Chapter-1

Introduction and Literature review

CHAPTER 1: Introduction and Literature Review

1.1 Overview

We have come a long way in the history of our civilization and our needs are increasing day by day. The world's energy consumption is growing considerably in the current period to meet the needs of an expanding global population and the desire for higher standard of living[1]. Fig. 1 depicts the global energy production (or consumption) scenario from 2000 to the present and also predicted until 2050. According to the report of Energy outlook 2021, The consumption of world energy is expected to increase by nearly 50% in next 30 years[2]. However, on a large scale, for realization of the demand of the energy, we are relying on non-renewable sources. According to the Global energy statistical yearbook 2021[3], 74% of the world's energy demand and 81 % in India are fulfilled by non-renewable energy sources. The past couple of years have revealed the flaws of a system severely contingent on the fuels of the 20th century. The significant dependence on fossil fuels has a massive impact on the environment. Global warming, depletion of the ozone layer, and extreme weather widespread environmental concerns. The effects of global warming have never been so significant, with the past decade (2010–19) being the warmest on record. This is due to our continued dependence on fossil fuels. With an average annual growth of 1.8% over the past two decades, CO_2 emissions have soared by 43%[4]. The air pollution from fossil fuel also triggers various health issues including heart diseases, cancer, asthma, and premature death. Generating power without harming the environment and health is a task that compels the scientific community to search for alternative energy sources which are cost-effective, efficient, and have minimal environmental warning gaseous emissions. These challenges establish that renewable energy sources will play a substantial part in the satisfying present and future energy needs to meet the worldwide increase in energy demand, particularly for ecofriendly energy supply[5].

Natural resources that regenerate themselves over time without depleting Earth's resources are the source of renewable energy. These resources also have the advantages of being cheap, accessible almost everywhere, and causing little to no environmental devastation. Reducing carbon emissions, expanding energy sources, stimulating economic growth, and creating jobs in manufacturing and installation are just a few of the many environmental and economic advantages that renewable energy offers to individuals, businesses, and the world Several renewable energy technologies are being established in recent years, such as Solar energy, Bioenergy, Hydropower energy, Wind energy, and geothermal energy[6]. However, all these renewable sources have their constraints and limitations. Some of the renewable technologies are completely dependent on the weather (solar and wind energy). Low efficiency level is another factor. The efficiency of solar panel has about 22% of efficiency in its most advanced running system. Some also requires a huge upfront capital outlay and specific region (open windy fields for wind energy). These are some interruptions which suggest that it can’t be solely reliable for power and it is better to look towards other alternative options.

The restriction of renewable energy sources aimed the interest of a part of scientific community towards the electrochemical devices. These devices are being developed for substantial-scale energy conservation and storage applications. Electrochemical devices either generate electricity through chemical reactions or use electrical energy to cause a chemical reaction. These devices present important roles in diverse fields of energy[7], healthcare[8], environmental protection[9], and security[10]. Fuel cell is such electrochemical energy conversion device. Fuel cells are electrochemical devices that produce electricity with low environmental impact and excellent efficiency by transforming fuel and oxidizer into products through electrochemical reactions. Fuel cells are the prominences as a reliable source of electricity if the fuel is supplied continually. Unlike other renewable energy sources, it can be easily relied on as a sole power source [11]. Fuel cells can serve as primary as well backup power sources [12], [13]. The overview, working principles and types of fuel cells are discussed in details in subsequent section.

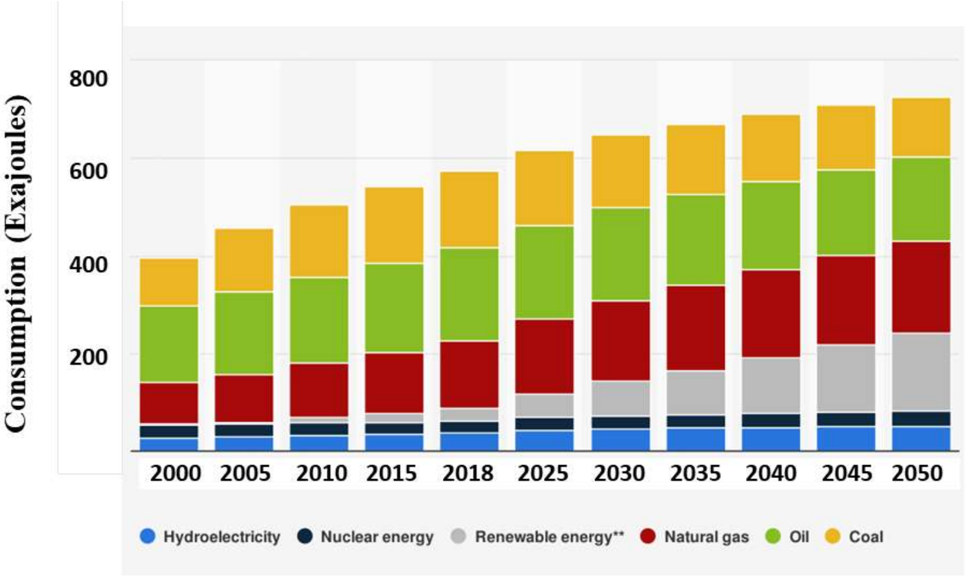

Figure 1.1: Worldwide energy consumption forecast till 2050[14].

1.2 Fuel Cells Basics

Fuel cells are energy conversion device in which chemical energy is converted into electricity through an electrochemical reaction. Fuel cell is a very promising technology for energy conservation, an area which is dominated by the traditional technologies such as internal combustion engine and gas turbine. Fuel cells have higher electrical efficiency (greater than 40%) as compared to the traditional power systems such as turbine generator (30-40%), reciprocating engine (≈35%). Fuel cells combine the best properties of an engine and a battery, and they can function as long as fuel is supplied, much like an engine. Their traits are identical to a battery under load conditions[15]. Fuel Cells are simple device, containing no moving parts and only four functional components: anode, cathode, electrolyte, and interconnect. Since the energy is generated without combusting the fuel, the environmental benefits are significant. All fuel cells operate and function essentially in the same ways. At the anode, an oxidation takes place, whereas at the cathode, reduction takes place. A charged species that migrates across the electrolyte and electrons that pass through the external circuit connect these two reactions. Fuel cells typically use compressed hydrogen as fuel and oxygen (from the air) to sustain the chemical reaction. Special fuel cell types have been developed in order to gain advantages from various electrolytes and fulfil a variety of application requirements. Despite the fact that, the fuel and the charged species which migrates through the electrolyte in these fuel cells may be different, the basic principle of these fuel cells is the same.

1.2.1 History of Fuel Cell:

The scientific community has well-known about fuel cells for over 150 years. William Nicholson and Anthony Carlisle defined the electrolysis process in 1800, in which water is broken down into hydrogen and oxygen using electricity[16]. Sir Humphrey Davy successfully validated the first-ever concept of a fuel cell in 1801[17]. This was followed by the groundbreaking work of Prof. Christian Friedrich Schőnbein, who discovered the fuel cell's principle in 1838 [18]. Sir William Robert Grove, a British physicist, chemist, and lawyer, is extensively recognized with developing the first fuel cell in 1839 based on the reverse electrolysis of water [19]. While investigating coal gas fuel cells in 1899, scientist Ludwig Mond and his colleague Charles Langer coined the name "fuel cell." They achieved 6 mA/cm^2 (electrode area) at 0.73 volts using electrodes made of thin, perforated platinum[20]. Friedrich

Wilhelm Ostwald, one of the originator of physical chemistry, experimentally described the functions and interconnections of various fuel cells in 1893[18]. A revolution in energy research started in 1962 when researchers at Westinghouse Electric Corporation (now Siemens Westinghouse) demonstrated how it was feasible to generate electricity from a device known as a solid electrolyte fuel cell. Fuel cell development has speeded up swiftly since the early 1990s due to the commercialization of numerous applications. Fuel cell can be used in broad array of applications. Their applications may be divided generally into three categories: Stationary power generation[21], [22], Portable power generation[23], and power for transportation[24]. Fuel cell technology is on the forefront as our next technological revolution due to significant advancements in the development of low-cost fuel cells, increasing costs of existing power generation, and fuel resources.

1.2.2 Working principle of Fuel cell

A fuel cell consists of two electrodes, namely anode and cathode, which are separated by an electrolyte membrane. Fuel cells use different types of electrolytes as per the application need and due to this, their operation is a bit different from each other, but their basic geometrical features remain the same. In general terms, the redox reactions (the reaction between hydrogen and oxygen) require the transfer of electrons that leads to the conversion of chemical energy into electrical energy. Fuel is delivered to the anode end individually, whereas at cathode end, oxygen is supplied. On the anode side, hydrogen split into hydrogen ions and electrons through the catalyst present at anode side. These both will try to move towards the cathode end through the different pathway. The ion moves from the anode to the cathode via the electrolyte, whereas the electron moves through the external circuit, causing in direct current. At the cathode end, ion-electron and oxygen combine to generate the water molecules as a by-product (Proton-conducting fuel cell). In some fuel cells, the electron is picked up by oxygen, and oxygen ion passes through the electrolyte to the anode, where it react with hydrogen ions (Oxide ion-conducting fuel cell)[25]–[27].

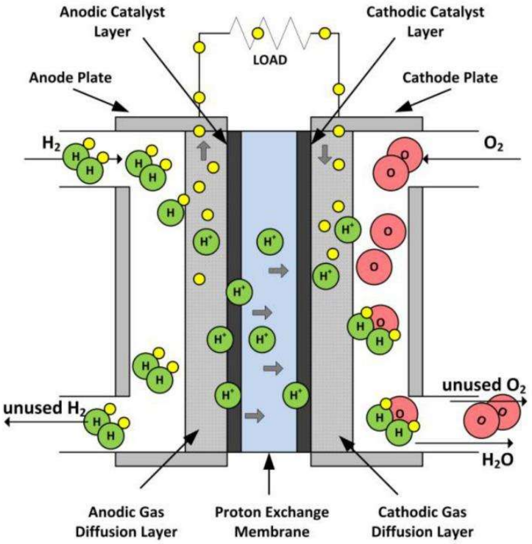

Figure 1.2: Schematic diagram of Proton conducting fuel cell[28]

The electrical energy obtained in fuel cell through chemical energy is displayed in terms of electrical current output and cell potential. For the maximum possible current output or cell potential, fuel cell needs to be operated under thermodynamically reversible conditions. However, some of the energy in fuel cell also dissipated in terms of heat. The efficiency of fuel cell is not constrained by any thermodynamic constraint, such as Carnot proficiency[29]. It is because there is not any intermediate step of mechanical work and generally production of heat is not permitted in case of fuel cell. It generates electrical energy more efficiently compared to traditional devices like combustion engines. The difference between the efficiency of a fuel cell and conventional heat engine is shown in figure 1.3. Conventional techniques entail the conversion of fuel to heat, mechanical work, and then electrical power, and are typically restricted to low efficiency of nearly 30%. Fuel cell circumvents the intermediate energy losses and produces electrical energy with superior efficiencies greater than 50%[30]–[32].

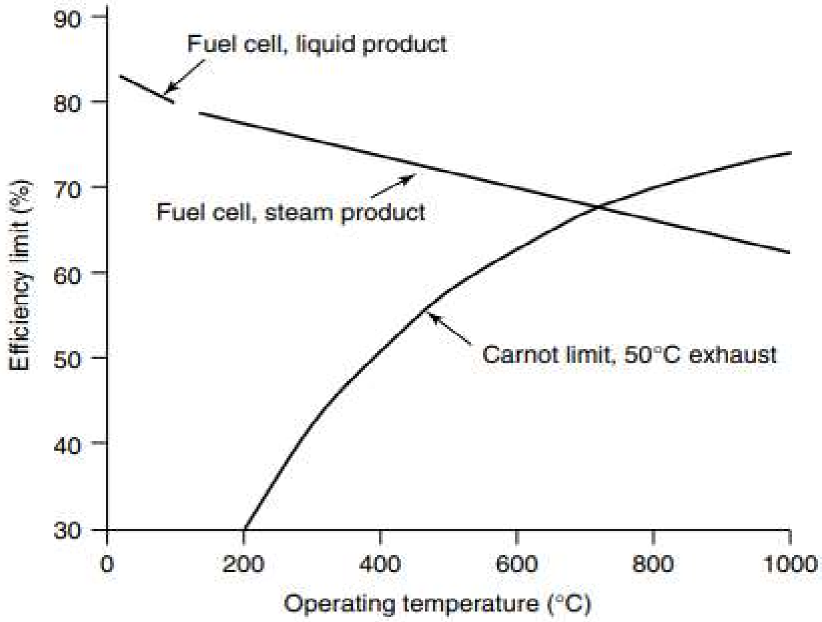

Figure 1.3: Maximum efficiency of hydrogen fuel cell with the steam produced compared to Carnot limit with 50 ºC exhaust temperature[33]

The fundamental working of the fuel cell may not be challenging to demonstrate but building an efficient and reliable fuel cell is far more complex. The voltage of a unit fuel cell is around 0.7 V[34]. Many cells must be attached in series to obtain a larger voltage and current. Such a collection is mentioned to as a "fuel cell stack" or simply "stack."' To overcome the voltage, drop during a stack, 'bipolar plate' is used for cell interconnection. It links the anode of one cell to the surface of the next cell's cathode. Apart from the stack, several other subsystems and components are also required; they are referred to as balance of plant (BoP). BoP, when connected with the stack, forms a functional fuel cell system[35].

1.2.3 Types of Fuel cells

Fuel cells are usually classified on the basis of electrolyte they employ. This classification also establishes the mandatory fuel, the operating temperature, the kind of electro-chemical reaction taking place, the type of catalyst, and other factors. This classification, in turn, affects the application for which these are most applicable. Six types of fuel cells have emerged as visible systems for the present and near future[36]. Basic information and their comparison are listed in table 1.1.

The commercialization of fuel cells deals with two most important: improving durability and reducing the costs. The production of hydrogen is the most difficult challenge for cost-effective commercialization. Since the last decade, lots of research has been accomplished on all sorts of fuel systems. The Solid oxide fuel cell (SOFC) has the most extended development period, starting from the late 1950s. SOFC has fascinated much research interest right through the world in recent years for its potential market competitiveness, including high efficiency, fuel flexibility, low price, and long-life expectancy. The current focus of SOFC research is on the identification and synthesis of novel materials that can lower SOFC manufacturing cost and extend their lifetime. The reduced price will boost the production of SOFC and make it a sustainable substitute of conventional power technologies[37]–[40]. In the next section, the working principles, component, applications and challenges in the field of SOFC will be discussed briefly.

Fuel cell type	Mobile ion	Operating temperature	Fuel supplied	Application and Efficiency
Alkaline Fuel Cell (AFC)	OH^-	65-220 °C	Hydrogen or NH_3	Space vehicle (50-55 %)
Proton Exchange Membrane Fuel Cell (PEMFC)	H^+	40-100 °C	Liquid ethanol	Vehicle and mobile application, for lower power CHP system (50-55 %)
Direct Methanol Fuel cell (DMFC)	H^+	20-90 °C	Methanol	The portable electronic system of low power (30-40 %)
Phosphoric Acid Fuel Cell (PAFC)	H^+	160-220 °C	Hydrogen	Power plants of up to 200 KW (40-50 %)
Molten Carbonate Fuel Cell (MCFC)	CO_3^{2-}	600-800 °C	Hydrogen, CO, Natural gas, or propane	Suitable for medium to large CHP system, up to MW capacity (45-50 %)
Solid Oxide Fuel Cell (SOFC)	O^{2-}	500-1000 °C	Natural gas or propane	Suitable for all sizes of CHP system, 2KW to multi-MW (45-60 %)

Table 1.1: Comparison of different types of Fuel Cell

1.3 Solid Oxide Fuel Cell (SOFC)

The solid oxide fuel cell (SOFC) is promising and potentially revolutionary technology for the cost-effective manufacture of electricity as compared to the available fossil fuels. This is a result of the growing demand for reliable, high-quality energy and the increasing prospects for environmental safeguards. SOFC is an indispensable energy conversion device that produces electricity through electrochemical reactions at high temperatures (600-1000 °C) by combining fuel and an oxidant over an ion-conducting oxide electrolyte. SOFC utilizes the solid ceramic material as an electrolyte. The high operating temperature of SOFC enhances the reaction kinetics, which eliminates the need for any metal catalyst. SOFCs have considerable efficiency benefits over current thermally generated electricity technologies[37], [41], [42]. SOFC systems alone are up to 50 - 55% efficient, and, in combination with heat regeneration and cogeneration technologies, the overall efficiency can be lifted to 70 - 75%. Pollution levels are markedly reduced with 20 - 40% CO_2 levels per kW of electricity produced. There are also reductions by 1 - 2 orders of magnitude in the nitrogen and Sulfur-based gases responsible for acid rain and other worsening health conditions. Furthermore, SOFC system efficiencies can be improved by the internal reforming of natural gas within the fuel cell stack. With modular construction, it is likely to adapt SOFC systems to match the load requirement and, if fuel is present, the SOFC can run steadily in almost any environment.

Depending on the electrolyte, SOFCs can either proceed via oxide ion or proton conduction. Electrical power generated from SOFC has the following general highlights:

- It has high efficiency for power generation.
- High thermal efficiency
- Long term performance and stability
- A wide variety of hydrocarbons can be used as fuel.
- It eliminates the problem of corrosion and liquid management that usually occurs in PAFC and MCFC

1.3.1 The basic operation of SOFC

A SOFC is made up of dense, oxygen ion-conducting electrolyte placed between two porous electrodes (cathode and anode). Proton conductors and oxide ion conductors are the two different types of SOFC electrolytes. Although the two types of conduction methods are very different, their operating principles are the same. The schematic diagram of both type of SOFC is shown in figure 1.4. In solid oxide, fuel cell oxygen ions are conducting species. Oxygen supplied at the cathode end is reduced to oxygen ion (O^{2-}), diffuses into the electrolyte, and transfers to the other side of the anode. This oxide ion reacts with the fuel at the anode side, giving up electrons and producing byproducts and heat. The interconnect is used to transport the electron through an external circuit.

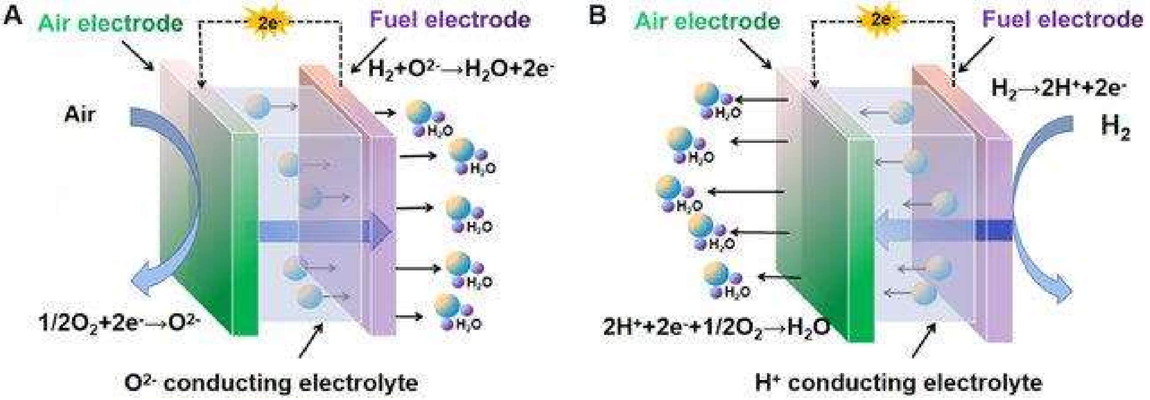

Figure 1.4: Schematic diagram of (A) oxygen-ion and (B) proton conduction in a solid oxide fuel cell[43].

Proton conducting SOFC differs from the traditional SOFC in sense that the electrolyte membrane transports protons instead of oxygen ions. At the anode side of the cell, hydrogen is oxidized to protons and conducted through the electrolyte until it combines with oxygen at the cathode side to produce water. The electrons generated from the partial reaction are routed through the external circuit and thus produce electricity.

The electrochemical reactions that are associated with hydrogen fuel in conventional SOFC are represented as:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \text{ (At cathode end)} \qquad (1.1)$$

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \text{ (At anode end)} \qquad (1.2)$$

The overall reaction can be written as:

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

The corresponding Nernst equation for this reaction will be:

$$E = E^0 + \frac{RT}{2F}\ln\left(\frac{PH_2PO_2^{1/2}}{PH_2O}\right) \qquad (1.4)$$

Where E denotes the cell potential (or Nernst Potential), E_0 is the standard potential at unit activity, R is ideal gas constant, T is temperature, F is Faraday constant and PH_2, PO_2 and PH_2O is the partial pressure of hydrogen, oxygen and water respectively.

1.3.2 Components of SOFC

The SOFC comprises different components like cathode, anode, electrolyte, interconnects, materials for sealing, and fuel distribution system. Some several criteria and properties need to be retained by each material to operate in a distinct capacity. The SOFC components, along with their requirement, are mentioned below:

1.3.2.1 Electrolyte:

In SOFC, the electrolyte has a task to conduct the oxide ion from cathode end to anode end. As the name itself said, SOFC uses solid oxide ion conductors as electrolyte material. In electrolytes, oxide ion conduction occurs via a thermally activated oxygen vacancy hopping mechanism. The main prerequisite for the electrolyte materials is:

- Sufficient oxide ion conductivity (>0.1 S/cm at operating temperature) without any significant electronic conductivity
- Fully dense with no open porosity

- Compatibility of Thermal expansion coefficient (TEC) with another component of the cell
- Electronic transference number should be low ($< 10^{-3}$)
- Chemical and thermodynamic stable over a wide range of temperature (RT to 1000 °C) over a wide range of oxygen partial pressure ($1\text{-}10^{-22}$ atm)
- It should be Chemical inert towards cathode and anode
- Negligible evaporation
- It should have reliable mechanical properties (such as facture strength should be greater than 400 MPa)

1.3.2.2 Anode:

The primary objective of an anode is to provide a place for the reaction of oxide ions with the gas fuel. The anode material of SOFC must comply with the following requirement:

- High electronic activity
- High electrocatalytic activity
- High porosity for mass transport of reactant and product gases
- Comparable thermal expansion coefficient with electrolyte
- Good microstructural strength to operate SOFC at working temperature
- Stable under the reducing atmosphere of fuel.
- It should be able to handle a variety of fuels and not react with the SOFC's commonly used fuel.
- It must resist the action of byproduct (H_2O) (especially metal anode)

1.3.2.3 Cathode:

In a solid oxide fuel cell, the reduction of oxygen occurs at the cathode end. To serve the better, the cathode material in SOFC has needed to be fulfilled the following requirements:

- High electronic conductivity (preferably greater than 100 S/cm in an oxidizing atmosphere is preferable)
- Enough porous for fast diffusion of molecular oxygen from cathode to cathode/electrolyte interface.
- High catalytic activity for oxygen reduction reaction (ORR).
- The thermal expansion coefficient (TEC) needs to be matched with the other component of the cell.
- Good chemical and dimensional stability during cell operation and fabrication of interconnection, and fuel electrode layers.
- Good chemical compatibility with electrolyte and interconnect materials as well minimum interaction with electrolyte.

1.3.2.4 Interconnect:

The interconnection is the connection between the adjacent cell in the SOFC stack. It connects the cathode of one cell to the anode of the next cell through an electrical connection. It also serves as a physical hurdle between the oxidizing (at the cathode) and the reducing (at the anode end) atmosphere. The interconnect material must fulfill the following selection benchmarks for proper SOFC operation:

- Electrical conductivity of nearly 100% with area-specific resistance (ASR) less than $0.1\Omega\ cm^{-2}$.
- Structural, chemical, and phase stable at the extreme operating environment of SOFC in reducing and the oxidizing atmosphere.
- Non-reactivity towards electrode and electrolyte material.
- Matching Thermal expansion coefficient with the other component of the cell.
- Moderate mechanical strength.
- Low permeability for hydrogen (fuel) and oxygen to avoid the direct combination of oxidant and Fuel.

1.3.2.5 Sealing materials:

The function of sealants material is to avoid any leakage of either fuel or air from their respective chamber of SOFC stacking. In some configurations, it also offers mechanical bonding of components as well in some designs, and it provides electrical insulation between the stack components. The sealing material needs to fulfill the following demand for the SOFC device to function properly:

- It should have high hermeticity (i.e., no gas leak)

- The thermal expansion coefficient should be similar to the other cell component.
- Insulating in nature
- Long term chemical stability (>40,000 h) under oxidizing/wet fuel
- Enough toughness under external static and dynamic force.
- Chemical compatible with adjoining SOFC components.
- Admirable bond strength to prevent leakage, as well as compressive loading to support the stack load.
- Enough tolerance to thermal shocks.

Solid oxide fuel cells have five major components and each component has specific working principle and mechanism. Although major of the work in this thesis is dedicated to the air-electrode and electrocatalyst. Therefore, it is important to understand the basic mechanism of air electrode. The reaction occurs in air electrode and its kinetic mechanism is discussed in details in next section.

1.4 Reaction and Kinetic mechanism for the air electrode

At the cathode end in SOFC, normally, air is supplied; therefore, it is called an air electrode. Since this research work is based on the air electrode materials, therefore it is worthwhile to discuss the kinetics and chemical reactions taking place at air electrode (cathode). The ORR takes place at the cathode end in SOFC, and the equation followed for the reduction is already mentioned in equation 1.1. However, this reaction is quite distinct from the other catalytic reactions in many ways. It is usually assumed that a cathodic reaction can occur at the Triple phase boundary (TPB). TPB is defined as that site where oxide ion conductor, electron conductor, and gas-phase come together simultaneously. The illustration of TPB is shown in figure 1.5. Although overall ORR looks very straightforward, the elementary steps associated with the ORR are quite Complex.

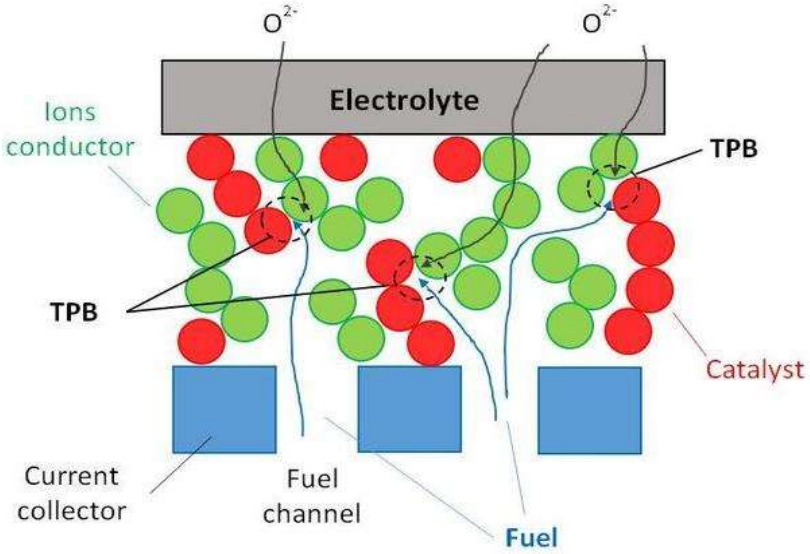

Figure 1.5: Schematic representation of Triple Phase Boundary[44]

1.4.1 Mechanism of Oxygen Reduction Reaction (ORR)

Single diatomic oxygen (O_2) must be transformed in some 'electroactive' state by one or more steps for the ORR to take place. The overall ORR reaction entails different bulk and surface step and can be divided into three key steps revealed as follows[45]–[47] :

(i) The reduction of oxygen molecules into oxide ions and their adsorption, dissociation, and incorporation into the cathode lattice.

(ii) Ionic transport through the cathode towards the electrolyte.

(iii) Jumping of oxygen anion into electrolyte site.

For SOFC cathodes, there are three possible pathways out of which cathodic reactions can occur (figure 1.4)[48] :

1. **The Electrode Surface Path**: This path is appropriate in the case of the electronic conductor. This path includes diffusion of oxygen followed by the adsorption of oxygen and diffusion of dissociated oxygen (and partly ionized) along the surface towards the TPB (Fig. 1.6 a) At TPB, complete ionization of oxygen species takes place and then ionic transfer into the electrolyte. Integration into the electrolyte doesn't require to occur directly at TPB. Broadening of the incorporation zone can be initiated via surface or interface diffusion of ionized oxygen.
2. **The Bulk Path**: This path is followed by a Mixed ionic-electronic conductor (MIEC). This path comprises of the diffusion and adsorption of oxygen gas on the cathode surface and the dissociation and ionization of oxygen into oxide ion, followed by the incorporation of ion into the cathode (Fig. 1.6 b). The electrode transport oxidized ion into the electrolyte.
3. **The Electrolyte Surface path:** This route is appropriate for the cases of the composite conductor. This pathway considers adsorption and ionization of oxygen species on the electrolyte surface followed by the migration of species through the electrolyte surface towards the TPB (Fig. 1.6 c). This path is identical to the electrode surface pathway from a geometrical point of view. However, in favor of the electrode surface pathway, this path is overlooked. An active zone for the cathodic reaction is confined very close to the TPB because of the low electronic conductivity of the most suitable electrolyte.

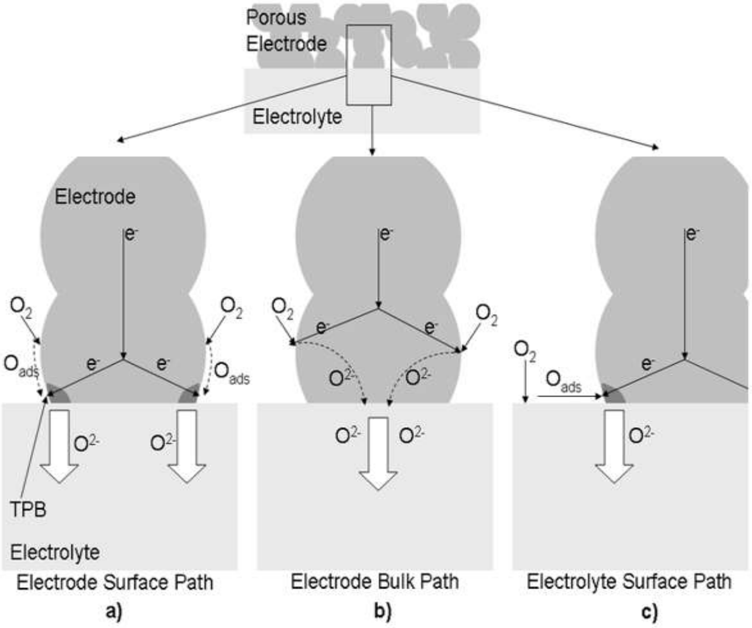

Figure 1.6: Schematic illustration of three reaction paths for the cathodic reaction [48]

The ORR can take place in any of the three paths mentioned above, and each path may have one or more elementary steps that are rate-defining step. It is not always possible to predict which elementary reaction is the rate-restricting step for ORR. The path which has the fastest rate-determining step will dominant the overall reduction reaction rate. To understand the rate-limiting step along with the dominant pathway, numerous studies have been employed, including various techniques such as cyclic voltammetry (CV)[40],[41], electrochemical impedance spectroscopy (EIS)[42],[43], isotope exchange depth profile (IEDP)[53], [54], steady Stade polarization[55] and actual fuel cell testing[56], [57]. These all studies provided crucial information regarding the element reaction occurring during the ORR. However, in this thesis, we focus only on CV due to the following reasons:

1. *CV is widely used to access the catalyst activity and is valuable for discovering the electrochemically active surface area (ECSA)*[58].

2. *CV can be used to acquire information about electrochemical reactions, including kinetics, mechanism of reactions, reversibility, and electrocatalytic process. Besides ORR, the application of this technique is also quite common in Oxygen evolution reaction (OER) and hydrogen evolution reaction. (HER)*[59].

1.4.1.1 Catalyst for Oxygen reduction reaction (ORR)

The details of ORR and possible path for it in any electrode material is already discussed in previous sanction. In terms of electron pathway, this reaction can be occurred in two possible ways. One is two electron pathways whereas other is four electron pathways. The supplied fuel (oxygen) reduced to water by 4-electron pathway and to hydrogen peroxide through 2-electron pathway. The most desirable pathway for ORR is 4-electron pathway. However, ORR is the fuel cell reactions that occurs the most slowly in any fuel cells. in any condition. Higher bond energy of oxygen molecule is one of the associated reasons for this. In order to achieve the high current density for electrode, this activation barrier needs to be breached. Thus, there is a demand of electrocatalyst for ORR. For a good electrocatalyst for ORR, following properties are required:

(i) High electronic conductivity
(ii) High chemical and electrochemical stability
(iii) High catalytic activity towards ORR
(iv) Highest interaction between catalyst particle and support interface.
(v) High catalytic stability

Most of the requirement are same as per the requirement for cathode in SOFC. All electrodes do not, however, need to simultaneously satisfy these conditions. It can differ based on the applications and external factors where catalysts are employed. Catalyzing the oxygen reduction reaction is a multi-step reaction. Therefore, the rate of the rate-determining step is more crucial than the overall reaction rate. The fundamental mechanism of ORR for four-electron pathway can be stated as the following equation sequence on a metal surface.

$$O_2(g) + * \rightarrow O_2^* \qquad (1.5)$$

$$\frac{1}{2}O_2^* \rightarrow O^* \qquad (1.6)$$

$$O^* + H^+(aq) + e^- \rightarrow HO^* \qquad (1.7)$$

$$HO^* + H^+(aq) + e^- \rightarrow H_2O^* \qquad (1.8)$$

1.4.2 Mechanism for Oxygen Evolution Reaction (OER)

OER is the core reaction of fuel cell to carry out its reversible process along with ORR. Besides fuel cell, OER plays vital role in several other energy system such as metal-air batteries, water electrocatalysis. The reversible reaction of OER is Hydrogen evolution reaction (HER). OER is heterogenous reaction and basically the half reaction of water splitting. OER usually takes place at anode end whereas HER take place at cathode end. The mechanism of OER is different under different electrolyte mediums (acidic or alkaline)[60]. All the steps involved in OER are thermodynamically uphill process, and the step with highest energy barrier become the rate-limiting step of OER[61].

The mechanism of OER under acidic or alkaline mediums proceed in four to five steps described in following equations[62]:

- For acidic environment:

$$M + H_2O \rightarrow MOH + H^+ + e^- \quad (1.9)$$

$$MOH + OH^- \rightarrow MO + H_2O + e^- \quad (1.10)$$

$$2MO \rightarrow 2M + O_2 \quad (1.11)$$

$$MO + H_2O \rightarrow MOOH + H^+ + e^- \quad (1.12)$$

$$MOOH + H_2O \rightarrow M + O_2 + H^+ + e^- \quad (1.13)$$

- For alkaline environment:

$$M + OH^- \rightarrow MOH + e^- \quad (1.14)$$

$$MOH + OH^- \rightarrow MO + H_2O + e^- \quad (1.15)$$

$$2MO \rightarrow 2M + O_2 \quad (1.16)$$

$$MO + OH^- \rightarrow MOOH + e^- \quad (1.17)$$

$$MOOH + OH^- \rightarrow M + O_2 + H_2O + e^- \quad (1.18)$$

Here M represent the active site in both cases.

1.4.2.1 Catalyst for Oxygen Evolution Reaction (OER):

As mentioned earlier, HER and OER occurs simultaneously. The overall reaction of water electrolysis, which involved both HER and OER required a theoretical voltage of 1.23 V between cathode and anode in order to proceed the electrolysis reaction. Additionally, an overpotential (η) is also applied which account the potential loss resulting from kinetic limitations that may arise during the electrochemical reaction. Thus, overpotential can be lower through electrocatalysts by kinetically accelerating the water-splitting reaction either in OER or HER. Beside it, it is general concept that the OER is much more sluggish than the HER because of four-electron involving nature of OER. Thus, the development of effective OER catalysts is crucial to improve the overall efficiency overall reactions. The general requirement for OER catalyst is quite similar to the requirement of ORR catalyst such as

(i) It should have highly active surface area that can facilitate the rapid removal of products and also good accessibility to reactants.
(ii) Its electrical conductivity should be high in order.
(iii) It should be stable Electrochemically, chemically and mechanically.
(iv) It should have low intrinsic overpotentials for OER and HER.

In recent years, many materials have been suggested as electrocatalyst noble metal for OER. Most commonly, noble metal catalyst such as Ru, Pd, Pt, Ir has been used for such a long time. In addition, there oxide (IrO_2, RuO_2) is used as electrocatalyst for alkaline medium[63]. Alternatively, non-noble metal catalyst such as transition metal (Ni, Co, and Fe compounds). In recent studies, Nickel oxides are found good candidate for OER because of its resistant behavior to corrosion in alkaline media[64]. A comparative study of Ni based compound with other non-noble metal catalyst shows its superiority as OER catalyst. Electrochemical performance in transition metal compound is found in the order of Ni>Co>Fe[65].

1.5 Electrodes for fuel Cells: An Overview

The selection of the electrode is crucial not only in SOFCs but also in all others fuel cells as well. As a cathode, a wide range of materials have been investigated. These materials can be categorized widely in the category as mentioned below:

1.5.1 Magnetite based cathodes

Oxygen non-stoichiometry and defects have a considerable influence on the electronic and ionic transport properties of cathode materials. Lanthanum magnetite-based Oxides have either oxygen-deficient or excess non-stoichiometry. This is the most studied material, which lies under this category[66]–[68]. The general formula is $Ln_{1-x}A_xMnO_{3-\delta}$, where A is a divalent cation. Most commonly, Strontium (Sr) is used as a dopant for Lanthanum magnetite because its size matches with lanthanum. Doping of Sr enriches the electron-hole concentration, which results in higher conductivity. However, the conductivity of Lanthanum magnetite based cathode lie between 200 S/cm to 300 S/cm[69], [70], and also the electrical properties of Lanthanum magnetite-based cathode are not suitable for the temperature range below than 800 °C. For that, Lanthanum (La) can be substituted with the other rare earth elements. Sr doped $PrMnO_3$ revealed low overpotential, and its TEC is also compatible with Yttrium-based Zirconia (YSZ)[71].

The majority of the work in Lanthanum magnetite is centered on the doping on Sr-doped A-site. However, Ca doped Magnetite has also exhibited good performance as cathode materials. $Pr_{0.7}Ca_{0.3}MnO_3$ showed chemically compatible, and its TEC is well-matched with YSZ, and also its conductivity lies to the close of Sr doped $PrMnO_3$[72].

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. Sc doped magnetite $La_{0.8}Sr_{0.2}Mn_{1-x}Sc_xO_{3-\delta}$ is a potential cathode material for IT-SOFC[73]. However, the high cost of Sc is a concern in this category of cathode materials.

$Sr_{1-x}Ce_xMnO_{3-\delta}$ ($0.1 \le x \le 0.3$) system is another choice of cathode materials under this category. The TEC value of these cathode materials varies between 10.1×10^{-6} -12.6×10^{-6} K^{-1}, which lie close to the CeO_2 based electrolyte[74]. Doping of Cobalt on B-site lowers the Area Specific resistance (ASR) and enhances the catalytic activity. ASR of $Sr_{0.8}Ce_{0.2}Mn_{0.8}Co_{0.2}O_{3-\delta}$ is 20 times lower than that of $Sr_{0.8}Ce_{0.2}MnO_{3-\delta}$ and has high catalytic activity for ORR at the temperature range of 700 °C - 800 °C[75].

1.5.2 Ferrite based cathodes

In ferrite-based cathodes, the mobility of electrons or holes is considerably higher than that of oxygen ions. As a result, the hole-conduction process directs the total conductivity of these cathodes. The reactivity of Ferrite based cathodes with YSZ is substantially reduced, and also, the TEC is lying close to the YSZ and CGO electrolytes. Lanthanum ferrite ($LaFeO_3$) is expected to remain stable because of the stable electronic configuration of Fe^{3+} ion ($3d^5$ configuration).

The addition of Sr to $LaFeO_3$ created charge unbalancing, maintained by forming Oxygen vacancy or Fe^{4+} ion. Sr-doped $LaFeO_3$ (LSF) cathodes exhibit promising power density and stability at 700 °C[76]. The ASR value of LSF can be reduced by incorporating La deficiency. ASR value of $La_{0.8}Sr_{0.2}FeO_3$ is reported as 0.1Ω cm^2 at 800 °C and TEC of $La_{0.75}Sr_{0.25}FeO_3$ closely matches with YSZ and CGO electrolyte[77].

Doping of Cu in lanthanum strontium ferrite improves the kinetic activity for ORR, and also copper doping reduces the sintering temperature for electrode fabrication[78], [79]. However, Cu-doped composition interact chemically with YSZ (above then 950 ^{0}C).

1.5.3 Cobaltite based cathode

Cobalt-based cathode materials exhibit higher electronic and ionic conductivity than that of the other cathode materials. $LaCoO_3$ (LCO) has a high electronic density of states near the Fermi level (E_F). Sr doped LCO ($La_{1-x}Sr_xCoO_3$) has high oxygen diffusivity and high oxygen molecule dissociation ability, marking its electrode activity. However, a large amount of cobalt increases the TEC value. The significant value of TEC in cobalt-based perovskite is due to the formation of oxygen vacancy. Replacing lanthanum (La) with another rare earth elements (Pr, Nd, Sm, and Gd) can reduce the TEC and ASR. Among all rare earth elements, Pr^{3+} have the highest electronic conductivity and lowest overpotential because of the Pr^{3+}/Pr^{4+} valency change.

Doping of Cu in the Co site is anticipated to increase the catalytic activity and ionic conductivity. Although, the conductivity of Cu-doped LCO is less than LCO[80]. A combination of Pr, Sr on A-site and Cu, Co on B-site ($Pr_{0.7}Sr_{0.3}Co_{0.9}Cu_{0.1}O_{3-\delta}$) records the maximum power density as 481 mW/cm^2 at 750 °C[81]. Besides Pr, Sr doped Samarium cobalt is another widely studied composition for cathode material. The electrical conductivity of this composition reaches up to 1000 S/cm at a temperature range of 800 °C - 1000 °C and shows metal-like behavior [82].

Mn doping on B-site along with the Sr doping on A-site also lowers the cathode overpotential. The lowest overpotential was observed in $Pr_{0.6}Sr_{0.4}Co_{0.9}Mn_{0.1}O_{3-\delta}$ among the tested $Ln_{0.6}Sr_{0.4}Co_{0.9}Mn_{0.1}O_{3-\delta}$ (Ln= La, Pr, Sm, and Gd). The electrical conductivity of $Pr_{0.6}Sr_{0.4}Co_{0.9}Mn_{0.1}O_{3-\delta}$ also reached 1400 S/cm at 500 °C[80].

1.5.4 Ferro-cobaltite based cathode

Lanthanum strontium cobalt ferrite is one of the primary cathode materials used for SOFC manufacturing. $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ (LSCF) has an excellent electrical conductivity, high oxygen diffusion coefficient, and high surface exchange coefficient. The TEC value of LSCF is also well matched with the frequently used electrolyte. The Sr concentration affects the ionic conductivity of LSCF at A-site, where electronic conductivity is influenced by the Fe and Co concentrations at B-site. LSCF based cathodes outperform LSM cathodes at lower temperatures. However, LSCF perovskite is generally incompatible with YSZ electrolytes. Substitution of Pr cation in the place La cation at A-site improves the cathode performance. The composition $Pr_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (PSCF) shows the highest conductivity, 1040 S/cm at 300 °C, and also ASR of PSCF-GDC(Gadolinium doped ceria) is 0.046 Ω cm^2 at 800 °C indicating that PSCF is promising cathode material[82].

Barium strontium cobalt ferrite has also been studied as a cathode material in SOFC using hydrogen as fuel. $Ba_{0.5}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (BSCF) cathode along with Samarium doped ceria (SDC) electrolyte and NiO-SDC anode in a anode supported cell reached 1010 mW/cm^2 at 600

°C and ASR of this material is 0.055-0.071 Ω cm^2[83]. However, the TEC of BSCF is much higher, with a value of 20×10^{-6} K^{-1} in the temperature range 50-800 °C[84].

1.5.5 Nickelate based cathodes

Nickelate-based perovskite cathodes ($LnNiO_{3-\delta}$) are stable only below 1000 °C; further heating of these perovskites will lead to the K_2NiF_4- type structure. This transformation restricts the use of $LnNiO_{3-\delta}$ and can be utilized by doping into Nickel sublattice[85].

Iron-doped nickelate ($LaNi_{1-x}Fe_xO_{3-\delta}$) exhibits high electronic conductivity, moderate TEC, and phase stability in air. $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF) has been explored as the option of cathode for IT-SOFC. The electric conductivity of LNF is reported at 580 S/cm at 800 °C [86]. However, LNF is more reactive towards the ZrO_2 based electrolyte rather than the conventional electrolyte.

Sr doped LNF (LNSF) is another choice of cathode under this category. The electrical conductivity of LNSF depends on the concentration of Ni/Sr and the temperature range. The highest electrical conductivity value in LNSF is achieved when the total concentration of Ni and Sr is about 0.6 at 600 °C[87].

1.6 State of the Art: Nickelate based cathode

The present scenario of the number of papers published in cathode in the last five years (source: Web of Science, WOS) has been represented in Fig. 1.7. Here, we are representing the data up to June 2022. It means that, during the last five years, most publications have been focused on ferrites. Despite having promising properties as electrode, an insignificant number of publications are published in nickelate. This motivated us to work on the Nickelate-based cathode. In the upcoming section, we will discuss the possible structure for nickelate cathode.

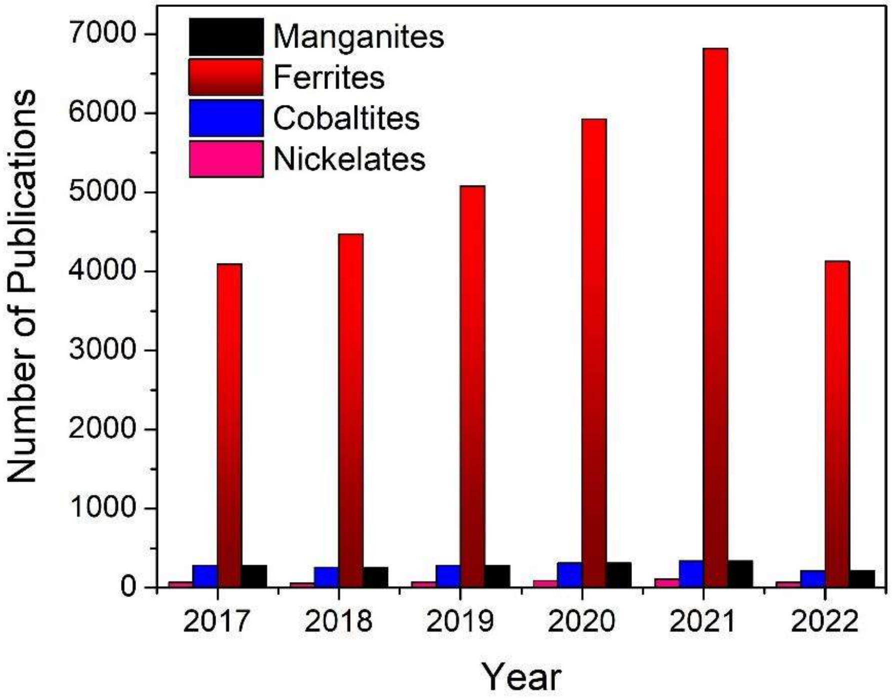

Figure 1.7: Number of publications in the last 5 years the for the keyword of cathode materials

1.6.1 Perovskite structure

Perovskite structure has a general formula unit of ABO_3, where A represents the larger cation with coordination number 12 and B represents the smaller cation with coordination number 6. In the case of SOFC electrodes, A cation can be alkaline earth metal/rare earth metal, or other whereas B cation can be many transition metals [88]. The ideal structure of perovskite is cubic. The structure deviation of perovskite from its perfect structure is measured in the form of tolerance factor given by the following equation:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \qquad (1.19)$$

The perovskite structure has relatively stable tolerating high-level oxygen vacancy compared to the other structure; therefore, it provides significant oxygen-ion conduction. Octahedral symmetry of oxygen around the reducible transition metal located at B-site provides rapid electron conduction. Therefore, some perovskites are good mixed ionic-electronic conductors (MIEC) and are strong candidates for the cathode materials for SOFC.

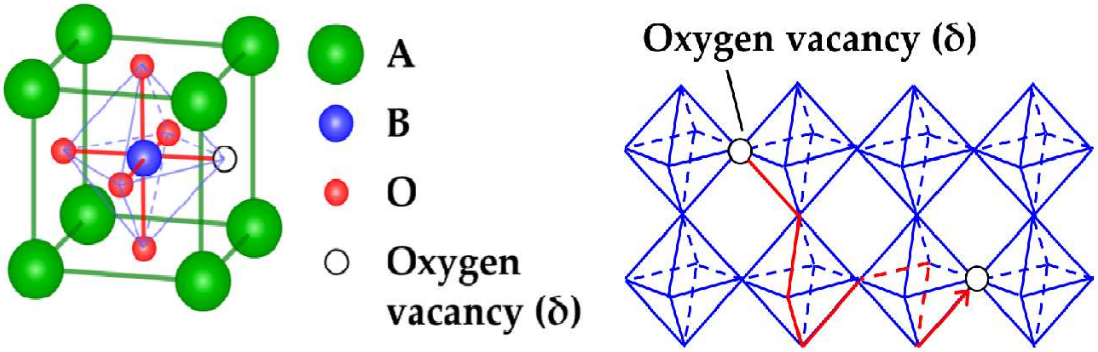

Figure 1.8: (a) Atomic structure in mixed conducting perovskite, left image represents ions' position in a cubic structure, and right image represents the BO_6 octahedra with oxygen vacancy migration path[88]

Among the nickel-based perovskite oxide, the parent oxide $LaNiO_3$ (LNO) itself possessed a very good electrical conductivity in order of 100 S/cm[89]. However, as mentioned earlier, at elevated temperature, it gets decomposed to the K_2NiF_4 type lattice structure and NiO. In order to stabilize the LNO at higher temperature, partial substitution of foreign ion (Fe, Al, Mn, Co) at Ni site is tried. It is well reported that 40% doping of Fe at Ni site ($LaNi_{0.6}Fe_{0.4}O_3$) satisfied the requirement of cathode materials. In order to improve the catalytic activity for ORR, cobalt ($LaNi_{1-x}Co_xO_3$)[90] and Molybdenum ($LaNi_{1-x}Mo_xO_3$) is also doped on B-site of LNO[91].

1.6.2 Ruddlesden-popper type oxide:

The general formula of Ruddlesden-Popper-type (RP) metal oxides is $A_{n+1}B_nO3_{n+1}$ (n=1,2,3). In this type of structure, n-ABO_3 perovskite layers are sandwiched between two AO rock-salt layers and are arranged along the c-axis(as shown in figure 1.9)[92]. K_2NiF_4 structure is supposed to the first element of the RP series. Most commonly, Lanthanide is placed at K.

This particular structure of RP has capability to conduct the oxygen ion through intrinsic oxygen, without the formation of oxygen hypo-stoichiometry. In addition, TEC of Ln_2NiO_4 is also considerably lower than that of the conventional perovskites and also close to the LSGM based electrolyte[93]. The thermo-chemical stability of K_2NiF_4 type structure is higher than corresponding perovskite type oxides[94]. Among the Ln_2NiO_4 materials, Pr_2NiO_4 was suggested to have the best performance for ORR at high temperatures[95]. Under the operating conditions of fuel cells, Nd_2NiO_4 also demonstrated good phase stability in terms of CO_2 poisoning and resistances against Chromium contamination [96]. In the next sanction, the details of layered Ln_2NiO_4 nickelates is discussed.

1.7 Layered $Ln_2NiO_{4+\delta}$ nickelates:

The oxide $Ln_2NiO_{4+\delta}$ (Ln = La, Nd, and Pr) materials belongs to the Ruddlesden-Pooper (RP) family. These oxides have layered structure with general formula $A_{n+1}B_nO_{3n+1}$ ($n \geq 1$). The $Ln_2NiO_{4+\delta}$ nickelates have wide range of applications because of its numerous outstanding properties. It has applications in oxygen-containing electrolytes, solid oxide electrochemical cells, and proton conducting analogues. The RP structure of $Ln_2NiO_{4+\delta}$ is formed through the consecutive block of perovskites, which are alternating with rock-salt-type AO layers along the *c*-axis. The structural stability of A_2BO_4 phases is controlled by the bond length between the perovskite and rock-salt-type layers. It can be explained though Goldschmidt tolerance factor, which is given by:

$$t = \frac{r_{Ln} + r_O}{\sqrt{2}(r_{Ni} + r_O)} \qquad (1.20)$$

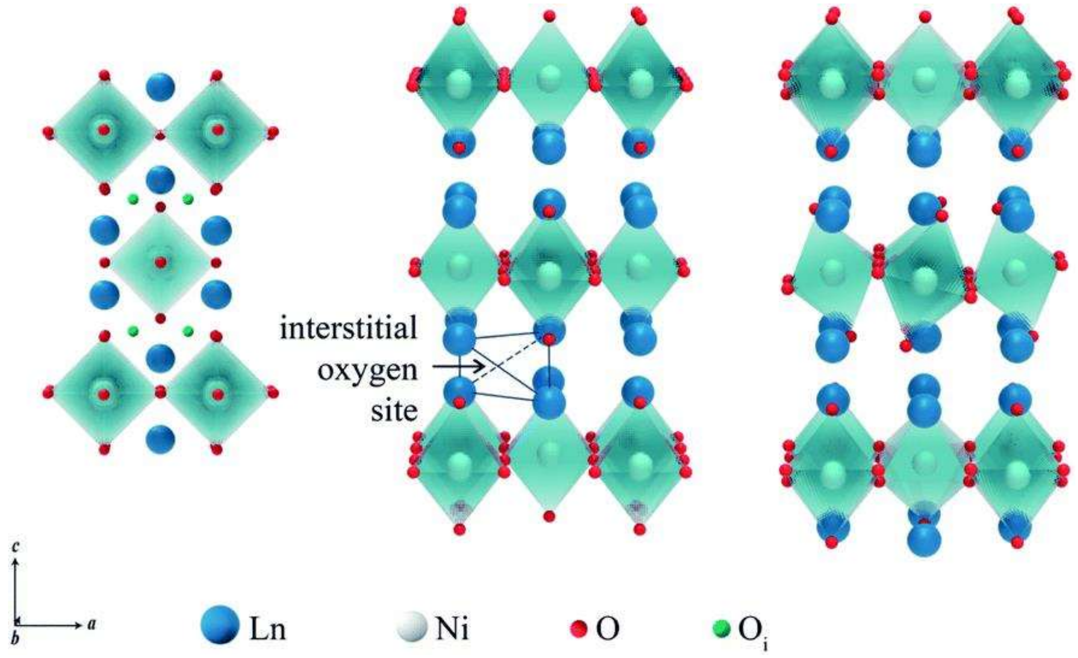

Figure 1.9: Crystal structures of A_2BO_4 phases (A = Ln and B = Ni)[97]

The K_2NiF_4-structure is recognized as being connected to the perovskite structure because it can be imagined of being constituted on the premise of the unit cell of a cubic perovskite ($Pm\bar{3}m$). In an ideal cubic structure ABX_3, A- cation is located on the edges of the unit cell, B-cation is body centered and X-anion arrange on the face centered (Fig. 1.10 a) In the perovskite structure, *B*-cations are octahedrally coordinated by the *X*-anions while *A*-cations are surrounded by the anions *X*. The unit cell of the ideal tetragonal K_2NiF_4-structure (*I*4/mmm) is shown in figure 1.10(b). The perovskite block is located at the center of the K_2NiF_4. At center, Ni ion is octahedrally coordinated by the 6 anions. The perovskite block is present additionally above and below of the center. However, they moved towards the (ab)- plane relative to the center. This movement is to enhance the electrostatic attraction between anions and cations. The stacking arrangement of the K_2NiF_4 unit cell is shown in figure 1.10(c). The stacking arrangement of K_2NiF_4 represent the 2-dimensional nature of the compound, which is made up of the single perovskite layers stacked along the c-axis. For the closest approach of anions in one perovskite layer and cations in the following layer, adjacent perovskite layers are displaced by $\left(\frac{1}{2},\frac{1}{2}\right)$ in the (a, b)-plane. When the region between successive perovskite layers is examined more precisely, this becomes apparent that the geometric configuration of the cations and anions are identical to that of rock salt. Therefore, K_2NiF_4 can be considered of as a compound that accumulates between rock salt and perovskite structures.

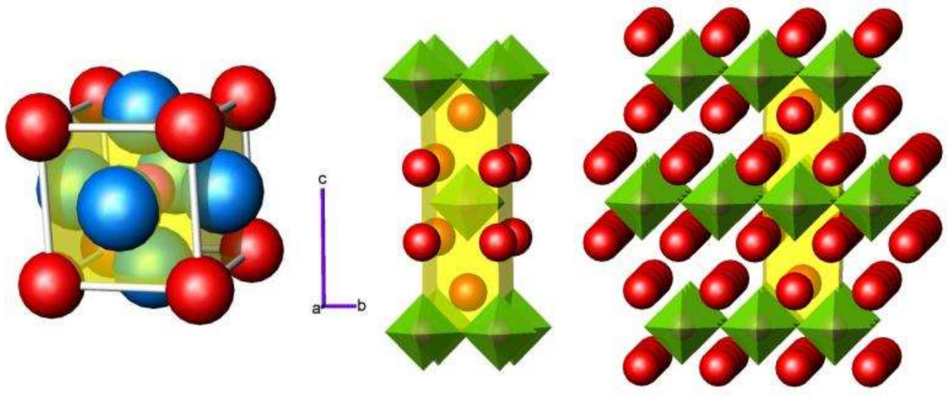

Figure 1.10: (a) The unit cell of the ideal perovskite structure, building block of ideal tetragonal K_2NiF_4-structure. (b) Unit cell of K_2NiF_4 along the (a, b)-directions (c) Two-dimensional character of the K_2NiF_4-structure. Unit cells are outlined yellow[98].

The orthorhombic-tetragonal transition is shifted to a higher temperature as a result of the decrease in the ionic radius of the Ln^{3+} cations in the order La > Pr > Nd in Ln_2NiO_4[99]. Because of this decrease in ionic radius, there is a corresponding rise in the oxygen content, which compensate the identical conditions. The Ln_2NiO_4 structure is highly adaptive for addition of A-site cation deficiency as well the different substitution in both sublattice. This substitution affects the structural properties, electrocatalytic properties, ionic and electronic transport and other pertinent properties.

The most important characteristics of the nickelates is their ability to accommodate excess oxygen. This property is established through numerous investigations such as coulometric titration, density measurements, thermogravimetric analysis, neutron diffraction and iodometric titration. The amount of oxygen absorbed into the nickelate depends upon various factor such as temperature, doping on A-site and B-site, oxygen partial pressure and also on rare earth element. The value of oxygen over stoichiometry for rare earth nickelates lie in the range 0.05 to 0.25 at normal conditions. This strong tendency of nickelates towards oxygen incorporation is due to the reduction of the size mismatch between perovskite and rock salt layers. There are two reasons that can adequately explain this phenomenon:

(i) There is a partial oxidation of Ni^{2+} to Ni^{3+} and because of this, there is a decrease on the average Ni-O bond distance.

(ii) There is an increase in the average *Ln*-O distance due to a higher average coordination numb of the lanthanide ions[100].

$Ln_2NiO_{4+\delta}$ and its compositions primarily exhibit the p-type electronic conductivity. At low temperature, undoped $Ln_2NiO_{4+\delta}$ exhibits thermally activated conductivity but at high temperature (350 ℃ to 500 ℃), these compositions exhibit a seamless transition from semiconducting to metallic-like behavior. The semiconducting behavior at low temperature is explained by splitting of the $\sigma_{x^2-y^2}$ band caused by antiferromagnetic ordering, or by intraatomic exchange interactions with localized $d_z{}^2$ electrons. This can also correlated with the orthorhombic–tetragonal transition[101], [102].

$Ln_2NiO_{4+\delta}$ based oxide materials are known as mixed ionic-electronic conductors (MIEC). The MIEC behavior of RP perovskites is because of the either redox reactions or change in the valence state of B-site ions.[103]. However, at higher temperature (500 °C - 1000 °C), the electronic conductivity of these RP perovskites is three times higher in magnitude than the ionic conductivity (σ_o). The $Ln_2NiO_{4+\delta}$ oxides have strong anisotropy of oxygen-ionic transport because of its layered structure. Additionally, oxygen migration in these materials may involve either oxygen vacancies or oxygen interstitials, or both. This can be correlated through the oxygen hyper stoichiometry of $Ln_2NiO_{4+\delta}$ phases under oxidizing conditions. Furthermore, interstitial oxygen ions are also highly mobile.

Thus, family of $Ln_2NiO_{4+\delta}$ based RP materials offer promising alternative for conventional ABO_3 perovskite for their applications in electrochemical cells, proton ceramic electrolysis cells and protonic ceramic fuel cells.

1.7.1 Overview of $Sm_{2-x}Sr_xNiO_{4-\delta}$

The possibility of K_2NiF_4 type structure is predicted through Goldschmidt tolerance factor as mentioned in previous sanction. According to this relation, the K_2NiF_4 is stable over the range for $0.866 \leq t < 1$. The tetragonal/orthorhombic structure is present for $0.866 \leq t \leq 0.88$ and tetragonal structure is present for $0.88 \leq t \leq 0.99$ [104]. Because of this limitation, neodymium is the smallest lanthanide that can form the K_2NiF_4 type structure. Samarium (Sm), which is smaller than the neodymium cannot form the K_2NiF_4 structure. Therefore, $Sm_2NiO_{4-\delta}$ cannot be formed. However, by partial substation of Sr^{2+} for Sm^{3+}, a stable structure $Sm_{2-x}Sr_xNiO_{4-\delta}$ can be formed.

Partial substitution of Sr^{2+} for Sm^{3+} increase the radius of A-site ions and decrease the radius of B-site ions. This occurs due to of the oxidation of B-site ion into a higher valence state. This

Sr^{2+} substation in $Sm_2NiO_{4-\delta}$ triggers a drastic shift in the O(II) ions along the c axis from Sm(or Sr) towards Ni while affecting the NiO_4 in the basel plane.

Strontium doing in $Sm_2NiO_{4-\delta}$ contributed to the giant temperature stable dielectric constant. This excellent dielectric properties of the $Sm_{2-x}Sr_xNiO_{4-\delta}$ is because of the small polaron hopping, induced from the charge ordering[100].

These all points indicate the potential of $Sm_{2-x}Sr_xNiO_{4-\delta}$ and lead to the fact that $Sm_{2-x}Sr_xNiO_{4-\delta}$ is an interesting compound to carry out the research work.

1.8 The objective of the Present Research Work

The prime objective of this thesis is to contribute in alternative solutions of nonrenewable sources which are cost effective, efficient and have minimum impact on environment. An extensive literature survey showed that electrochemical devices have that potential to be the alternative energy sources. Among available electrochemical devices, fuel cells have been chosen because of their promising applications such as, a solo power source, a primary power source as well as a backup power source.

Each type of component used in fuel cells has a specific application. It was observed that the oxygen reduction reaction (ORR), which occurs at the cathode end of these components, is a critical factor in determining any fuel cell's efficiency. Moreover, the oxygen evolution reaction (OER) is also a key fuel cell reaction, which also occurs with its complementary process (HER) along with ORR. In addition to this, OER is essential for other electrochemical devices. Therefore, it is required to investigate such type of materials which are high electrocatalytic active for ORR and OER. Our objective in the present research work, is to find the electrode material that could potentially operate as a catalyst for both OER and ORR together.

In order to meet this objective, Ruddlesden-popper oxides (RP) material is chosen because of its impressive but less explored properties. For this purpose, RP perovskite $SmSrNiO_{4-\delta}$ and its compositions have been chosen for investigation as air electrodes for fuel cell applications.

The following steps were taken to investigate the ORR and OER along with other electrochemical properties of the RP perovskite $SmSrNiO_{4-\delta}$ system.

1. The layered perovskite $SmSrNiO_{4-\delta}$ were synthesized and their physical and chemical properties, such as structural, microstructural, electrical, and electrochemical properties under different optimization conditions were measured and discussed. This investigation is reported in chapter 3.
2. It has been observed that 'A' site ordering and morphology change enhances oxygen ion diffusivity in bulk materials. As a result, second objective is to study the influence of different crystalline phase in $Sm_{2-x}Sr_xNiO_{4-\delta}$ for ORR/OER. This study is discussed and reported in chapter 4.
3. In order to understand the catalytic property of A-site substituted $Sm_{2-x}Sr_xNiO_{4-\delta}$ for oxygen evolution reaction (OER). This system is investigated thoroughly and reported in chapter 5. Moreover, the possibility of synthesized materials for energy storage applications along with its electrochemical and structural properties are studied and reported in same chapter.
4. B-site cation has an important role to alter the catalytic behaviour of the electrode in fuel cell applications. Therefore, it is vital to investigate the properties of B-site cation

in details. In this regard, the catalytic activities of transition metal oxide in different media (alkaline/KOH, acidic/H_2SO_4, and neutral/Na_2SO_4) have been investigated and reported in chapter 6.

The details of the synthesis process and measurement techniques for studied compounds have been described in the next chapter (Chapter 2). The outcome of all the chapters and scope of research in this field in near future are summarized in chapter 7.