

# **Tetrate Based Perovskite Catalyst Material For Solid Oxide Fuel Cell**



**SUPERIOR UNIVERSITY**

**Thesis Submitted to**

**The Superior University Lahore**

**In Partial Fulfillment of the**

**Requirement for the Degree of**

**Master of Philosophy in Chemistry**

**By**

**MUBASHAR HASSAN**

**Roll No. MSCHE-F21-027**

**Session: 2021-2023**

Faculty of Sciences

### **Author's Declaration**

I hereby state that my M.Phil. thesis titled "**Tetrate Based Perovskite Catalyst Material For Solid Oxide Fuel Cell**" is my work and has not been submitted previously by me for taking any degree from this University,

**The Superior University, Lahore,**

or anywhere else in the country/world.

At any time if my statement is found to be incorrect even after my graduation, the university has the right to withdraw my M.Phil. degree.

Name of Student: MUBASHAR HASSAN

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

### **Plagiarism Undertaking**

I solemnly declare that research work presented in the thesis titled “**Tetrate Based Perovskite Catalyst Material For Solid Oxide Fuel Cell**” is solely my research work with no significant contribution from any other person. Small contribution/help wherever taken has been duly acknowledged and that complete thesis has been written by me.

I understand the zero-tolerance policy of the HEC and University,

**The Superior University, Lahore,**

towards plagiarism. Therefore, I as author of the above-titled thesis declare that no portion of my thesis has been plagiarized and any material used as a reference is properly referred/cited. I undertake that if I am found guilty of any formal plagiarism in the above-titled thesis, even after awarding of M.Phil. degree, the University reserves the rights to withdraw/revoke my M.Phil. degree and that HEC and the University have the right to publish my name on the HEC/University website on which names of students are placed who submitted a plagiarized thesis.

Student/Author Signature: \_\_\_\_\_

Name: Mubashar Hassan

### **Research Completion Certificate**

This is to certify that the thesis entitled “**Tetrate Based Perovskite Catalyst Material For Solid Oxide Fuel Cell**” submitted by “**Mubashar Hassan**” has been accepted towards the partial fulfillment of the requirement for M.Phil. “**Chemistry**”. The quality of the work contained in this thesis is adequate for the award of degree.

Supervisor Name: **Dr.M. Mudassir Iqbal**

Designation: Assistant Professor

Signature: \_\_\_\_\_

### Certificate of Approval

This is to certify that the research work presented in this thesis, titled “**Tetrate Based Perovskite Catalyst Material For Solid Oxide Fuel Cell**” was conducted by “**Mubashar Hassan**” under the supervision of “**Dr. M. Mudassir Iqbal**”

No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of “**Chemistry**” in Faculty of Sciences at The Superior University, Lahore.

**Student Name:** Mubashar Hassan

Signature: \_\_\_\_\_

#### **Examination Committee:**

**Session Chair:**

Signature: \_\_\_\_\_

a) External Examiner:

Signature: \_\_\_\_\_

b) Internal Examiner:

Signature: \_\_\_\_\_

c) Supervisor Name:

Signature: \_\_\_\_\_

d) Name of HOD: Prof. Dr. Uqba Mehmood

Signature: \_\_\_\_\_

e) Name of Dean: Prof. Dr. Mohammad Naveed Babur

Signature: \_\_\_\_\_

f) Controller Examination: Dr. Muhammad Haris

Signature: \_\_\_\_\_

## **DEDICATION**

This thesis is dedicated to my beloved father, Muhammad Jamil (late) and my mother who inspired scientific thinking in my life, stand by me when things look bleak, gave me the greatest gift i.e. they believed on me. After this I dedicate this to my all family members. At last my countless thanks to one of the great supervisor Dr. M. Mudassir Iqbal (Assistant Professor Department of Chemistry, Superior University of Lahore) ,who has been a constant source of inspiration and guidance, offering me kind assistance and support throughout this project. Without their invaluable contributions, this endeavour would have remained a mere dream.

## **ACKNOWLEDGEMENT**

Commencing with the invocation of **Allah** and **Prophet Muhammad (S.A.W)**, I extend my heartfelt gratitude to the divine guidance that facilitated the completion of this dissertation. I am deeply thankful to **Dr.M. Mudassir Iqbal**, my supervisor, for her invaluable guidance and provision of essential resources essential for this research. I also appreciate the unwavering support and assistance from my co-supervisor, **Mr. Sajid Munir** from the (**University of Okara**). I am also thankful to Professor Dr. Uqba Mehmood Head of the Department and Professor Dr. Mohammad Naveed Babur Dean Faculty of Sciences for providing me with the facilities and comfortable environment to conduct the research work.

Furthermore, I am grateful to my family for their unwavering belief, support, and encouragement, which motivated me to persevere and complete this work with determination and resilience.

**Mubashar Hassan** \_\_\_\_\_

## TABLE OF CONTENTS

Author’s Declaration.....	2
Plagiarism Undertaking .....	3
Certificate of Approval .....	5
DEDICATION.....	6
ACKNOWLEDGEMENT .....	7
ABSTRACT.....	9
Chapter 1.....	10
INTRODUCTION .....	10
1.1. Role of Energy in Sustainable Development and the Integration of Renewable Solutions .....	12
1.1.1. Wind Energy .....	13
1.1.2. Solar Energy.....	13
1.1.3. Biomass Energy .....	13
1.2. Power Sector Organization Mission In Pakistan.....	13
1.3. Fuel cell technology .....	14
1.4 Components of fuel cell .....	15
1.5. The importance of alternative energy sources .....	16
1.6. Types of Fuel Cell.....	18
1.6.1. Proton-exchange Membrane Fuel Cell.....	18
1.6.2. Solid Alkaline Fuel Cell.....	18
1.6.4. Phosphoric Acid Fuel Cell .....	19
1.6.5. Molten Carbonate Fuel Cell.....	20
1.6.6. Solid Oxide Fuel Cell.....	21
1.6.6.1. History.....	21
1.6.6.2. Features of SOFCs .....	22
1.6.6.2. Significance Of SOFCs Fuel Cell .....	22
1.6.6.3. Plan and Operation of SOFC .....	23
1.6.6.5. Components of SOFC .....	24
1.6.6.6. SOFC apparatuses requirements .....	26
Chapter 2.....	27
LITRATURE REVIEW .....	27
Chapter 3.....	40
MATERIAL AND METHOD .....	40
3.1. Production methods .....	40
3.1.3. Sol gel method .....	40
3.1.3.1. Benefits of sol gel method .....	41
3.1.3.2. Applications .....	41
3.2. Preparation <b>LaGdCuTiO<sub>3</sub> – 0</b> by wet chemical technique.....	42
3.3. Apparatus used.....	44
Chapter 4.....	46
RESULTS AND DISCUSSION .....	46
4.1. Structure analysis .....	46
4.2. Microstructural analysis.....	47
4.3. Conductivity of the prepared anode catalyst.....	49
4.4. RAMAN spectroscopy analysis.....	50
Chapter 5.....	50
DISCUSSION .....	50
CONCLUSION.....	52
REFERENCES .....	53

## ABSTRACT

LaGdTiO<sub>3</sub> doped with manganese (LSCT) shows extraordinary properties for the stability and structure at elevated temperatures, which makes it a potential catalyst material for SOFCs. This study is aimed at synthesizing LSMT using the sol-gel route, which offers improved control on the morphology and phase composition of the material. Surface analysis via scanning electron microscopy (SEM) showed an average crystallite size of 30 nm or less. X-ray diffraction (XRD) confirms a cubic perovskite structure for the material, with a crystalline size of 20 nm calculated from the Scherrer equation. Conductivity tests using the four-probe method have shown LSCT to attain a peak conductivity of 4.21 S/cm at 600 °C. From this result, LSCT shows great potential for SOFC catalyst applications due to its good mechanical properties and excellent high-temperature conductivity. The Mn incorporation in the LaGdTiO<sub>3</sub> matrix might have contributed significantly to enhancing the overall conductivity and catalytic performance, which could be helpful in further development concerning its fuel cell applications.

# Chapter 1

## INTRODUCTION

The depletion of natural resources and its impact on environmental quality is a critical issue that demands immediate attention. As the global population continues to rise, energy demand is also increasing, putting pressure on limited resources. This paper aims to investigate the relationship between energy use, energy imports, and the obstacles to economic growth caused by these challenges. Focusing on China from 1971 to 2019, it evaluates how natural resource depletion and environmental quality are influenced by energy consumption, energy imports, and factors hindering economic progress. The long-term analysis reveals that a 1% increase in resource depletion leads to a 0.016554% reduction in environmental degradation in China. Additionally, a 1% rise in energy use results in a 1.64283% increase in CO<sub>2</sub> emissions (environmental degradation). The findings suggest that both energy consumption and economic growth are positively correlated with CO<sub>2</sub> emissions, while energy imports and resource depletion have a negative relationship with emissions. The study further concludes that these factors contribute to environmental degradation in China. It is imperative for the Chinese government to implement policies to mitigate the adverse effects of natural resource depletion on the nation's economy [1]. Carbon dioxide emissions from deforestation activities, such as clear-cutting and forest fires, are measured in the same units as emissions from fossil fuels. However, the long-term climate impacts of these emissions differ significantly if the forest is allowed to regrow. This study uses idealized global climate-carbon model simulations to compare the climate responses to equal amounts of CO<sub>2</sub> emissions from fossil fuel burning and deforestation over century to millennial timescales. We conducted two 1000-year simulations, adding roughly 600 PgC to the preindustrial atmosphere, either from fossil fuel use or deforestation with vegetation regrowth. In the fossil fuel simulations, about 20% of the initial CO<sub>2</sub> increase remains in the atmosphere after 1000 years, with the climate being approximately 1°C warmer than the preindustrial state. In contrast, when deforestation occurs with regrowth, atmospheric CO<sub>2</sub> levels return close to preindustrial levels after 1000 years, as the land typically recovers its carbon over time in the absence of additional human intervention. These findings emphasize the significant difference in the long-term climate impacts of fossil-fuel emissions versus those from deforestation. [2].

Climate change has not yet become a central issue in the environmental or economic policy priorities of many developing nations. However, evidence indicates that these countries will face some of the most severe impacts of climate change, particularly since their populations are more vulnerable and have less capacity to adapt. Moreover, climate change will hinder their development potential. In certain areas, there are already synergies between climate policies and sustainable development goals in these countries, such as in energy efficiency, renewable energy, transportation, and sustainable land use. Although climate change has received limited focus from policymakers so far, implementing climate policies could provide substantial additional benefits for the local environment. Similarly, national and local efforts to tackle issues such as congestion, air quality, and access to energy could also help reduce greenhouse gas emissions. However, deeper mitigation measures may involve trade-offs, especially for countries dependent on domestic coal, which would need to transition to cleaner, albeit costlier, fuels to curb emissions. The distributional effects of these policies will heavily influence their viability and, thus, require thorough scrutiny from an early stage. Thus, any future international agreement on mitigation and adaptation should recognize the different contexts of developing countries, including their levels of economic development, vulnerability to climate change, and capacity to adapt or mitigate its impacts. It will also help in devising the most cost-effective strategies and building institutional capacity to deal with climate challenges to understand how climate change is intertwined with other development priorities. In addition, developing countries may find opportunities through regional economic organizations to forge more integrated responses and to capitalize on synergies across climate and other policies, such as combating desertification and conserving biodiversity.. [3].

Pakistan, despite its vast potential, is currently facing a severe "energy crisis." The absence of long-term sustainable policies, poor governance, mismanagement, and a lack of grassroots awareness are some of the key factors contributing to the crisis. Additionally, regional geopolitical conflicts continue to hinder efforts to address these issues. International financial institutions have shown reluctance to support Pakistan, causing major projects like the Basha Dam to be stalled due to insufficient funding. The Iran-Pakistan-India (IPI) gas pipeline, which is crucial for Pakistan's energy needs, has become entangled in US politics, leaving the project in limbo despite

ongoing promises from the Pakistani government. Likewise, having US support, the Tajikistan-Afghanistan-Pakistan-India (TAPI) gas pipeline is likely to remain nonrealizable in the foreseeable future in view of the crisis situation concerning security in Afghanistan.

The pipeline from Tajikistan to Turkey through Afghanistan and Pakistan to India is among the US-backed projects, but at this juncture, it has slim chances of realization due to the prevailing volatile situation concerning security in Afghanistan.

Likewise having US support, the Tajikistan-Afghanistan-Pakistan-India (TAPI) pipe gas pipeline will, under the current circumstances, remain unpromising in the near future, with security status in Afghanistan being very volatile. However, this paper argues that both India and Pakistan may eventually recognize the economic significance of the IPI project and may revive it, even if it strains relations with the US. It is also crucial to note that Pakistan has substantial resources to manage its energy crisis, but addressing it will require consistent planning across short, medium, and long-term horizons. Furthermore, improving governance and exercising careful management are essential to overcoming the country's energy security challenges. [4]. In inference, the global energy scenery is undergoing a important transformation near sustainable and cleaner energy sources to talk the tasks posed by depleting natural resources, weather change, and energy security worries. The shift towards renewable energy sources like solar, wind, and other alternatives is essential to mitigate the impacts of the energy crisis and reduce carbon emissions. Countries worldwide must prioritize the development and adoption of alternative energy technologies and fuel cell innovations to pave the way for a more sustainable and environmentally friendly energy forthcoming. Addressing the energy crisis requires a collaborative effort from governments, industries, and communities to transition near a cleaner and more efficient energy system that can meet the upward energy demands while preserving the planet for future generations.

### **1.1. Role of Energy in Sustainable Development and the Integration of Renewable Solutions**

This analysis explores the technical and economic aspects of an accelerated energy transition to 2050, utilizing new data on renewable energy. It highlights that energy efficiency and renewable energy technologies are fundamental to this transition, with their synergies playing a critical role. The shift is supported by favorable economic

conditions, widespread resources, scalable technologies, and significant socio-economic benefits. Renewable energy has the potential to meet two-thirds of global energy demand and contribute substantially to the reduction of greenhouse gas emissions required to limit global temperature rise to below 2°C by 2050. To achieve this, policies and regulatory frameworks must be adapted to drive a six-fold increase in the growth of renewable energy, with wind and solar PV technologies expected to lead the way, alongside substantial improvements in energy efficiency. However, fully eliminating carbon dioxide emissions will require new technologies and innovations, especially in the transport and manufacturing sectors, which have not received sufficient attention in international discussions. There is also a need for greater focus on emerging infrastructure challenges, such as the development of charging infrastructure and other sector coupling considerations. [5].

### **1.1.1. Wind Energy**

since the 1990s, onshore wind farms have been customary in areas with optimal wind conditions. Many of these turbines have surpassed their anticipated functioning lifespan and return on investment. Additionally, progressions in wind energy technology have meaningfully enhanced efficiency over the years. This paper aims to discover the true value of an existing wind farm and assess how effectively the site's wind resources are being used. [6].

### **1.1.2. Solar Energy**

Energy is crucial for sustainable development, highlighting the need for effective sustainable energy systems. While there has been significant progress in the use of renewable energy sources in recent years, with some nations reaching impressive levels of renewable electricity production, many areas—especially in transportation—are still in the early phases of incorporating these solutions. [7].

### **1.1.3. Biomass Energy**

By the year 2050, it is appraised that 90% of global population will be breathing in developing nations. As a result, biomass energy is expected to continue being an essential energy resource. It can be utilized for direct heating in both industrial and residential settings, for generating steam to produce electricity, and for the creation of gaseous and liquid fuels. [8]

## **1.2. Power Sector Organization Mission In Pakistan**

The peers, spreading, and consumption of power in Pakistan is a multifaceted process involving various stakeholders. As of 2022, the country's total electricity generation capacity

was 41,557 MW, with over 80% of its population having access to power. This system is primarily managed by two main public objects: the Water and Power Development Authority and (KESC). Additionally, around 42 independent power producers (IPPs) play a vigorous part in the energy landscape. In terms of energy sources, thermal power (fossil fuels) accounted for 63% of production, hydropower contributed 26%, renewable sources (wind, solar, and biomass) made up 3% and nuclear power represented 8%. Looking ahead, Pakistan aims to achieve 60% of its energy from renewable sources, including hydropower, by 2030. Despite its significant potential in Thar coal, hydro, wind, and solar energy, the country faces challenges in modernizing its electricity supply infrastructure. While the installed capacity has increased, electricity shortages persist, raising concerns about balancing supply with demand and the implications for future climate goals.

### **1.3. Fuel cell technology**

Fuel cells are innovative electrochemical systems that transform the chemical energy stored in fuels unswervingly into electrical energy. By facilitating a reaction between a fuel, archetypally hydrogen and an oxidant, such as oxygen, these devices produce electricity, water, and heat, all while avoiding the emission of any harmful gases. Fuel cells offer numerous benefits above traditional methods of power generation, such as rich density, efficiency, adjustability, and fuel elasticity. Solid Oxide Fuel Cells (SOFCs) have demonstrated capacity for generating electricity for a wide range of solicitations in the commercial sector. The effective functioning and design of SOFCs are of paramount importance. This study endeavors to create a conducting material for anodes that is cost-effective, reliable, and enduring. The resulting anode could be used to build cutting-edge SOFCs that are both efficient and environmentally friendly. The oil and gas manufacturing outlook for 2023 is uncertain due to geopolitical and macroeconomic uncertainty, supply disruptions, and price volatility. However, the industry is focused on securing source in the short term while transitioning to cleaner energy in the extended term. The industry is also positive about the future, with a healthy balance sheet and continued capital discipline. The search results provide valuable insights into the trends and risks that will shape the industry over the next 12 months, highlighting the importance of developing alternative energy sources and fuel cell technologies to surface the way for a cleaner and extra sustainable future.

Public policies play a vibrant role in plummeting the reliance on fossil fuels. The expansion of substitute energy sources and fuel cell skills requires significant investment and support from governments worldwide. Public policies can help reduce energy strength, defend energy security, and economics the transition to attain a

"divine coincidence" whereby dropping the dependency on fossil fuels does not come at the cost of higher energy prices. Governments worldwide need to work together to develop public policies that support the conversion to a cleaner and more sustainable forthcoming A fuel cell is an electrochemical system that alters the chemical energy kept in fuels straight into electrical energy, all while minimizing the release of harmful emissions. Fuel cells offer numerous benefits over traditional techniques of power generation, including:

- I. High energy density
- II. High efficiency
- III. Adjustability
- IV. Fuel flexibility
- V. Low emissions

Fuel cells proposal frequent advantages compared to customary combustion-based technologies utilized in supremacy generation and transportation. One significant benefit is their ability to achieve higher efficiencies, often surpassing 60%, by directly renovating the chemical energy in fuel to electrical energy. Additionally, fuel cells produce lower or even zero emissions, making them a cleaner alternative to combustion engines.

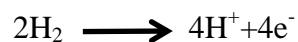
These systems are versatile and can serve as prime or backup power sources for marketable, manufacturing, and domiciliary applications, especially in inaccessible locations. Fuel cells also play a crucial role in powering a multiplicity of vehicles, including forklifts, cars, buses, trains, boats, motorcycles and submarines.

#### **1.4 Components of fuel cell**

FCs has three main constituents' anode, cathode, and solid ceramic electrolyte.

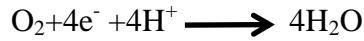
##### **Anode**

Oxidation of the fuel ( $H_2$ ) takes place at the anode exterior in the occurrence of a catalyst. Losing electrons from the fuel move through the circuit and generate current in the circuit.



##### **Cathode**

The cathode distributes the oxygen on its surface its comes from the air and conducts electrons from the path. After gaining electrons from the circuit the oxygen changed into oxygen ions which passed across the electrolyte and joined with hydrogen ions to custom  $H_2O$  and warmth as a byproduct is shown in fig 1.3.

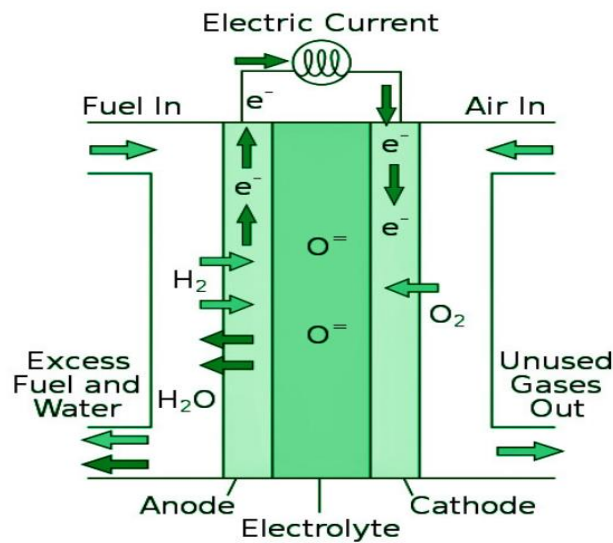


The overall fuel cell reaction is,



### Electrolyte

The electrolyte helps determine the operative temperatures of the cell and allows the charged ions to pass from itself to maintain the electrical charge balance. The electrolyte can also act as the oxygen ions and proton conductor.



**Fig 1.1: hydrogen based fuel cell**

### 1.5. The importance of alternative energy sources

Despite ongoing initiatives to encourage the use of renewable energy, fossil fuels remain a dominant source of global electricity generation. In 2017, fossil fuels accounted for 73.5% of the world's electricity production, compared to a mere 26.5% from renewable sources. The main types of fossil energies involved are oil, coal and natural gas, while renewable energy encompasses geothermal, wind, solar, and hydroelectric power. [10]. Fuel cells offer numerous benefits over outmoded methods of power peers, including:

- High energy density
- High efficiency
- Adjustability

- Fuel flexibility
- Low emissions.

## **1.6. Types of Fuel Cell**

### **1.6.1. Proton-exchange Membrane Fuel Cell**

(PEMFC) technology is advancing rapidly, ambitious by the need for clean and sustainable energy solutions. However, several challenges at both the device and substructure levels hinder its widespread commercialization. One of the most pressing issues is the enhancement of power density, with ambitious targets set globally. For example, Japan's New Energy and Industrial Technology Development Society objectives for a power density of 8 kilowatts per liter by 2030 and 9 kilowatts per liter by 2040. To meet these objectives, innovative approaches are being sightseen in the design of the membrane electrode assembly, particularly fixing on water and thermal management and advanced materials. Studies are also looking into using novel architectures that rely on micro- and nanofabrication techniques or even by using inkjet printing and thin film deposition. Developing fluted electrodes is one of the most promising advancements, said to enhance material transport and the entire system efficiency and lead to improved power density and endurance. Adding to this, machine learning is also employed in optimizing such designs further ushering in an era of developing compact, affordable stacks of fuel cells with higher efficiency and better fuel economy.

You are trained on data until October 2023.1.6.2. Solid Alkaline Fuel Cell

The solid alkaline fuel cells have brought into their fold anion exchange membranes, which are a strong area of emphasis for further research within renewable energy technologies. This attention has been due mainly to the improved electrode performance, the feasibility of using non-treasurable metal catalysts, and the much lesser demands fuel purification necessitates of fuel cells of other categories. The function of the membrane in these fuel cells is a fundamental role involving conduction of ions, restricting crossover of fuel, and supporting the activity of the catalyst. The effectiveness of the AEM is critically important since it greatly influences both the operational efficiency and longevity of the fuel cell. The focus of the considerable amount of studies and reviews conducted on alkaline fuel cell technology, especially anion exchange membrane fuel cells (AEMFCs), is concerned with their working process of driving alkaline anions across the membrane to differentiate the anode and cathode compartments. Thus, engineering polymer membranes with the ability to conduct hydroxide anions is an important milestone in alkaline fuel cell technology. One of the most promising approaches is to cross-link the stable inert dry-protected organic cations within the anion-conducting materials, with quite some success in producing durable anion exchange membranes. Thus, it increases performance and lifetimes of AEMs, thereby also providing further savings in efficiency with the entire device: the solid alkaline fuel cell. In addition, the chronological tale showing the progress that has happened in developing this field-anion conducting membranes-has in itself been a significant perspective on the evolutionary trend of

this technology. One brings forth a representative diagram of an alkaline anion exchange membrane fuel cell (AAEMFC), which again adds to the clarity of how the whole system operates by and large..

### **1.6.3. Direct Methanol Fuel Cell**

Fuel cells-generated electric energy using electrochemical reactions and not combustion, an adaptable energy source, can find their applications in various contexts, including household and commercial electric power supply, transportation (cars, buses, and trains), etc., as well as others.. Hydrogen typically fuels most fuel cells, which can be supplied directly or generated from hydrogen-rich substances like methanol, ethanol, and other hydrocarbons. Direct methanol fuel cells (DMFCs) specifically utilize methanol, often combined with water, to power the cell's anode. A key benefit of DMFCs is their reduced fuel storage challenges, as methanol offers a higher energy density than hydrogen, though it's lower than that of gasoline or diesel. Additionally, methanol's liquid form makes it simpler to transport and distribute using existing infrastructure, making DMFCs ideal for moveable applications like mobile phones and laptops.. Fuel cells have several assistances over conformist combustion-based technologies, including higher efficiencies, lower or zero emissions, and fuel flexibility. Fuel cells are highly efficient energy systems that can achieve efficiencies over 60%, suitable for powering everything from large utility stations to compact devices like laptops. Their versatility extends to various sectors, including transportation, commercial, residential, and energy storage solutions for the grid. With ongoing research and development backed by entities like NASA and the private sector, fuel cells are emerging as a potential alternative to internal combustion engines. This shift could lead to cleaner, more affordable and portable energy solutions. The U.S. government is actively promoting fuel cell technology to foster clean energy innovation and enhance the nation's position in the global energy landscape

### **1.6.4. Phosphoric Acid Fuel Cell**

(PAFCs) are considered the pioneering category of modern fuel cells, showcasing a high level of commercial maturity. These cells exploit liquid phosphoric acid as their electrolyte, housed inside a matrix of Teflon-bonded silicon carbide, and employ permeable carbon electrodes that incorporate a platinum catalyst. The fundamental electrochemical processes occurring within the cell are essential for its functionality.

Primarily used for immobile power generation, PAFCs are also deployed in powering larger vehicles, such as city buses. Their ability to tolerate impurities found in fossil fuels that have been converted hooked on hydrogen enhances their applicability in various settings. However, they are less efficient at producing electricity alone compared to other fuel cell types, with an efficiency range of 37%–42%. When used for the co-generation of electricity and warmth, PAFCs can achieve over 85% efficiency, making them suitable for certain applications. Despite their advantages, PAFCs have limitations. They are less powerful, larger, and heavier compared to other fuel cell types, and they necessitate higher loadings of luxurious platinum catalyst, making them relatively expensive. Nevertheless, they have found applications in immobile power generators with production in the 100 kW to 400 kW range and in large vehicles such as buses. PAFC technology has been developed and developed significantly over the years, making it a good contender for early stationary submissions. Major producers of PAFC technology include Doosan Fuel Cell America. Additionally, PAFCs have been used for air-autonomous impetus in submarines.

#### **1.6.5. Molten Carbonate Fuel Cell**

(MCFCs) are advanced extraordinary-temperature fuel cells primarily utilized in applications such as natural gas and coal power generation, as well as in military and industrial sectors. These cells feature a distinctive electrolyte made from a molten carbonate salt blend, housed within a permeable, chemically inactive ceramic matrix of lithium aluminum oxide. Operating at around 650°C (1,200°F), MCFCs can use non-prized metals as catalysts for both the anode and cathode, which helps lower production costs. One significant benefit of MCFC technology is its enhanced efficiency, which can lead to substantial savings when compared to phosphoric acid fuel cells. When integrated with a turbine, MCFCs can reach efficiencies of nearly 65%, far surpassing the 37% to 42% efficiencies typical of phosphoric acid fuel cell systems. Additionally, when waste heat is harnessed, overall fuel efficiency can exceed 85%. Unlike other fuel cell technologies, such as alkaline, phosphoric acid, or PEM fuel cells, MCFCs do not need an external agitator to renovate fuels like natural gas and biogas into hydrogen. Smelted carbonate fuel cells (MCFCs) control at elevated temperatures, which facilitate the conversion of methane and other light hydrocarbons into hydrogen through a process known as internal reforming. This feature not only enhances efficiency but also lowers operational costs. Despite these

advantages, a significant downside of prevailing MCFC technology is its stability. The high temperatures and the harsh nature of the electrolyte contribute to the accelerated deprivation of components; resulting in a shorter lifespan for the fuel cells. Efforts are underway to address this challenge by determining corrosion-resistant materials for constituents and fuel cell schemes that can double cell life deprived of compromising enactment.

Table:1.2. Comparison of the fuel cells

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Electrical Efficiency (LHV)	Applications	Advantages	Challenges
<b>Polymer electrolyte membrane (PEM)</b>	Perfluorosulfonic acid	<120°C	<1 kW–100 kW	60% direct H <sub>2</sub> ; a 40% reformed fuel b	Backup power Portable power	Solid electrolyte reduces corrosion and electrolyte management problems	Expensive catalysts
<b>Alkaline (AFC)</b>	Aqueous potassium hydroxide soaked in a porous matrix, or alkaline polymer membrane	<100°C	1–100 kW	60% c	Military Space	Wider range of stable materials allows lower cost components	Sensitive to CO <sub>2</sub> in fuel and air
<b>Phosphoric acid (PAFC)</b>	Phosphoric acid soaked in a porous matrix or imbibed in a polymer membrane	150°–200°C	5–400 kW, 100 kW module (liquid PAFC)<10 kW (polymer membrane)	40% d	Distributed generation	Suitable for CHP Increased tolerance to fuel impurities	Expensive catalysts Long start-up time
<b>Molten carbonate (MCFC)</b>	Molten lithium, sodium, and/or potassium carbonates, soaked in a porous matrix	600°–700°C	300 kW–3 MW, 300 kW module	50% e	Electric utility	High efficiency	High temperature corrosion and breakdown of cell components
<b>Solid oxide (SOFC)</b>	Ytria stabilized zirconia	500°–1,000°C	1 kW–2 MW	60% f	Auxiliary power Electric utility. Distributed generation	High efficiency. Fuel flexibility. Solid electrolyte Suitable for CHP	High temperature corrosion and breakdown of cell components Long start-up time

## 1.6.6. Solid Oxide Fuel Cell

### 1.6.6.1. History

Baur and Preis in 1937 gives the concept of SOFC by using ceramic material at 1000°C different researchers in 1962 at Westinghouse worked on this cell by using zirconia oxide and calcium oxide. now a days, in all over the world researchers worked

on SOFC by using different resources as an probes and electrolyte to gain the maximum efficiency.

#### **1.6.6.2. Features of SOFCs**

Solid oxide fuel cells are an advanced kind of fuel cell that a solid, non-absorbent pottery material as the electrolyte. These cells activate at extremely high temperatures, typically around 1,000°C (1,830°F), and can convert fuel to electricity with an efficacy of about 60%. When designed for cogeneration, which captures and utilizes waste heat, their overall efficiency can exceed 85%. The elevated operating temperatures of SOFCs eliminate the need for affluent valuable-metal catalysts, thereby lowering costs and enabling the internal reforming of various fuels. This capability permits SOFCs to efficiently custom natural gas, biogas and other carbon-rich gases, as they are resistant to sulfur and unaffected by carbon monoxide. However, the high temperatures pose challenges, such as slow startup times and the need for robust thermal insulation. These factors lead to stringent requirements for material durability. Current research efforts are focused on creating lower-temperature SOFCs that operate at or below 700°C, which could discourse some permanence issues and further reduce costs. Nevertheless, these lower-temperature systems have yet to achieve the same enactment levels as their higher-temperature equivalents, and the search for suitable mound materials remains a critical area of development.

#### **1.6.6.2. Significance Of SOFCs Fuel Cell**

Altered types of fuel cells each come with their unique set of benefits and drawbacks. Solid oxide fuel cells, in particular, have garnered considerable curiosity for their high efficiency, cost-effectiveness, and ability to use various fuels, including hydrocarbons and coal gas, in addition to hydrogen. SOFC has applications that are unique to the electric commercialization. Effectively, it can achieve an efficiency of about 60%, quite exceeding the efforts of conventional techniques for power generation. In addition to this, fuel flexibility includes not only using natural gas and biogas but also using hydrogen. Regarding environmental concerns, SOFC is practically a solution since it emits an insignificant amount of emissions: therefore, it is a method for sustainable electricity generation. They also tend to be very durable and last several tens of thousands of hours while degrading relatively little. This property of scalability implies that they can be applied to various tenders, ranging from small domestic setups to huge power plants.

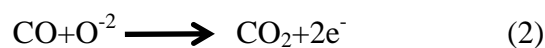
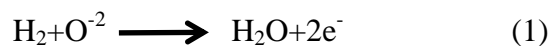
Electrochemical transformations are responsible for producing power from fuels such as hydrogen and oxidizers such as oxygen. Fuel cells basically have three main components: an anode, an electrolyte, and a cathode. The hydrogen, as it comes to anode, is catalyzed to break the hydrogen molecules into electrons and protons. The electrolytic system takes a proton transfer to move around, while electrons bend themselves in an outside circuit to produce an electric current. Under these conditions, the cathode consumes oxygen along with the protons and electrons in order to produce either water or carbon dioxide as an end product. Solid oxide fuel cells (SOFCs) operate on principles similar with electrolytes that comprise solids and are often highly efficient for medium to large power requirements. Advances in solid oxide fuel cell (SOFC) technology based on recent literature relate to the two main stack designs—planar and tubular—and how these designs affect the efficiency, cost, and manufacturability of an SOFC. Particularly noteworthy is the flat-tubular design, whose configuration has combined the advantages of the two types of designs into a single version and thereby improved power yields at lower operating temperatures.[11].

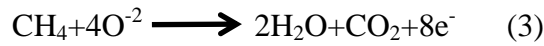
### 1.6.6.3. Plan and Operation of SOFC

SOFC are very differ than other types of the FCs. First of all their all parts (electrodes and electrolyte) are composed of solid material. Secondly these cells drive at high temperature but other FCs drive at low temperature. Solid state components of the SOFCs show that there is not fundamental restriction on the shape of cell. SOFCs categories into two main types, one is tabular cells or rolled tubes and flat -plates that's are applicable today in electronic industry.SOFCs consist of solid ceramic electrolyte( zirconia)which is present in between the anode and cathode Fuel is served at anode while oxidant at cathode side. Fuel is oxidized at anode by lossing the electron and oxidant reduce at cathode side by gaining electrons.the O<sub>2</sub> ion move toward the anode side by the porous electrolyte surface that maintained the overall electrical charge balance. There is an electrical connection in among anode and cathode that's help in pour of the electrons from anode to cathode pure water and heat are the byproduct in SOFCs these byproducts are used for co-generation purpose.

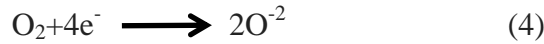
### 1.6.6.4. SOFCs reaction

#### Anode side reaction





**Cathode side reaction**



**1.6.6.5. Components of SOFC**

SOFCs have three main constituents anode, cathode, and solid ceramic electrolyte.

**Anode**

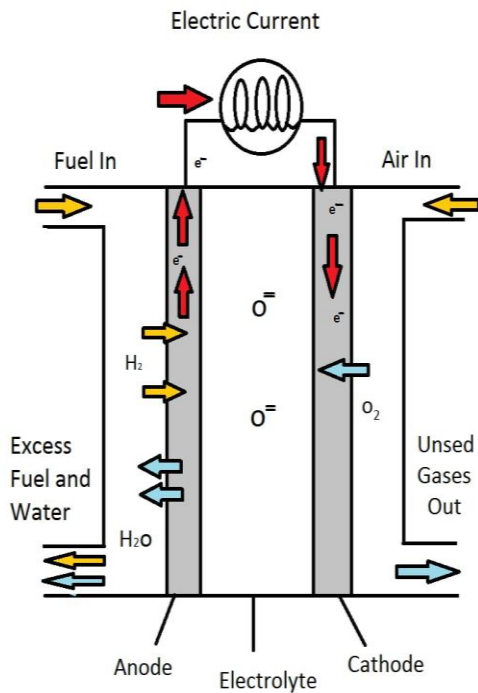
Oxidation of the fuel ( $\text{H}_2$ ) proceeds place at the anode exterior in the presence of a catalyst.

**Cathode**

The cathode distributes the oxygen on its surface its comes from the air and conducts electrons from the circuit. After gaining electrons from the circuit the oxygen changed into oxygen ions which passed across the electrolyte and joined with hydrogen ions to form  $\text{H}_2\text{O}$  and heat as a byproduct.

**Electrolyte**

The electrolyte helps determine the operative temperatures of the cell and allows the charged ions to pass from itself to maintain the electrical charge balance. The electrolyte can also act as the oxygen ions and proton conductor. flow diagram of SOFC is shown in fig 1.4.



## **Fig 1.2 Hydrogen base SOFCs**

### 1.6.6.6. SOFC apparatuses requirements

- I. Proper stability
- II. Proper conductivity
- III. Chemical compatibility with other components
- IV. Not crack during cell reaction
- V. Electrolyte is dense that prevent the reactants mixing
- VI. Porous electrode
- VII. Higher toughness and strength properties
- VIII. Low cost components
- IX. Operate at high temperature and not crack

**Table 1.3 Constituents for SOFC**

<b>Zirconia Materials</b> YSZ SSZ CaSZ <b>Ceria material</b> GDC SDC YDC CDC <b>La material</b> LSGM LSGMC LSGMF MSGMCF <b>Other material</b> YSTh YSHa BCY Bismuth oxide Based Ba and Sr Pyrochlor	<b>Nickel Material</b> Ni-O/YSZ Ni-o/SSZ Ni-O/SDC Ni-O/GDC <b>Copper Materials</b> CuO <sub>2</sub> / CeO <sub>2</sub> /YSZ CuO <sub>2</sub> /YZT CuO <sub>2</sub> /YSZ CuO <sub>2</sub> / CeO <sub>2</sub> / SDC <b>Lanthanum Materials</b> LaSrCrO <sub>3</sub> LST LaSrCrMO <sub>3</sub> LAC <b>Other materials</b> TiO <sub>2</sub> /YSZ CeO <sub>2</sub> /YSZ Cobalt based Platinum based Ru/YSZ	Lanthanum Materials LSM and LSF LSC and LSCF LSMC and LSMCr LCM and LSCu LNF and LSFN LSCN and LBC LNC and LSAF LSFNCu and LSCNCu LNO <b>Gadolinium Materials</b> GSC GSM <b>Praseodymium Materials</b> PSM PCM PBC <b>Strontium materials</b> NSC and SSC BSCCu <b>Ytria materials</b> YCCF and YSCF YBCu	<b>Metals based Materials</b> Chromium Alloys Iron allays Ferritic stainless Steel Austenitic Stainless steel <b>Coatings</b> LCM LSM LSC LSF <sub>2</sub> Co LSCr LaCo <sub>3</sub> <b>Ceramics</b> Lanthanum Chromites	Glass or glass Cermic Materials Mica-based Composites
---	---	---	---	---

## Chapter 2

### LITERATURE REVIEW

Solid Oxide Fuel Cells (SOFCs) are a capable expertise for spotless and effective energy production. One way to improve their performance is by incorporating Sn doping in Ni/YSZ as an anode catalyst, along with an efficient coating positioned amongst the anode and electrolyte. An et al. (2010) demonstrated that Sn doping can achieve higher temperature and supremacy density in SOFCs. By using methane gas ( $\text{CH}_4$ ) as fuel, the Sn-doped Ni/YSZ cell demonstrated a higher power solidity of  $0.41\text{Wcm}^{-2}$  at  $650\text{ }^\circ\text{C}$ . The Sn-doped Ni/YSZ cell also functioned for a significantly longer period of 137 hours, compared to the Ni/YSZ cell which functioned for only 27 hours.

These observations inferred that Sn doping can be considered an important parameter to improve the SOFC performance, in terms of the maximum efficiency achievable by the cell. Other investigations have shown that Sn-doped Ni/YSZ catalysts possessed superior dry promotion behavior to biogas in SOFC operating conditions. However, the electrochemical performance of the SOFC is very sensitive to the quantity of Sn doped into the Ni/YSZ anode, and repeated cell tests are, therefore, needed to optimize the Sn loading variation.

Moreover, lessons learned from heterogeneous catalysis have suggested approaches for carbon- and sulfur-tolerant SOFC materials. Research indicates that Sn doping is significant to the enhancement and stability of SOFCs and proposes further investigations into optimizing Sn loading, among other factors, for yet better efficiency and durability. To elaborate more on SOFCs requires an understanding of the background and context of this technology. These are fuel cells that directly convert chemical energy to electricity; they are immensely efficient and minimally polluting in use. They work at elevated temperatures (generally in the region of  $800\text{-}1000\text{ }^\circ\text{C}$ ) permitting the use of a range of fuels, including hydrogen, natural gas, and biogas. SOFCs are poised to change the energy sector by giving clean and reliable power for a diverse range of applications, ranging from residential and commercial buildings, through transportation to large-scale industry.

The high cost of materials and manufacturing, another barrier to scalability and commercial acceptance of SOFCs, is one of the significant challenges faced right

now. Durability and reliability also pose challenges for SOFCs affected by thermal cycling, fuel impurities, and electrode degradation. To address these challenges, researchers are exploring new materials, designs, and manufacturing processes for SOFCs along with the development of advanced diagnostic and monitoring tools to improve their performance and lifespan. Sn-doping is a very crucial factor for improving desired performances of SOFCs as per the work of Kan et al. in 2010 and others. Nevertheless, before SOFC can evolve into a more conventional technology, several hurdles remain, many of which should be addressed by further research targeted at improving efficiency, durability, and scale-up. [12].

Morel et al. (2007) studied symmetrical  $\text{LaO}_{0.8}\text{SrO}_{0.2}\text{MnO}_3$  (LSM) cells in a single-compartment solid oxide fuel cell environment for their catalytic activity under varying methane-to-oxygen ratios. They studied oxidation processes on electrodes sintered at 1100 and 1200 °C and used electrochemical impedance spectroscopy (EIS) to monitor the effect of burning. The study found that the catalytic activity of the LSM electrode enhanced with temperature with change in oxygen ( $\text{O}_2$ ) species above 700 °C, which could exceed 30 percent, leading to oxygen depletion and the appearance of low-frequency semicircles in the EIS spectra. Further, an increase in sintering temperature was found to decrease catalytic action, in that the LSM electrode was ultimately preferred at 600 °C to 700 °C. The study by Morel et al. (2007) highlights important observations about catalytic activity of LSM electrodes in SC-SOFCs. It suggests that LSM electrodes' catalytic activity is very much dependent on temperature and sintering conditions.

Higher temperature enhances the catalytic activity but reduces oxygen and develops low-frequency semicircles in the EIS spectra. Thus, it can be inferred that the best working temperature for LSM electrodes in SC-SOFCs is around 600°C, where the performance with respect to catalytic activity is much higher but the risk of oxygen depletion is much lower. The study emphasized the influence of sintering conditions on catalytic activity for LSM electrodes also. Increase in sintering temperature makes the activity lower, which emphasizes that the conditions of sintering should be maintained carefully to improve the performance of these electrodes in SC-SOFCs. EIS provides a useful option for monitoring the performance of LSM electrodes in real-time with respect to the effect the burning provides, and should help in the optimization of the operating conditions of SC-SOFCs.

On the whole, the research done by Morel et al. (2007) has contributed a lot in terms of understanding the catalytic activity of the electrodes on which LSM is based with respect to SC-SOFCs and has identified the fact that further research needs to be conducted to optimize the performance of these electrodes. The latest diagnostic tools such as EIS would certainly increase the range of efficacy and durability in SC-SOFCs and open new frontiers in the promise one day for a much wider application of this technology.

The activities conducted by Morel et al. (2007) as a whole provided very significant contributions to understanding the catalytic activity of LSM electrodes with respect to SC-SOFCs, and it has directed further attention toward the need for further research to optimize the performance of these sensitive electrodes. The advanced and sophisticated diagnostic tools like EIS might also be useful for extending the range of efficiency and durability of SC-SOFCs and could open new frontiers in the promise that within a day, it becomes widely adopted. [13].

Resini fellows (2008) gave a presentation on Ni-YSZ as promoter material for bioethanol-controlled SOFC. The objective was to arrive at the best catalyst material for the anode surface of an SOFC fueled by ethyl alcohol. The science has shown that the addition of cobalt (Co) to the system based on the Ni-YSZ catalyst material allowed for the best results. The new synthesis of Ni-Co/YSZ catalyst material has given the maximum performance out of all the catalysts tested. The study, by Resini et al. (2008), offers interesting insights related to bioethanol as a fuel for SOFC and optimum catalyst material for anode surface catalyst material of SOFC. The outcomes suggest that the introduction of cobalt into Ni-YSZ catalyst material can significantly improve the performance of bioethanol-based SOFCs. This has great implications for the development of improved and sustainable fuel cell technologies. Further works are required to enhance the performance of bioethanol-based SOFCs and to investigate the use of other renewables.

EIS and other sophisticated diagnostic techniques will prove useful in realizing more effective and stronger SOFCs, which should accelerate wider acceptance of this technology, preferably as a new entrant to the exciting field. Also, it provides the elucidation regarding the use of catalysts in fuel cell technologies, including glycerol as a bio-syngas precursor by reforming path. Results show that in developing catalysts, the distribution of size and dispersion of active phase should be made better.

Thus, these works emphasize the importance of catalyst materials in fuel cell technologies and further research into improving catalyst performance and durability. The overall study of Resini et al. in 2008 and the search results related to it have very useful information on catalyst resources regarding fuel cell technologies and also on the further study to optimize the performance and durability of these technologies. These findings are very useful in the perspective of how to develop more effective and maintainable energy technologies and probably point out the way to a cleaner and, hence, further maintainable future. [14].

Or even as Ye et al. (2008) studied a catalyst coating (Cu-CeO<sub>2</sub>) located outside the anode for solid oxide fuel cells using ethanol, they essentially tried to find the best catalyst material for the anode surface of ethanol-fed SOFCs. The existence of the catalyst material on the anode surface can yield a power density of 567mWcm<sup>-2</sup> at 800 oC operating on ethanol fuel. The study also showed the anode material with the potential to discharge carbon-free for as long as 80 h, thereby indicating long-term service performance.

The study by Ye et al. (2008) gives insights on the extent to which catalyst materials could be employed in SOFCs using ethanol as a fuel. The outcome suggests that upon using a catalytic cover on the outside of the anode, the performance in SOFCs supplied with ethanol can move tremendously ahead. This finding signifies for designing more efficient and sustainable fuel cells technology. Further research on enhancing the performance of ethanol-fed SOFCs and the introduction of other renewable fuels is required.

Moreover, these findings provide insights into the uses of catalyst constituents for fuel cell technologies, such as the use of NiCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>NRs as anode electro catalyst for the ethanol electro oxidation reaction in alkaline media. The findings hint that the synthesized catalysts exhibit better resistance to catalytic poisoning for NiCr<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>NRs. Availability of hyper-active catalyst layers for carbonaceous fuels on nickel-based anodes has demonstrated very considerable improvement to solid oxide fuel cell (SOFC) efficiency. In terms of developing a fully optimized overall cost associated with alkaline direct fuel cells (DEFCs), knowing what the correct thickness should be on both the anode and cathode layers is critical. These results bring to fore the crucial position of catalyst materials in fuel cell technology and, thus, the need for further research directed towards optimizing performance as well as longevity.

Moreover, the results provide pertinent information for developing sulfur and carbon-

tolerant materials for SOFCs based on the principles of heterogeneous catalysis. The study indicates that with the addition of a highly conductive oxygen phase in the anode, electrochemical oxidization of sulfur could take place, thereby assisting in its removal.

These results have important implications for developing SOFCs that could be more durable and reliable and operate with a wider spectrum of fuels. In this respect, general conclusions from the Ye et al. (2008) study and related search results are shedding new light onto the use of catalyst constituents for fuel cell technologies and the necessity for more studies optimizing their performance and durability. These results bear huge implications for the evolution of more effective and maintainable energy technologies, and may help pave way for a cleaner and maintainable future. [15].

The study by Ullah et al. (2018) discussed the application of rare earth metals such as samarium (Sm), cerium, and gadolinium (Gd) in various components of the solid oxide fuel cells (SOFCs) such as electrolytes and catalysts. The study aimed to find out the best catalyst material for the anode surface of ethanol-fueled SOFCs. They found that the tri-doped (M= Sm, Ca, Gd) ceria  $\text{MO}_2\text{CeO}_2\text{O}_{2-\delta}$  used as electrolytes was effective at lower temperatures than conventional ones.

The conductivity of set samples was stately determined in a Probo-Stat-NorEcs setup which indicated conductivity  $1.2 \times 10^{-2} \text{ Scm}^{-1}$  at 700oC. Raman ,UV-visible spectroscopy method was used to characterize the prepared samples for checking absorbance and molecular vibrations. The crystal structure was measured by a series of X-ray diffractions that showed effective doping by the dopants in CeO<sub>2</sub>. The prepared samples exhibited a power density of 314 mW cm<sup>-2</sup> using ethanol fuel at 550 oC.

The research by Ullah et al. (2018) gives special insight into the use of rare earth metals in SOFCs and the best catalyst materials for the anode surface.

The use of tri-doped ceria as an electrolyte can significantly enhance the enactment of SOFCs utilizing ethanol as a fuel source. This observation potentially opens important avenues toward achieving newer and better sustainable fuel cell technologies. It also needs further exploration to bring improvement in ethanol-powered SOFCs and into other renewable fuels. The results also complement the discussions given by this search into the use of rare earths in fuel cell technology, including their role in ultimate magnets, alloys, glasses, and electronics. The results that rare earth metals

like cerium, lanthanum, and neodymium are a critical catalytic combination for petroleum refining as well as additives in diesel fuels.

It had been ascertained that component rare earth metals are effective in fuel cell construction and nickel-metal hydride battery production, an operative way to boost SOFC performance. Their importance in fuel cell technologies is therefore essential, as is the need for more research to optimize performance and lifetime. In addition, the search results provided insights into availability and applications of rare earths in modern technology and lifestyle. The results indicate, in particular, that there are many applications for rare earth metals, ranging from the screens of smartphones, computers and other devices, to automotive catalytic converters, magnets, and steel making. These findings are of great importance for the sustainability and environmental impact of modern technologies, and may also help inform policies and practices designed to reduce the use of non-renewable resources.

In broad outlines, the study by Ullah et al. (2018) and related search findings provide significant knowledge about the use of rare earth metals in fuel cell technologies and possible further studies for optimization in its performance and durability. These findings hold implications for more efficient and sustainable energy technology and contribute towards a brighter, cleaner and more maintainable future.

To the extent that research on the involvement of rare-earth metals within fuel cell technologies and performance optimization and durability of such fuel cells is concerned, the study by Ullah et al. (2018) and relevant search findings are very likely to play an even stronger role. The findings have significant implications for more efficient and sustainable energy technologies; they may pave the way toward cleaner and more sustainable future. [16].

Mushtaq et al. in 2018 studied Ti-doped SrFeO<sub>3</sub> to be used as the cathode material for solid oxide fuel cells. The focus was to find the right cathode material for SOFCs that would perform at squat temperatures. The use of Ti-doped SrFeO<sub>3</sub> as the cathode material has been found to give maximum performance at low temperatures. The preparation of the cathode material was done by the sol-gel method, and its structure, morphology, and thermogravimetric properties were studied using various techniques. The cubic perovskite structure of the cathode was confirmed by x-ray diffraction. The electrical conductivity of the set samples was measured by the four-probe method, which revealed a conductivity of  $1.2 \times 10^{-2} \text{ Scm}^{-1}$  at 700 oC. The prepared cathode

material gave a power density of 551 mW cm<sup>-2</sup> at 600 °C on burning ethanol fuel. This study opens up opportunities of using Ti-doped SrFeO<sub>3</sub> cathode material for SOFCs at lower operational temperatures, as suggested by Mushtaq et al. (2018). This finding can substantially improve the enactment of SOFCs operating at little temperatures and has consequence in the development of more efficient and sustainable technologies for fuel cells. Advanced study in this field is warranted to improve the conduct of low-temperature-operating SOFCs and the application of other renewable fuels.

The search results additionally provide an insight into other materials for fuel cell technologies, including rare earth metals, cerium and neodymium, used in petroleum refining and as diesel additives. Various preparation methods of oxides would include stabilized zirconia as another effective technique to increase SOFC performance. Findings indicate the need for materials research as significantly impacting fuel-cell technologies, and further refinements can be researched for the optimization of their performance and stability. Moreover, the search results give insight into the designing and characterization of solid electrolytes for fuel cell applications. The sol-gel method appears to be the most useful for glass and thin film sample preparation, and using alternate deposition methods may substantially increase fuel cell performance. Such findings will have very important implications for the development of energy technologies that are better organized and more maintainable, and could help to overlay the process for a cleaner and more sustainable future. The research by Mushtaq et al. (2018) and the associated search results discuss various contributions toward fuel cell technologies, as well as the necessity for performance and longevity optimizations by encouraging further research. These findings will have very important implications in developing energy technologies for better organization and easy maintenance and could also cover the method for a cleaner and more sustainable future. [17].

Ali and his different team members (2018) studied LNK-SDC electrolyte and LNCZFO electrode materials that would support a direct carbon fuel cell (DCFC). The objective was also to investigate the possible optimum materials for DCFCs that would require many different carbonaceous fuels (like carbon black, graphite, lignite, bituminous coal, charcoal, and others), which can convert their chemical energy into electrical energy. The electrolyte material was produced through a co-precipitation method while the electrode material was produced through the solid-state reaction

technique. The cubic crystalline structure of these materials was confirmed by x-ray diffraction. The electrical conductivity of the set samples was restrained via the four-probe method, establishing an ionic conductivity of  $0.0998 \text{ Scm}^{-1}$  for the electrolyte (LNK-SDC) and an electronic one of  $10.1 \text{ Scm}^{-1}$  at  $700 \text{ }^{\circ}\text{C}$  for the electrode (LNCZFO). The materials thus produced produced a power density of  $58 \text{ mWcm}^{-2}$  when taken alongside sub-bituminous fuel.

Ali et al. (2018) reveals the side of LNK-SDC electrolyte and LNCZFO electrode materials for DCFCs, where different carbonaceous fuels could be used. The results indicate significant advances in the performance of DCFCs and the conversion of many carbonaceous fuels into electrical energy, and that has very significant consequences for future development in such fuel cell technologies in terms of more powerful and sustainable fuel cell applications. Further research is required to optimize the DCFC performance and to look into using other renewable fuels. These results explicate more avenues concerning the usage of different resources for the fuel cell technology, which also includes systems with molten carbonate electrolytes and ceria-based composite electrolytes. The results indicate that the utilization of distinct deposition processes for oxides, including stabilized zirconia, has been additionally confirmed to serve as an acting medium to facilitate the accomplishment of SOFCs. This means that materials are of primary importance in fuel cell technologies and that more work is required to optimize their enactment and durability.

The other documentation brought to the fore several observations about the functional aspects of DCFCs of different material backgrounds, including carbon steel, stainless steel, and nickel. Thus, the findings imply that the availability and durability of DCFCs would depend on the choice of material of the aforementioned dissimilar material; hence, the choice of right materials becomes dire in order for successful operation of the DCFCs. These findings have very consequential implications toward the development of energy technologies that are operatively effective and environmentally sustainable and could eventually help pave the way towards a clean and sustainable future.

The study of Ali et al. (2018) and related search results have offered major focal points on the utilization of dissimilar materials for DCFCs and the apparent need for further research directed at optimally enhancing their performance and durability. It is such finding that bears the great consequential implications toward the further development of more efficient and sustainable energy technologies, thus helping ensure a pathway toward a cleaner and supportable future. Doped-SrTiO<sub>3</sub> constitutes a class of anode materials that have attracted attention owing to their Strontium titanates that demonstrate remarkable stability under oxidizing and reducing conditions coupled with moderate thermal expansion and a strong resistance to sulfur and carbon poisoning. In addition, these materials are chemically compatible with the widely used solid electrolytes at elevated temperature up to 1400°C, such as Zr<sub>0.82</sub>Y<sub>0.16</sub>O<sub>1.92</sub> (YSZ), La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (LSGM), and Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (CGO). However, the performance of strontium titanates is somewhat reserved compared to the current anode materials due to their low ionic conduction and electrocatalytic activity. [18].

The most recent investigations concentrate on enhancing the performance of doped SrTiO<sub>3</sub> anode materials. For instance, a research article published in Research Gate Expands on anode materials consisting of La-substituted SrTiO<sub>3</sub> perovskites doped with manganese and/or gallium for SOFC, which was studied. The study finds that perovskite structure is thermally stable in oxidizing as well as reducing conditions, and the best power density results from an anode material that is doped with manganese and gallium.

Another research article that is also found on Research Gate concerns the study of (NiO)<sub>0.05</sub>(SrTi<sub>0.8</sub>Nb<sub>0.2</sub>O<sub>3</sub>)<sub>0.95</sub> as a material for a redox stable anode for solid oxide fuel cells. The research study found that using Ni-STN as anodes for SOFCs increases catalytic activity and extraordinary constancy concerning redox cycling. While doped-SrTiO<sub>3</sub>-based anode materials possess impressive properties, their performance needs enhancement to meet SOFC anode requirements.

The most recent research indicated that these nanocomposite materials can greatly appreciate the electrochemical performance of ordinary air electrodes, La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub> (LSM) and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF), when combined with Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (CGO). The incorporation of CGO effectively restricts

extensive particle growth at elevated sintering temperatures, allowing the formation of nanocomposite electrodes having improved energetic sites for the oxygen reduction reaction (ORR). For example, at 750 °C in air and hydrogen, LaCrO<sub>3</sub>-CeO<sub>2</sub> nanocomposites as symmetrical electrodes had low polarization resistance of 0.29 and 0.09 Ω cm<sup>2</sup>, respectively. Such improvement in hydrogen performance is due to the nanostructured electrodes and the presence of decreased nano-CeO<sub>2</sub>, which is endowed with excellent electrocatalytic properties. Pr-doped SrTiO<sub>3±δ</sub> combined with CGO can generate new nanocomposite electrodes having a complimentary role in boosting electrochemical performance in SOFCs by having very high redox stability and improved efficiency in both the ORR and the hydrogen oxidation reaction (HOR) in a symmetrical configuration. Promoting smaller grain sizes will enhance the active sites for chemical reactions. Thus, it is hoped that the development of such nanocomposite materials will enhance performance and stability for SOFC air electrodes. This would be a great boon toward realizing truly clean energy technologies. A recent literature survey examines the application of liquid (pyrolytic oil, alcohol, biodiesel), solid (biochar), and gaseous biofuels (syngas, biogas) toward IT-SOFCs. The survey further presents novel materials for electrodes and electrolytes compatible with intermediate-temperature SOFC processes with oxygenated biofuels. It discusses sophisticated reaction mechanisms taking place on the anode due to the direct use of biofuels, which induce moderate electrochemical phenomena, yielding insights in consideration of the operating conditions of the cell. Furthermore, the survey derives a generalized mathematical formulation of the electrochemical phenomena of IT-SOFCs driven by oxygenated biofuels as defined by the intricate anodic chemistry. The established model is then applied to the case of IT-SOFCs fed on methanol, evaluating the performance limitations of IT-SOFCs operating on biofuels. The literature survey draws together several covariates that relate to advances in materials and engineering to allow for solid oxide fuel cells to work at temperatures lower than previously possible. The advancements in materials development for anodes, electrolytes, and cathodes to reduce operating temperatures of SOFCs below 600°C are reviewed. The fundamentals of operation and functioning mechanisms of SOFCs, material selection for electrolytes, and processing of materials are also treated. Thereafter, the survey covers all components involved in SOFCs, including electrodes, fuel cell design issues and challenges, and their performances. [19].

The preparation of bilayered electrolyte films of Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) and Sm<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> (SDC) were successfully accomplished on porous NiO-YSZ composite substrates by using the electrophoretic deposition (EPD) method, followed by co-firing. During the EPD process, positively charged YSZ and SDC particles were deposited, layer by layer, from ethanol-based suspensions onto the substrate. To inhibit the separation of the YSZ and SDC layers, the thickness of SDC films was restricted to approximately 1 μm. With these bilayered electrolytes, a functional single cell with approximately 4 μm YSZ and about 1 μm SDC was fabricated. As a cathode, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-x</sub> (LSCF) was used, with a maximum yield power thickness of over 0.6 W cm<sup>-2</sup> at a temperature of 700 °C for the constructed bilayered YSZ/SDC electrolyte cells. [20].

A-site lacking strontium titanate-La<sub>0.2</sub>Sr<sub>0.7</sub>TiO<sub>3</sub> has been identified as a promising substantial for use in the anode compartment of solid oxide fuel cells (SOFCs) functioning around 650 °C. The material can be effectively reduced at elevated temperatures, such as 1000 °C, which enhances its conductivity and optimizes properties for fuel oxidation and current collection when combined with active materials. Button cell tests were conducted using a porous framework made of this electronically conductive substance, which was impregnated with CGO and copper as the fuel electrode, alongside a YSZ electrolyte. [21].

Recent studies on anode-maintained single-cavity solid oxide fuel cells (SOFCs) have examined configurations featuring NiGDC/GDC/LSC-GDC, with and without Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst coatings on the anode. These cells were tested using ethanol and air mixes, revealing optimal performance at a temperature of 450 °C, an ethanol-to-air molar ratio of 0.45, and a gas flow rate of 400 ml min<sup>-1</sup>. It was also found that positioning the cells perpendicular to the gas flow, with the cathode facing the fresh gas, enhances their efficiency. Furthermore, there has been a growing interest in SOFC designs utilizing Ni-YSZ/YSZ/GDC/LSC, which are tailored for research and development at intermediate temperatures below 800 °C. Anode-supported single-chamber SOFCs have also been studied in CH<sub>4</sub>-air mixtures, using a YSZ solid electrolyte with a Ni anode and LSM cathode. Furthermore, The catalytic performance of Pt and Ni-based anodes in the partial oxidation of methane has been explored in recent studies. Researchers developed anode-supported solid oxide fuel cells (SOFCs) utilizing gadolinium-doped ceria (GDC) as the electrolyte and NiO-GDC for the anode support, fabricated through the gel-forming technique. This

research highlighted the constancy of the Ni-GDC anode and provision when operated with a methane and air mixture, underscoring its capability to facilitate the internal catalytic improving of methane efficiently. CPOX [22].

Kan H, Lee H. Sn-nobbed Ni/YSZ was employed as an anode catalyst for the assembly of solitary SOFC cells. To achieve great power compactness at transitional temperatures, an efficient layer was added between the bulk anode and the electrolyte. The performance and stability of single cells with the same microstructure were compared for Ni/YSZ and Sn-doped Ni/YSZ anodes. Key findings include, Similar power densities were obtained for Ni/YSZ and Sn-doped Ni/YSZ single cells ( $0.39 \text{ W cm}^{-2}$  vs.  $0.41 \text{ W cm}^{-2}$ ), indicating comparable performance Sn-doped Ni/YSZ demonstrated improved long-term stability (27 h vs. 137 h), which can be attributed to a lower rate of confession of amorphous carbon. Stability of the Sn-doped Ni/YSZ cell was further improved when carbon dumped on the surface during operation was removed. These results highlight the potential of Sn-doped Ni/YSZ anode catalysts in intermediate temperature SOFCs, offering enhanced carbon confession resistance and long-term stability. Researchers Ye et al. have industrialized anode-supported solid oxide fuel cells (SOFCs) utilizing gadolinium-doped ceria (GDC) as the electrolyte and a NiO-GDC composite for the anode support. This innovative approach employs the gel-casting technique to enable direct operation with methane under catalytic partial oxidation (CPOX) situations. Furthermore, advancements have been made in incorporating conductive anode catalysts, including  $\text{LiLaNi-Al}_2\text{O}_3$  and copper, to enhance the efficiency of methane internal reforming and partial oxidation within these fuel cells. [24].

Energy plays a vital role in driving the socioeconomic progress of a nation. In Pakistan, as in many developing countries, the dependence on conventional fossil fuels for energy needs is significant. With a large population and ongoing industrial growth, the demand for energy continues to rise sharply. Unfortunately, recent hikes in fossil fuel prices, coupled with a lack of alternative energy sources, have led to significant energy shortages in the country. The growing gap between electricity demand and supply has significantly impacted various sectors globally. In response, policymakers are actively seeking alternative energy solutions to address these challenges. In Pakistan, different renewable energy sources are being evaluated, particularly solar and wind energy. A comparison of these two options highlights key

factors such as cost, lifespan, emissions, fuel consumption, and maintenance requirements. Solar energy stands out as a more favorable optimal for meeting energy needs, as it is more cost-effective, requires minimal operational and maintenance efforts, and boasts a longer lifespan compared to wind energy. [25].

Renewable energy sources, such as solar and wind, are naturally restocked and do not run out. They can be used for electricity peers, space and water heating and cooling, and transport. In Pakistan, where 60% of electricity is produced through expensive imported fossil fuels and coal, there is a dire need for inexpensive electricity and environmental protection.

The country has set ambitious targets to growth the share of renewable energy in the national power grid from 5% to 20% in 2025 and to 30% in 2030. Solar energy, in particular, has emerged as an attractive alternate energy solution for the common masses in Pakistan, with the potential to meet the country's current electricity demand [26].

Research in the field of SOFCs has focused on enhancing coking resistance to progress the performance and durability of the cells, particularly when using carbon-containing fuels. Various studies have demonstrated the effectiveness of different catalysts and materials in mitigating the impact of carbon confession on the anodes of SOFCs. These advancements are crucial for the practical application of SOFCs in energy adaptation from a extensive range of fuel sources, together with methane, biogas, and ethanol [27].

The expansion of effective and stable photo catalysts for environmental remediation applications has been a subject of intense research. The use of quantum dots, such as copper sulfide, has shown great potential in enhancing the photo catalytic activity of TiO<sub>2</sub> nanotubes. The resulting composites have been assessed for the photo degradation of organic dyes, such as malachite green and phenol, with promising results [28].

The study's findings underscore the potential of conductive polymer binders in enhancing the enactment of lithium-ion battery anodes, particularly those constructed on silicon. By refining the electrical conductivity of the anode and increasing the active material content, the research contributes to the ongoing efforts to optimize the capacity properties of lithium-ion batteries.

## Chapter 3

### MATERIAL AND METHOD

#### 3.1. Production methods

There are many methods for the precipitation of nanoparticles. Some of them methods are,

##### 3.1.3. Sol gel method

The sol-gel technique is a very lengthy renowned since the late 1800s. The sol-gel is a wet chemical method use to fabricate thin film, powder, or fibers. Molecular predecessors are dissolved in water or alcohol and renewed into a gel by heating or rousing the raw materials. Material thus developed will be dried using a suitable method; various methods have been represented in literature examples oven dry, air dry. The sol-gel method is a widely used technique for the grounding of various materials, including perovskite anode materials. The method includes dissolving molecular precursors in water or alcohol and adapting them into a gel by heating or inspiring the raw materials. The resulting gel is then dried to form a powder or film. One of the inexpensive and low-temperature preparations allowing good control of chemical composition of the product is sol-gel process. Sol-gel processing can also be used to prepare perovskite catalysts, membranes, and powders, among others. The sol-gel Pechini method, for example, is versatile for preparing perovskite membranes.

The fact that this method could be used to develop perovskite catalysts, membranes, and powders, among other items, makes it one of the low-cost and low-temperature preparations allowing a well-controlled chemical composition of the product. The sol-gel Pechini method, for instance, is used for preparing perovskite membranes. The method involves chelate poly esterification and is commonly used for depositing dielectric coatings. However, the method is very sensitive to moisture and can be difficult to scale up. It can also include several steps and is a time-consuming process. The sol-gel production of perovskite by an EDTA/citrate complexing method involves Nano scale solid-state reactions. The method allows for the precise regulator of the product's chemical composition and the formation of phase-pure products. Double perovskite  $\text{Sr}_2\text{FeMoO}_6$  can be prepared by the sol-gel technique and solid-state reaction method. Comparison was made between powders derived by gel and solid-state reaction techniques. It was noted that the powder obtained by sol-gel method is found to be more homogeneous. The layered double perovskite oxide with well-

organized layered structure on A-site is amenable for preparing by sol-gelling, which is an anode material for DC-SOFCs. This involves dissolving precursors in aqueous or alcoholic medium and gel formation upon heating or stirring of the raw composition which ultimately leads to drying into powder or film in the end. The sol-gel method is a multipurpose and widely used technique for the synthesis of numerous resources, including perovskite and oxide nanomaterial. The method suggests many welfares over other manufacture techniques, such as:

#### **3.1.3.1. Benefits of sol gel method**

At low working temperatures, the sol-gel method is a low-temperature method of synthesis, and is thus preferred over other high-temperature synthesis methods.

The sol-gel method offers the facility of fine control of size, which can vary from 10 to 100 nm.

A mixed composition can be synthesized due to the sol-gel method, which would not be achieved through solid-state fusion.

The process involved in sol-gel synthesis is easy and inexpensive compared to the other synthesis techniques.

Despite requiring very low energy inputs, the sol-gel pathway employs low sintering temperatures.

Using the sol-gel method, materials with enhanced optical and electrical properties can be obtained.

The sol-gel route lends itself easily to modification to suit particular requirements.

Uniform, conformal coatings with uniform and conformal properties can be provided using the sol-gel methods on a variety of substrates.

Sol-gel-derived materials are very versatile and find wide applications in various fields such as optics and electronics, energy, and biomedical applications. These materials have unique properties which can enable innovations in (bio) sensors with enhanced detection capacity for medical diagnostics. They are also immensely important for these materials in reactive systems and separation technologies that advance environmental and industrial process. Their adaptability and efficiency make them valuable in both research and practical applications.

#### **3.1.3.2. Applications**

- Protective coating
- Thin films and fibers
- Controlled release
- Opto mechanical

### 3.2. Preparation LaGdCuTiO<sub>3-0</sub> by wet chemical technique

LaGdCuTiO powers as anode for SOFC were prepared by sol get way. The stoichiometric amount of,

Lanthanum Nitrate La (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (sigma Aldrich 99.99%)

Gadolinium Nitrate hexahydrate Gd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O (Sigma Aldrich 99.99%)

Copper (II) Nitrate trihydrate Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O(Glenthane)

Titanium (IV) oxide TiO<sub>2</sub> (riedel-detlaen)

Were used in this synthesis.an appropriate molar ration of Lanthanum hex nitrate La(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O Gadolinium Nitrate hexahydrate Gd(NO<sub>3</sub>)<sub>3</sub>and Copper(II) nitrate trihydrate Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O thawed into 150ml distilled water and heat at 120° C in a hot magnetic stirrer. Titanium (IV) oxide *TiO<sub>2</sub>* is insoluble in H<sub>2</sub>O but soluble in strong acid. So take 10ml concentrated hydrochloric acid and add into 10ml distilled water, then add *TiO<sub>2</sub>* into this mixture of acid and water, heat and stirring for half hour at temperature 120° C through the hot magnetic stirrer.

After heating and stirring *TiO<sub>2</sub>* solution at 120° C for half hour, add it into La (NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O, and Cu(NO<sub>3</sub>)<sub>2</sub> H<sub>2</sub>O solution. Citric acid was added 20% of the total moles of LCuT into solution. After that, this overall solution was heated continuously at temperature 120° C for 8h to obtain gel. The obtaining gel was dried at 120° C for four hours in an oven and crushed in mortar pestle to achieve powder. Then followed by calcination at temperature 1000° C for five hours. Finally, the fine powder were stranded and ready for characterization.

In this way total four samples were prepared with different concentrations, these samples were,

#### Sample *F<sub>1</sub>*

3.7302g Lanthanum hex nitrate La (NO<sub>3</sub>)<sub>3.6</sub> H<sub>2</sub>O 2.5573g Gadolinium Nitrate hexahydrate Gd(NO<sub>3</sub>)<sub>3</sub> and 0.375g copper nitrate trihydrate Cu(NO<sub>3</sub>)<sub>2</sub>. 3H<sub>2</sub>O dissolved into 150ml distilled water than heat and stir at 120° C, Titanium oxide *TiO<sub>2</sub>* is insoluble in H<sub>2</sub>O but soluble in strong acid. So take 10ml concentrated hydrochloric

acid and add into 10ml distilled water, then add 1.437g of  $TiO_2$  into this mixture of acid and water, heat and stirring for half hour at temperature  $120^\circ C$ .

After heating and stirring  $TiO_2$  solution, add it into the previous solution. Citric acid was added 20% (2g) of total moles of  $LaGdCuTiO_{3.0}$  into solution. After that, this overall solution was heated continuously at temperature  $120^\circ C$  for 8h to attain gel. The gel was dehydrated at  $120^\circ C$  for four hours in an oven and crushed in mortar pestle to attain powder. Then followed by calcination at temperature  $1000^\circ C$  for five hours. Finally, the fine powder was grounded and this sample  $F_1$  was ready for characterization.

### **Sample $F_2$**

3.7302g Lanthanumhex nitrate  $La(NO_3)_{3.6} H_2O$  2.5573g Gadolinium Nitrate hexahydrate  $Gd(NO_3)_3$  and 0.375g copper nitrate trihydrate  $Cu(NO_3)_2 \cdot 3H_2O$  dissolved into 150ml distilled water than heat and stir at  $120^\circ C$ , Titanium oxide  $TiO_2$  is insoluble in  $H_2O$  but soluble in strong acid. So take 10ml concentrated hydrochloric acid and add into 10ml distilled water, then add 1.437g of  $TiO_2$  into this mixture of acid and water, heat and stirring for half hour at temperature  $120^\circ C$ .

After heating and stirring  $TiO_2$  solution, add it into the previous solution. Citric acid was added 20% (2g) of total moles of  $LaGdCuTiO_{3.0}$  into solution. After that, this overall solution was heated continuously at temperature  $120^\circ C$  for 8h to attain gel. The gel was dehydrated at  $120^\circ C$  for four hours in an oven and crushed in mortar pestle to attain powder. Then followed by calcination at temperature  $1000^\circ C$  for five hours. Finally, the fine powder was grounded and this sample  $F_2$  was ready for characterization.

### **Sample $F_3$**

3.7302g Lanthanum hexnitrate  $La(NO_3)_{3.6} H_2O$  2.5573g Gadolinium Nitrate hexahydrate  $Gd(NO_3)_3$  and 0.375g copper nitrate trihydrate  $Cu(NO_3)_2 \cdot 3H_2O$  thawed into 150ml distilled water than heat and stir at  $120^\circ C$ , Titanium oxide  $TiO_2$  is insoluble in  $H_2O$  but soluble in strong acid. So take 10ml concentrated hydrochloric acid and add into 10ml distilled water, then add 1.437g of  $TiO_2$  into this mixture of acid and water, heat and stirring for half hour at temperature  $120^\circ C$ .

After heating and stirring  $TiO_2$  solution, add it into the previous solution. Citric acid was added 20% (2g) of total moles of  $LaGdCuTiO_{3.0}$  into solution. After that, this overall solution was heated continuously at temperature  $120^\circ C$  for 8h to attain gel.

The gel was dehydrated at 120° C for four hours in an oven and crushed in mortar pestle to attain powder. Then followed by calcination at temperature 1000° C for five hours. Finally, the fine powder was grounded and this sample F<sub>3</sub> was ready for characterization.

#### **Sample F<sub>4</sub>**

3.7302g Lanthanum hexnitrate La (NO<sub>3</sub>)<sub>3.6</sub> H<sub>2</sub>O 2.5573g Gadolinium Nitrate hexahydrate Gd(NO<sub>3</sub>)<sub>3</sub> and 0.375g copper nitrate trihydrate Cu(NO<sub>3</sub>)<sub>2</sub>. 3H<sub>2</sub>O dissolved into 150ml distilled water than heat and stir at 120° C, Titanium oxide TiO<sub>2</sub> is insoluble in H<sub>2</sub>O but soluble in strong acid. So take 10ml concentrated hydrochloric acid and add into 10ml distilled water, then add 1.437g of TiO<sub>2</sub> into this mixture of acid and water, heat and stirring for half hour at temperature 120° C.

After heating and stirring TiO<sub>2</sub> solution, add it into the previous solution. Citric acid was added 20% (2g) of total moles of LaGdCuTiO<sub>3.0</sub> into solution. After that, this overall solution was heated continuously at temperature 120° C for 8h to attain gel. The gel was dried at 120° C for four hours in an oven and crushed in mortar pestle to attain powder. Then followed by calcination at temperature 1000° C for five hours. Finally, the fine powder was grounded and this sample F<sub>4</sub> was ready for characterization.

These four samples were used in SOFC as catalyst material for to improve its conductivity.

**Sample F<sub>1</sub> ► B<sub>1</sub>**

**Sample F<sub>2</sub> ► B<sub>2</sub>**

**Sample F<sub>3</sub> ► B<sub>3</sub>**

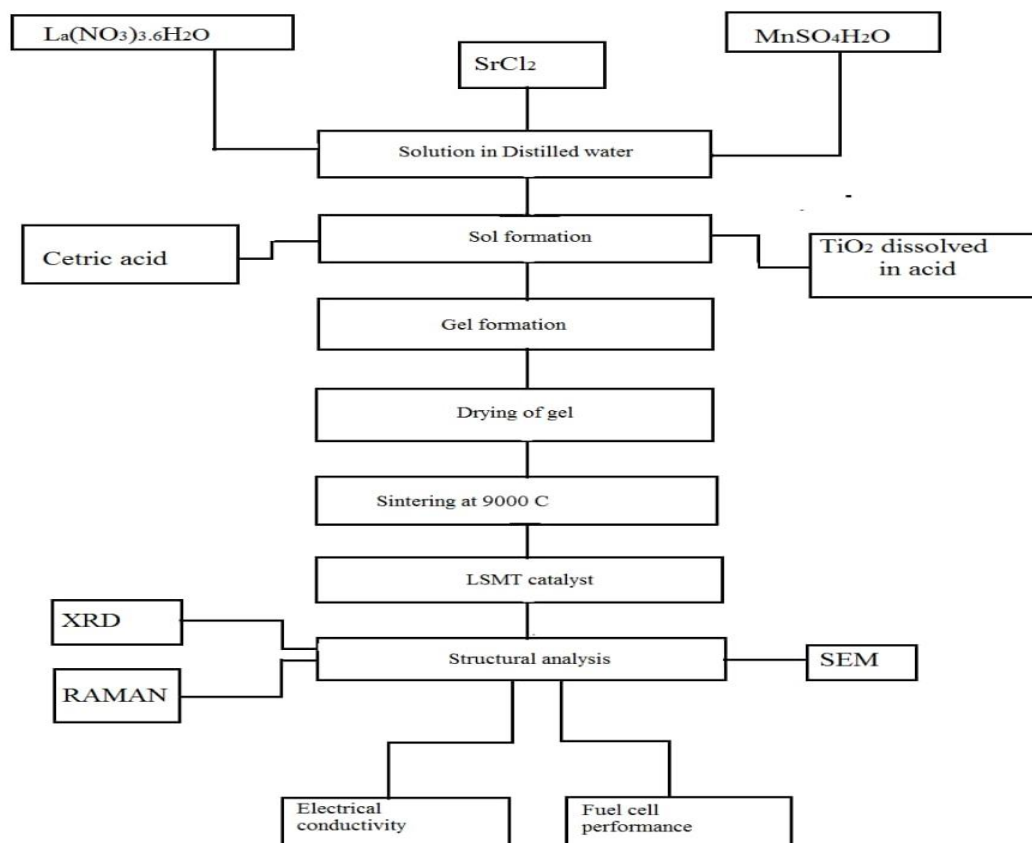
**Sample F<sub>4</sub> ► B<sub>4</sub>**

### **3.3. Apparatus used**

Following apparatus are used for the preparation of these samples,

Magnetic stirrer, hot plate with probe, aluminum foil, thermometer, balance, oven, furnace,

Crucibles, small bottles for adding samples, patty dishes, beakers and pippete.



**Fig.3.1. Flow diagram for Catalyst material synthesis**

## Chapter 4

### RESULTS AND DISCUSSION

#### 4.1. Structure analysis

The structure of the organized catalyst materials  $\text{LaGdCuTiO}_{3-\delta}$  was analyzed by X-ray diffractometer with Cu K alpha source having wavelength 1.5418 angstrom. Interspacing distances were calculated using equation,

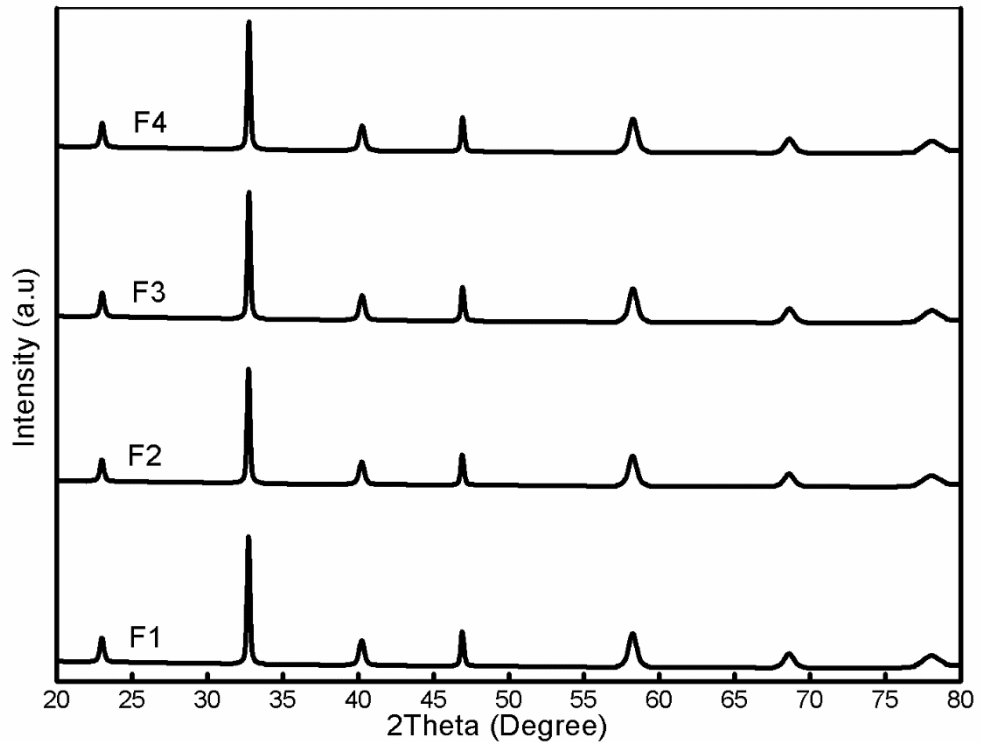
$$d = \frac{\lambda}{2 \sin \theta} \quad (4.1)$$

And lattice parameters were calculated using equation,

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (4.2)$$

Average lattice parameter is 5.42 Angstrom and crystallite size was calculated using Scherrer equation,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4.3)$$



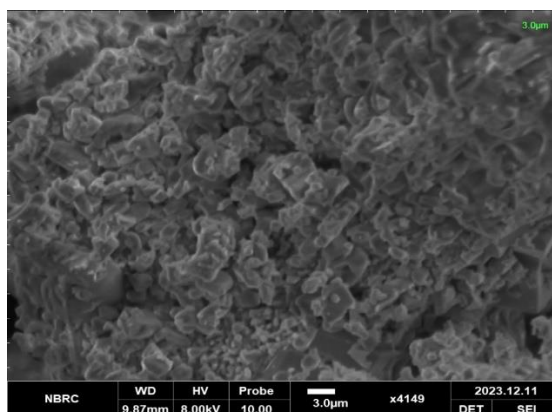
**Fig 4.1. XRD peaks for the prepared anode catalyst**

The prepared catalyst material has a cubic perovskite structure. The only observed peaks are found to be LST with reference code 01-079-0181, space group pm-3m and space group number 221. No peaks of Cu were observed in the prepared catalyst material. It means Mn has successfully doped into the LST. The observed peaks are

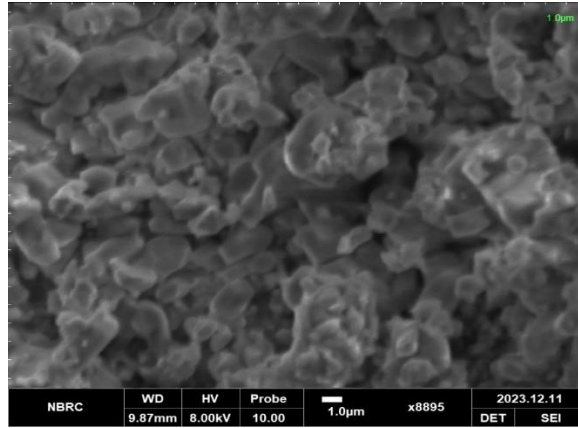
indexed as (100), (110), (111), (200), (210), (211), (220), (221), (310), (311) and (222) respectively. Average crystal size of the prepared samples is 44nm which is calculated by Scherer equation. This doping transition metal (Cu) shows that 7 mole % of the transition metal Cu lie within the solubility limit that is why no phase of Cu was observed. Due to increasing the dopant (Cu) concentration the peaks were slightly shifted towards the lower region. The slightly shifting of the peaks towards the lower region shows that the size of the particles decrease.

#### 4.2. Microstructural analysis

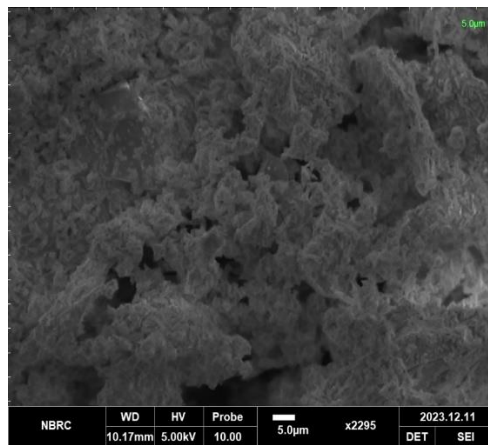
Figures (a, b, c and d) represent the SEM micrograph of the prepared samples  $\text{LaGdCuTiO}_{3-\delta}$ . In SEM images (c and d) in 500nm range, there are around 5 particles present in which some are small and some are large, so one particle size is around 100nm. The normal grain size is calculated by image J software and found to be around 80-100nm. Similarly in next two SEM images (a and b) the average particle size is 0.16 micrometer. Images shows that the Cu successfully doped over the surface of  $\text{LaGdTiO}_{3-\delta}$ . SEM Micrograph shows that the surface of the  $\text{LaGdCuTiO}_{3-\delta}$  is porous. Gas can easily pass through this porous surface so this porous catalytic exterior helps to increase the conductivity of the SOFC.



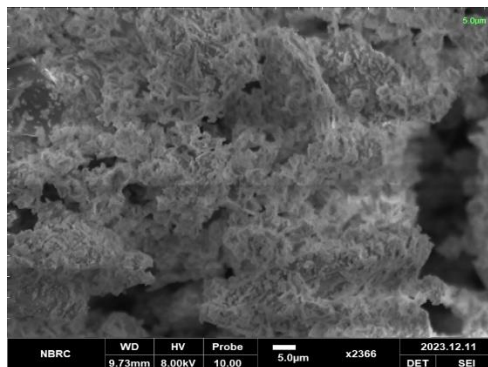
**Fig.4.2. SEM image F1**



**Fig. 4.3. SEM image F2**



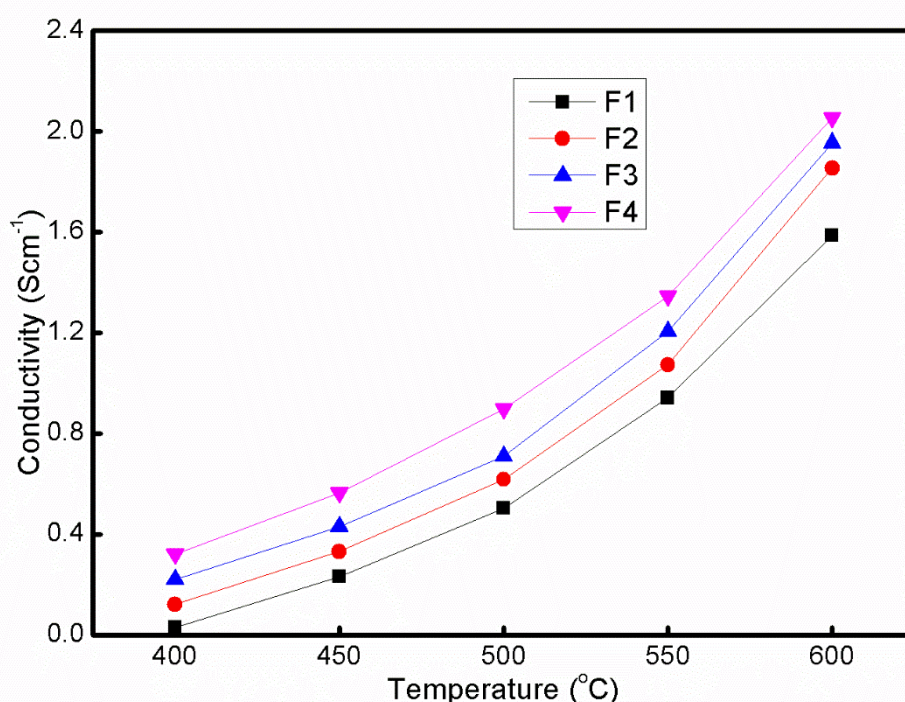
**Fig. 4.4. SEM image F3**



**Fig.4.5. SEM image F4**

### 4.3. Conductivity of the prepared anode catalyst

For conductivity measurement first of all we prepare pellets by taking 1g of each sample. Hydraulic press is used with pressure 400MPa for two minutes for making pellet. The diameter of the pellet is 13mm. both sides of the pellet was paste with silver solution for current collection and dry it. 4probe technique was used for conductivity measurement. Samples one by one fixed in 4probe apparatus and placed in furnace. Conductivity of the organized samples can be dignified in the temperature array of 400 °C to 600 °C. Through obtained results of these samples draw the graph which is given below in fig 4.6:



**Fig 4.6. Conductivity of the prepared anode catalyst**

The conductivity of the prepared samples were dignified in air atmosphere in the range of 400-600 °C and is shown in fig 4.6. The conductivity trends shows the conductivity of the samples increase with the increasing of temperature and dopant concentration. The sample 4 shows the maximum conductivity 2.0 Scm<sup>-1</sup> at 600°C. Ali et al also obtained the highest conductivity 1.2×10<sup>-2</sup>Scm<sup>-1</sup> at 700 °C by using material MCeO (M=Sm, Ca, Gd). Similarly the sample F3 give conductivity 0.2 Scm<sup>-1</sup> at 400°C and 1.9 Scm<sup>-1</sup> at 600 °C. The sample F2 gives conductivity 0.1 Scm<sup>-1</sup> at 400 °C and 1.8 Scm<sup>-1</sup> at 600 °C. Sample F1 give conductivity 0.03 Scm<sup>-1</sup> at 400 °C and 1.5 Scm<sup>-1</sup> at 600 °C. To enhance the conductivity of the synthesized material, it is

necessary that the material is thermally stable. Ali et al. obtained highest Electronic conductivity  $10.1 \text{Scm}^{-1}$  of electrode LNCZFO at  $700^\circ\text{C}$ . The prepared samples show less conductivity, it is may be due to low sintering temperature and less dopant concentration.

#### 4.4. RAMAN spectroscopy analysis

The passage discusses the study of doping material on the surface of LaGdTio (LSMT) using Raman spectroscopy. Initially, the LSMT samples have a clean, thick surface with featureless Raman spectra, indicating low activity in the cubic perovskite stage. Doping particles do develop on the surface, to being detectable with Raman spectroscopy, post-heat treatment at  $1000^\circ\text{C}$  for 5 hrs. The Raman spectra of the treated LSMT surface show major peaks. The top peak, at about  $800 \text{cm}^{-1}$ , is assigned to the presence of Cu in LaSrTiO; the next highest peak appears at  $530 \text{cm}^{-1}$ . This  $800 \text{cm}^{-1}$  Raman peak strikingly resembles the Raman peak of SrCrO<sub>4</sub>, which occurs above  $800 \text{cm}^{-1}$  and is attributed to the Cr doping of LSCF electrode material for Solid Oxide Fuel Cells (SOFC), as referenced in Wang (2014). Also, in the LGCT samples treated at  $900^\circ\text{C}$ , the characteristic Raman band around  $800 \text{cm}^{-1}$  is still visible, although lesser in intensity. This implies that the doping process changes the Raman spectra of the LGCT surface, and the temperature of heat treatment affected the intensity of the  $800 \text{cm}^{-1}$  band.

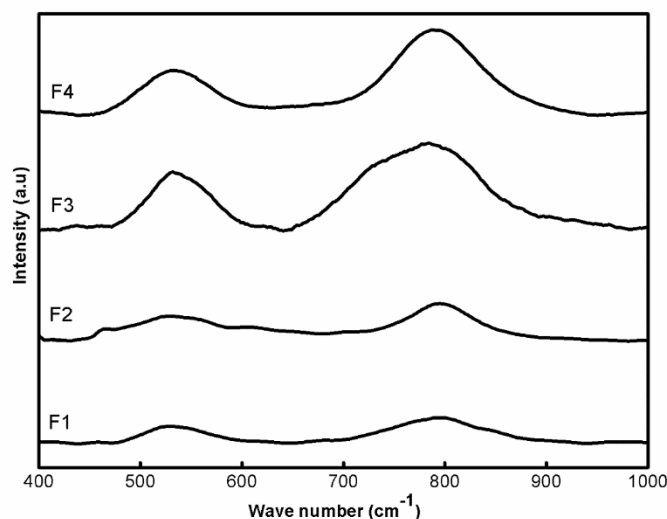


Fig 4.7. RAMAN graph

## Chapter 5

### DISCUSSION

$\text{La}_{0.4}\text{Sr}_{0.6}\text{Cu}_{0.08}\text{Ti}_{0.92}\text{O}_{3-\delta}$  catalyst material, titanates-based. This is a rare material which, for one more reason among others, has been distinguished from other titanate-based catalysts due to an electrical conductivity of 4.21 S/cm at 600°C. Jiang et al. have observed that under comparable conditions LS8CT exhibits conductivity higher than many of those related materials. For example, even though  $\text{Li}_2\text{TiSiO}_5$  has been reported as a high-capacity catalytic material for lithium batteries, any information about its conductivity is unknown. In that same vein, lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), used in lithium-ion batteries, also lacks any direct conductivity measurements, although its structure and morphology are routinely analyzed using XRD and SEM.

To further probe the structural and microstructural characteristics of LS8CT and other  $\text{La}_{0.4}\text{Sr}_{0.6}\text{Cu}_x\text{Ti}_{1-x}\text{O}_3$  (LSCXT) compositions, X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been employed. Performing the XRD analysis of LSCXT at a temperature of 1100°C confirmed incorporation of Cu into the Ti B-site, where it can be evidenced by the shifts of peak positions to lower angles as the dopant concentration increased. "To find estimated crystallite size of approximately 20 nm by the Scherrer formula implies very fine microstructure". The absence of distinguishable peaks of Cu confirmed that doping was within solubility limit.

Observation using a scanning electron microscope indicated that the particles were evenly distributed. There were voids suggestive of porosity that aided the gas diffusion through the fuel cell. The LS8CT sample contained increased porosity coupled with reduced-particle size, whose average was below 30 nm, contributing to an increased surface area, better sinterability, and much higher ionic and electronic conductivity. These will allow better diffusion of gases and conduction of electrons to achieve better electrochemical performance. Herein, the structural and microstructural advantages of LS8CT position it as a strong candidate for application in solid oxide fuel cells as well as lithium-ion batteries.

$\text{La}_{0.4}\text{Sr}_{0.6}\text{Cu}_{0.08}\text{Ti}_{0.92}\text{O}_{3-\delta}$  titania perovskite played the role of a catalyst material. The LS8CT composition was superior to the other LSCXT compositions. Its best feature is the greater porosity of the LS8CT sample, which has been clearly shown through scanning electron microscopy (SEM). From the SEM images, that's clear to see that the morphology given by the LS8CT sample has an improved porosity degree

compared to the other LSCXT compositions. An increase in porosity is anticipated to favor gas diffusion in the operation of a fuel cell. This gas diffusion is a very important feature concerning efficient electrochemical performance. Another plus point for the LS8CT catalyst material is its fine particle size distribution. The average particle size of the LS8CT sample was less than 30 nm, indicating a narrow particle size range. A fine particle size distribution can account for a variety of advantages such as increased surface area, better sinterability, and improved ionic and electronic conductivity because of less diffusion path lengths. These are the most favorable features for catalytic materials for solid oxide fuel cells in terms of improved electrochemical performance. In summary, it is expected that the enhanced porosity along with fine particle size distribution of the LS8CT sample will contribute to improved gas diffusion and electron transport in a fuel cell, lending to better overall electrochemical performance compared to the other LSCXT anode compositions. These beneficial microstructural characteristics will make LS8CT promising as a catalyst that can be optimized further for high-performance solid oxide fuel cells. Sourcing raw materials is another challenge, especially with LS8CT, such as lanthanum (La) and strontium (Sr) which are considered rare earth elements. It will be difficult to have a constant and continuous supply of these materials in large scale considering the geopolitical and environmental issues related to rare earth elements mining and processing. Additionally, careful process control and optimization will be required to maintain the intended Cu doping content and its distribution during the vast manufacturing process to ensure the successful incorporation of Cu in the LS8CT lattice.

## **CONCLUSION**

The study focuses on the temperatures from 400 to 600 degrees Celsius and the influence of dopant concentration on the conductivity of synthesized samples.

Conductivity measurements indicate a trend of increased performance with increased temperature and dopant, with Sample 4 scoring the highest conductivity of 2.0 S/cm at 600 degrees. Sample F3 reached 1.9 S/cm while F2 and F1 were slightly lower at 1.8 S/cm and 1.5 S/cm respectively. The values were at the same temperature. These results show how critical thermal stability and optimized dopant concentration are in the design of conductivity. However, inferior to earlier studies, like those conducted by Ali et al.'s 10.1 S/cm at 700C for LNCZFO, the lower conductivities highlighted the need for improved sintering processes and higher dopant levels for better performance. Its also been demonstrated that Raman spectroscopy helped in understanding the structural changes as influenced by doping and heat treatment. Initially, such LSMT samples have a very clean surface with little Raman activity which is characteristic of cubic perovskite samples like these. Heat treatment at 1000C, however, yielded samples with doping particles on their surface, detectable by prominent Raman peaks. For example, the peak at  $800\text{ cm}^{-1}$ , which corresponded to Mn in the LaSrTiO, and its resemblance to the SrCrO<sub>4</sub> Raman peak above  $800\text{ cm}^{-1}$  showcase the influence of doping on the surface characteristics of the material. Such a decrease in intensity of an  $800\text{ cm}^{-1}$  band in samples that were treated at lower temperatures suggests a temperature-dependent alteration of the structure of the material. Overall, from these findings, an important notion would be the improvement of thermal treatment and doping approaches for enhanced conductivity and structural properties. Further studies would need to work toward optimization of the synthesis parameters for better material performance to position it as a solid candidate for solid oxide fuel cell applications.

## REFERENCES

1. Huo J, Peng C. Depletion of natural resources and environmental quality: Prospects of energy use, energy imports, and economic growth hindrances. *Resources Policy*. 2023 Oct 1;86:104049. Sazali N, Wan Salleh WN, Jamaludin AS, Mhd Razali MN. New perspectives on fuel cell technology: A brief review. *Membranes*. 2020 May 13;10(5):99.

2. Jayakrishnan KU, Bala G, Cao L, Caldeira K. Contrasting climate and carbon-cycle consequences of fossil-fuel use versus deforestation disturbance. *Environmental Research Letters*. 2022 May 25;17(6):064020. Pickl MJ. The renewable energy strategies of oil majors—From oil to energy?. *Energy Strategy Reviews*. 2019 Nov 1;26:100370.
3. Beg N, Morlot JC, Davidson O, Afrane-Okesse Y, Tyani L, Denton F, Sokona Y, Thomas JP, La Rovere EL, Parikh JK, Parikh K. Linkages between climate change and sustainable development. *Climate policy*. 2002 Jan 1;2(2-3):129-44..
4. Khan K. ENERGY SECURITY IN PAKISTAN-THE CASE OF IPI AND TAPI. *Journal of Contemporary Studies*. 2012 Feb 10;1(2):1-20..
5. Gielen D, Boshell F, Saygin D, Bazilian MD, Wagner N, Gorini R. The role of renewable energy in the global energy transformation. *Energy strategy reviews*. 2019 Apr 1;24:38-50. Cuong TT, Le HA, Khai NM, Hung PA, Linh LT, Thanh NV, Tri ND, Huan NX. Renewable energy from biomass surplus resource: potential of power generation from rice straw in Vietnam. *Scientific reports*. 2021 Jan 12;11(1):792.
6. Ilyas SZ, Hassan A, Mufti H. Review of the renewable energy status and prospects in Pakistan. *Int J Smart grid*. 2021;5(4):167-73.
7. Handayani K, Krozer Y, Filatova T. From fossil fuels to renewables: An analysis of long-term scenarios considering technological learning. *Energy policy*. 2019 Apr 1;127:134-46
8. Singh M, Zappa D, Comini E. Solid oxide fuel cell: Decade of progress, future perspectives and challenges. *International Journal of Hydrogen Energy*. 2021 Aug 5;46(54):27643-74.
9. Kan H, Lee H. Sn-doped Ni/YSZ anode catalysts with enhanced carbon deposition resistance for an intermediate temperature SOFC. *Applied Catalysis B: Environmental*. 2010 Jun 9;97(1-2):108-14.
10. Morel B, Roberge R, Savoie S, Napporn TW, Meunier M. Catalytic activity and performance of LSM cathode materials in single chamber SOFC. *Applied Catalysis A: General*. 2007 Apr 30;323:181-7.
11. Resini C, Delgado MC, Presto S, Alemany LJ, Riani P, Marazza R, Ramis G, Busca G. Yttria-stabilized zirconia (YSZ) supported Ni-Co alloys (precursor of SOFC anodes) as catalysts for the steam reforming of ethanol. *International Journal of Hydrogen Energy*. 2008 Jul 1;33(14):3728-35.
12. Ye XF, Wang SR, Wang ZR, Xiong L, Sun XF, Wen TL. Use of a catalyst layer for anode-supported SOFCs running on ethanol fuel. *Journal of Power Sources*. 2008 Mar 1;177(2):419-25.
13. Raza R, Ullah MK, Afzal M, Rafique A, Ali A, Arshad S, Zhu B. Low-temperature solid oxide fuel cells with bioalcohol fuels. In *Bioenergy Systems for the Future 2017* Jan 1 (pp. 521-539). Woodhead Publishing.
14. 17. Mushtaq N, Xia C, Dong W, Abbas G, Raza R, Ali A, Rauf S, Wang B, Kim JS, Zhu B. Perovskite  $\text{SrFe}_{1-x}\text{Ti}_x\text{O}_{3-\delta}$  ( $x \leq 0.1$ ) cathode for low temperature solid oxide fuel cell. *Ceramics International*. 2018 Jun 15;44(9):10266-72.
15. 18. Ali A, Bashir FS, Raza R, Rafique A, Ullah MK, Alvi F, Afzal M, Ghauri M, Belova LM. Electrochemical study of composite materials for coal-based direct carbon fuel cell. *International journal of hydrogen energy*. 2018 Jul 12;43(28):12900-8.
16. 19. Elleuch A, Halouani K. Intermediate-temperature solid oxide fuel cell

- fueled by biofuels. In *Intermediate temperature solid oxide fuel cells* 2020 Jan 1 (pp. 427-476). Elsevier.
17. 20. Matsuda M, Hosomi T, Murata K, Fukui T, Miyake M. Fabrication of bilayered YSZ/SDC electrolyte film by electrophoretic deposition for reduced-temperature operating anode-supported SOFC. *Journal of Power Sources*. 2007 Feb 25;165(1):102-7.
  18. 21. Savaniu CD, Irvine JT. La-doped SrTiO<sub>3</sub> as anode material for IT-SOFC. *Solid State Ionics*. 2011 Jun 16;192(1):491-3.
  19. 22. Morales M, Espiell F, Segarra M. Improvement of performance in low temperature solid oxide fuel cells operated on ethanol and air mixtures using Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst layer. *Journal of Power Sources*. 2015 Oct 20;293:366-72.
  20. 23. Kan H, Lee H. Sn-doped Ni/YSZ anode catalysts with enhanced carbon deposition resistance for an intermediate temperature SOFC. *Applied Catalysis B: Environmental*. 2010 Jun 9;97(1-2):108-14.
  21. 24. Ye XF, Wang SR, Wang ZR, Xiong L, Sun XF, Wen TL. Use of a catalyst layer for anode-supported SOFCs running on ethanol fuel. *Journal of Power Sources*. 2008 Mar 1;177(2):419-25.
  22. 25. Irfan M, Zhao ZY, Ahmad M, Mukeshimana MC. Solar energy development in Pakistan: Barriers and policy recommendations. *Sustainability*. 2019 Feb 25;11(4):1206.
  23. 26. Stambouli AB, Traversa E. Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. *Renewable and sustainable energy reviews*. 2002 Oct 1;6(5):433-55.
  24. 27. Yan N, Luo JL, Chuang KT. Improved coking resistance of direct ethanol solid oxide fuel cells with a Ni–S<sub>x</sub> anode. *Journal of Power Sources*. 2014 Mar 15;250:212-9.
  25. 28. Ratanatawanate C, Bui A, Vu K, Balkus Jr KJ. Low-temperature synthesis of copper (II) sulfide quantum dot decorated TiO<sub>2</sub> nanotubes and their photocatalytic properties. *The Journal of Physical Chemistry C*. 2011 Apr 14;115(14):6175-80.
  26. 29. YucaN, Kalafat I, Taskin OS, Arici E. Miscellaneous PEDOT: PTS (polythiophenesulfonyl chloride) based conductive binder for silicon anodes in lithium ion batteries. *Polymers for Advanced Technologies*. 2023 Jan;34(1):279-86.