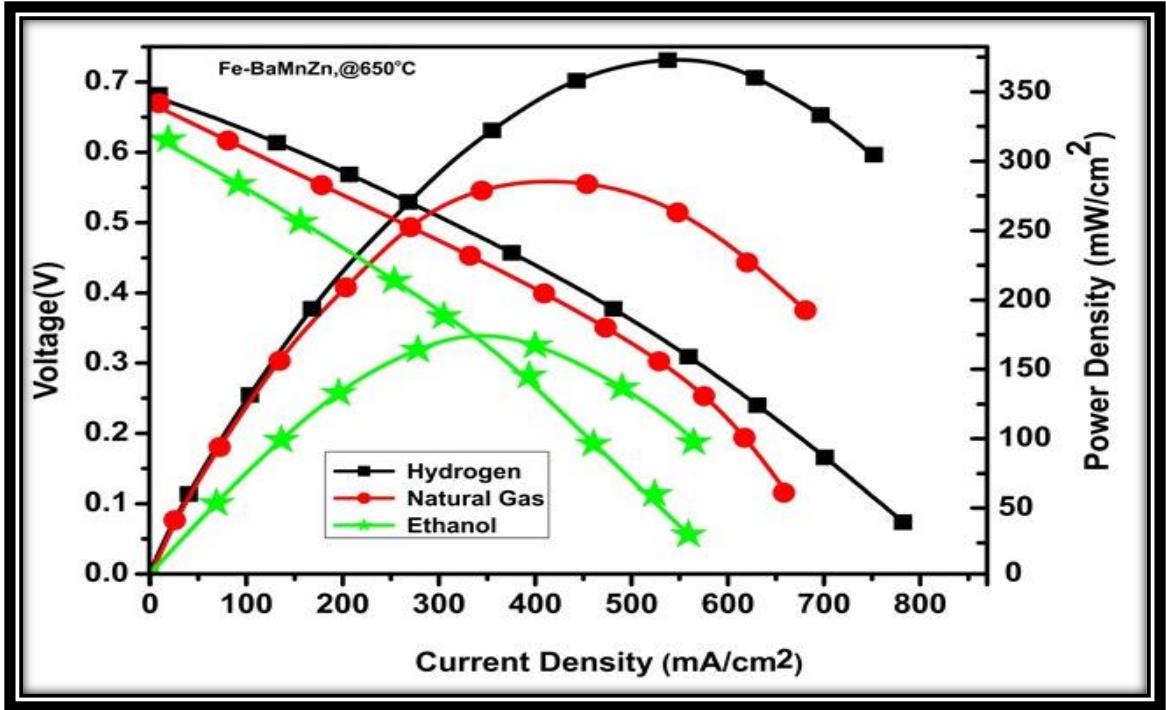
This graph represents the fuel cell performance of sample BaZnMn-Cu in which copper is used as a catalyst. Similarly, here we used the same fuels and performance was measured. Here also maximum power density was recorded by the hydrogen fuel as compared to natural and ethanol. The measured power densities are 400 mW/cm<sup>2</sup>, 300 mW/cm<sup>2</sup> and 150 mW/cm<sup>2</sup> respectively. The open circuit voltage for hydrogen and natural gas are almost the same in this sample 0.8 V. But for ethanol, the open circuit voltage is 0.7 V. The maximum current density found for this sample is 1200 mA/cm<sup>2</sup>. As we see from the graph when the open circuit voltage is started to decrease than the current density will start to increase.



**Figure 4.6:** Performance result of BaZnMn-Cu with different fuels

#### 4.4.3 Analysis of sample BaZnMn-Fe:

Fuel cell performance of BaZnMn-Fe shown in figure [4.7] which demonstrates the current density decreases as compared to other samples. Same as open circuit voltage is also decreased by increasing temperature but deliver maximum value on 650 which have consistency to the law of thermodynamic. OCV is the inverse of Gibbs free energy. Power density determined by I-V data that have a maximum value of 400 mW/cm<sup>2</sup>. That's shows electrons are executed through prepared BaZnMn-Fe. But iron poses less catalytic activity as compared to copper and silver due to strong iron oxide bonding. Manganese with iron oxide phase provides a pathway to the migration of ions from splitting area of gasses into ions to the Nano core triple phase boundary at inter phase of electrolyte.



**Figure 4.7:** Performance result of BaZnMn-Fe with different fuels

From the above graphs of fuel cell performance, we conclude that the best performance among these three samples BaZnMn-Ag, BaZnMn-Cu, BaZnMn-Fe is given by the sample of BaZnMn-Ag. The reason is that silver behaves like a good catalyst as compared to that of copper and iron. Silver as a catalyst is good against the deposition of the carbon layer on the fuel cell. Since the Ag-C bond is too powerless to even consider breaking the C-O or C-H bond, as per the bond request preservation hypothesis. We also conclude that performance is best through hydrogen fuel as compared to natural gas and ethanol.

## Conclusion:

In this research work, the nanocomposite materials BaZnMn-Ag, BaZnMn-Cu, BaZnMn-Fe based on the mixed conductivity were synthesized for the fuel cell. After that, these nanocomposite materials were described with the assistance of various characterization procedures to research and study its different properties. Following ends was drawn from this exploration work.

- Synthesis by sol gel method
- Effect of different is analyzed.
- X- Ray diffraction shows the crystalline structure. The crystallite size of the three samples anode material was determined from the XRD data by applying Scherer's formula.
- For sample 1 and 3 two phases structure were observed one is hexagonal and other is tetragonal. For sample, 2 phase structure is hexagonal and cubic.
- The average particle size calculates in the range of 19nm to 90nm.
- From the three prepared samples, the maximum conductivity was found to be 4.8 S/cm at a temperature of 600 °C with a silver catalyst. Silver at a lower temperature is thermally active so it gives maximum conductivity at a temperature of 600 °C as compared to the other sample.
- From the graphs of fuel cell performance, we conclude that the best performance among three prepared samples is given by the sample BaZnMn-Ag. The reason is that silver behaves like a good catalyst as compared to that of copper and iron.
- The maximum OCV of about 0.9V, 0.8V and 0.7V and maximum power density of about 500 mW/cm<sup>2</sup>, 400 mW/cm<sup>2</sup> and 400 mW/cm<sup>2</sup> are observed by hydrogen fuel.



## References

1. Abbas, T., et al., Greener energy: Issues and challenges for Pakistan-geothermal energy prospective. *Renewable and Sustainable Energy Reviews*, 2014. 31: p. 258-269.
2. Bazmi, A.A. and G. Zahedi, Sustainable energy systems: Role of optimization modeling techniques in power generation and supply—A review. *Renewable and Sustainable Energy Reviews*, 2011. 15(8): p. 3480-3500.
3. Raza, R., et al., Fuel cell technology for sustainable development in Pakistan – An over-view. *Renewable and Sustainable Energy Reviews*, 2016. 53: p. 450-461.
4. Bhutto, A.W., A.A. Bazmi, and G. Zahedi, Greener energy: Issues and challenges for Pakistan—Solar energy prospective. *Renewable and Sustainable Energy Reviews*, 2012. 16(5): p. 2762-2780.
5. Bhutto, A.W., A.A. Bazmi, and G. Zahedi, Greener energy: Issues and challenges for Pakistan—wind power prospective. *Renewable and Sustainable Energy Reviews*, 2013. 20: p. 519-538.
6. Bhutto, A.W., A.A. Bazmi, and G. Zahedi, Greener energy: Issues and challenges for Pakistan-hydel power prospective. *Renewable and Sustainable Energy Reviews*, 2012. 16(5): p. 2732-2746.
7. Bhutto, A.W., et al., A review of progress in renewable energy implementation in the Gulf Cooperation Council countries. *Journal of Cleaner Production*, 2014. 71: p. 168-180.
8. Kousksou, T., et al., Energy storage: Applications and challenges. *Solar Energy Materials and Solar Cells*, 2014. 120: p. 59-80.
9. Twidell, J. and T. Weir, *Renewable energy resources*. 2015: Routledge.
10. Qureshi, M.I., A.M. Rasli, and K. Zaman, Energy crisis, greenhouse gas emissions, and sectoral growth reforms: Repairing the fabricated mosaic. *Journal of Cleaner Production*, 2016. 112: p. 3657-3666.
11. Rauf, O., et al., An overview of energy status and development in Pakistan. *Renewable and Sustainable Energy Reviews*, 2015. 48: p. 892-931.

12. Khoso, S., et al., An overview on emerging water scarcity in Pakistan, its causes, impacts and remedial measures. *Journal of Applied.Engineering Science*, 2015. 13(1): p. 35-44
13. Awan, A.B. and Z.A. Khan, Recent progress in renewable energy–Remedy of energy crisis in Pakistan. *Renewable and Sustainable Energy Reviews*, 2014. 33: p. 236-253.
14. Chaudhry, M.O., M.Z. Faridi, and S. Riaz, Energy Crisis and Macroeconomic Stability in Pakistan. *Pakistan Journal of Social Sciences (PJSS)*, 2015. 35(1): p. 425-436.
15. Sher, H.A., et al., Pakistan’s progress in solar PV based energy generation. *Renewable and Sustainable Energy Reviews*, 2015. 47: p. 213-217.
16. Chaudhry, M.A., R. Raza, and S. Hayat, *Renewable energy technologies in Pakistan: prospects and challenges*. *Renewable and Sustainable Energy Reviews*, 2009. **13**(6): p. 1657-1662.
17. Yang, Z., et al., Recent progress in doped carbon nanomaterials as effective cathode catalysts for fuel cell oxygen reduction reaction. *Journal of Power Sources*, 2013. 236: p. 238-249.
18. Conway, B.E., *Electrochemical supercapacitors: scientific fundamentals and technological applications*. 2013: Springer Science & Business Media.
19. M. W. Ellis et al; “Fuel Cell Systems: Efficient, Flexible Energy Conversion for the 21st Century”, *Proceedings of the IEEE*, Vol. 89, NO. 12, Dec 2001.
20. Cavendish, R., *Structural analysis of nickel doped cerium oxide catalysts for fuel reforming in solid oxide fuel cells*. 2012, Arizona State University.
21. Schlögl, R., *Sustainable Energy Systems: The Strategic Role of Chemical Energy Conversion*. *Topics in Catalysis*, 2016. 59(8-9): p. 772-786.
22. Xu, Y., et al., *Synthesis and catalytic water oxidation activities of ruthenium complexes containing neutral ligands*. *Chemistry–A European Journal*, 2011. **17**(34): p. 9520-9528.
23. Clark, W.W., et al., *Hydrogen energy stations: along the roadside to the hydrogen economy*. *Utilities Policy*, 2005. **13**(1): p. 41-50.

24. Sharaf, A.M. and M.A. El-Sayed. *Dynamic Control of Fuel Cell Powered Water Pumping Station*. in *International Conference. ICREPQ-2009*. April. 2009.
25. Perdikaris, N., et al., *Design and optimization of carbon-free power generation based on coal hydrogasification integrated with SOFC*. *Fuel*, 2009. **88**(8): p. 1365-1375.
26. Blomen, L.J. and M.N. Mugerwa, *Fuel cell systems*. 2013: Springer Science & Business Media.
27. Barbir, F., *PEM fuel cells: theory and practice*. 2012: Academic Press.
28. Rembelski, D., et al., *Characterization and Comparison of Different Cathode Materials for SC-SOFC: LSM, BSCF, SSC, and LSCF*. *Fuel Cells*, 2012. **12**(2): p. 256-264.
29. Wang, W., et al., *Progress in solid oxide fuel cells with nickel-based anodes operating on methane and related fuels*. *Chemical reviews*, 2013. 113(10): p. 8104-8151.
30. Hanna, J., et al., *Fundamentals of electro-and thermochemistry in the anode of solid-oxide fuel cells with hydrocarbon and syngas fuels*. *Progress in Energy and Combustion Science*, 2014. 40: p. 74-111.
31. Stambouli, A.B. and E. Traversa, *Fuel cells, an alternative to standard sources of energy*. *Renewable and Sustainable Energy Reviews*, 2002. **6**(3): p. 295-304.
32. Pandey, Jaya. "An overview of Ullmann Reaction, Its importance and applications in synthesis of Dibenzopyranones."
33. Tian, Na, Zhi-You Zhou, Shi-Gang Sun, Yong Ding, and Zhong Lin Wang. "Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity." *science* 316, no. 5825 (2007): 732-735
34. Nobrega, S. D., Gelin, P., Georges, S., Steil, M. C., Augusto, B. L., Noronha, F. B., & Fonseca, F. C. (2014). A fuel-flexible solid oxide fuel cell operating in gradual internal reforming. *Journal of The Electrochemical Society*, 161(3), F354-F359.
35. Zhang, Y., Yu, F., Wang, X., Zhou, Q., Liu, J., & Liu, M. (2017). Direct operation of Ag-based anode solid oxide fuel cells on propane. *Journal of Power Sources*, 366, 56-64..

36. Jiang, S. P., Ye, Y., He, T., & Ho, S. B. (2008). Nanostructured palladium–La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> composite anodes for direct methane and ethanol solid oxide fuel cells. *Journal of Power Sources*, 185(1), 179-182.
37. Han, B., Zhao, K., Hou, X., Kim, D. J., Kim, B. H., Ha, S., ... & Ahn, B. G. (2017). Ni-(Ce<sub>0.8-x</sub>Ti<sub>x</sub>)Sm<sub>0.2</sub>O<sub>2-δ</sub> anode for low temperature solid oxide fuel cells running on dry methane fuel. *Journal of Power Sources*, 338, 1-8.
38. Pillai, M. R., Kim, I., Bierschenk, D. M., & Barnett, S. A. (2008). Fuel-flexible operation of a solid oxide fuel cell with Sr<sub>0.8</sub>La<sub>0.2</sub>TiO<sub>3</sub> support. *Journal of Power Sources*, 185(2), 1086-1093.
39. Raza, R., Wang, X., Ma, Y., & Zhu, B. (2010). A nanostructure anode (Cu<sub>0.2</sub>Zn<sub>0.8</sub>) for low-temperature solid oxide fuel cell at 400–600° C. *Journal of Power Sources*, 195(24), 8067-8070.
40. Abbas, G., Chaudhry, M. A., Raza, R., Singh, M., Liu, Q., Qin, H., & Zhu, B. (2012). Study of CuNiZnGdCe-nanocomposite anode for low temperature SOFC. *Nanoscience and Nanotechnology Letters*, 4(4), 389-393.
41. Batool, R., Gill, R., Altaf, F., Ahmad, M. A., Raza, R., Khan, M. A., ... & Abbas, G. (2019). Structural and electrochemical study of Ba<sub>0.15</sub>Cu<sub>0.15</sub>Ni<sub>0.10</sub>Zn<sub>0.60</sub> oxide anode for low temperature solid oxide fuel cell. *Journal of Alloys and Compounds*, 780, 653-659.
42. Hussain, F., Ahmad, M. A., Raza, R., Khan, M. A., Rehman, Z. U., Riaz, R. A., & Abbas, G. (2019). Electrochemical investigation of multi-fuel based low temperature nano-composite anode for solid oxide fuel cell. *Journal of Power Sources*, 425, 147-152.
43. Imran, S. K., Raza, R., Abbas, G., & Zhu, B. (2011). Characterization and development of bio-ethanol solid oxide fuel cell. *Journal of Fuel Cell Science and Technology*, 8(6), 061014.
44. Liu, J., Madsen, B. D., Ji, Z., & Barnett, S. A. (2002). A fuel-flexible ceramic-based anode for solid oxide fuel cells. *Electrochemical and solid-state letters*, 5(6), A122-A124.
45. West, A. R. (2006). Inorganic functional materials: optimization of properties by structural and compositional control. *The Chemical Record*, 6(4), 206-216.

46. Mogensen, M., Lybye, D., Bonanos, N., Hendriksen, P. V., & Poulsen, F. W. (2004). Factors controlling the oxide ion conductivity of fluorite and perovskite structured oxides. *Solid State Ionics*, 174(1-4), 279-286.
47. Li, Z. C., & Bergman, B. (2005). Electrical properties and ageing characteristics of BaTiO<sub>3</sub> ceramics doped by single dopants. *Journal of the european ceramic society*, 25(4), 441-445.
48. Hussain, F., Abbas, G., Ahmad, M. A., Raza, R., Rehman, Z. U., Mumtaz, S., ... & Dilshad, S. (2019). Comparative electrochemical investigation of zinc based nano-composite anode materials for solid oxide fuel cell. *Ceramics International*, 45(1), 1077-1083.