CHAPTER - 1

INTRODUCTION

The energy requirement is growing rapidly day by day due to the exponential growth in population, thereby imposing immense pressure on the primary energy sources (Khan et al. 2021, Liddle et al. 2014, Rehman et al. 2022). Khan et al. 2021 address the concern of effect on energy consumption due to increase in population. Khan et al. 2021, reported that the increased population severely increase the energy consumption leading to the highly CO_2 emission. The primary energy sources are coal, petroleum and natural gasses. The applications of coal are extensive and have had a considerable impact throughout history, particularly in electricity generation, where coal-fired power stations play a major role. Moreover, coal has traditionally served as a predominant fuel for industrial operations, particularly in steel manufacturing, and continues to be a crucial energy resource in numerous areas like of heating and generating power. Fossil fuel coal affects the environment through environmental pollution despite of its historical importance. The combustion of coal combustion emits huge quantities of carbon dioxide (CO_2) and other contaminants into the atmosphere, such as SO_x, NO_x and CO, making a substantial contribution to both global warming and air pollution (Li et al. 2023, Mastral et al. 2000). Furthermore, the process of coal mining can lead to the destruction of habitats, erosion of soil, and pollution of water, emphasizing the immediate requirement for cleaner and more sustainable alternatives. The liquid fossil fuel petroleum is widely used in the transportation sector as the principal energy source for automobiles, airplanes, ships, and many forms of public and private transportation. It is also a crucial raw material for petrochemical industries. Similar to coal, petroleum combustion also emits greenhouse gases, including CO_2 and unburnt hydrocarbons, which contribute to climate change when released into the atmosphere (Jafarinejad 2016, Ragothaman and Anderson 2017). Furthermore, the process of extracting and transporting oil have adverse effects on marine ecosystems and coastal areas (Ramirez et al. 2017). However, limited reserves of petroleum also raise concerns about the long-term security of the energy supply, which is prompting research into alternative and ecologically benign energy sources. Although natural gas is often considered as a cleaner energy source, it still poses some environmental challenges. The main constituent of natural gas is methane (CH_4), which is a powerful greenhouse gas, and its release during the extraction and distribution processes can contribute to climate change. Additionally, the extraction method, typically hydraulic fracturing (fracking), has been linked to water pollution and disturbance of natural habitats (Smil 2015). Thus, the use of fossil fuels, coal, petroleum, and natural gas is being restricted in shaping the modern era. The significant environmental and sustainability issues of fossil fuels motivate us to reassess our energy landscape.

The shift towards cleaner and more sustainable alternatives would be the most suitable option for a robust and balanced coexistence with the resources of our world. In view of this, other alternative sources of energy are being tried and widely tested to the current energy requirement and to diminish the toxic pollutants that are emitted by fossil fuels. Solar energy is a type of renewable energy that is present in abundant amounts. Solar energy has many obstacles such as (Tripathi et al. 2023):

- Intermittent nature of solar enegy.
- Problem of efficient storage.
- Weather and climate dependency.

The availability of solar energy fluctuates due to temporal and meteorological factors and thus, requiring efficient energy storage technologies to be utilized during periods of reduced sunlight (Tripathi et al. 2023). The wind energy, harnessed by wind turbines, has become very popular as a renewable and environmentally friendly source of energy. The wind energy also faces some majoe issue such as (Dhar et al. 2020, Raga et al. 2022):

- The variability of wind.
- Variable power generation.
- Manufacturing and disposal of turbine component.

Hydropower is a reliable energy source. The dams for hydroelectric and run-of-river systems exploit river kinetic energy to generate power. Large dams change ecosystems, displace communities, and damage aquatic habitats (Hunt et al. 2021). Geothermal power plants harness the energy from hot reservoirs to generate steam and power turbines. Geothermal energy is environmentally favorable, but only in places with high-temperature reservoirs. These reservoirs are expensive to dig, and trace gases and minerals released during extraction may harm neighboring environments (Yuksel et al. 2022).

In this regard, the fuel cell is an excellent energy device that converts the chemical energy of supplied fuel and oxidant into electrical energy as long as fuel is supplied to the anode side and oxidants are supplied to the cathode side. The fuel cell technology is the most promising technological advancement to address the issue among all the various forms of renewable energy. There are many advantages of fuel cell over other conventional energy sources, such as it does not produce toxic gasses like SO_x and NO_x, very high theoretical efficiency, simple operation and it works silently (Carrette et al. 2000, Wilberforce et al. 2016). The fuel cell was first introduced by lawyer and scientist William Grove in 1839. Fuel used in the fuel cell is generally hydrogen or hydrogen rich compounds such as methanol, ethanol, glycerol, sodium borohydride, etc (Din et al. 2023, Hren et al. 2023, Sangkheaw et al. 2020 Yin et al. 2022). The oxidants used are oxygen from the air, pure oxygen, hydrogen peroxide, sodium hypochlorite etc. (Seo et al. 2008, Zeng et al. 2022, Jiang et al. 2020, Panjiara and Pramanik 2022).

The working principle of a simple hydrogen/oxygen fuel cell, also known as Proton exchange membrane fuel cell (PEMFC) is shown in **Figure 1.1**. The fuel hydrogen is supplied to the anode side where it produces hydrogen ion (H^+) and electron (e^-) due to electrooxidation of H_2 over Pt based anode electrocatalyst (Equation 1.1).

Anode:

$$2H_2 \rightarrow 4H^+ + 4e^- \tag{1.1}$$

Cathode:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{1.2}$$

Overall reaction:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1.3}$$

The electrons produced at the anode pass through the external circuit, creating an electric current. The proton (H^+) generated at the anode passes through the membrane electrolyte while the electron passes through the external circuit. The oxidant oxygen, combined with the electron and proton, produces water via a reduction reaction at the cathode (Equation 1.2). Thus, the hydrogen/oxygen fuel cell produces electricity, heat and water as the final outcome. It should be noted that all the electrochemical reactions of the anode and cathode occur at the electrocatalyst layer. Initially, the liquid electrolyte was used for ion transportation, but it came up with many disadvantages, such as leakage of electrolyte, low contact area between the gas, the electrode and the electrolyte and large distance between the electrodes causing increased resistance (Gupta and Pramanik 2018). To overcome the disadvantages of liquid electrolytes, a thin layer of solid polymer film was introduced as an electrolyte in the fuel cell for the transportation of ions. The polymer membrane electrolyte Nafion®, which is also known as proton exchange membrane (PEM) is very popular for its highest ionic conductivity in the order of 0.1 Scm^{-1}.

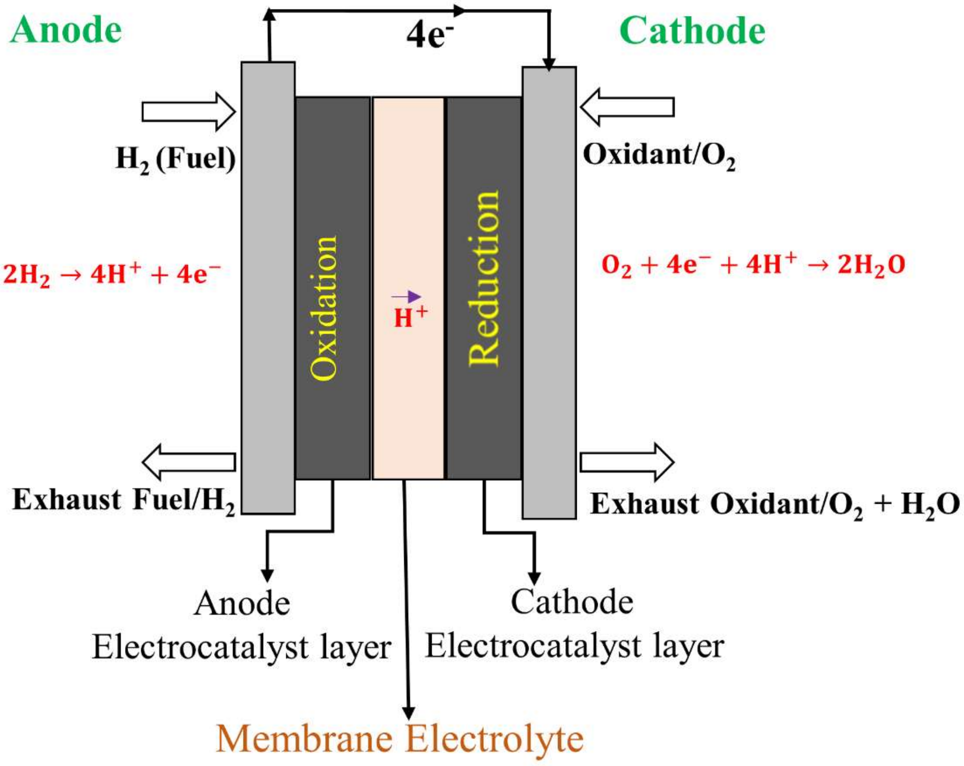

Figure 1.1 Schematic of working principle of hydrogen/oxygen fuel cell.

There are various types of fuel cell developed so for. On the basis of temperature, fuel cell is divided into low temperature fuel cell and high temperature fuel cell. The low temperature fuel cell are proton exchange membrane fuel cell (30-100 ^oC), direct alcohol fuel cell (20-90 ^oC), phosphoric acid fuel cell (~220 ^oC) and alkaline fuel cell (50-200 ^oC). On the other hand, high temperature fuel cell are molten carbonate fuel cell (~ 650 ^oC) and solid oxide fuel cell (500-1000 ^oC) (Larminie and Dicks 2003). The low temperature fuel cell may use the electrolyte, either acidic or alkaline type. In acidic environment/medium, cathode reduction is sluggish in nature. Moreover, an acidic medium does not favour anode electrooxidation of many fuels like methanol and borohydride (Shah et al. 2022, Mahapatra and Datta 2011, Ko et al. 2022). In view of these, the study of fuel cell using some common fuels like methanol, ethanol, glycerol and $NaBH_4$ in alkaline medium has become very popular nowadays.

The methanol fuel cell has many disadvantages, such as its neurotoxic characteristics, volatility, and flammability, methanol poses a number of potential safety concerns. In addition to this, it is generated using intricate chemical processes using non-renewable resources. It presents crossover issues through the electrolyte of ionomeric membranes (Choudhary and Pramanik, 2020a). Moreover, using methanol as fuel, the electrocatalyst like platinum is highly susceptible to CO poisoning and it has low theoretical open circuit voltage (1.21 V at 25 ^oC) (Larminie and Dicks 2003, Gagliardi et al. 2023). Ethanol as fuel is better than methanol in many aspects as it is renewable in nature, high energy density (8.6 kWh/kg) than methanol (6.1 kWh/kg), non-toxic, safer and less permeable through membrane due to its larger size (Choudhary and Pramanik, 2020a). However, using ethanol as anode fuel offers several challenges, such as the difficulty of splitting the ethanol C-C bond and the sluggish ethanol electrooxidation kinetics at low temperatures on present Pt-based electrocatalyst. Even the breaking of the C-C bond of ethanol molecule via the electrochemical reaction process is kinetically hindered due to several reasons, such as geometrical inaccessibility, the little electron affinity and ionization energy between two atoms (Shen et al. 2010). Hydrogen is a very popular fuel used in fuel cell due to its simple molecular structure and hydrogen fuel has the highest energy density of 32 kWh/kg. However, hydrogen fuel in fuel cell has many challenges. Fuel cell requires ultrapure hydrogen; any impurities in hydrogen may poison the electrocatalyst and, hence, slowed down the reaction rate (Du et al. 2021). It is well known that commercial hydrogen obtained from the hydrocarbon via reforming or cracking and thus, has a high possibility of CO with hydrogen even after purification (Schneider et al. 2020). The production of ultrapure hydrogen increases the cost of the fuel. In addition, hydrogen is highly explosive in nature and due to this, any mishandling can cause huge damage to property and life. Furthermore, the processes of handling and storing hydrogen are not yet completely advanced (Alias et al. 2020).

In recent time, hydrogen rich molecule, sodium borohydride is being used as an excellent fuel in fuel cell. Sodium borohydride has high hydrogen content (10.6 wt. %) and a high energy density of 9.3 kWh/kg (Raman et al. 2007). Furthermore, for $NaBH_4$ fuel, the fuel cell does not suffer from storage issues like pure hydrogen gas does. It means that the fuel cell using $NaBH_4$ as fuel can be safely run without any risk, as it is nonflammable. The open circuit voltage (OCV) of a direct sodium borohydride fuel cell (DSBFC) is theoretically high, measuring 1.64 V at a temperature of 25 °C (Yadav and Pramanik 2023). Additionally, the processes occurring at the anode and cathode do not produce any CO_2 or other harmful gases. Table 1.1 shows the various types of fuel cell highlighting their various adavnatages and limitations (Huang et al. 2023, Mekhilef et al. 2012, Shah et al. 2022, Mahapatra and Datta 2011, Ko et al. 2022 Choudhary et al. 2020a, Larminie et al. 2003, Gagliardi et al. 2023, Shen et al. 2010, Yadav and Pramanik 2024a, Raman et al. 2007, Du et al. 2021).

Table 1.1: Comparative analysis of types of fuel cell based on nature of electrolyte and types of fuel used in the fuel cell.

Based on the nature of electrolyte		
Type of Cell	**Advantages**	**Limitations**
Acidic (PEMFC)	High power density, high ionic conductivity, relatively quick start	Precious electrocatalyst favorable, high cost, less efficient than alkaline fuel cell
Alkaline Fuel cell	Low cost non-noble metal electrocatalyst usable, low cost, high efficiency, faster oxygen reduction reaction	Relatively low ionic conductivity, formation of carbonate in case of liquid electrolyte
Based on the fuel utilization		
Hydrogen Fuel Cell	Simple molecule structure, very high energy density (32 kWh/kg)	Hydrogen is highly explosive in nature, storage and transportation problem, electrocatalyst poison
Direct Methanol Fuel Cell	Methanol electrooxidation is faster than methanol, simple methanol structure, rapid refueling	Methanol fuel is neurotoxic, volatile flammable, low open circuit voltage, methanol crossover
Direct Ethanol Fuel Cell	Non-toxic, safer and less permeable through membrane due to its larger size	Sluggish ethanol electrooxidation kinetics, slow start
Direct Sodium Borohydride Fuel Cell	High hydrogen content (10.6 wt. %), high energy density of 9.3 kWh/kg, no storage issue, nonflammable, safer, no CO_2 emission, high open circuit voltage	Hydrolysis of $NaBH_4$ to hydrogen, borohydride ion crossover, stable only in alkaline solution

The $NaBH_4$ is easily available and commercially produced using the Brown–Schlesinger process in which trimethyl borate reacts with extremely fine sodium hydride in high boiling hydrocarbon oil at about 523-553 K (Equation 1.4) (Santos et al. 2011):

$$\mathrm{B(OCH_3)_3 + 4NaH \rightarrow NaBH_4 + 3NaOCH_3} \tag{1.4}$$

The other industrial method for the production of $NaBH_4$ was developed by Bayer (Buchner et al. 1997, Santos et al. 2011). Bayer synthesized $NaBH_4$ by using sodium, hydrogen and borosilicate glass as given by Equation 1.5:

$$Na_2B_4O_7 + 7SiO_2 + 16Na + 8H_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3 \tag{1.5}$$

The $NaBH_4$ from the product mixture borohydride-silicate is removed using liquid ammonia under pressure. The majority of the energy required for the production of $NaBH_4$ using the Brown–Schlesinger process and Bayer process is mainly attributed to the form of electricity used to make sodium metal (Santos et al. 2011). Thus, the production of $NaBH_4$ from the above discussed method mainly depends on the sodium metal and boron resources. The boron resources like fossil fuel are in limited which make the $NaBH_4$ non-renewable. To make the $NaBH_4$ renewable, other methods are also developed to produce $NaBH_4$ from $NaBO_2$ which is termed as electrosynthesis of $NaBH_4$ (Santos et al. 2010).

The electrosynthesis of $NaBH_4$ in aqueous strong alkaline media involve the anodic and cathodic reaction as reaction as given by the Equation 1.6 and Equation 1.7, respectively (Santos et al. 2010):

$$8OH^- \rightarrow 2O_2 + 4H_2O + 8e^- \qquad (E^o = 0.40\ V) \tag{1.6}$$

$$NaBO_2 + 6H_2O + 8e^- \rightarrow NaBH_4 + 8OH^- \qquad (E^o = -1.24\ V) \tag{1.7}$$

The production of $NaBH_4$ from the electrosynthesis method, makes the $NaBH_4$ recyclable which makes the $NaBH_4$ more sustainable. The electrosynthesis process for the production of $NaBH_4$ is still under investigation.

It is important to mention that borohydrides such as $NaBH_4$ or KBH_4 exhibit instability in both neutral and acidic environments. Typically, borohydride-based fuel cells, also known as direct borohydride fuel cell (DBFC), are operated in an alkaline medium. Consequently, the issue of borohydride instability caused by hydrolysis in an acidic or neutral medium does not occur in an alkaline medium (Ko et al. 2022). The sodium borohydride is electrochemically highly active and one mole of $NaBH_4$ produces eight moles of electrons in an alkaline medium (Equation 1.8) at the anode and oxygen reacts with water and electron produce eight moles of hydroxyl ion at the cathode (Equation 1.9) and byproduct $NaBO_2$ is not harmful to the environment (Kadioglu et al. 2020):

Anode:

$$\mathrm{NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-} \qquad (E^o = -1.24\ V) \qquad (1.8)$$

Cathode:

$$\mathrm{2O_2 + 4H_2O + 8e^- \rightarrow 8OH^-} \qquad (E^o = 0.40\ V) \qquad (1.9)$$

Overall reaction:

$$\mathrm{NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O} \qquad (E^o = 1.64\ V) \qquad (1.10)$$

In view of these, $NaBH_4$ is recommended as the fuel in the thesis work. The oxidant of the cathode was oxygen and in some cases NaOCl.The important components of the direct sodium borohydride fuel cell are fuel, oxidant, electrocatalyst, and membrane electrolyte. The central part of the fuel cell consists of a membrane electrolyte through which the transportation of ions takes place. The membrane electrolyte is called the heart of any type of fuel cell. The membrane electrolyte in the direct sodium borohydride fuel cell can be used as a cation exchange membrane (CEM) and anion exchange membrane (AEM). Amendola et al. 1999 first introduced a direct sodium borohydride fuel cell with air cathode that used anion conducting commercial polymer membrane electrolyte (2259-60 Pall RAI, Hauppauge, NY). The cell was constructed with an air cathode and an anode current collector made of highly dispersed gold/platinum particles supported on a high surface area of carbon silk. Due to the high crossover of borohydride ions through anion conducting membrane, some researchers tried to develop an alternative to anion conducting membrane by modifying the Nafion® like proton exchange membrane with the help of NaOH doping (Ko et al. 2022, Ertürk et al. 2022, Wang et al. 2020, San et al. 2014). The doping of NaOH to the Nafion® membrane enables the interchange of Na^+ ions across the membrane electrolyte which is called cation exchange membrane (CEM) or Na^+ form membrane electrolyte. This helps to mitigate the issue of BH_4^- crossover that typically arises in traditional anion exchange membrane electrolytes.

However, the modified Nafion®/CEM membrane has additional drawbacks, such as slower Na^+ ion conduction in an alkaline environment compared to the pure Nafion® membrane in a PEMFC (Liu et al. 2005). Furthermore, the proton conduction mechanism in water-containing PEM differs from that of Na^+ ion conduction (Choudhury et al. 2009). The main problem with using CEM in DSBFC is that it decreases the alkali concentration in the fuel solution on the anode side, leading to instability and inefficient utilization of borohydride fuel. On the other hand, the accumulation of alkali/NaOH on the cathode side is caused by the movement of Na^+ through the CEM and its reaction with OH^- produced by the oxygen reduction reaction (**Figure 1.2**). Additionally, the high cost of Nafion® materials is a significant obstacle to the commercialization of direct borohydride fuel cells (DBFC).

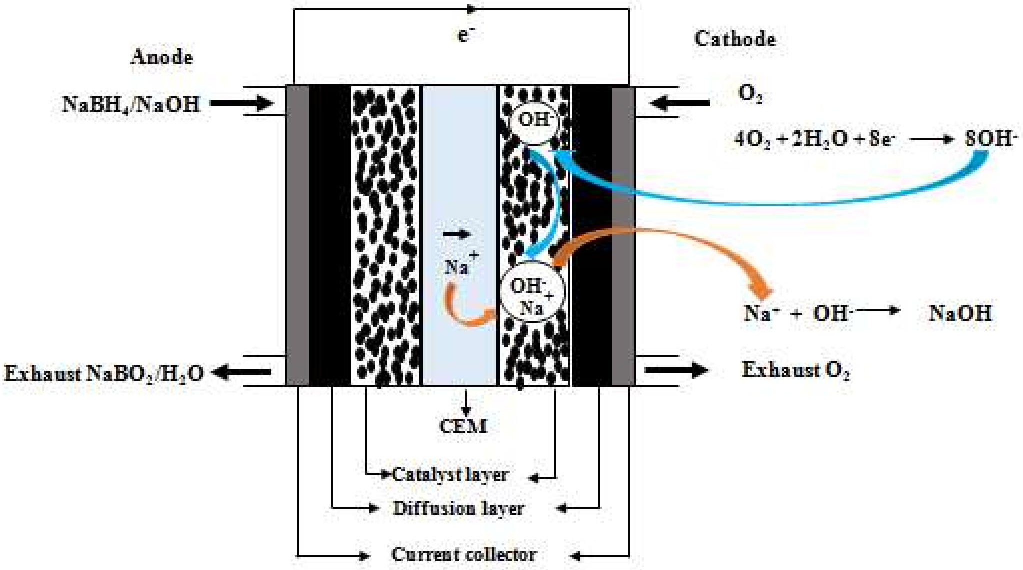

Figure 1.2 The schematic of DSBFC having cation exchange membrane/CEM electrolyte.

Thus, the development of an alternative to Nafion® modified CEM membrane is very much essential to overcome the above drawback of NaOH doped Nafion® membrane.

Till now, there is limited progress in the development of solid alkaline electrolytes. Very scanty literature is found in the published open literature search. Moreover, only a few literature is available on the performance of such alkaline membrane electrolytes for the direct sodium borohydride fuel cell. The utilization of commercial alkaline membrane electrolytes as anion exchange membranes (AEM) in direct sodium borohydride fuel cells is very expensive due to its generally high cost and limited availability.

In view of this, many other researchers recently synthesized alkaline membrane electrolytes for the improvement of DSBFC better performance in terms of power density and stability. Till now, the membrane electrolytes synthesized and examined in fuel cells include polyether sulfone (Wang et al. 2019), polyether ketone (Wang et al. 2021), polyphenylene oxide (Zhang et al. 2021), polybenzimidazole (Wang et al. 2021) and poly (N-allylisatin biphenyl)-co-poly (alkaline biphenyl) (Zhang et al. 2020a). The polymer structures contain aryl ether linkage, which is susceptible to attack by OH groups, potentially leading to membrane degradation. Furthermore, the production of the above-mentioned membrane electrolytes (Wang et al. 2019, Wang et al. 2021, Zhang et al. 2021, Wang et al. 2021, Zhang et al. 2020a) is complex and the cost of materials is also rather expensive.

Thus, the synthesis of an alkaline membrane electrolyte that is inexpensive is highly important in this context because it is necessary to get a high power density from a direct sodium borohydride fuel cell (DSBFC) at temperatures ranging from ambient temperature to moderate temperature. Polyvinyl alcohol is a very promising polymer which has excellent film forming capability, non-toxic, low cost and present in abundant amounts. It is well known that the PVA is highly hydrophilic and mechanically weak in nature. Thus, the PVA membrane must be modified before it is used as a membrane electrolyte in the fuel cell. There are various methods adopted to improve the mechanical and chemical properties of the PVA membrane. The PVA membrane blend with other polymers (Yang et al. 2015, Yagizatli ey al. 2022, Gouda et al. 2021), doped with various inorganic compounds (Pagidi et al. 2020, Yang et al. 2008, Yang et al. 2011, Sahin 2018) and the crosslinking of PVA membrane (Gupta and Paramanik, 2018, Aparicio et al. 2019, González et al. 2018) was done to improves its properties. The polyvinyl alcohol polymer contains a large number of reactive hydroxyl groups, which enable PVA to react with various compounds. The inorganic compound such as Zirconium phosphate (Pagidi et al. 2020), zeolites (Nishihara et al. 2018), titanium oxide (TiO_2) (Yang et al. 2008), silicon dioxide (SiO_2) (Yang et al. 2011) and tetraethyl orthosilicate (TEOS) (Sahin 2018) are most common material which is doped in PVA membrane to improve its properties. Among these, TEOS is a potential precursor of silica, which has excellent compatibility with PVA membranes. The TEOS forms a strong hydrogen bond with the PVA membrane, which eventually increases its mechanical strength. The TEOS is hygroscopic in nature and has the ability to retain NaOH, which can improve the water uptake and NaOH uptake of the PVA membrane and, hence, could improve the ionic conductivity of the PVA membrane electrolyte (Yang et al. 2011). The crosslinking of the PVA membrane could be done by either chemical crosslinking or by physical crosslinking. The chemical crosslinking method involves the addition of external chemical agents which react with polyvinyl alcohol. The use of a chemical crosslinker, on the other hand, may result in unfavorable effects, and the crosslinkers themselves are not only expensive but also toxic. The physical crosslinking method, such as heat treatment (Zhang et al. 2020b), irradiation method (Nho et al. 2002, Wong et al. 2020) and freeze-thaw method (Gupta and Pramanik 2018) does not involve any external chemical agents. On the other hand, the physical crosslinking method changes the physical condition of the polyvinyl alcohol by changing the temperature, which eventually leads to the crosslinking of PVA. Among the physical crosslinking methods, the freeze-thaw method is a very effective, non-hazardous, easy-to-use physical crosslinking technique for enhancing the characteristics of PVA membranes (Muangsri et al. 2022).

Thus, in the present thesis work, the low-cost PVA-TEOS composite membrane was prepared and this PVA-TEOS membrane was doped with NaOH to make it a hydroxyl ion (OH^-) conducting membrane electrolyte. Firstly, the NaOH doped pristine PVA-TEOS membrane electrolyte was prepared and characterized by various characterization techniques. The performance of NaOH doped PVA-TEOS membrane electrolyte was tested in a direct sodium borohydride fuel cell. Further, the PVA-TEOS membrane was further improved by the freeze-thaw physical crosslinking method. The physical crosslinking was done by different freeze-thaw cycle to find the best cycle that can give the best performance in direct sodium borohydride fuel. This physically crosslinked NaOH doped PVA-TEOS membrane electrolyte was also characterized and tested in DSBFC to achieve the highest power density. In all the single cell test, oxidant oxygen was used at the cathode. Only a few experiments were conducted using the sodium hypochlorite in NaOH solution was used as an oxidant and its performance was tested in half-cell analysis and single direct sodium borohydride fuel cell. The statistical method, i.e., response surface methodology (RSM) was used for the optimization of the process parameter of NaOH doped physically crosslinked PVA-TEOS membrane electrolyte to achieve the highest power density in DSBFC. The RSM model was validated by the experimental results.

The current energy scenario from fossil fuel and other renewable energy sources, along with its various drawbacks with a detailed discussion of the suitability of direct sodium borohydride fuel cell are discussed in the introduction **Chapter 1**. The **Chapter 2** contains a detailed literature review research along with the research gap and objectives of the thesis. The **Chapter 3** consists of the material required through the experiment and detailed experimental procedure of the synthesis of the synthesis of the membrane electrolyte, physical and electrochemical characterization of the prepared membrane electrolyte, preparation of the catalyst slurry and electrodes, half-cell study and single cell study. The optimization and validation of the process parameter of the physically crosslinked membrane electrolyte by response surface methodology to achieve the highest power density from direct sodium borohydride fuel cell are discussed in **Chapter 4**. The results and discussion of the characterization of the synthesized membrane electrolyte, as well as the study of the half-cell and single cell studies of the DSBFC, are presented and discussed in **Chapter 5**. The various types of characterization techniques used were water and NaOH uptake, swelling ratio, ion exchange capacity, ionic conductivity measurement by electrochemical impedance spectroscopy (EIS), FTIR analysis, XRD analysis, scanning electron microscopy (SEM), mechanical strength test and cyclic voltammetry (CV). **Chapter 6** presents an extensive summary of the key findings and discussions presented in the thesis, along with significant recommendations for future research in this field.