CHAPTER-1

INTRODUCTION AND LITERATURE REVIEW

CHAPTER 1: Introduction and Literature Review

1.1 Present Energy Scenario

The rapid depletion of fossil fuels such as coal, petroleum, and natural gas has created an urgent requirement for the efficiently harnessing green energy sources to support human activities in a conclusive environment. To sustain the growth, there is an increase in the demand for energy and electricity[1]. The main sources of energy till now have been fossil fuels, which are mainly formed by natural processes, which are primarily constitute by carbon, petroleum, coal, and natural gases. Moreover, considering fossil energy resources as a long-term energy solution will have severe impacts on the environment due to the emission of harmful gases such as carbon dioxide, greenhouse gases etc. The energy consumption pattern in different sectors up to the year 2030 is shown in Fig1.1. A rapid increase in energy consumption calls for alternative fuels and energy systems to address global energy demand and mitigate the impact of greenhouse gases and other pollutants. Several fully renewable energy sources, like solar, wind, hydro, biomass, etc. are used to solve this issue but they are still looking for adequate energy for the foreseeable future.

Globally, demand of energy is increasing exponentially with the population, advent of high-tech cities, fast urbanization etc. The U.S. Energy Information Administration (EIA), International Energy Agency (IEA), and the European Environment Agency regularly collect and disseminate updates on energy consumption data. Since long time, coal remained the predominant energy source, with significant increases in the utilization of oil and natural gas. This was followed by notable growth in hydropower and renewable energy sources[2][3].

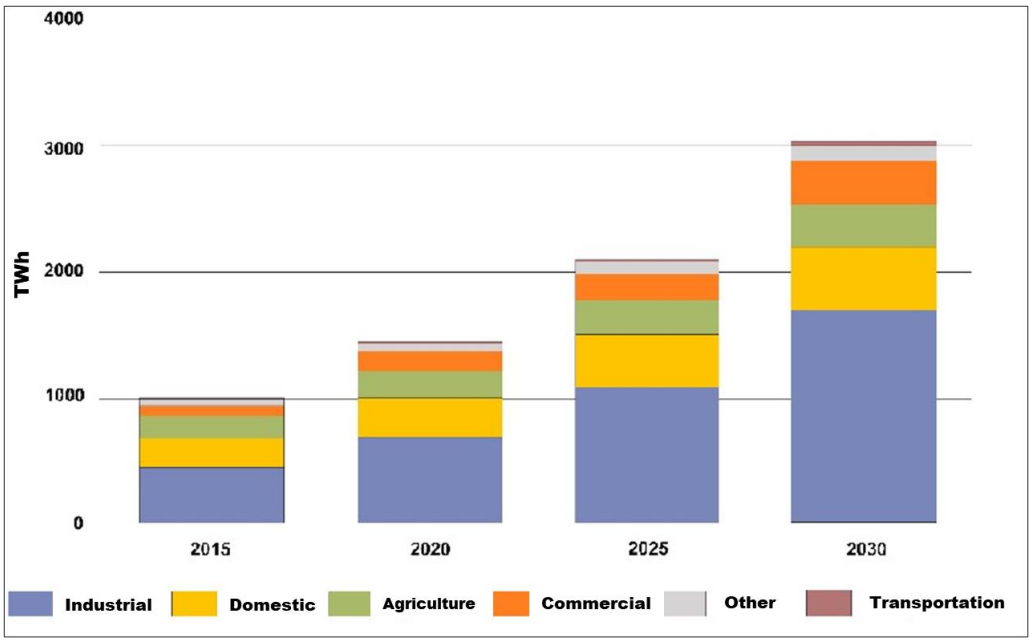

Figure.1.1 World energy consumption by different energy sources with projection from 2010 to 2030 [1].

In 2022, global energy demand increased by 1.1% marking a new record, albeit slower than the 5.5% growth seen in 2021. Renewable energy continued to increase strongly, with solar and wind contributing to a 7.5% share of primary energy consumption, up nearly 1% from the previous year. Renewable power, excluding hydro, experienced a 14% growth in 2022, slightly lower than the previous year's 16% rate. Meanwhile, there was a 0.6% increase in global coal demand, reaching its peak since 2014 and exceeding the 10-year average growth rate of 0.2%. China and India were the main drivers of this rise, with a 1% and 4%. Furthermore, global coal production increased by more than 7% compared to 2021, with China, India, and Indonesia accounting for over 95% of this surge[4][3][2].

Oil demand increased by 3.1% in 2022, surpassing the 0.9% growth average observed over the past decade. This robust increase was attributed to the continuing global economic recovery following the Covid-19 pandemic. However, despite this increase, consumption level remained 0.7% below those of 2019. In 2022, Brent crude oil prices averaged $101 per barrel(/bbl),

reaching their highest value since 2013. Despite this, the growth in oil consumption was moderate, rising by 2.9 million barrels per day (b/d) to 97.3 million b/d, a smaller increase compared to the year 2020 and 2021. Among all countries, Saudi Arabia (1,182,000 b/d) and the USA (1,091,000 b/d) experienced the most significant increase[4].

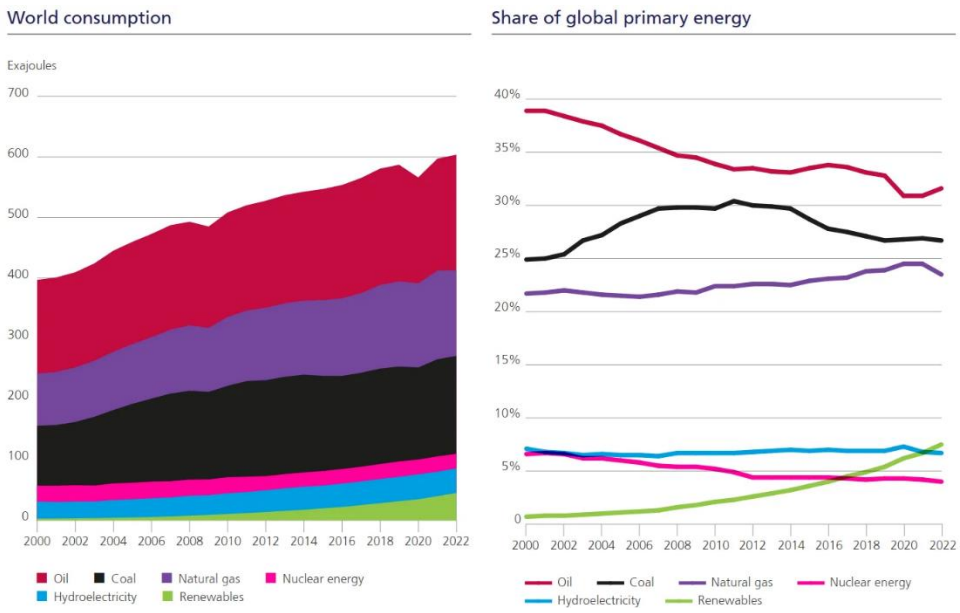

Figure 1.2 Primary Global Energy Consumption 2023 [4]

In 2022, global natural gas demand experience a 3% decline, dipping below the landmark of 4 Trillion cubic meters reached for the first time in 2021. Its contribution to primary energy decreased marginally from 25% in 2021 to 24% in 2022. This decrease was influenced by unprecedented price spikes in Europe and Asia during the year, with prices nearly tripling in Europe and doubling in the Asian LNG spot market. In 2022, there was a 3% decrease in global natural gas demand, falling just below the 4 trillion cubic meters for the first time in 2021. Additionally, its contribution in primary energy experiences a marginal decrease to 24% in 2022, down from 25% in 2021[4].

Global electricity generation increased by 2.3% in 2022which was steady compared to the previous Years's growth rate of 6.2%. Significantly, wind and solar reached a pinnacle, constituting 12% of power generation. Solar energy witnessed a remarkable 25% surge in output, while wind power experienced a growth of 13.5%.

Coal retained its position as the primary fuel for global power generation in 2022, holding steady at around 35.4% of the share, slightly down from 35.8% in 20201. Natural gas-fired power generation also remained stable, maintain a share of around 23%. However, output from nuclear power decreased by 4.4%. In 2022, renewables excluding hydro took on a significant role, fulfilling a substantial 84% of the net electricity demand growth. Concurrently, coal prices reached to record high in 2022, with European prices averaging $ 294/tonne and the Japan CIF spot price averaging $225/tonne, marking a remarkable increase of 145% and 45% respectively compared to the previous year. Despite this increased process, coal consumption continued its upward trajectory, rising by 0.6% from 2021 to reach 161 exajoules (EJ), the highest rise since 2014. The growth was primarily fuelled by increases in China (1%) and India (4%), contributing a combined growth of 1.7 EJ. Furthermore, global coal production experienced a significant increase of over 7% compared to 2021, reaching a record high of 175 EJ. The majority of this increase, over 95%, was attributed to China, India, and Indonesia [5].

The share of renewables comprising solar, wind, geothermal, biomass, and waste, excluding hydro in primary energy consumption reached 7.5%, marking a nearly 1% rise from the previous year. Fossil fuels maintained their stronghold on primary energy consumption, holding steady at 82%.

Complications arises when burning fossil fuels such as coal, coke, petroleum oil etc. generates a substantial of greenhouse gases (GHGs), leading to adverse impact on our environment. Carbon dioxide (CO_2) emissions from energy use, industrial processes, flaring and methane (in CO_2 equivalent terms) continued to increase to 0.8% in 2022 to 39.3 $GtCO_2e$, with emissions from energy use rising 0.9% to 34.4 $GtCO_2e$. Juliet Davenport, President of EI, highlighted, "Despite the notable expansion of wind and solar in the power sector, global energy-related greenhouse gas emissions have once again increased. Our trajectory remains contrary to the goals set by the Paris Agreement." The report thoroughly detailed the impact of human activity on atmospheric CO_2 concentration, elucidating the consequences on carbon storage in land and ocean reservoirs, climate change, and both anthropogenic and natural alterations during the pre-industrial period. If this upward trend persists, surface temperatures are projected to rise by approximately 3.7−4.8 ℃ in the twenty-first century.

1.2 Alternative Solutions

Years ago, Sorensen [6] demonstrated that renewable resources could fulfill all societal energy needs. The defining characteristic of renewable energy resources is their capability for indefinite replenishment. Sun, wind, solar, and biomass energies are a continuous source of energy to the Earth. Renewable energy resources are virtually boundless, replenished through natural processes. Solar energy alone theoretically offers a daily supply sufficient to fulfill humanity's energy needs for an entire year. However, these resources are imperfect due to geographical and temporal variations in accessibility.

We require an alternative source of energy which can consider the concerns related to fossil fuels. According to oxford dictionary the definition of alternative energy is given like this:

Energy fueled into ways that do not use up natural resources or harm the environment [7]. One of the main features of these alternative energies is the usage of the renewable as well as environmentally friendly fuels for different applications. Among different types of alternative energy resources for the replacement of fossil fuels, the encouraging way is the formation of chemical energy through the usage of solar energy which covers the exciting applications like solar cell, photoelectrochemical water splitting, photocatalytic water splitting etc. [8]. In this solar to chemical energy conversion technology, one of the attractive applications is photocatalytic water splitting which utilizes water which is an inexpensive renewable resource to produce hydrogen which is the most promising clean-burning fuel with high energy density (~122 kJ/g) with the help of natural resource sunlight and this is also the least cost-effective process among other solar to chemical energy conversion technology [9][10]. One of the greatest challenges now-a-days is to store these intermittent energies available from renewable resources. Different metal-ion batteries, metal-air batteries, and fuel-cells have caught the interest of most researchers attributable to their diverse possible applications. These are becoming the promising candidates for the energy storage technology. In the next section we will discuss some alternative green and clean energy resources.

1.2.1 Fuel Cells

The fuel cell is able to convert a variety of fuels, including hydrogen, hydrocarbons, etc., directly into electricity. Generally, the efficiency of the fuel cell is high, and a key benefit is that fuel cells are cleaner and quieter than conventional energy sources.

It is an electrochemical device that converts chemical energy into electrical energy and heat without emitting harmful substances. A fuel cell comprises three main components: the anode,

the cathode, and the electrolyte. Fuel (typically hydrogen) is fed from the anode side in an FC. In the presence of catalysis, hydrogen splits into hydrogen ion, H^+ and electron, e^-. These electrons travel through the external circuit to produce electricity. At the cathode, oxygen in the air is reduced to the oxygen ion (O^{2-}) and then transported to the electrolyte via different kinetics. The hydrogen present at the anode oxidizes the fuel, producing water as a byproduct. The basic diagram of the fuel cell is shown in Fig. 1.3. Fuel cells offer noise-free operation and nearly zero emissions of pollutants like CO_2, etc. They can be used in different ways, like small devices e.g. mobile phones, laptop, computers, household, hospitals, power plant, and transportations.

The electrochemical reaction at the cathode and anode of the fuel cell are as follows:

Anode: (electrochemical oxidation) $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (1.1)

Cathode: (electrochemical reduction) $^1/_2\, O_2 + 2e^- \rightarrow O^{2-}$ (1.2)

Overall Reaction: $H_2 + {}^1/_2\, O_2 \rightarrow H_2O$ (1.3)

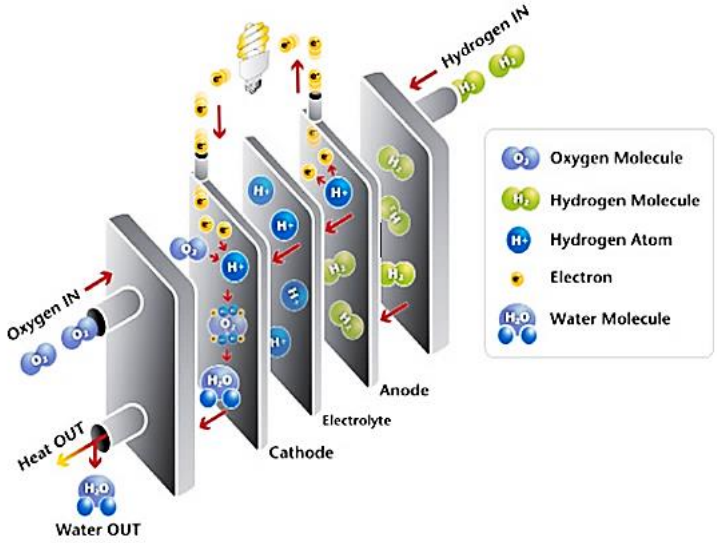

Figure 1.3 Working of a Fuel Cell.

The classification of FCs is primarily based on the electrolyte being utilized and the temperature at which they operate. A list of the most promising type of fuel cells with their characteristics and reactions are depicted in Table 1.1. Each system has its own advantages and disadvantages. Thus, distinct types of fuel cells are used for different applications.

1.2.1.1 Fuel Cell Components

I. Electrolyte

The electrolyte of the FCs must possess sufficient ionic conductivity and a non-porous structure for the mobility of the ions. Yttria stabilized zirconia (YSZ) stands as the most common electrolyte material for the FCs due to its good stability in both reducing and oxidizing atmospheres. There are many literatures available on the other electrolyte materials with conductivities higher than that of YSZ[11]. It should have high porosity and density to prevent gas permeation, matched thermal expansion coefficient with other components of the fuel cell.

Yttria stabilized zirconia (YSZ), Scandia stabilized zirconia, Bi_2O_3 based oxides, Sr & Mg-doped Lanthanum gallate (LSGM), Sm/Gd doped ceria, Lanthanum silicate apatite, Gadolinium doped ceria are severely used electrolyte material for the fuel cell.

II. Anode

The anode must have proper catalytic properties for the electrochemical oxidation of the intended fuel. Unlike the electrolyte, it must have sufficient catalytic activity for the oxidation reaction of hydrogen and adequate porosity to provide gas diffusion to the triple phase boundaries (TPBs) and ensure good electronic and ionic conductivity. It is also known as the fuel cell electrode. The anode role is to oxidize the fuel and provide the sufficient transfer of electrons from the reaction sites to the current collector, along with facilitating the movement of oxygen ions from the electrolyte sites[12]. Ni-stabilized zirconia, Cu-Gadolinium doped ceria, Ni- Gadolinium doped ceria (Ni-GDC), La doped Strontium titanate are few well-known materials.

III. Cathode

It is one of the main components of FCs, where the electrochemical reduction of oxygen takes place at the cathode. This oxygen reduction reaction occurs at the vicinity of the electrolyte/electrode/gas interface or the gas/electrode interfacial areas[13]. The partially reduced oxide ions are then transferred either along the surface pathways or through the bulk to reach the electrode/electrolyte/gas interface. From there, they diffuse through a dense electrolyte to reach the anode. The process of electrochemical reaction occurs at the cathode near triple phase boundaries (TPBs), where the electronic conductor, oxygen ion conductor and the gas phase converge. ORR cannot occur if any one of the three phases is

disconnected[14]. These materials must possess properties like high ionic conductivity, high porosity, high electrochemical activity, and matched thermal expansion coefficient (TEC). The most common feature of cathode materials is their tendency to readily form oxygen adsorption bonds. The important reaction occurring at the cathode is the oxygen adsorption process. It is also known as air electrode material, as air flows from this side[14]. Doped lanthanum cobaltite & manganite, Lanthanum-Barium cobaltite, lanthanum strontium cobalt ferrite (LSCF) are some well-known cathodes material.

Table.1.1 Different types of fuel cells with their characteristics.

Fuel Cell Systems	**Electrolyte**	**Mobile ion**	**Operating Temperature (℃)**	**Fuel Supplied**	**Application/ Efficiency**	**Catalyst**	**Efficiency**
Proton exchange membrane (PEMFC)	Sulfonated PTFE membrane	H^+	30−100	H_2, methanol (DMFC)	• Backup power • Portable power • Transportation • Special vehicles	Pt/C	50-55%
Alkaline (AFC)	Potassium hydroxide	OH^-	50−100	H_2	• Space-vehicles • Military • domestic	Pt,Transition-metal/C	50-55%
Phosphoric acid (PAFC)	Phosphoric acid	H^+	~200	H_2, CO	• Large scale CHP	Pt/C	40-50%
Molten carbonate (MCFC)	Alkali metal carbonate	CO_3^{2-}	~650	H_2, CH_4, natural gas	• Electric utility • Medium to large scale CHP	Nickel and Nickel Oxide	45-50%
Solid oxide (SOFC)	Ceramic	O^{2-}	~500−1000	H_2, CH_4, natural gas	• Auxiliary power • Electric utility • Small to large scale CHP	Pervoksite	45-60%

1.2.2 Batteries

While fuel cells offer efficient energy conversion, metal-air batteries present an alternative with distinct advantages. They boast a compelling combination of affordability, extended shelf life, and an impressive theoretical energy density of 1084 Wh Kg^{-1}[15][16]. It is an electrochemical cell in which pure metal is used as an anode and ambient air as cathode with an electrolyte between the two electrodes. Depending upon the nature of the electrolyte there are two types of the cell system. The cell system that is insensitive to moisture, employs aqueous electrolyte, whereas moisture-sensitive cell systems are employed with organic or aprotic solvents. Based on the working principle, batteries are majorly categorized into two types: rechargeable and non-rechargeable (refer to Fig 1.4).

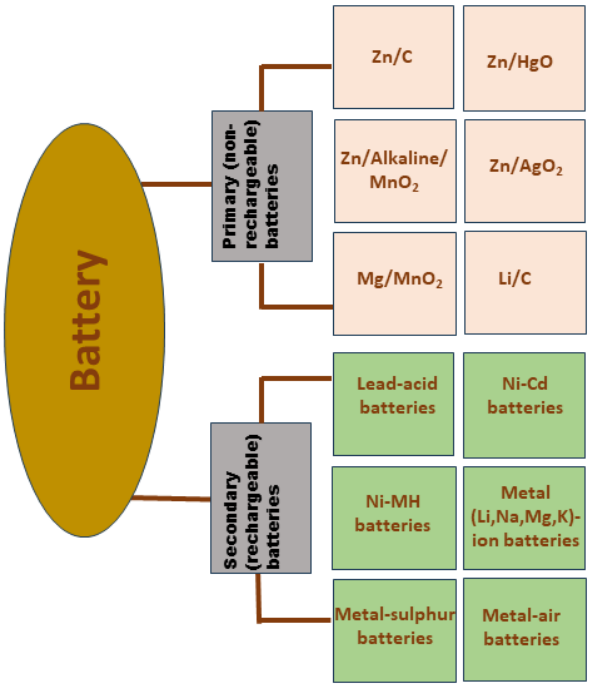

Figure 1.4 Types of primary and secondary batteries.

Primary batteries are typically single-cell, low-cost, portable, and widely used in a variety of household items such as cameras, watches, gadgets, etc. Once drained, they are no longer usable and cannot be recharged. The most common form of the primary battery is zinc/carbon (Zn/C) types which later updated to Zn/alkaline MnO_2 batteries having higher energy density. The other example of primary batteries such as Mg/MnO_2, Li/C, Zn/AgO_2, and Zn/HgO. These often represent a significant danger to the environment due to high operating alkaline conditions and leakage problems[17]. Secondary batteries, on the other hand, are rechargeable and often found in gadgets such as smartphones, computers, and cars. Lead-acid batteries are one of the first technologies in this category. Since they are usually low-cost and can deliver high energies, they are commonly employed in automobiles. However, due to the toxicity of Pb, there is a constant search for a new type of secondary battery. Lithium-ion batteries (LIB) are current state-of-the-art storage technology in rechargeable technologies for most portable electrical and electronic devices. Nevertheless, limited resources led to the development of Na-ion batteries, Mg-ion batteries, and so on. With promising energy densities, metal-air batteries are emerging as a viable alternative to metal ion batteries. Aqueous cell systems have used a variety of metals, including Ca, Al, Fe, Cd, and Zn while in aprotic electrolytes, Li, K, Na, and Mg are employed as the anode. Because of its higher corrosion resistance in alkaline electrolytes, Zn was determined to be the most appropriate metal for aqueous cell systems [18]. The Metal-air batteries operate with the charging and discharging phenomenon. In discharging process, the metal anode (M) gets oxidized to release metal ions (Mn^{+}) and electrons. The produced electrons move through an external circuit towards the cathode where oxygen reduction reaction (ORR) occurs from air to produce hydroxyl ions (OH^{-}) (eq. 1.4). These hydroxyl ions pass through the separator and electrolyte where they react to produce Zn (OH^{4-})

(eq. 1.5) which further decomposes to give metal oxides (eq. 1.6). During charging of the air batteries, the process is reversed oxygen evolution reaction (OER) takes place at the air electrode and oxygen is evolved from the water molecules and metal oxide at anode reduced to solid metal.

$$O_2 + 2H_2O + 4e^- \leftrightarrow OH^- \quad (1.4)$$

$$Zn + 4OH^- \leftrightarrow Zn(OH)^{4-} + 2e^- \quad (1.5)$$

$$Zn(OH)^{4-} \leftrightarrow ZnO + H_2O + +2OH^- \quad (1.6)$$

$$Zn + 2OH^- \leftrightarrow ZnO + H_2O + 2e^- \quad (1.7)$$

1.2.3 Water Splitting

The decomposition of water by any method leads to the production of hydrogen and oxygen i.e. splitting of water into its components. The hydrogen production from electrochemical methods is one promising pathway as it comes most cleanly. Being a low-cost method as compared to other fuel energy systems, it explores the carbon-neutral method of hydrogen production by renewable and environment-friendly energy sources[19]. Thus, it provides a suitable and ideal pathway to hydrogen and oxygen production. Encouraged by solar-driven photosynthesis that generates energy from sunlight and releases oxygen molecules, water electrolysis is carried out by applying a certain potential to split water into hydrogen and oxygen molecules (refer to Fig 1.5). By connecting these small units in a parallel manner, a considerable amount of hydrogen and oxygen can be generated and the emitted H_2 can be directly supplied in fuel cells e.g. PEMFCs as a fuel to generate energy.

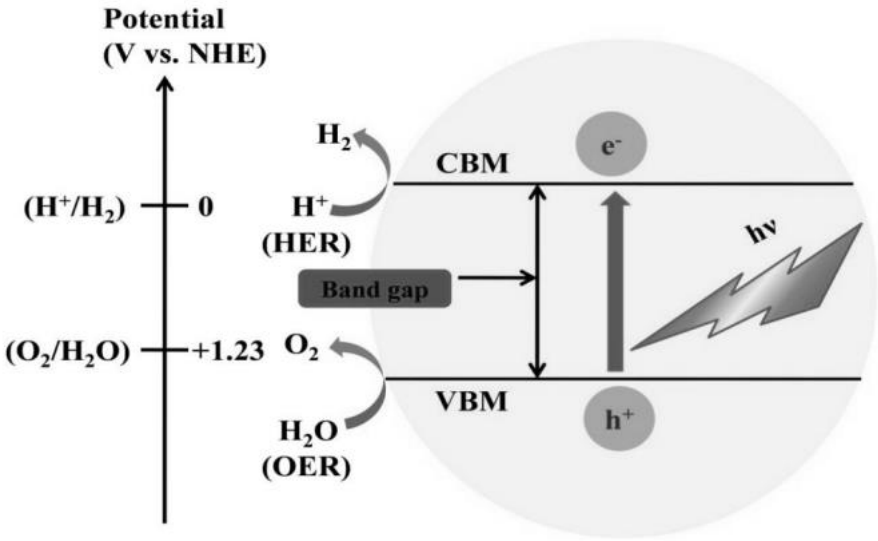

Figure 1.5 Schematic illustration of water splitting.

There are two half-cell reactions in the electrochemical water splitting, namely hydrogen evolution reaction (HER) which occurs at the cathode and oxygen evolution reaction (OER) at the anode. Both the reaction requires certain overpotentials to occur. Due to sluggish OER kinetics, the reaction proceeds at higher potentials than the thermodynamic values (+1.23 V vs. RHE), while high current density for HER can be achieved at lower overpotentials. The quest for a suitable material capable of efficiently splitting water to generate hydrogen is increasingly vital. This endeavor seeks to harness clean and renewable energy while adhering to rigorous environmental standards, devoid of any pollution or unwanted byproducts.

These applications convert and store renewable energy in the form of chemical energy. The aforementioned sustainable energy applications involve key reactions i.e., oxygen evolution reactions (OER), oxygen reduction reactions (ORR), and hydrogen evolution reactions (HER). The significance of these reactions will be thoroughly discussed here.

1.3 Importance of Electrochemical Reaction

The electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are vital aspects of the various mentioned renewable energy platforms, particularly for fuel cells and rechargeable air batteries. As a result, the progress of these renewable technologies is largely dependent on electrochemistry. To make fuel cells and metal-air batteries usable and practical, ORR/OER-active catalysts must be employed to accelerate the electrochemical process. The ORR and OER are, however a set of sluggish reactions which are typically catalyzed by noble metals as efficient catalysts. Currently, platinum is the best-known catalyst for ORR, however, its high cost and scarcity, and poor methanol tolerance hindered its commercial use for large-scale applications[20]. Despite recent advances in lowering the cost and increasing the efficiency of fuel cells, basic research to produce cost-effective catalysts that can survive severe operating conditions and have high catalytic activity toward ORR is still needed. All of the previously discussed systems operate on the same principle where oxygen is reduced at the cathode as the associated half-cell reaction by the electrons generated from the anode. Provided that the charging cycle of Zn–air batteries are powered by OER kinetics, while ORR catalyzes the discharge mechanism on the air-cathode. Similar to ORR, catalytic water splitting is entirely restricted by a sluggish OER mechanism at the anode and requires higher overpotentials than thermodynamic potential (+1.23 V) to overcome the reaction barrier. To date, ruthenium and iridium oxides (IrO_2 and RuO_2) have been widely utilized catalysts for OER due to their impressive OER. Designing efficient, cost-effective, and stable OER catalysts present a tough challenge due to their high cost, limited availability, and low long term stability [21]. The detailed study of catalysts and various reaction mechanisms will be discussed in the next section.

1.3.1 Catalysts

Catalysis mainly enhances the electrochemical reaction rate without being consumed. Introducing a custom designed material at the electrode surface can provide a new reaction pathway, thereby increasing the reaction rate. In the modified electrodes, catalysis occurs at the electrode-electrolyte interface[22][23]. In the late eighties, the development of the new hybrid materials made electrocatalysis an integral part of electrochemistry. Construction of an effective electrocatalytic platform depends on concepts such as controlled surface roughness, defined catalytic sites, and understanding the mechanism of electrochemical reactions. Catalysis is defined as the electron transfer reaction occurring at the electrode-electrolyte interface. When mediated by an immobilized redox couple, it reduces the overpotential as compared to a bare electrode and accelerates the given electrochemical process[24][25]. The schematic representation of catalytic processes at the electrode surface is shown in Fig 1.6.

There are two types of catalysis processes:

1. **Homogeneous catalysis**: In this type, both the substrate and the catalyst are present in the electrolytic solution. The catalytic reaction occurs within the solution, and catalyst are free to diffuse in the solution[26]. Metal coordination complexes or bio enzyme are few examples of it.
2. **Heterogeneous catalysis:** Unlike homogeneous catalysis, this process involves the adsorption of the catalyst onto the electrode surface to help the electron transport. During this process, the substrate diffuses towards the electrode surface from the solution, where the electron is the reason behind the chemical reaction between the substrate and catalyst. After the electrochemical reaction, the formed product diffuses away from the electrode

surface [25]. In this scenario, the catalyst is immobilized and the products diffuse into the bulk solution[27][28]. Platinum surface or metal nanoparticles are few examples of it.

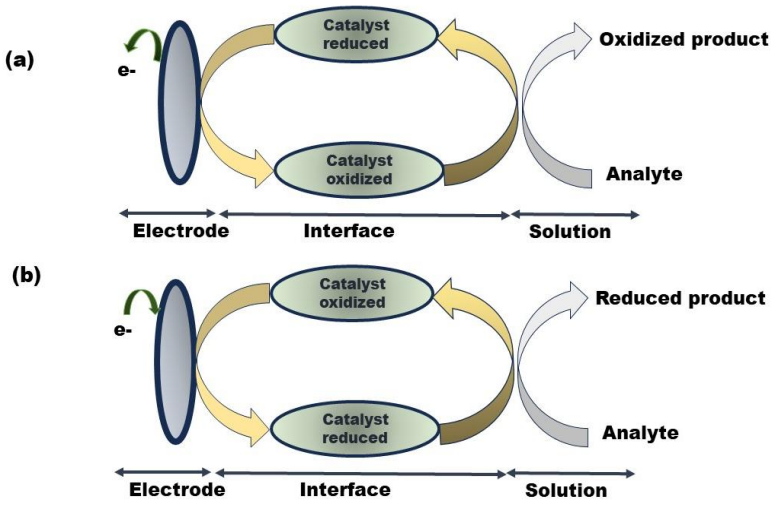

Figure 1.6 Schematic of catalytic process at the electrode surface.

Catalysis process is the backbone of several electrochemical reaction-like sensors, batteries, and fuel cells[29]. The catalytic activity is determined by the d band of transition metals and the partial substitution occurring at the cation site, leading to defect formation that directly influences catalytic activity [31]. Additionally, the ionic conductivity of the electrolyte and rates of gas transport through the porous electrode contribute significantly to the overall performance [36].

1.3.2 Reaction Kinetics and Mechanism

There are several kinetics involved in the chemical reactions take place at the electrode end of a fuel cell. These kinetics are discussed in this section and listed below-

1. Oxygen Evolution reaction (OER)

2. Oxygen Reduction Reaction (ORR)
3. Hydrogen Reduction reaction (HER)

1.3.2.1 Oxygen Evolution reaction (OER)

OER is a key reaction upon which various advanced electrochemical storage and conversion technologies are based. It occurs at the anode of the fuel cell. It is complex mechanism due to the multiple electron transfer process, requiring a four-electron process. In comparison to acidic media, alkaline media offer a relatively milder corrosive environment, which is why catalysts are more stable in alkaline media[30]. The OER mechanism in acidic and alkaline medium shown in Fig. 1.7.

Equation 1.8 and 1.9 represents the overall reaction involved in different media[31] –

In acidic condition,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^0 = 1.23\ RHE \qquad (1.8)$$

In Alkaline condition,

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad E^0 = -0.40\ RHE \qquad (1.9)$$

Metal oxides and hydroxides are widely explored catalyst for OER. Oxides-based catalysts are considerably more stable in the alkaline media, although the reactions are kinetically slow. Catalysts based on the oxides are categorized into noble metal-based and transition metal-based catalyst[32]. This mechanism involves the formation of oxides layers on the catalyst surface, even when noble materials are employed. This indicates that oxides, hydroxides and layered double hydroxides are extensively explored materials for OER applications.

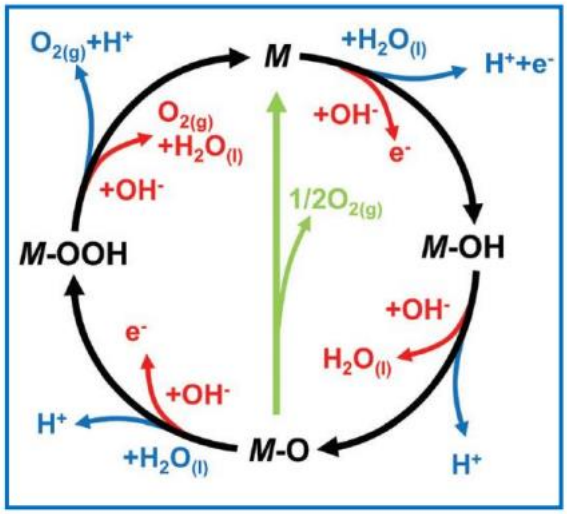

Figure 1.7 Reaction mechanism for Oxygen Evolution Reaction (OER) mechanisms in both alkaline (red) and acidic (blue) media[30].

IrO_2 and RuO_2 are widely used oxides for the OER, but they are highly unstable in both the electrolyte. Therefore, transition metal-based oxides are potential alternative for the catalyst. These are classified into the spinels, and perovskites. They are stable in alkaline solution and have multiple oxidation states, such as tetrahedral and octahedral sites, for the fastest and tunable OER behavior. Additionally, they are affordable, widely available and offer low corrosion resistance.

The initial catalyst based on raw transition metals include Cobalt (Co), Manganese (Mn), Nickel (Ni), and Iron (Fe).

1.3.2.2 Oxygen Reduction Reaction (ORR)

It is the key reaction for fuel cells and the metal-air batteries occurring at the cathode of the fuel cell. Unlike OER, they proceed in two different path reactions –

1. Two-electron transfer process (forming hydrogen peroxide)
2. Four-electron transfer process (forming water)

The four-electron path reaction has been the most preferred pathway because it doesn't produce the peroxide species, which causes electrode degradation mechanisms[33][34].

Two-electron pathway proceeds through an associative mechanism, which involves the formation of hydrogen peroxide ions before the complete reduction of the O_2 molecule. However, the four-electron process follows a dissociative mechanism, involving the separation of O=O bonds and the production of OH^- ions in an alkaline medium. The reaction mechanism shown in Fig. 1.8.

The reaction mechanism of ORR in different media is given below in the equations –

In acidic medium,

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.23\ V_{RHE} \qquad (1.10)$$

$$O_2 + 2H^+ + 2e^- \rightarrow 2H_2O_2 \qquad E^0 = 0.70\ V_{RHE} \qquad (1.11)$$

In alkaline medium,

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^0 = 1.23\ V_{RHE} \qquad (1.12)$$

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \qquad E^0 = 0.70\ V_{RHE} \qquad (1.13)$$

The kinetic impact on reaction efficiency is very evident for both the two-electron and four-electron ORR processes, as the accessibility of O_2 and H_2O to the active site plays an important role.

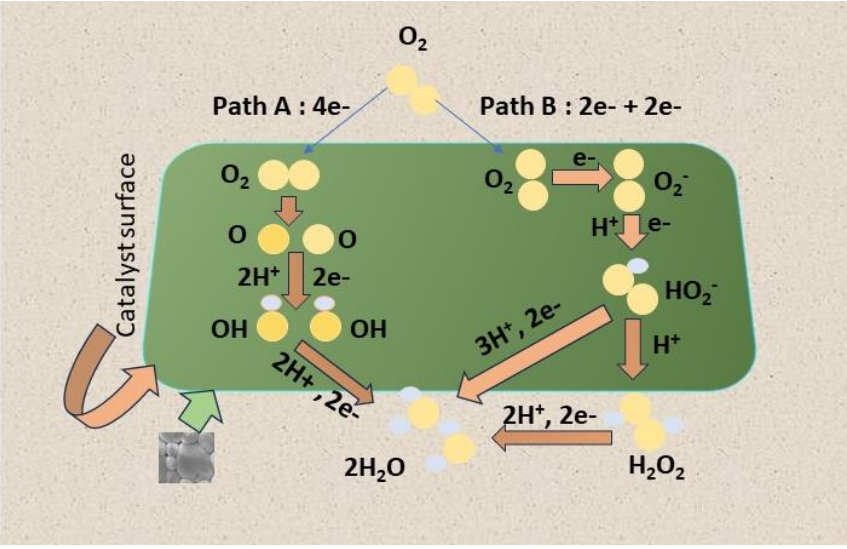

Figure 1.8 Reaction mechanism for ORR.

1.3.2.3 Hydrogen Evolution Reaction (HER)

This reaction occurs at the cathode of the fuel cell and is also used in the water splitting devices. It involves a two-electron transfer process, which is why it's less sluggish compared to the Oxygen Evolution Reaction (OER)[30].

The overall reaction is presented in the equation[31] –

In acidic media-

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = 0\ V_{RHE} \qquad (1.14)$$

In alkaline media ,

$$2H_2O + 2e^- \rightarrow H_2 + 4OH^- \qquad E^0 = 0\ V_{RHE} \qquad (1.15)$$

In alkaline medium, HER involves a two-step process known as the Volmer step in which water dissociates (equation 1.16), and Heyrovsky step, where desorption of adsorbed hydrogen

species occurs (equation 1.17), or the Tafel step, where the recombination of adsorbed hydrogen species occurs according to equation 1.18.

These equations are given as follows:

Volmer step: $$H_2O + e^- \rightarrow H^* + 4OH^- \quad (1.16)$$

Heyrovsky step: $$H^* + H_2O + e^- \rightarrow H_2 + OH^- \quad (1.17)$$

Tafel step: $$2H^* \rightarrow H_2 \quad (1.18)$$

Here, HER occurs via two path reaction: either it follows the Volmer-Heyrovsky or Volmer-Tafel pathway during the reaction at the cathode end of the fuel cell[31]. "*" denotes the catalytic sites in all cases.

Platinum (Pt) is a potential catalyst for HER, but its utilization is limited for large-scale application. Therefore, alternatives exist in the form of transition metals, alloys, and some transition metal sulphides or carbides.

1.3.3 Bifunctional/Multifunctional Catalysts

As previously discussed, various types of reaction mechanisms, such as OER, ORR, and HER, play a crucial role in the operation of fuel cells, metal-air batteries. OER and ORR are fundamental reactions in fuel cells, while HER and OER occur in water splitting or production processes. Thus, material that are active in catalyzing ORR and OER or HER and OER are known as bifunctional catalysts, and the corresponding behavior is known as the bifunctional behavior.

Extensive studies focus on investigating bi-functional oxygen catalysts within alkaline electrolytes, such as potassium hydroxide (KOH) and sodium hydroxide (NaOH). These electrolytes allows us to substitute the of expensive precious metal catalysts, like platinum and

iridium on carbon, with cheaper metal or metal-free catalysts. This is possible due to their less corrosive nature when compared to acidic electrolytes. However, studies in the neutral medium are comparatively few. In this thesis, the discussion of the materials used is available for all three media: acidic, alkaline, neutral.

Bi-functional materials can be divided into three major groups-

1. **Non-precious metal catalysts**- oxides (spinels, perovskites etc.), sulfides, nitrides etc. This category includes a considerable number of published reports, each demonstrate sufficiently high rates for bi-functional oxygen reactions. Other compounds like nitrides and sulfides are also exhibit the bi-functional activity[32][31].

2. **Metal-free carbons-** Hetero-atom doped graphitized carbons like graphene nanosheets and carbon nanotubes belong to this category. Due to the presence of electronic structure and defects in the carbon species these shows the improved catalytic activity and high ORR process. In this the OER study is still in process. They are extensively studied for the ORR for fuel cell applications. Transition metal-N/C complexes, graphene-based materials, carbon nanotubes-based materials are lying in this category.

3. **Hybrids – consist of both metal oxide and carbon-** The combination of these two materials, metal oxide and carbon, for the formation of hybrid bi-functional catalysts is explored to enhance OER and ORR activities. To improve the activity of ORR, the active carbon act as the oxygen electrocatalyst while metal oxides facilitate OER.

   In addition to this discussion, other parameters are also taken into account for the bifunctional catalyst, such as tolerance for a broad pH range, ability to operate at moderate overpotentials with high current density, long-term stability, and cost-

effective with simple preparation. Selecting the suitable catalyst for a specific application will be crucial in exploring their potential as bi-functional catalysts across a wide pH range[35].

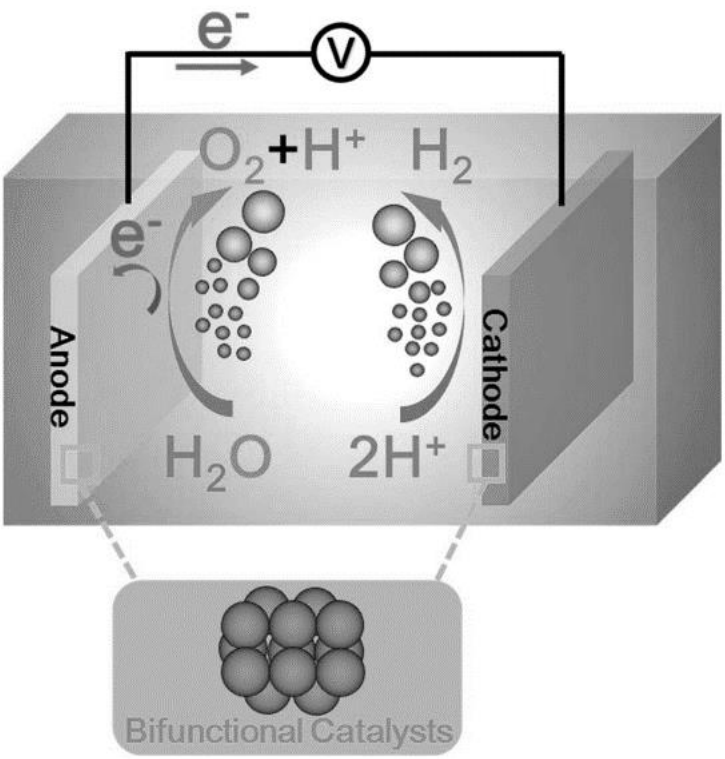

Figure 1.9 Schematics of occurring reaction on bifunctional catalyst[31].

In this thesis, bifunctional activity is observed in perovskites oxides, which also acts as electrode materials for fuel cell applications. The activities were studied mainly in two different electrolytes: acidic and alkaline. In this discussion, Na_2SO_4 was also considered as a neutral electrolyte to evaluate the performance of materials and compare them with the other two electrolytes.

Perovskite oxide are widely recognized forms of bi-functionally active oxygen catalysts. Their flexible compositions, mainly determined by the transition metal ions they contain, contribute significantly to their enhanced performance. These compositions enable the formation of redox

couples and defects through oxygen vacancy or excess, resulting in excellent mobility of oxygen anion. The active site for the electrocatalytic oxygen reactions on perovskite oxide surfaces is generally associated with B-site cation. There are many varieties of perovskite are available, all of which exhibit bifunctional activities. For example- BaTiO, LaFeO, LaCoO, LaMnO, LaNiMnO, LaNiFeO, LaCaCoO, LaSrMnO [26].

1.4 Perovskites for Energy Application

This section describes the importance of Fe-based perovskite that have been used in previous studies. Subsequently, $LaFeO_3$ will be introduced, and ongoing investigations and advancements related to it will be discussed.

1.4.1 Perovskite Oxide

The Perovskite structure has successfully incorporated a wide variety of compositions, encompassing nearly all elements found in the periodic table. It is a three- dimensional array of corner sharing octahedral, using a general formula ABO_3 where A and B are metal cations and O is the charge-balancing anion, have a wide range of potential applications due to their highly tunable and scalable properties. The properties of perovskite oxides can be varied for the desired application by controlling the A- and B- site cations. The Fig 1.10 illustrates the general structure of a cubic perovskite oxide.

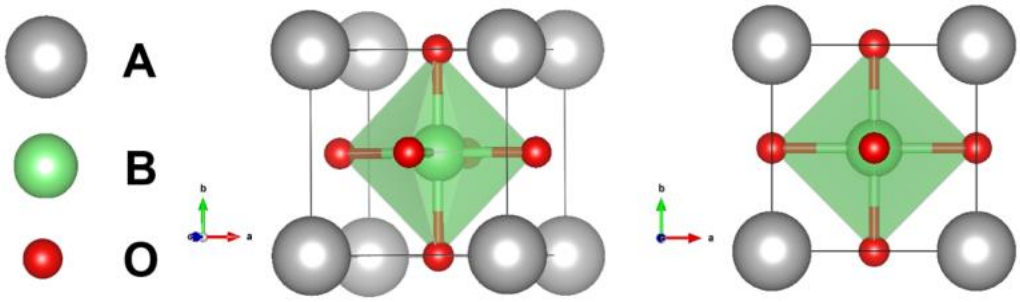

Figure 1.10 Structure of perovskite oxide.

Synthesizing the perovskite structure with different combinations of elements is quite simpler compared to pyrochlore and perovskite – related compounds. The ease of synthesis can be attributed to several factors:

- Two different sizes of ions can accommodate A and B sites.
- Structural distortions of the ideal cubic perovskite structure facilitate further flexibility of accommodation cations of different sizes.
- These structures are notably tolerant for vacancy formation and inter-growths in atomic scale.

As illustrated in Fig. 1.10, an ideal perovskite has a cubic structure with 12 coordinated large cations of A and 6 coordinated small cations of B. The total charge on A and B (+6) can be achieved by a variety of combinations such as 1+5, 2+4, 3+3. The cubic structure shows that the BO_6 octahedra form a corner-shared network, with the voids filled by cation A. However, the cubic structure often distorts to rhombohedral, orthorhombic, monoclinic, or tetragonal symmetry due to the tilting and stretching of the BO_6 octahedra.

The Goldschmidt tolerance factor gives the degree of distortions in the ABO_3 perovskite and can be given as:

$$t = \frac{(r_A + r_0)}{\sqrt{2}(r_B + r_0)} \quad (1.19)$$

where r_A, r_B, and r_O, correspond to the ionic radii of the cation A, cation B, and oxygen respectively. The value of t is used to qualitatively determine the stability of perovskites. For t between 0.9 to 1.0, it represents the ideal case of the cubic structure, while t greater than unity indicates a hexagonal perovskite. Similar results discussed in Table 1.2. A decrease in A or increase in B cations leads to a lowered tolerance factor, resulting in cation displacement and tilting of corner-sharing BO_6 octahedra towards an orthorhombic symmetry.

Table 1.2 Structural Predictions for the Goldschmidt tolerance factor

Tolerance factor (t)	**Explanation**	**Structure**
>1	A-site too large or B-site too small	Hexagonal/Tetragonal
1	Optimized A-B size ratio	Cubic
0.71-0.99	A-site too small/B-site too large	Orthorhombic/Rhombohedral/ Monoclinic

Most of the perovskite compounds exhibit good electrical resistivity, therefore they can be classified as insulators, semiconductors, supercapacitors and ionic conductors [36]. Perovskite-based oxides exhibit excellent thermal and mechanical stability. They are mixed ionic-electronic conductors, which reduce the polarization resistance occurring at the electrode/electrolyte interface. Also, they possess improved ionic and electronic conductivity with good catalytic activity after tunable doping at the A and B site of the structure. Different materials used, consist the alkaline or rare earth cations such as La, Sr, Ca, and Ba at A-site, while reducible transition metals like Fe, Co, Ni, and Ti are used at the B-site. The B-site provides the redox mechanism. In order to improve the catalytic activity, catalytic particles are

doped at the B-site of the perovskite structure. Conventionally, the B-sites within the perovskite lattice consist of relatively small cations arranged within oxygen octahedra, while at the A-sites, larger cations are present, forming a twelve-fold coordination with oxygen. Some well-known perovskite is listed in the Table 1.3.

Table 1.3 List of well-known perovskites.

Insulating	**Metallic**	**Magnetic**
$SrTiO_3$	$SrNbO_3$	$LaCrO_3$
$BaTiO_3$	$LaTiO_3$	$CaMnO_3$
$LiNbO_3$	ReO_3	$LaMnO_3$
$NaTiO_3$	$KMoO_3$	$LaFeO_3$
$KTaO_3$	$NaWO_3$	$LaCoO_3$

1.4.1.1 Applications of Perovskite

Perovskites have distinct applications in electronics, refractories, and ceramics. Table 1.4 outlines the applications of frequently studied perovskites. The utilization of perovskite devices primarily depends on factors such as specific surface area, surface morphology, crystallite structure, particle size, lattice plane, and porous structure[37].

Table 1.4 Applications of frequently studied perovskites.

Perovskites (ABO_3)	
Compounds	**Applications**
$LaCrO_3$	Metallic conductor
$BaTiO_3$	Multilayer Capacitor
$BaZrO_3$	Thick film resistor
$LaFeO_3$	Photocatalyst, electrode material
$LaCoO_3$	Refractory electrode
$LiNbO_3$	Switch

The perovskite oxides are extensively studied due to their intruding and rare physical characteristics, ferromagnetism, insulating, semiconducting, superconducting, highly photochemical and electro-chemical active materials to be used as bi-functional electrocatalyst, photocatalyst, energy storage and electrochemical energy applications. Conventionally, the physical properties such as, structural, optical, dielectric, and magnetic properties of these perovskites depend on the selection of elements A, B and doping element either A or B site or by leaving from the ideal stoichiometry. The remarkable versatility displayed by transition metal perovskites has positioned perovskite at the forefront of materials science research, symbolizing one of the most pivotal and dynamic areas of exploration within the field.

1.4.1.2 Catalytic Activity of Perovskite

The perovskite oxides have been also used as catalysts due to their characteristics, including high thermal stability, cations exchangeability, and the presence of oxygen vacancies. The catalytic performance depends on the presence of surface transition metal ions with an oxidation state different from 3+, thereby emphasizing their non stoichiometric nature. The investigation of surface properties, specifically in terms of degree of surface nonstoichiometric

becomes crucial for understanding catalytic phenomenon. The activity is based on a significant ratio of surface activity to oxygen reduction, a consequence of the abundant oxygen vacancies governed by the principle of electroneutrality[38].

The most of the elements from the periodic table exhibit stability within a perovskite structure. Partial substitution can be applicable without disrupting the lattice structure, with variable oxidation state of cations and enhancing the presence of oxygen vacancies. Consequently, these oxides are of great interest in scientific research due to their adaptability as combustion catalysts. They can undergo significant substitutions in one or both cationic sites while maintaining the original crystal structures[39][40]. Oxides with specific morphologies shows unique characteristics in both the bulk and surface components. Among different types of alkaline earth substituted perovskites, lanthanum perovskites such as $LaBO_3$ (B = Mn, Ni, Co, Fe, Cr) compounds have been used as catalysts. The stabilities of these catalysts depend on the B atom, varying in the order, $LaCrO_3 > LaFeO_3 > LaMnO_3 > LaCoO_3 > LaNiO_3$ [41].

Oxygen species play an important role in catalysis with adsorbed oxygen facilitating superficial catalysis, while lattice oxygen contributes towards interfacial catalysis. ABO_3 tends to catalyze the superficial reaction, while the distinction between superficial and interfacial catalysis is dependent on the mobility of oxide ions within perovskites. When oxide ions are mobile enough then those ions in subsurface layers will participate in interfacial catalysis. Conversely, the presence of immobile oxide ions favors a superficial mechanism. This undergoes the importance of defect structures in perovskite catalysis. Superficial catalysis occurs when the catalyst's outermost surface acts as a fixed template, providing atomic orbitals of suitable symmetry and energy for the adsorption and intramolecular reactions of the reactants involved. On the other hand, Interfacial catalysis occurs at relatively higher

temperatures, contingent upon the combination of the reduction-oxidation cycle of the catalysts [42].

1.4.1.3 Mixed Ionic Electronic Conductors

Currently, mixed ionic-electronic conductors (MIECs) represent a class of materials known for their high ionic and electronic conductivity properties. They have attracted great interest in electrode applications due to their ability to enhance ionic and electronic conductivity, expanding the scope for oxygen reduction reactions. With an increased surface area, the reaction rate also increases, consequently enhancing the overall activity of the fuel cell.

Fig. 1.11 illustrates the difference between the active sites involved in the oxygen reduction reaction within a mixed ionic-electronic conductor and a purely electronic conductor.

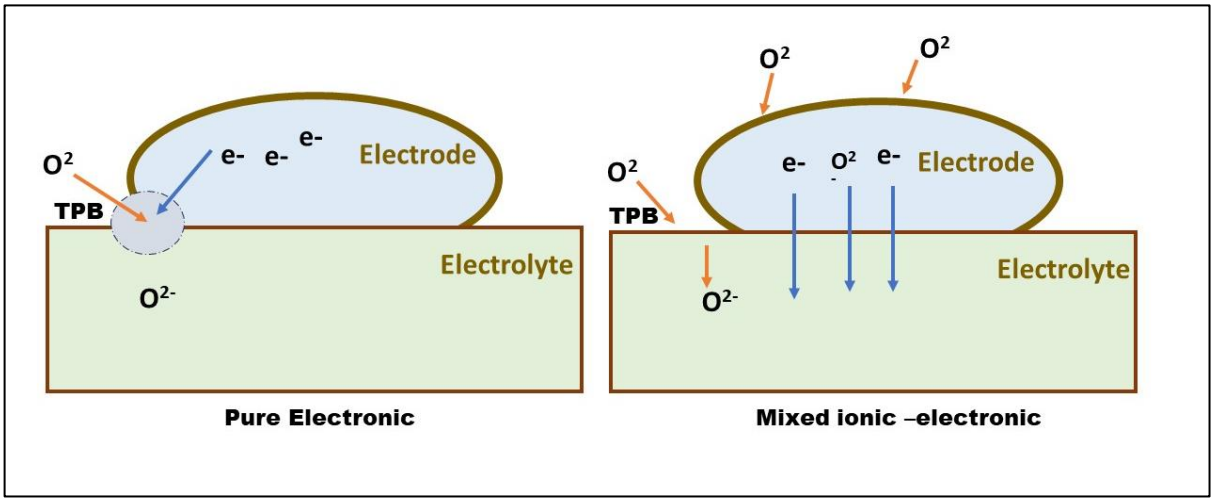

Figure 1.11 Difference between the active site involved in pure electronic and mixed ionic electronic conductor.

Perovskite oxides, such as $La_{1-x}Sr_xCoO_3$, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, have used as the basis for numerous Mixed Ionic-Electronic Conducting (MIEC) electrode materials. The performance of these mixed-conducting electrode is influenced by various

factors, including the electronic conductivity of the electrocatalyst and the catalytic activities occurring at the triple phase boundary within the electrodes in the fuel cells (FCs). There has been an increasing focus on these materials due to their desirable attributes such as low warm-gas emissions, high fuel-to-electricity conversion efficiency, surface properties, compactness, and good fuel flexibility.

1.4.1.4 Magnetite

Magnetite-based Oxides have either oxygen-deficient or excess non-stoichiometry. These oxygen non-stoichiometry and defects shows a significant change in the electronic and ionic properties of the materials. Lanthanum magnetite oxides are the most studied material with formula $Ln_{1-x}A_xMnO_{3-\delta}$, where A is a divalent cation. In literature, Strontium (Sr) is commonly used as a dopant for Lanthanum magnetite due to identical size matches with lanthanum[46][47] . Doping of Sr enriches the electron-hole concentration, which results in higher conductivity. However, the conductivity of Lanthanum magnetite for the electrode material lies between 200 S/cm to 300 S/cm[48][49] and the electrical properties are not reliable for the lower temperature. Numerous of work in Lanthanum magnetite is focused on the doping of Sr at A-site. However, Calcium (Ca) doped Magnetite has also displayed good performance as electrode materials. As for the B-site doping, Scandium (Sc) is a favorite choice. The doping of Sc introduced the nonstoichiometric defect in the perovskite lattice of lanthanum magnetite, which increased the oxygen ion mobility. However, the high cost of Sc poses a challenge.

$La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) is a traditional electrode material used in different energy application such as fuel cell and batteries. These operates at temperatures around 800 ℃ to 1000 ℃ [50]. It exhibits high electrochemical activity in oxygen reduction reactions along with strong

thermal and chemical stability. It also possesses good compatibility with common electrolytes, such as strontium-doped yttria zirconia (YSZ) and gadolinium-doped ceria (GDC), at operating temperatures[51]. The electrical conductivity and catalytic activity increased upon introducing Sr at the A-site of $LaMnO_3$[52]. The presence of Sr2+ leads to a charge imbalance, compensated by forming a hole on the B-site. The observed conductivity increases as the concentration of holes increases due to Sr doping. However, this increase in Sr content also leads to a higher formation of $SrZrO_3$ at the interface of LSM with YSZ[53]. $SrZrO_3$ is a poor conductor, limiting the reaction area of the oxygen reduction reaction and its activity, which affects the efficiency of the FC.

These materials are also incompatible with widely used interconnect materials like stainless steel, which contains Chromium (Cr). These Cr species interact with the LSM surface and decrease the activity of the FC[13].

These challenges outline the need for alternative materials to replace LSM for electrode applications. The need for materials that exhibit both ionic and electronic conductivity has led to an interest in mixed ionic-electronic conductors (MIECs). These materials exhibit both properties without the processing complexities associated with composite materials. Moreover, cobaltite-based $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), a promising MIEC material, has shown resistance to poisoning from Cr species compared to LSM. This characteristic has increased interest in LSCF as a potential alternative material[54], which we will discuss in the next section.

1.4.1.5 Cobaltite

In comparison to other materials used for the energy application Cobalt-based materials exhibit higher electronic and ionic conductivity. Introduction of Strontium (Sr) into $La_{1-x}Sr_xCoO_3$

(LCO) increases its oxygen diffusivity and promotes efficient dissociation oxygen molecule, thereby emphasizing its electrode activity. However, a large amount of cobalt increases the thermal expansion coefficient (TEC) value due to the formation of oxygen vacancy. Also, doping of Copper (Cu) in the Cobalt (Co) site is expected to increase the catalytic activity and ionic conductivity. Although, the conductivity of Cu-doped Lanthanum cobaltite (LCO) is less than LCO [55]. Manganese (Mn) doping on B-site along with the Sr doping on A-site also lowers the electrode overpotential.

Strontium (Sr) at A-site and Cobalt (Co) at B-site substituted $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) is a doubly doped perovskite oxide material with high electronic and ionic conductivity. It has high catalytic activity and a low thermal expansion coefficient[56]. With an increase in the Sr content on the A-site, there is an increase in the oxygen non-stoichiometry and ionic conductivities[57]. After an inevitable increase in Sr (x=0.5), there is a subsequent decrease in conductivity. Additionally, the thermal expansion coefficient (TEC) of the material rises with higher strontium (Sr) content, making it less compatible with conventional electrolyte materials[57][58]. Cobalt (Co) at B-site is responsible for the catalytic activity and stability of the material. A higher proportion of Co enhances the activity in the oxygen reduction reaction. However, TEC of the material increases with the increase of Co content, and material's stability decreases in oxidizing atmospheres[57]. In reaction with the common electrolyte YSZ, they form insulating layers of $La_2Zr_2O_2$ or $SrZrO_3$, which significantly reduces the activity of the electrode [11][59]. However, other electrolytes, like GDC or a GDC layer between electrode and electrolyte, enhances their performance[60]. Other potential issues include strontium accumulation on the electrolyte surface, sulphur poisoning, and coarsening of the LSCF micro-structure[61][56].

1.4.1.6 Ferrites

Ferrites are the significant category of ceramic oxides in magnetic materials, which exhibit insulating and conducting properties with larger number of applications in vast fields. Ferrites are categorized in cubic or spinel ferrite, garnet ferrite, hexagonal ferrite and ortho ferrite form. They are generally presented with the formula $M^{2+}OFe^{2+}O_3$ where M is a divalent metal ion that may or may not be magnetic in nature. The structure of ferrite is based on naturally occurring spinel $MgO.Al_2O_3$. The spinel structures of ferrite occur in two forms i.e. normal and inverse. The normal spinel possesses two sub-lattices A and B. Metal ions on A sub-lattices is surrounded by four O^{2-} ions on tetrahedral coordinates while the B sub-lattices are surrounded by six O^{2-} in octahedral co-ordinate[62][63].

Ferrites are highly prized for their excellent properties, such as electrical resistivity, thermal stability, permittivity, high electrical and magnetic properties, low dielectric loss, and eddy current. These characteristics make ferrites indispensable in a wide range of applications, including as electrodes for fuel cell, batteries, magnetic sensors, storage materials, as adsorbents in waste water treatment, and in the photocatalysis. The physical properties of ferrites are delicate to several factors; likely, preparation methods and conditions, nature of substituent[64]. A slight alteration in these factors may lead to a modification in the properties of ferrite.

The main motivation of the extensive study of these ferrites was the requisite combination of suitable properties to develop a material, which could show superior electrical, electrochemical, and micro structural properties. Ferrites, which possess a wide range of these electrical, magnetic and micro structural properties, are the most suitable materials for such a requirement and hence find a large number of applications in electronics, energy conversion

and storage applications. The crystallography, electrical and electrochemical properties of ferrites depend upon the A-site and B-site substitution during the sample's preparation. These properties are also affected by different synthesis method. Ferrites-materials have been the subject of extensive research for their valuable electromagnetic properties, making them suitable for numerous applications [65][66].

Ferrites, while considered venerable materials, continue to maintain their relevance and attractive in the research field. This enduring interest is attributed to their versatile applications and dynamic range of magnetic, optical, electrical and electrochemical properties. Examining prior research conducted by various research groups is crucial to gain a comprehensive understanding of the materials discussed in this thesis. This review provides valuable insights into the perspectives surrounding the issues addressed in the research.

1.5 Background For Proposed Work (Motivation)

1.5.1 Why Fe-based Perovskites?

Fe-based perovskite materials play a crucial role in comprehending how crystallographic defects impact their properties. Due to their excellent material stability, nonstoichiometric properties, and good phase stability, these are used as oxygen catalyst. In recent years, there has been significant research focus on mixed oxides containing iron (Fe) with a perovskite structure, denoted as A-FeO_3, where A = Mn, Co, or La. The objective of research is to create catalysts that can replace metals and function as catalysts for the environmental purification. The valence states of Fe in perovskites are important for understanding defects and have a considerable impact on mobility and electrical conductivity[67].

Marezio and Dernier elucidated the temperature and doping-dependent alterations in the crystal structure of $LaFeO_3$, an Fe-based perovskite[68]. Kotomin and his colleagues discovered that despite $SrFeO_3$ and $CaFeO_3$ being isoelectronic species, variations in their structural geometry arise from differences in their respective ionic radii[69]. Maity et al. employed the sol-gel technique to fabricate $GdFeO_3$ and Mn-doped $GdFeO_3$. In both cases, the orthorhombic phase of $GdFeO_3$ with the Pbnm space group was observed. Substituting 30 percent of Fe with Mn retains the O-type orthorhombic phase, characterized by reduced unit volume and enhanced photocatalytic activity[70]. Fe-based perovskite presents a range of intriguing characteristics like ferromagnetic observed in $BaFeO_3$, along with enhanced ferromagnetism in A-FeO_3 compounds (where A = Ba, Ca, Sr, or La), electrical conductivity, and catalytic activity. Table 1.5 compiles several well-known Fe-based perovskites along with their corresponding properties[71].

Table 1.5 List of Fe-based perovskites and their properties.

Fe-based Perovskite	**Distinctive Property**
$BaFeO_3$, $GdFeO_3$	Ferromagnetic property
$SrFeO_3$	Electrical conductivity
$LaFeO_3$, $SmFeO_3$	Magnetic property, electrode
$SrFeO_3$, $BiFeO_3$	Catalytic property
$NdFeO_3$	Ferroelectric

1.5.1.1 Electrical Conductivity

Electronic conduction is the primary property in perovskite-type oxides. In many fuel cells applications, like solid oxide fuel cells (SOFCs), electrode materials are required to exhibit high conductivity in both oxidizing and reducing conditions. While these materials demonstrate high conductivity in oxidizing environments, they face challenges in reducing atmospheres[72]. Anikina et al. studied the conductivity of $SrFe_{0.9}Nb_{0.1}O_3$ has the highest value in the reducing environment[73]. Lan et al. observed the conductivity of $SrFe_{0.9}Nb_{0.1}O_3$ is 30 S/cm in a reducing environment, which is significantly greater than previously reported values. Also, if the Fe is partially replaced with Cu in $SrFe_{0.9}Nb_{0.1}O_3$, can increase conductivity even further[74].

1.5.1.2 Catalytic Properties

The abundant presence of oxygen vacancies in Fe- based perovskites contributes significantly to their high catalytic activity, making them suitable for various environmental catalytic reactions. B-site doping enhances its stability along with catalytic activity [75]. These are the promising material for the photocatalytic and photo electrocatalytic applications. Vincent et. al used magnetron sputtering to deposit $LaFeO_3$ film together with g-C3N4 in order to study its photocatalytic properties and observed hydrogen generation of 74% at a rate of 10.8 mol/hr/cm^{-2} for $LaFeO_3$/g-C3N4[76]. Ibrahim et al. investigated $LaFeO_3$ perovskites for their potential in hydrogen generating photocatalytic generating properties and developed a cost-effective, and robust electrochemical cell for the solar energy conversion[77]. Kim et al. reported that Fe-doping in Co based perovskite oxide can be explored as the catalysts for the OER in the alkaline media. They observed that with the B-site doping in Fe- based oxides enhances the efficiency and stability of oxygen evolution reaction (OER) [78].

In comparison to the photocatalytic degradation of organic pollutants, photoelectrochemical degradation is identified as a more reliable process. These Fe-based perovskite are pivotal in the degradation of organic pollutants as photo electrocatalysts. Nkwachukwu et al. investigated the La doped $BiFeO_3$ for the photo electrocatalytic degradation property on dyes (orange II, Congo red, and methylene blue) and pharmaceutical pollutant[79]. Joshi et al. discovered that $BiFeO_3$ is a promising material for the photoelectrochemical water splitting and can be employed as a photocatalyst [80].

1.5.1.3 Applications in Sensors and Absorbent

Since, Fe-based perovskites exhibit thermal stability and catalytic properties, they are applicable in various applications including sensor and adsorbent. These have been used as a sensor for detecting gases like carbon monoxide (CO) and oxygen (O_2). Lantto et al. have studied the gas sensing property for $LaFeO_3$ [81]. Fabio et al. developed a gas sensor for detecting gases under reducing or oxidizing pressure range[82]. Ma et al. studied $PrFeO_3$ (praseodymium ferrite) nanofibers for the sensing property towards acetone[83]. Yang et al. also developed porous $LaFeO_3$ for HCHO sensing[84].

A number of literatures are also present for the Fe-based perovskite to work as adsorbent. Adsorption depends on several factors including surface area, porosity, surface charge, and size distribution density. Shima et al. use the $La_{0.9}Sr_{0.1}FeO_3$ nano-perovskite to remove the congo red dyes in aqueous and real samples[85]. Deng et al. performed the adsorption of rhodamine B by $LaFeO_3$-ACF [86].

Fe-based perovskites find utility in a wide range of energy applications, including solar cells, photoelectrochemical cells, excellent photocatalytic properties, sensors, solar cells, fuel cells,

and catalysis. These are promising materials for their high stability and durability under various conditions. Also, these are cost effective element for large-scale production. Consequently, our study delves into the investigation of Fe-based perovskite.

1.5.2 Lanthanum-Doped Fe-based perovskites (La-FeO_3)

Numerous studies have been conducted on the A-site and B-site doping of $LaFeO_3$. It is well-known process of increasing the ionic and electronic conductivities of the $LaFeO_3$ with enhanced electrochemical performance. Efforts to enhance A-site doping strategies have focused on integrating divalent alkali earth metals. Their similar size to La3+ ion facilitates easy incorporation into the perovskite structure without inducing strain. The reduced valence of these dopant ions encourages the formation of charge-compensating elements for conductivity, specifically oxygen vacancies and holes [87][88][89]. Also, this affects the structural, transport and electrical properties.

Primarily, previous studies on doping the A-site of $LaFeO_3$ have focused on Strontium (Sr), and sometimes Calcium (Ca) as an alternative[88][89][90].

Hung et al. studied Calcium (Ca) doped $LaFeO_3$ (LCF) and observed similar electronic conductivity as Strontium (Sr) doped $LaFeO_3$ (LSF)[91]. Ortiz-Vitoriano et al. suggest that substituting strontium with Calcium does not yield a significant difference in the electrochemical performance of $La_{1-x}Sr_xFe_{0.8}Ni_{0.2}O_{3-\delta}$. Their findings indicate that Calcium is the prime A-site dopant among the alkali earth metals, as it is significantly cost-effective compared to Strontium and also exhibit comparable electrochemical performance[90]. Bidrawn et al. studied that Calcium (Ca)-doped $LaFeO_3$ demonstrates lower ionic conductivity than $La_{0.8}Sr_{0.2}FeO_3$ (LSF) and exhibit higher activation energy for ionic transport. This implies

that it will be less active compared to $La_{1-x}Sr_xFeO_3$[89]. Hung et al. directly stated that further substitution of other transition metals onto the Fe-site of LCF is expected to enhance the electrical conductivity[91].

There is an evident requirement for clarity concerning A-site dopants in $LaFeO_3$, specially for the Sr doped study at A-site. Our research investigated the impact of Sr substitution at the A-site of $LaFeO_3$ as both an electrode material and a catalyst for fuel cells and batteries application.

Further, studies on B-site doped $LaFeO_3$ have emphasized on divalent first row transition metals. By introducing divalent transition metals, it is possible to tuned the magnetic properties and electrical conductivity of $LaFeO_3$[88][92] [93][94]. Similar to the limited nature of prior research on A-site dopants in $LaFeO_3$, studies on B-site dopants have predominantly focused on two elements: cobalt (Co) and nickel (Ni). The substitution of cobalt into $LaFeO_3$ increases its electronic and ionic conductivity[95]. Since Co is more reactive than iron (Fe), electronic conductivity of $LaFe_{1-x}Co_xO_3$ increases with the Co concentration. This readily increase its valence state, and facilitate the conductivity via electron 'hopping'[96]. Meanwhile, the formation energies of oxygen vacancies in cobalt-based perovskites contribute to the increase in ionic conductivity[97]. However, drawbacks such as high thermal expansion coefficients (TEC) and reactivity towards common electrolyte material are likely to be consistent when cobalt is used as a dopant. Therefore, small quantities of cobalt are usually introduced to mitigate these disadvantages[98].

Nickel as a dopant on the B-site in $LaFeO_3$ increases the mobility of charge carriers, thereby increasing the material's conductivity[93]. Coffey et al. observed that when nickel was introduced at the B-site in LSF, while increasing the electronic and ionic conductivity of the

material, led to higher power densities being achieved with the undoped material[99]. In support of this, Coffey also proposed that while nickel increased the number of active sites for the oxygen reduction reaction (ORR), it simultaneously reduced their activity[99].

As illustrated in the study by Coffey et al., previous investigations on B-site dopants in $LaFeO_3$ has primarily focused on enhancing the properties of LSF [99][100].

In recent years, optical properties, electrical conductivities, magnetic properties, photocatalytic, and electrochemical properties of $LaFeO_3$ is of great interest. The effect of structure, doping, and composition on the electrochemical property has to be explored further. The significance of Fe in improving OER, HER, and ORR activity and stability has remained unexplored in the broad spectrum. As of now, there is a lack of literature available on $LaSrFeTiO_3$, regarding its study as a catalyst with good long-term stability in environment friendly medium. Table 1.6 provides a summary of the cyclic stability of previously investigated perovskites in various electrolytes.

In our work, we explore the impact of substitution of Strontium (Sr) at the A-site and Titanium (Ti) at the B-site in $LaFeO_3$, aiming to address the limitations observed in the previous work. Furthermore, our study aims to elucidate the catalytic behavior of these modified compositions across a wide range of pH and check their stability under varied environmental conditions. This work contributes to an enhanced understanding of the property alterations induced by substitution and co-substitution in $LaFeO_3$.

Table 1.6 Summary of cyclic stability of previously investigated perovskites.

Material	Methods	Electrolyte	Stability (in cycles)	References
$CaMnO_3$	Sol-gel	1LiPF6	10	[101]
$Ca_{0.95}Li_{0.05}MnO_3$-	Sol-gel	1LiPF6	10	[101]
$CaSnO_3$	-	-	30	[101]
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	Pechini method	1LiTFSI	24	[102]
$LaMnO_3$	Electrostatic Interaction	$1KHCO_3$	10	[103]
$La_xSr_{1-x}Co_{0.01}Mn_{0.9}O_{3-\delta}$	Electrostatic spinning	$1Na_2SO_4$	24	[104]
$BiFeO_3$	Hydrothermal Method	0.1KOH	10	[105]
$NdFeO_3$	Co-precipitation method	0.1KOH	20	[106]
$BaCe_{0.95}Nd_{0.05}O_{3-\delta}$	Hydrothermal method	0.1KOH	10	[107]
$LaFeO_3$	Hydrothermal method	0.1KOH	50	[108][109]

1.6 Overview of Lanthanum Ferrite ($LaFeO_3$)

$LaFeO_3$ (LF) exhibits ionic and electronic conductivities, which can be improved through doping, making it highly interesting for electro ceramic-based applications. The characteristics of $LaFeO_3$ significantly depend on its defect chemistry, possible dopants, and surface chemistry, all of which will be thoroughly discussed in the upcoming chapters. There's a concise overview in this previous work regarding these areas, which has established the groundwork for our conducted research.

LF has the orthorhombic perovskite form with the space group Pbnm (number 62)[110]. It is described in Glazer notation that orthorhombic structure is a distorted form of the cubic

perovskite, with neighboring octahedra tilted in alternate directions as $a^{+}b^{-}b^{-}$[111][112]. The unit cell contains 20 atoms, with the Iron (Fe) atom residing at octahedral centers and forming six covalent bonds with the neighboring oxygen atoms. The octahedra tilt to adjust the disparity in atomic radius between iron and lanthanum (La)[113]. Within this structure, the oxygen atoms fall into two distinct categories: one type is situated in the FeO_2 plane, called equatorial Fe-O bonds, while the other resides in the LaO plane, known as axial Fe-O bonds.

The existence of two different Fe-O bond lengths gives rise to two dissimilar oxygen environments, called O1 for the axial bonds and O2 for the equatorial bonds (refer to Fig. 1.12). This nomenclature is further used in thesis chapters. Within LF, both the La and Fe atoms are in a 3+ oxidization state, transferring three electrons to the neighboring oxygen atoms. This electron transfer indicates that iron possesses a d^5 electronic configuration.

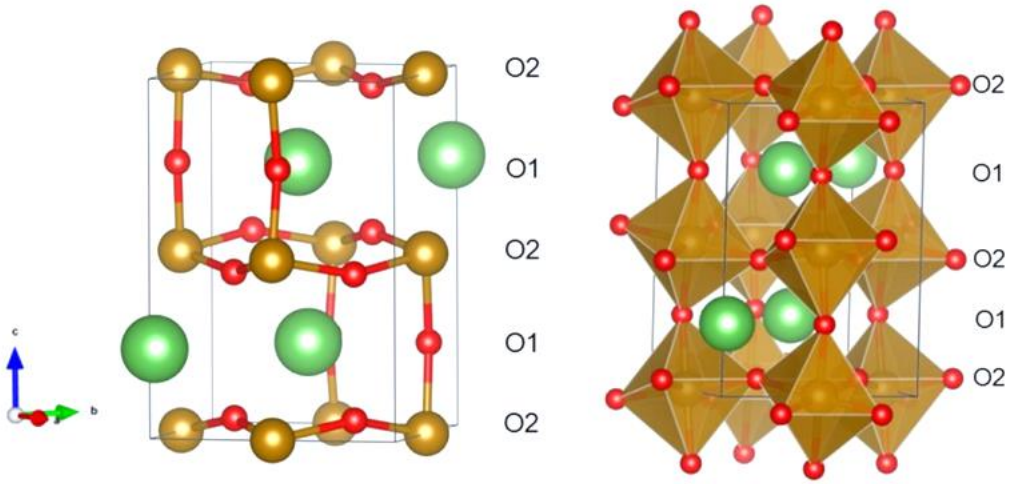

Figure 1.12 Orthorhombic structure of $LaFeO_3$, Lanthanum is shown in green, Iron in gold and Oxygen in red.

Oxide perovskites are used for catalytic applications. Among various perovskites, $LaFeO_3$ is one of the intriguing and widely studied perovskites for many applications. Several examples of such applications are listed here.

- Gas sensors.
- Magnetic devices.
- Solid Oxide Fuel cells.
- Catalyst.
- Chemical sensors.
- Thermo-electric.
- Photocatalytic Properties.
- Oxygen permeation membranes.

There are several key factors on which the material properties depend, like structure, conductivity, and material's defect chemistry. To study a material for specific application, it is necessary to comprehend its defect properties for effective optimization. On introducing dopants on either the A-site or B-site of a perovskite oxide can increase the ionic and electronic conductivity. Sr doping on the A-site of lanthanum ferrite-based perovskite is most common[114]. It affects its structural, transport, and electrical properties. Therefore, the choice of strontium content is an equilibrium between adequate conductivity properties and long-term fuel cell stability. Otherwise, it will lead to lower activity and efficiencies.

Further doping at the A-site should be considered to resolve this issue. As a part of our work, we are considering the effect of individual dopants on $LaFeO_3$ to optimize them for use in energy applications.

1.7 Motivation and Concluding Remarks

Lanthanum Ferrite materials have unique properties and vast application in the energy storage and conversion like fuel cells, batteries, supercapacitors, catalysis application, and magnetic

storage media[115][116]. Motivation behind the present work is to understand the role of dopants and their influence on structural, electrical, optical, electrochemical, and catalytic properties of $LaFeO_3$ for the energy application. From the literature, it is observed that $LaFeO_3$ has been extensively studied but there has been limited research conducted on the electrochemical study of $LaSrFeTiO_3$ and $LaSrFeO_3$, across a wide pH range along with cyclic stability. Present work provides the cumulative effect of rare earth and transition metal ion in La-Fe-O lattice.

In this introduction, we have described the main objective of our work by providing a comprehensive discussion on different energy applications including fuel cells and batteries with the explanation of important electrochemical reactions. The attention is on the electrode and their possible characteristics as catalyst, where we introduce materials undergoing extensive research. These materials include perovskite oxides, MIECs, Ruddlesden Popper oxides, cobaltite, magnetite, ferrites, and their pros and cons. The final section introduces the primary focus of this thesis: $LaFeO_3$.

1.8 Objective of the Present Research Work

The main objective of the present investigation is to develop and explore the physical and catalytic properties of cost-effective electrode materials for energy applications. For this purpose, lanthanum ferrite system has been selected as the ferrite-based material. The structural, thermodynamic, optical, electrical, and electrochemical properties of these materials were studied, establishing correlations among them. Additionally, these materials were explored as bifunctional catalysts for energy applications. To meet the objectives, the thesis has been planned to:

1. Synthesize Lanthanum ferrite and study the effect of A-site and B-site co-substitution on structural, morphological, electrical and electrochemical properties using various characterization techniques.
2. Study the charge dynamics and electrochemical behavior of pure $SrTiO_{3-\delta}$.
3. Study the $La_{0.5}Sr_{0.5}Fe_{0.5}Ti_{0.5}O_3$ as a robust and efficient catalyst for the fuel Cell.
4. Study the ZnO intercalation in $La_{0.5}Sr0_{.5}Fe_{0.5}Ti_{0.5}O_3$ via PLD for improved multifunctional behavior.
5. Study the effect of Sr substitution on the structural and electrochemical properties of $LaFeO_3$ using different synthesis methods: conventional Solid State Reaction Method and hydrothermal method.

The details of the synthesis and characterization techniques for the studied systems are discussed in the next chapter. The findings from this investigation will be elaborated upon and analyzed in the subsequent sections of the thesis.