CHAPTER 2

LITERATURE REVIEW AND OBJECTIVES

In this chapter, a comprehensive literature review is reported on the fundamentals of direct sodium borohydride fuel cells (DSBFC) along with the various types of membrane electrolytes, the synthesis of membrane electrolytes, the characterization of membrane electrolytes, the various key components, and the fabrication procedures for these components. Based on the comprehensive literature review, significant research gaps have been identified on borohydride fuel cell. These research gaps need to be addressed in order to develop this technology further and achieve the goal of generating low-cost power. The objectives of the thesis are decided based on the thorough literature review which is presented at the end of this chapter.

2.1 Fundamental of DSBFC

Direct sodium borohydride fuel cell (DSBFC) works on the similar principle of galvanic cell (Li et al. 2005). The details of functioning of DSBFC are already discussed in the Introduction (**Chapter 1**) (page no. 10). The DSBFC uses $NaBH_4$ as fuel at anode and oxidant like oxygen from air or pure oxygen or any other oxidant at the cathode side. The first DSBFC was reported by Indig and Snyder 1962 were the first to introduce the DSBFC and reported that it could be practical to generate direct power from borohydride ions. However, Amendola et al. 1999 was first to report the performance of DSBFC in which they used the anion exchange membrane electrolyte. The key advantage of a Direct Sodium Borohydride Fuel Cell (DBFC) in comparison to Proton Exchange Membrane Fuel Cells (PEMFC) and Direct Methanol Fuel Cell (DMFC) is the absence of CO poisoning to anode catalyst (Zhiani and Mohammadi 2016). Theoretically, the open circuit voltage (OCV) that DSBFC may achieve is 1.64 V, which is roughly 1.3 times higher than that of PEMFC

(Larminie and Dicks 2003) and 1.35 times higher than that of DMFC (Gagliardi et al. 2023) and the other advantages of the DSBFC are already discussed in **Chapter 1 (**page no. 10**)**. During the course of time DSBFC proved to be excellent fuel cell device. The details of the major components of the DSBFC are discussed in the following section.

2.2 DSBFC components

The DSBFC comprises of three major components such as (i) membrane electrolyte, (ii) anode and (iii) cathode. The heart of the fuel cell is membrane electrolyte through which the transport of ion takes place. The important characteristics of membrane electrolytes are mechanical and chemical stability and ionic conductivity, which control the performance of DSBFC and any other type of fuel cell. The detailed literature review and discussion on electrolyte is reported in the following **section 2.2.1**. The anode and cathode also play important role for the electrooxidation of fuel at anode and reduction of oxidant at cathode and thereby continuous generation of electrons at anode and recombination of electrons at cathode takes place. It helps in maintaining cell response current and voltage during operation. The fuel used in DSBFC is sodium borohydride ($NaBH_4$) mixed in NaOH solution, which has excellent characteristics over other fuels such as ethanol, methanol and hydrogen as discussed in **Chapter 1**. The oxidants generally used in DSBFC are oxygen and hydrogen peroxide. The choice of oxidants is also important to obtain the high performance from DSBFC, which is discussed in the subsequent section (page no. 46). The details of anode and cathode are discussed in the **section 2.2.2** and **2.2.3**, respectively.

2.2.1 Electrolyte

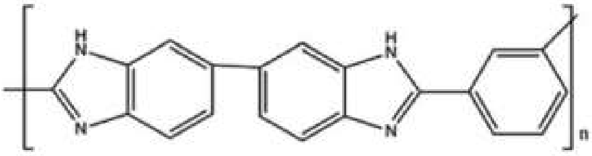
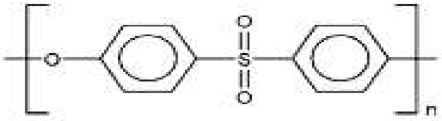
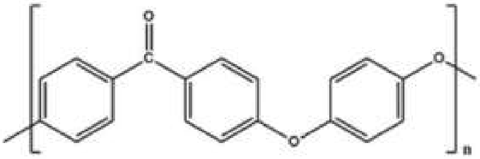
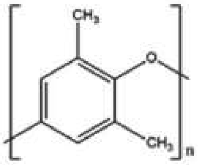
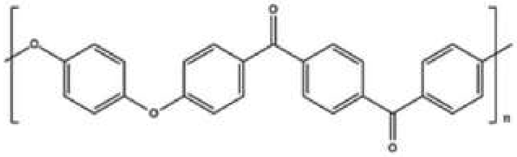
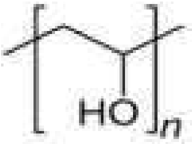
The DSBFC performance is highly dependent on the membrane electrolyte used in the cell. The membrane electrolyte used in the DSBFC are of two types (i) alkaline (ii) acidic. Acidic and alkaline electrolyte are available in solid and liquid form both. However, solid electrolyte is preferred over liquid electrolyte due to several benefits of solid form of electrolyte like very thin, highly conducting, no corrosion problem. The $NaBH_4$ is stable in an alkaline medium and also reaction kinetics of $NaBH_4$ is faster in alkaline medium. In addition, cathode reduction of oxygen or ORR is better in alkaline medium (Kumar et al. 2016). Thus, in the present work, $NaBH_4$ electrooxidation and cathode reduction both were performed in alkaline medium. Keeping in mind reactions in alkaline medium, solid alkaline membrane electrolyte or anion exchange membrane was selected for the transport of hydroxyl (OH^-) ions from cathode to anode. It is seen from thorough literature review that only few studies are available on the commercial anion exchange membrane for the DSBFC in open literature. No such work on the AEM synthesis studies and subsequent use are found in open literature. Duteanu et al. 2007 used the commercial anion exchange membrane (AEM) (ADP-Morgane, Solvay S.A.) electrolyte in direct sodium borohydride fuel cell. The fuel used was 1 M $NaBH_4$ in 1 M NaOH and the oxidant was pure oxygen. The anode and cathode electrocatalysts were Pt-Ru and Pt/C, respectively. The maximum power density obtained was 77.78 mW/cm^2 at the cell temperature of 30 ^{o}C. The commercial AEM (University of Cranfield, UK) was also used in DSBFC by Coowar et al. 2008. The gold (Au) was used as an anode electrocatalyst and MnO_2 as the cathode. The fuel used was 5 wt. % $NaBH_4$ in 6 M NaOH and the oxidant used was air. The maximum power density of 28 mW/cm^2 was obtained from the cell at room temperature. The reported power density was very low. No information on the AEM properties was provided in those studies. Moreover, the use of commercial alkaline membrane electrolytes as AEM in direct sodium borohydride is not very economical owing to the fact that its cost is generally high and not easily available. The other factor was the low performance of AEM due to the high crossover of BH_4^- through alkaline membrane electrolytes (Gouda et al. 2021). To overcome the borohydride ion crossover in some studies, CEM electrolyte were used instead of AEM electrolyte. The most common CEM electrolyte was NaOH modified Nafion® membrane. However, the NaOH doped CEM has several demerits like alkali reduction at the anode side, the NaOH accumulation at the cathode side (**Figure 1.2**) (page no. 12) and the high cost of Nafion® membrane electrolytes. Due to several disadvantages of CEM and commercial AEM, the researchers recently focused on the development of low cost alkaline membrane electrolyte for direct borohydride fuel cell. The synthesis of the highly conducting alkaline or anion exchange membrane electrolyte in laboratory is essential to obtain the high power density from the DSBFC. In the following section, literature review on electrolyte synthesis is thoroughly discussed. The suitable method and material are also identified for the present thesis work.

2.2.1.1 Electrolyte synthesis

The main substrate of the solid alkaline membrane electrolyte or anion exchange membrane is the polymer matrix. The synthesis of the membrane is done by various methods such as the, block polymerization (Hu et al. 2016), the sol-gel technique (Tripathi et al. 2010), copolymerization (Wang et al. 2019), paste method (Tanaka et al. 2011) pore- filling method (Maurya et al. 2015, Son et al. 2020), plasma polymerization (Munsur et a. 2020, Zhang et al. 2011) and solution casting method (Kaker et al. 2019). The block polymerization is a method employed to synthesize membrane polymer by combining various monomers in alternating or sequential blocks (Ex. Quaternary ammonium poly(arylene ether sulfone)) (Hu et al. 2016). The block polymerization method requires the multiple steps and precise control making the process highly difficult. However, the procedure needed specialized equipment, chemicals, and knowledge, making it highly costly. The membrane prepared by the sol-gel method involves the transformation of a colloidal solution (sol) into a gel-like network structure, eventually forming a thin and uniform membrane (Tripathi et al. 2010) (Ex. Polybenzimidazole (Xiao et al. 2005). The copolymerization is a process where two or more different monomers are polymerized together to produce a copolymer containing distinct repeating units from each monomer (Ex. poly(ether ether ketone)) (Wang et al. 2019). Copolymerization can produce a polydisperse distribution of chain lengths and compositions in the resultant polymer matrix and it susceptible to impurities and contaminants. The membrane preparation method by paste method often denotes a combination of solid particles that are distributed in a liquid media (Ex. Glycidyl methacrylate (GMA)/divinylbenzene (DVB)) (Tanaka et al. 2011). This paste can be placed as a coating onto a substrate. The paste preparation method is a straightforward approach used to prepare membranes, especially in situations when a thick or porous covering is required. Paste method of preparation of membrane faces problem of uniformity, mechanical strength and longer operation of time. The membrane preparation method by pore filling method typically denotes the procedure of infusing a substance into the pores or voids of a membrane material to alter its characteristics, such as permeability or selectivity (Ex. Poly(phenylene oxide)) (Son et al. 2020). The pore-filling preparation procedure may consist of a range of techniques, which are selected based on the specific demands of the membrane. Pore-filling method is suitable only for specific type of material. Plasma polymerization technique involves the generation of a plasma that contains vapors of monomers. The monomers are subsequently polymerized and deposited onto the substrate, forming a thin coating of polymer (Ex. Poly(vinylbenzyl chloride)) (Zhang et al. 2011). Plasma polymerization can be employed to synthesize membranes with controlled characteristics. The solution casting method is widely adopted for the synthesis of the membrane electrolyte. In this method, a polymer is made to dissolve in a suitable solvent to prepare a solution and, followed by solvent evaporation to prepare the membrane. Plasma polymerization method require specialized equipment and this method also not suitable for all type of materails. The solution casting method is widely used and reported in open literature for the fuel cell application (Prapainainar et al. 2020, Simari et al. 2020, Gupta and Pramanik 2018) due to its several advantages like versatility, uniformity, control over membrane thickness and uniformity. In view of this, in the present study, the solution casting method is adopted to synthesize the membrane electrolyte.

There are various types of membranes synthesized by researchers using the above solution casting technique for fuel cell application. Some important and popular membranes viz polybenzimidazole, polyether sulphone, poly(ether ether ketone), polyphenylene oxide, polyether ketone ketone, polyvinyl alcohol (Wu et al. 2018, Zhao et al. 2013, Aristizábal et al. 2019, Parrondo et al. 2016, Swier et al. 2004, Aslam et al. 2018) with their structures is shown in **Table 2.1**. The membranes which are shown in **Table 2.1** are synthetic in nature. The natural derived membrane is also synthesized such as Chitosan (CS) (Choudhury et al. 2011), nanofibrillar cellulose (CNF) (Bayer et al. 2021) and nano-crystalline cellulose (CNC) (Thakur et al. 2021). Among all the synthesized membranes, polyvinyl alcohol (PVA) membranes doped with suitable alkali NaOH or KOH are proven to be promising for anion exchange membranes as it is very cheap and excellent film forming capability as discussed in **Chapter 1 (**page no. 13).

Table 2.1 The various type of synthetic membrane used for the fuel cell application.

Membrane Types	**Structure**	**References**
Polybenzimidazole		Wu et al. 2018
Polyether sulphone		Zhao et al. 2013
Poly(ether ether ketone)		Aristizábal et al. 2019
Polyphenylene oxide		Parrondo et al. 2016
Polyether Ketone Ketone		Swier et al. 2004
Polyvinyl Alcohol		Aslam et al. 2018

The modification of PVA membrane is a necessary step to improve its properties such as mechanical and chemical stability, swelling ratio, ionic conductivity etc. The PVA membrane are of two types (i) Pristine and (ii) crosslinked. Bothe membrane could be modified with inorganic fillers. The pristine PVA membrane is modified by adding inorganic fillers with PVA solution to react with the PVA membrane matrix. On the other hand, the crosslinked PVA membrane are synthesized by crosslinking either by chemically or physically. Similar to the pristine PVA modified membrane, the crosslinked membrane are also modified by adding inorganic fillers with PVA solution to get the modified membrane matrix of PVA. Subsequently, the synthesized membrane is doped with alkali like NaOH or KOH to make the PVA membrane matrix suitable for OH^- conducting. These two types of modified PVA membranes are discussed in the following section.

2.2.1.1.1 Pristine PVA membrane electrolyte

The pristine PVA without modification is generally not recommended for the use in fuel cell due to some demerits as already discussed. The important properties of the pristine PVA membrane, such as chemical and thermal stability, mechanical strength and electrochemical properties are improved by the addition of inorganic fillers. The inorganic filler involves alkoxysilane and oxides such as TiO_2 (Yang et al. 2008b, Aiswarya and Joseph 2020), ZrO_2 (Mehto et al. 2023), ZrP (Pagidi et al. 2020), geolites (Nishihara et al. 2018), HAP (Yang et al. 2008a), SiO_2 (Yang et al. 2011), TEOS (Sahin 2018), Al_2O_3 (Chand et al. 2011) and nano carbons such as carbon nanotube (CNT) (Huang et al. 2016) and graphene (Beydaghi et al. 2014). Yagizatli et al. 2020 synthesized the PVA based membrane electrolyte and TiO_2 was used as additive for proton exchange membrane fuel cell. It is reported that the addition of TiO_2 nanoparticles to the membrane has a good impact on their mechanical and thermal properties. It was also observed that water uptake and ion exchange capacity also get improved on addition of TiO_2. Aiswarya and Joseph 2020 also synthesized PVA-TiO_2 membrane electrolyte for an alkaline direct methanol fuel cell. The PVA-TiO_2 membrane electrolyte was used as a cation exchange membrane electrolyte and it was also observed that the addition of TiO_2 improved the thermal stability, water uptake and ionic conductivity. Yang et al. 2008b also observed a similar trend for PVA-TiO_2 membrane electrolytes when tested in an alkaline direct methanol fuel cell. The addition of zirconium phosphate (ZrP) in the PVA membrane matrix mainly improves the protonic conductivity along with mechanical and thermal stability Pagidi et al. 2020. The distribution of nano-sized Al_2O_3 filler particles within the PVA membrane is anticipated to significantly hinder the crystallization process in polymer-based nanocomposite electrolytes. As a result, this is expected to enhance the ionic conductivity, mechanical strength, and electrochemical stability of the material, making it suitable for long-term use in electrochemical devices (Chand e et al. 2011, Mohamed et al. 2022). The incorporation of hydroxyapatite (HAP) ceramic filler into the polymer matrix resulting in decrease in the glass transition temperature (Tg) and crystallinity of the PVA polymer. Additionally, it promotes an increase in the amorphous phases of the polymer matrix, hence enhancing the ionic conductivity of the membrane electrolyte (Yang et al. 2008a). Although, using inorganic fillers such as TiO_2, ZrP, Al_2O_3, and HAP enhance the different properties of the PVA-based membrane electrolyte, these fillers have some drawbacks such as a complicated production process, negative environmental impact, and concerns over the cost of these nanofillers.

Recently the addition of nano carbon such as carbon nanotube and graphene in PVA membranes also receives much attention. Carbonaceous nanofillers possess the ability to contribute a range of unique features to PVA membranes, including proton conduction, fuel separation, and mechanical strength. These qualities are determined by the nanofillers' specific attributes, such as their particle size, shape, porosity, and surface functional groups. Huang et al. 2016 synthesized the PVA membrane electrolyte functionalized by carbon nano tubes for application in alkaline direct ethanol fuel cell. It was concluded that the addition of carbon nano tube decreases the crystallinity, improve the water uptake and ionic conductivity of the membrane electrolyte. Pan et al. 2011 reported similar features when they synthesized the PVA/multiwalled carbon nanotube membrane electrolyte for the direct methanol alkaline fuel cell. Apart from many advantages of CNT, they suffer many disadvantages of aggregation in PVA matrix, difficulties in the preparation of PVA/CNT composite membrane, high concentration of CNT can damage the membrane and high cost of CNT is also a major problem (Li et al. 2022).

Another inorganic filler, silicon oxide, also referred to as silica (SiO_2), is a frequently employed metal oxide nanofiller in the membrane electrolyte for the application in fuel cells (Vani et al. 2019). The nano SiO_2 possesses a three-dimensional network structure, and the presence of siloxane and silanol groups on its surface significantly enhanced its hydrophilic characteristics. Vani et al. 2019 synthesized the PVA-SiO_2 membrane electrolyte using colloidal silica (LUDOX HS-30 colloidal silica − 30 wt. % suspension in water). It was observed that the addition of silica in the PVA membrane electrolyte improves the mechanical strength, water retention capacity and ionic conductivity. The PVA-SiO_2 membrane electrolyte was also prepared by Das et al. 2014 for fuel cell application. The silica (SiO_2) nanoparticles (10-20 nm diameter) were used for the preparation of PVA-SiO_2 composite membrane electrolyte. Das et al. 2014 reported that the addition of silica in the PVA membrane matrix improves the water retention properties, increases the amorphous nature of the membrane matrix and improves the ionic conductivity. The addition of silica in the PVA membrane could be done by the addition of tetraethyl orthosilicate (TEOS) also. The tetraethyl orthosilicate is an excellent precursor of silica. The TEOS is a precursor that performs a hydrolysis and condensation reaction to create silicon dioxide. This reaction can lead to a closer integration of SiO_2 with the polymer matrix. The **Figure 2.1** shows the reaction between PVA and TEOS in an acidic environment (Kittur et al. 2013, Yadav and Pramanik, 2023):

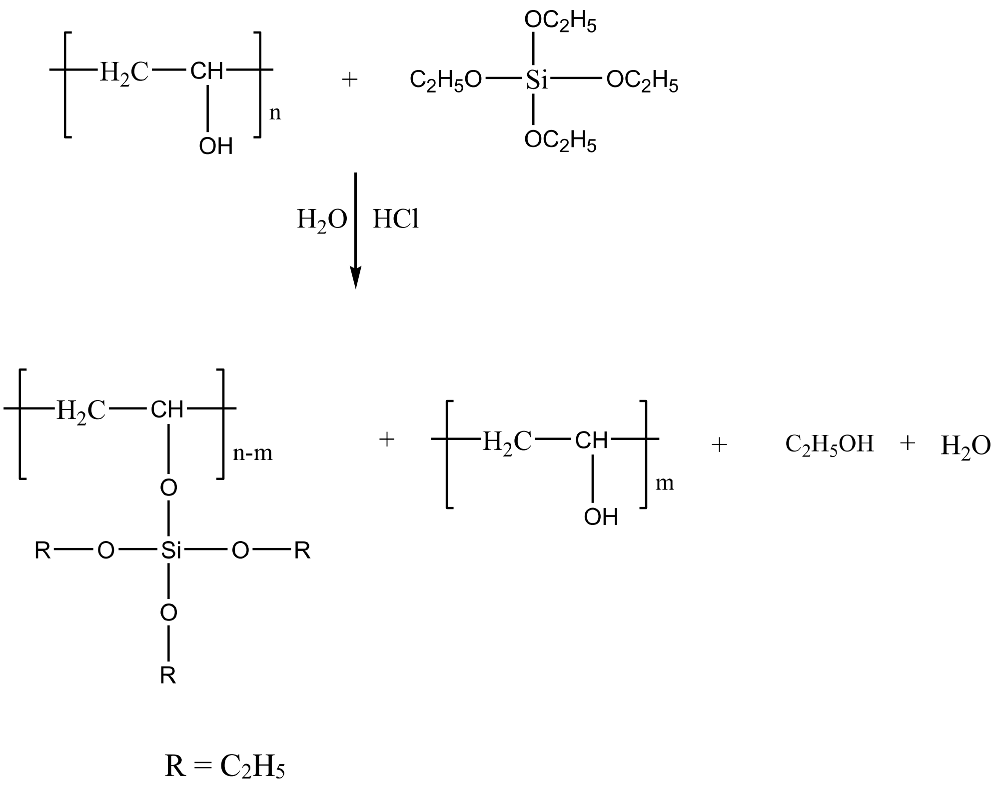


Figure 2.1 The reaction scheme and interaction between PVA and TEOS.

The silica obtained from TEOS has good compatibility with the PVA membrane, giving a robust solid electrolyte structure with good mechanical and chemical stability, which are required for low to moderate temperature fuel cell applications. The TEOS enables enhanced control of the SiO_2 concentration and arrangement within the membrane, resulting in greater accuracy and control.

This can be beneficial for modifying some essential characteristics viz water and NaOH uptake, mechanical stability and ionic conductivity of membrane electrolyte. The TEOS utilization can mitigate SiO_2 aggregation concerns, resulting in a more uniform dispersion inside the membrane. It is possible that TEOS, which involves in the controlled formation of SiO_2, can provide superior ionic conductivity in comparison to SiO_2, that is directly added. The TEOS is added in the membrane electrolyte either by direct blending method or sol-gel method. The TEOS directly blended into the PVA matrix can lead to agglomeration on the PVA surface and result in relatively low mechanical strength. However, incorporating TEOS using the sol-gel process into the PVA matrix results in a more uniform homogeneous membrane and increased mechanical strength. Thus, in the present study, modified pristine PVA membrane is synthesized by adding TEOS in the membrane matrix by sol-gel method.

2.2.1.1.2 Crosslinked PVA membrane electrolyte

The crosslinked membrane chemically and mechanically more stable than Pristine PVA and modified pristine PVA. The crosslinking of the polymer membrane electrolyte is generally done by physical crosslinking and chemical crosslinking method. The chemical crosslinking of the membrane involves the addition of an external chemical agent or crosslinking agent into the polymer matrix. The crosslinking agent reacts with the polymer membrane backbone and forms a strong bond between the polymer chain. The chemical crosslinking of the membrane improves the mechanical strength, thermal and chemical stability of the polymer matrix. It is seen from the reported literature that chemically crosslinked PVA membrane are synthesized by using multifunctional aldehyde molecules like glutaraldehyde (Aparicio et al. 2019), glyoxal (Gadhave et al. 2019), sulfosuccinic acid (SSA) (González et al. 2018), poly(ethylene glycol) diglycidyl ether

(PEGDGE) (Ari et al. 2019) and species that contain borate (Lu et al. 2017). Among all the glutaraldehyde is widely used as chemical crosslinker to improve the properties of the PVA membrane as it forms strong bond with PVA backbone (**Figure 2.2**) (Yan et al. 2015a). However, using a chemical crosslinker is not advantageous as the crosslinker are toxic, expensive and some of them are not environment friendly.

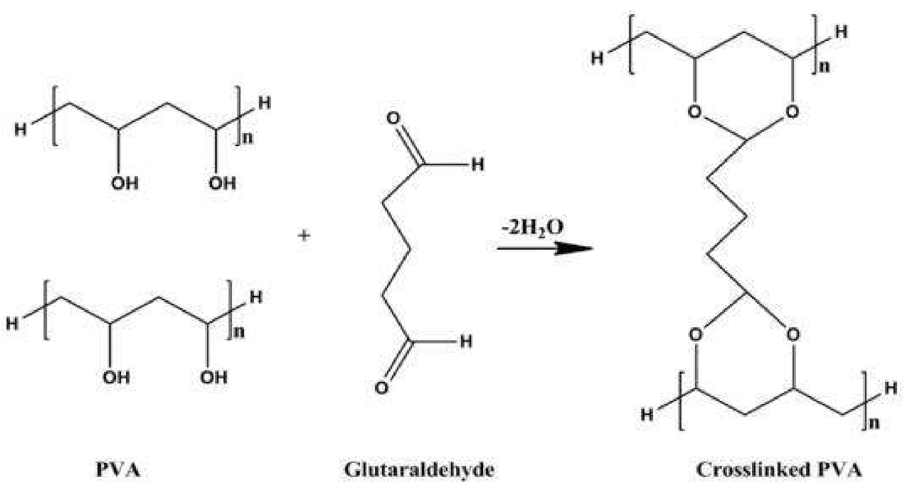


Figure 2.2 The reaction scheme and interaction between PVA and glutaraldehyde (Yan et al. 2015).

On the other side, physical crosslinking of PVA does not require any expensive and toxic chemical crosslinking agent. The physical crosslinking is generally done by freezing and thawing (Gupta and Pramanik 2018), heat treatments (Zhang et al. 2020b) and irradiation methods (Nho and Park 2002, Wong et al. 2020). The physical crosslinking of the membrane electrolyte by irradiation is done by exposing the membrane material to ionization radiation such as gamma rays, X-rays or electron beams, resulting in the creation of connections between polymer chains. This method is employed to change the properties of polymers, forming a network structure that improves mechanical strength, thermal stability, and other desirable properties (Nho and Park 2002, Basfar and Lotfy 2015). The physical crosslinking of the membrane by heat treatment is termed as thermal crosslinking, in which interconnection of polymer chains is established with the help of heat treatment. This technique enhances the mechanical and thermal characteristics of polymers (Diantoro et al 2018). The physical crosslinking method by freeze-thaw is an excellent, harmless and simple physical crosslinking method to improve the important properties of the PVA membrane (Muangsri et al. 2022). The physical crosslinking by freeze-thaw method is preferred over irradiation and heat treatment, it is due to freeze-thaw uses comparatively moderate processing conditions and irradiation can create chemical changes in the material, whereas heat treatment can cause thermal deterioration. In addition, the degree of crosslinking easily controlled in freeze-thaw process by adjusting number of freeze-thaw cycle and it promote uniform crosslinking throughout material. Thus, the physical crosslinking by freeze-thaw method has advantages of harmless, easy processing, cheap, uniform and controlled crosslinking. During the physical crosslinking of PVA by freeze-thaw method, the temperature of PVA solution is brought to below 0 ^{o}C temperature (freezing) for a certain interval of time and then brought back to room temperature (thawing). Initially, the PVA solution is mobile in nature, but during the freezing process of the PVA solution, the molecules come in contact with each other for a longer period of time, may leading to the intermolecular interaction between PVA chains, which is likely to result in hydrogen bond formation (Hatakeyema et al. 2005). This interaction may have promoted to yield physically entangled three-dimensional zone (Ru-yin et al. 2008). The schematic of the freeze-thaw process is shown in **Figure 2.3** (Adelnia et al. 2022). In the present study, the physical crosslinking by freeze-thaw method is adopted to synthesize the NaOH doped PVA-TEOS membrane electrolyte. The pristine PVA and pristine PVA-TEOS membrane electrolyte are also synthesized and studied for comparison purpose.

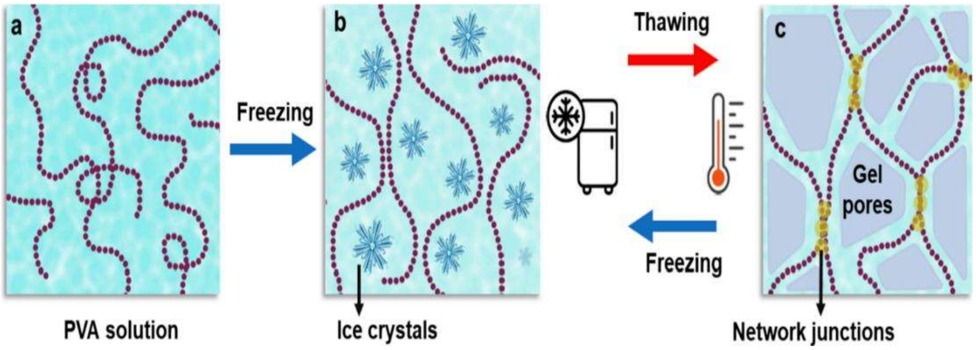


Figure 2.3 The schematic of freeze-thaw process of PVA solution (Adelnia et al. 2022).

To make the synthesized membrane OH^- ion conducting, the polymer membrane is generally treated with various concentration of NaOH or KOH alkaline solution (Huang et al. 2013). Gupta and Pramanik 2018 synthesized physically crosslinked KOH doped PVA membrane alkaline electrolyte. The highest conductivity of 5.67×10^{-3} S/cm was reported. Similarly, Zugic et al. 2013 synthesized physically crosslinked KOH doped PVA membrane electrolyte and highest conductivity of 1.2×10^{-2} S/cm was reported. Similar to the KOH modified membrane electrolyte, NaOH is also incorporated in some membrane electrolyte synthesis (Huang et al. 2013). Huang et al. 2013 synthesized NaOH doped PVA/CNT membrane electrolyte. The highest ionic conductivity of 6.62×10^{-2} S/cm was reported for the NaOH doped PVA/CNT membrane electrolyte at temperature of 30 ^{o}C. In view of this, in the present work, the synthesized membrane electrolyte was doped with NaOH solution to make the membrane matrix ionically conducting enabling transportation of OH^- ions. **Figure 2.4** shows the types of membrane electrolyte which are synthesized and named in reference to the types of electrolyte used and crosslinking method. The selected membrane electrolyte and method are highlighted by green colour.

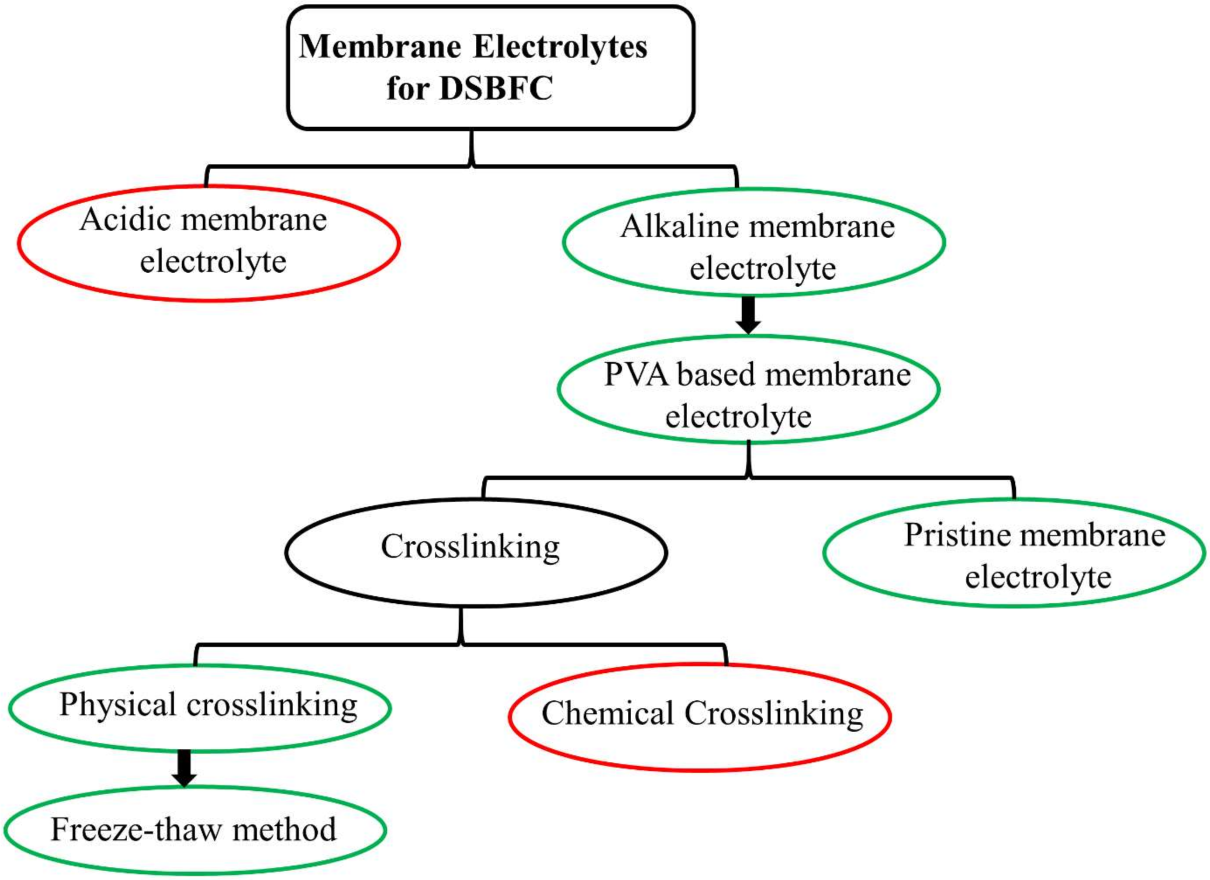


Figure 2.4 Flow diagram of selection of membrane electrolyte of alkaline DSBFC.

2.2.1.2 Electrolyte Characterization

2.2.1.2.1 Physical Characterization

2.2.1.2.1.1 X-ray diffraction

The X-ray diffraction (XRD) analysis of the membrane electrolyte is an important physical characterization method which gives the information on the nature of the membrane. The XRD analysis of the PVA membrane electrolyte is generally performed to study the crystallinity of the PVA membrane. The PVA membrane is semicrystalline in nature which is confirmed by the XRD analysis. The semicrystalline nature of the PVA polymer is well known, and it exhibits a significant peak at a 2θ angle of about 19.61° that corresponds to the (110) plane and a tiny peak at 2θ of 40.38° that corresponds to the (041) plane (ICDD No. 00–061-1401). It is seen from the literature that the addition of inorganic material into the PVA membrane decreased the semicrystalline nature and the PVA membrane becomes amorphous in nature (Pagidi et al. 2020). This phenomenon is desirable as the increase in the amorphous nature of the membrane improves the ionic conductivity of the membrane, which helps to increase the power density of the fuel (Fu et al. 2010). Fu et al. 2010 also reported that the addition of KOH in the PVA membrane augmented the amorphous nature of the membrane. Yang et al. 2008a studied the XRD analysis of the PVA and PVA/hydroxyapatite (HAP) composite membrane, as shown in **Figure 2.5.** It is seen from **Figure 2.5** that the PVA membrane exhibited a significant peak at around 2θ equal to 20° a small peak at around 2θ equal to 40°. It is also seen from the **Figure 2.5** that the peak intensity decreases and the broadening of the peaks occurs on the addition of ceramic filler HAP into the PVA matrix, which demonstrates that the amorphous nature of the PVA/HAP membrane increased. This indicates that the XRD analysis is necessary to study the crystallinity of the PVA composite membrane. In the current thesis, XRD was performed to study the semicrystalline nature of PVA, PVA-TEOS and NaOH doped PVA-TEOS composite membrane electrolyte.

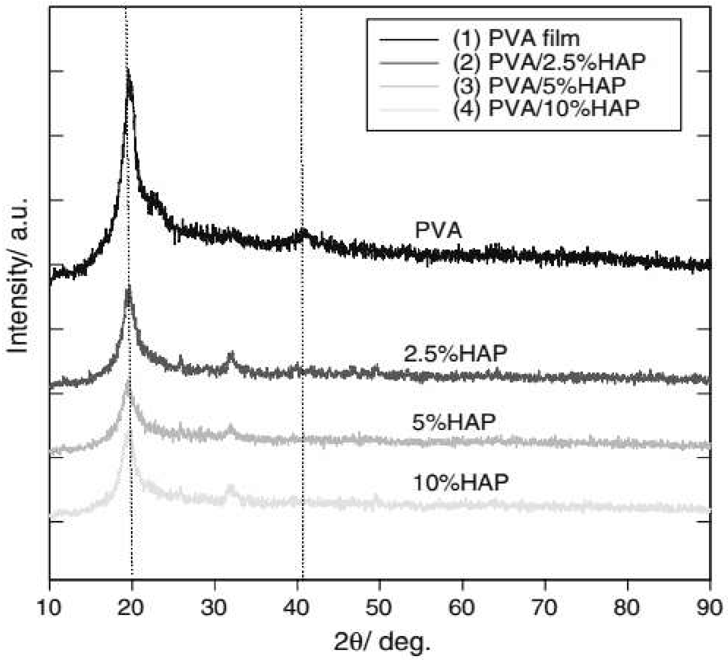


Figure 2.5 XRD spectra for the PVA/HAP composite polymer membranes at different HAP compositions (Yang et al. 2008a).

2.2.1.2.1.2 Scanning electron microscopy (SEM)

The surface morphology of the synthesized membrane electrolyte is studied by scanning electron microscopy (SEM). The SEM analysis gives the information of the surface properties of any substance. The surface of the PVA membrane is homogeneous and uniform if it is synthesized at standard conditions (Sahin 2018). However, the surface morphology of the various synthesized composite membranes will have different surface morphology which is essential to investigate to correlate with the results of membrane electrolyte performance. Moreover, after the addition of inorganic filler in the PVA matrix distribution of inorganic filler can be easily detected and confirmed by the SEM analysis. However, it does not analyze about the size of the particle present on the surface of the PVA membrane. Chaudhari et al. 2020 prepared the PVA-TEOS membrane and studied the surface morphology of the membrane through SEM. The y observed that the PVA TEOS membrane showed a smooth and continuous surface with no cracks or defects.

2.2.1.2.1.3 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared Spectroscopy (FT-IR) analysis is used to identify the significant functional groups that were present in the membrane electrolyte matrix. The FT-IR analysis of the PVA membrane was performed to study the various functional group present in PVA membrane. The addition of inorganic material or the addition of crosslinking agent in the PVA membrane matrix results in the presence of a new functional group in the membrane matrix which can be confirmed by FT-IR analysis. Sahin 2018 studied the FT-IR analysis of the SPEEK/PVA/TEOS composite membrane electrolyte to detect various distinct functional groups present in the synthesized composite membrane electrolyte are shown by FT-IR analysis (**Figure 2.6**). The broad absorption peak at wavenumber 3200-3500 is due to presence -OH functional group, C-H functional group is shown at wavenumber 2950 and 1350 of the PVA membrane. The addition of TEOS resulted in the presence of Si-O-Si, Si-O and Si-O-C functional groups at 1040-1120, 830 and 610, respectively. The C-N and O=S=O at 1580 and 1250, respectively is due to the SPEEK membrane. Thus, it can be concluded that FT-IR analysis is an important physical characterization method to study the insight of synthesized composite membrane electrolyte (Sahin 2018).

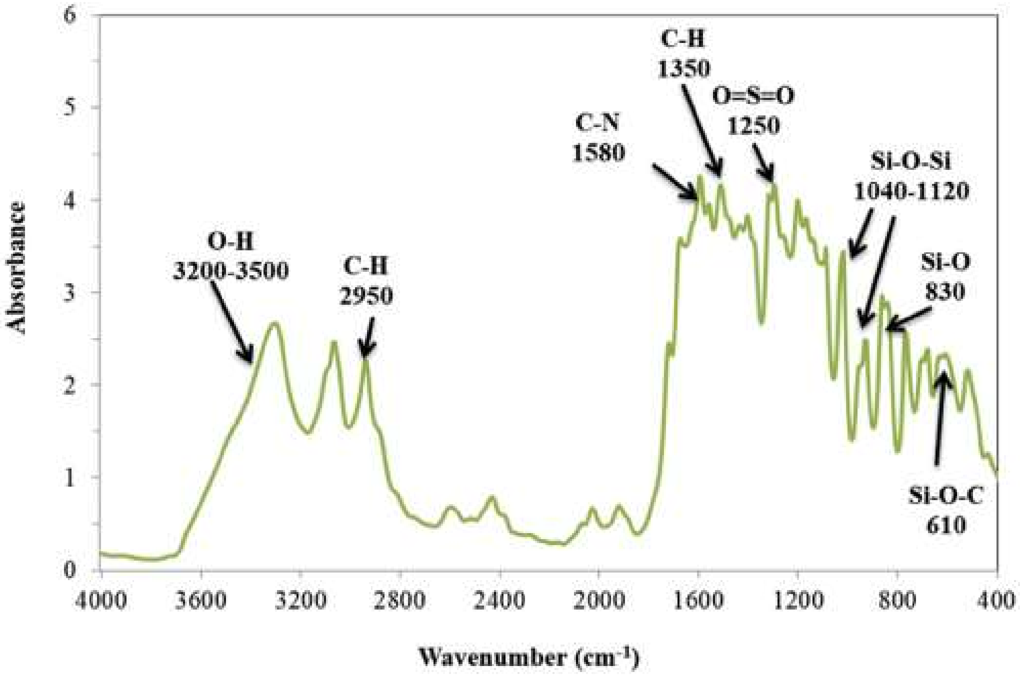


Figure 2.6 FT-IR spectra of the SPEEK/PVA/TEOS composite membrane (Sahin 2018).

2.2.1.2.1.4 Mechanical Properties

The mechanical strength of the membrane electrolyte should be high to sustain the fuel cell component load. The mechanical stability test is done by the universal testing machine (Gupta and Pramanik 2019a). The mechanical stability test evaluates the resilience to mechanical stress and deformation under a variety of situations of PVA membrane. It is an important evaluation method for ensuring the durability and dependability of PVA membranes for a variety of applications. The mechanical stability test ensures the compatibility between PVA and inorganic fillers. This is due the fact that the tensile strength of the PVA membrane increases due to better interaction between PVA and inorganic filler like TEOS. The high interaction between PVA and inorganic filler leads to less elongation which can easily detect by the stress-strain curve. Tong et al. 2017 and Jessie et al. 2007 reported the similar behavior of tensile strength and elongation of the synthesized PVA-

SiO_2 membrane. The similar type of increase in tensile strength and decrease on elongation are also reported for crosslinked PVA membrane electrolyte (Gupta and Pramanik 2019a, Adelnia et al. 2022).

2.2.1.2.2 Electrochemical study/ Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) study is one of the important characterizations of any membrane electrolyte to measure the ionic conductivity of the membrane electrolyte. The ionic conductivity of the membrane electrolyte using EIS technique is done by measuring the impedance response to an applied AC voltage. A typical EIS setup consists of a three-electrode cell with a reference electrode typically a conventional calomel or Ag/AgCl/KCl electrode, a counter electrode i.e., generally an inert material such as platinum, and a working electrode. For the ionic conductivity measurement of membrane electrolytes, the two-probe through plane EIS setup is widely used (Gupta and Pramanik 2019a). The components of the two-probe through plane EIS setup is systematically discussed in the **Chapter 3, Experimental** (page no. 64,65). The EIS uses an alternating current signal at various frequencies, often ranging from millihertz to megahertz. This frequency sweep allows us to evaluate the activity of the system across a variety of time scales, providing detailed information on the electrochemical characteristics or EIS. The Nyquist plot is widely used as the graphical representation of EIS data. A Nyquist plot consists of an imaginary part (y-axis) and a real part (x-axis) and the plot is generally exhibiting a semicircle and a straight line. The EIS plot is mainly divided into high-frequency and low-frequency zones. The high-frequency zone is related to the ionic conductivity of the solid electrolyte membrane (Yang et al. 2006). The **Figure 2.7** shows the typical EIS plot of the alkaline PVA/sulfosuccinic acid (SSA) membrane electrolyte at various temperatures (Yang et al. 2006). The intercept of the curve on the x-axis (real part) shown in the inset and represented by R_b (**Figure 2.7**) is considered as membrane resistance which used to measure the ionic conductivity of the membrane eletrolyte

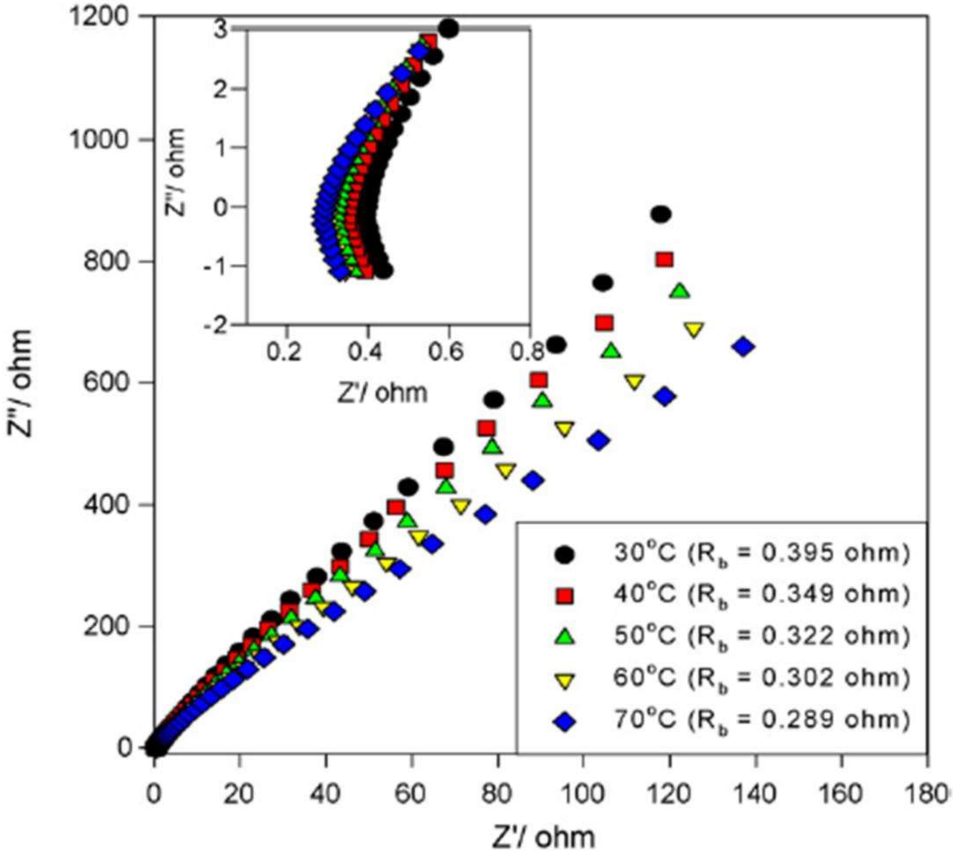


Figure 2.7 EIS plot of the alkaline PVA/SSA polymer membrane electrolyte at various temperature (Yang et al. 2006).

2.2.2 Anode Electrode

2.2.2.1 Electrocatalysts

The selection of electrocatalyst is tricky for direct sodium borohydride fuel cell. This is due to the high affinity of $NaBH_4$ towards its hydrolysis to produce hydrogen, which eventually reduces fuel efficiency. The electrooxidation of $NaBH_4$ depends upon various parameters such as the nature and structure of the electrocatalyst, electrode design, pH, temperature and fuel concentration (Molina et al. 2011, Finkelstein et al. 2013). Till date, many materials as electrocatalysts have been studied for the electrooxidation of $NaBH_4$ in alkaline media. The electrocatalysts material used for the electrooxidation of $NaBH_4$ in alkaline media are mainly categorized into non-noble/transition metal electrocatalyst and noble metal electrocatalyst.

2.2.2.1.1 Non-noble metal electrocatalysts

Non-noble metals used for the electrooxidation of $NaBH_4$ are cost-effective, abundant and stable in alkaline environments, making them attractive for $NaBH_4$ electrooxidation (Santos et al. 2016, Hosseini et al. 2012). Non-noble/transition metals such as Ni (Santos et al. 2016, Oshchepkov et al. 2019), Co (Liu et al. 2009) and Zn (He et al. 2011, Hosseini et al. 2012) are tested for electrooxidation of $NaBH_4$ in alkaline media. Santos et al. 2016 utilized nickel based alloy electrocatalyst for the oxidation of $NaBH_4$ in alkaline media. According to Santos et al. 2016, the nickel based alloy electrocatalyst are lower-cost alternative to noble metals, allowing for the construction of more cheap fuel cell devices, the nickel based alloy electrocatalyst demonstrates good electrocatalystic activity. However, it is reported that only 1.4 to 2.5 electrons are able to utilized out of 8 electrons which makes them less effective than platinum electrocatalyst. Hosseini et al. 2012 successfully synthesized zinc and nickle based electrocatalyst for oxidation of borohydride in alkaline media. The prepared electrocatalyst has shown good electrocatalytic acitivity towards oxidation of $NaBH_4$, however, the activity is still lower than the platinum electrocatalyst. Thus, the transition metal electrocatalyts are cost effective and stable in alkaline media but have inherent limits, notably poorer catalytic efficiency than noble metals.

2.2.2.1.2 Noble metal electrocatalysts

Noble metals have high catalytic activity and resistance to passivation, making them appealing for effective $NaBH_4$ electrooxidation (Kadioglu et al. 2020). Although, noble metals are expensive, their high catalytic activity toward electrooxidation of $NaBH_4$ negate their limitations. The noble metal electrocatalyst like Pt (Wang et al. 2015, Yi et al. 2018, Bortoloti 2017, Kadioglu et al. 2020), Pd (Cheng et al. 2017, Duan et al. 2015a, Martins 2017), Au (Yan et al. 2015b, Li et al. 2019, Wei 2009, Karabiberoglu et al. 2023), Ag (Duan et al. 2015b, Duan et al. 2016, Dey et al. 2022) and Os (Atwan et al. 2005, Lam et al. 2012) are widely used for the electrooxidation of $NaBH_4$ in alkaline media. Among all noble metal electrocatalysts, it is found that Au and Ag are effective for the electrooxidation of $NaBH_4$ in terms of the generation of electrons. Chatenet et al. 2006 reported that 7.5 out of 8 electrons were produced during the electrooxidation of $NaBH_4$ in an alkaline medium employing an Ag and Au electrocatalyst. However, it is seen that the activity of electrooxidation reaction is very slow due to slow reaction kinetics towards the electrooxidation of $NaBH_4$, resulting in low power density (Santos et al. 2010, Valiollahi et al. 2016, Concha et al. 2009). On the other hand, Pt electrocatalyst demonstrated excellent electrooxidation of $NaBH_4$ in alkaline media, resulting in a high power density (Liu et al. 2004, Gyenge et al. 2005, Ma et al. 2010). In the present work Pt electrocatalyst is taken as anode electrocatalyst to achieve the high power density from DSBFC.

2.2.2.2 Electrode characterization

2.2.2.2.1 Physical characterization through scanning electron microscopy (SEM)

The electrode generally prepared by the painting the electrocatalyst ink on the gas diffusion layer (GDL) or carbon substrate. The electrocatalyst layer on the GDL should be uniformly distributed.

The electrocatalyst loading plays an important role in the uniform distribution of electrocatalyst on the GDL i.e., at low to moderate loading, the electrocatalyst may uniformly distribute but at very high loading, the agglomeration of the electrocatalyst may occur. The SEM analysis of the prepared electrode provides the microstructure analysis of the prepared electrode and help in the analysis of the fuel cell performance with respect to various electrocatalyst loading. **Figure 2.8** shows the FE-SEM image of blank GDL and an electrode prepared of Pt-Ru-Re electrocatalyst (Chaudhary and Pramanik 2021). **Figure 2.8 (A)** shows the FE-SEM image of the blank GDL in which large pores and carbon fibers are clearly visible. On the other side, **Figure 2.8 (B)** shows FE-SEM image of the prepared electrode in which the electrocatalyst are uniformly distributed over GDL surface.

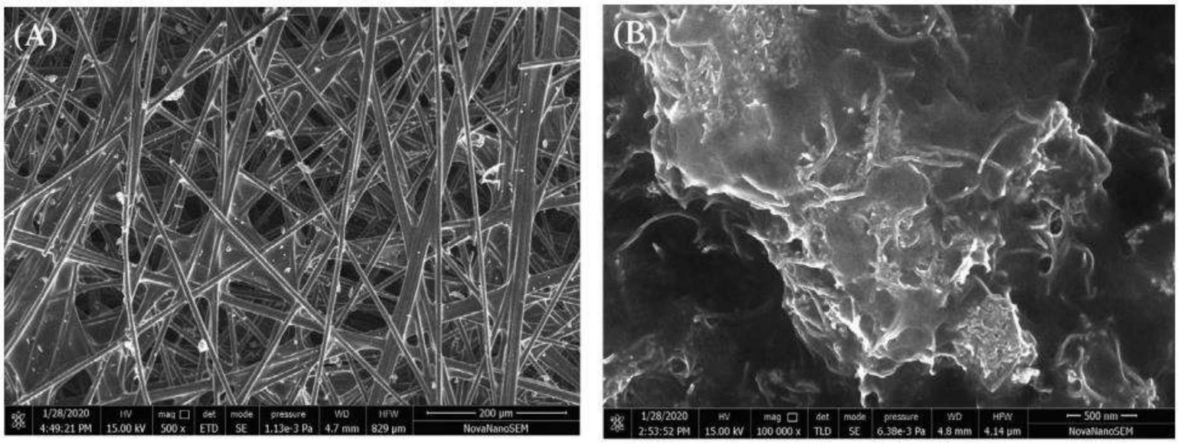


Figure 2.8 FE-SEM images of (A) blank GDL) (B) electrode of 0.5 mg/cm^2 loading of Pt-Ru-Re electrocatayst (Chaudhary and Pramanik 2021).

2.2.2.2.2 Electrochemical characterizations

2.2.2.2.2.1 Cyclic voltammetry (CV) study

The cyclic voltammetry (CV) is an effective and widely used electrochemical technique for studying the reduction and oxidation processes of molecular species that involve electron transfer.

The CV approach is widely utilized as it provides valuable insights into the kinetics and thermodynamics of electrochemical systems (Elgrishi et al. 2018). All significant variations of electrochemical processes have been able to be quantitatively interpreted in terms of their voltametric response. In addition, voltametric curve calculations for intricate electrochemical processes are made easier by contemporary numerical techniques (Heinze et al. 1984, Batchelor-McAuley et al. 2015). A cyclic voltammogram can provide qualitative insights on the rate of reaction and reactant diffusion in an electrochemical system.

The electrooxidation of $NaBH_4$ in an alkaline medium at the anode releases theoretically eight electrons ($8e^-$) as shown in Equation 2.1 (Wang et al. 2023):

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^- \qquad (2.1)$$

However, the electrooxidation of $NaBH_4$ is a little complex, it shows the different pathways with different electrocatalysts. The reason for the different pathways of electrooxidation is due to simultaneous catalytic hydrolysis of borohydride which early occurs at the electrode surface. Tarozaitė et al. 2009 conducted the cyclic voltammetry of $NaBH_4$ in NaOH solution on platinum electrocatalyst and reported that the peak at 0.2 V in the forward scan might be due to electrooxidation of BH_3OH^- (Equation 2.3). A distinct peak at -0.7 V was also observed, which may be due to the electrooxidation of H_2 generated from catalytic hydrolysis of borohydride (Equation 2.3).

$$BH_3OH^- + 4OH^- \rightarrow BO_2^- + 2H_2 + 2H_2O + 4e^- \qquad (2.2)$$

$$BH_4^- + H_2O \rightarrow BH_3OH^- + H_2 \qquad (2.3)$$

It should be noted that a distinctive peak between the range of 0 to 0.1 was also observed in the forward scan and this peak may be due to the direct oxidation of BH_4^-. This observation was also reported by many other researchers (Gyenge 2004, Martins and Nunes 2008).

Thus, it is concluded that the electrooxidation of $NaBH_4$ is a complex process and may vary with the electrocatalyst used for the electrooxidation process. It should be noted that the electrooxidation of $NaBH_4$ depends upon various parameters such as the nature and structure of the electrocatalyst, electrode design, pH and concentration of fuel (Molina et al. 2011, Finkelstein et al. 2013) as discussed in **section 2.2.2.1**. Moreover, the electrooxidation of the hydrogen produced during catalytic hydrolysis of borohydride may not occur as it can easily escape from the electrode surface (Zhang et al. 2023). Due to this, a peak in the cyclic voltammetry curve may not appear.

2.2.2.2.2.2 Chronoamperometry (CA) Test

The chronoamperometry (CA) is an electrochemical method that shows the behavior of electrodes by applying a constant voltage and measuring the resultant current over time. The chronoamperometry (CA) involves applying a continuous voltage to the working electrode and measuring the resultant current (Choudhary and Pramanik 2020). This technique provides information about the kinetics of electrochemical reactions occurring at the electrode surface. The chronoamperometry (CA) studies steady-state current behavior while keeping a constant potential, giving information regarding electron transfer mechanisms, adsorption/desorption phenomena, and mass transport constraints (Gyenge et al. 2005). The CA test is generally done by the same apparatus as CV study is performed in a three-electrode cell system. This study also helps to detect rapid catalyst poisoning during electrochemical reaction. Gyenge et al. 2005 performed the CA test of Pt and Pt-Au in 0.5 M $NaBH_4$ in 2 M NaOH solution to study the electrocatalyst performance. Oliveira et al. 2018 studied the performance of the Pt/polypyrrole-carbon electrocatalyst in 0.3 M $NaBH_4$ mixed in 2 M NaOH solution as well as in 0.05 M H_2O_2 mixed in 0.1 M HCl for the duration of 1 h. The CA test of Pt/polypyrrole-carbon(35 wt. %) in fuel mixture showed that the stable current generation of 6 mA/cm^2. On the other hand, CA test of Pt/polypyrrole-carbon(35 wt. %) in the N_2 saturated oxidant (0.05 M H_2O_2 / 0.1 M HCl) showed the stable activity by generating stable current density. However, the electrocatalyst Pt/polypyrrole-carbon(5 wt. %) and Pt/polypyrrole-carbon(20 wt. %) exhibit the unstable activity in both fuel mixture and the oxidant in CA test. Thus, CA is an important characterization to test the activity of electrocatalyst.

2.2.3 Cathode electrode

2.2.3.1 Electrocatalysts

2.2.3.1.1 Non-noble metal electrocatalysts

The benefit of the alkaline medium being non-corrosive allows the use of non-noble metal for the oxidation reduction reaction. The non-noble metal like Fe (Bezerra et al. 2008a), Co (Niu et al. 2013), Ni (Song et al. 2019), Mn (Bai et al. 2019) or MnO_x (Pickrahn et al. 2012) based material was extensively used for ORR in alkaline medium to the cathode side. The pyrolysed catalyst like Fe-N-C showed catalytic activity comparable to Pt based electrocatalyst in alkaline media (Davydova et al. 2018). Bai et al. 2019 prepared manganese based electrocatalyst for the oxidation reduction in alkaline media. According to Bai et al. 2019, manganese electrocatalysts efficiently catalyze ORR with high activity and durability. Metals such as cobalt and nickel, generally in the form of oxides or alloys, have good catalytic activity and stability under alkaline conditions Co

(Niu et al. 2013, Song et al. 2019). Zeng et al. 2022 synthesized transition metal nitrides as oxygen reduction reaction electrocatalyst for alkaline fuel cell. Zeng et al. 2022 reported that the metal nitrides of cobalt, manganese and iron supported on carbon demonstrated promising ORR activity. Non-noble metal-based electrocatalysts can also be modified by doping with nitrogen or integrating into carbon-supported frameworks (Bai et al.2019), to increase their activity and durability. Despite these benefits, transition metals have lesser catalytic efficiency than noble metals.

2.2.3.1.2 Noble metal electrocatalysts

The electrocatalysts used for the oxidation reduction reaction (ORR) are generally noble metals like Pt and Pd (Guo et al. 2018, Erikson et al. 2019). Noble metals, notably platinum, are regarded as benchmark catalysts for oxygen reduction due to their high activity and selectivity. The Pt and Pd metals were also used in combination of other metals such as Sn (Kim et al. 2009, Borbáth et al. 2021), Co (Todoroki et al. 2018, Singh and Pramanik 2023), Ru (Yu et al. 2004, Ravichandran et al. 2022), Pb, Au (Huang et al. 2019), Ag (Yin et al. 2014), Ni (Yin et al. 2014, Singh and Pramanik 2024) or Cu (Yin et al. 2014, Ye et al. 2022). Among all noble metal electrocatalyst, platinum electrocatalyst is a popular choice for the oxygen reduction reaction in DSBFC at the cathode due to its high activity for oxygen reduction reaction, electrical conductivity, and chemical stability (Cheng et al. 2006). Cheng et al. 2006 and Cheng and Scott 2006a used the impregnation method to synthesize the various cathode electrocatalysts and tested their oxygen reduction reaction activity in DSBFC. The Pt/C showed the highest catalytic activity and stability for oxygen reduction reaction in comparison to Pd/C, Ag/C, and Ni/C cathode catalysts, (Cheng et al. 2006). In view of this in the present thesis work, Pt based cathode electrocatalyst was selected. **Figure**

2.9 shows the flow diagram of the selection of electrocatalyst for the anode and cathode required for the alkaline DSBFC and the selected electrolcatalyst for the present work is highlighted by green color.

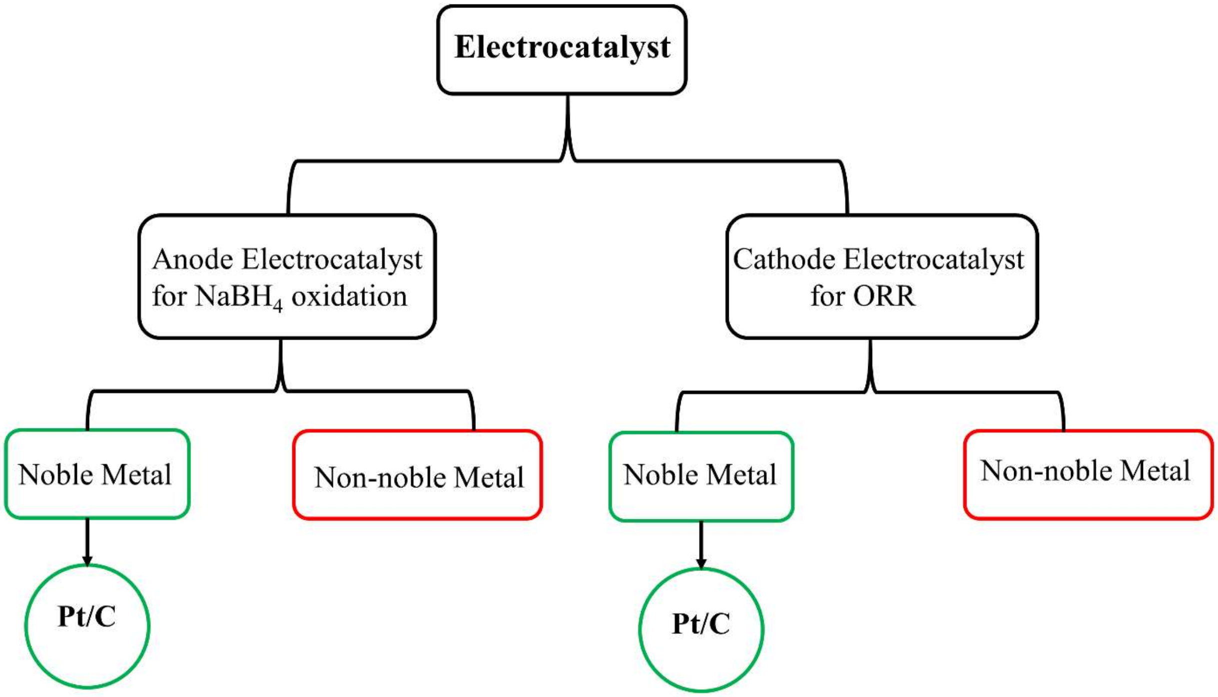


Figure 2.9 Flow diagram of selection of anode and cathode electrocatalyst for $NaBH_4$ electrooxidation and oxygen reduction reaction (ORR), respectively.

2.2.3.2 Cathode Oxidants

The most commonly used oxidants in the fuel cell are oxygen from the air (Atyabi et al. 2023, Yang et al. 2008c) and pure oxygen (Chu et al. 2020, Choudhary and Pramanik 2020, Singh and Pramanik 2023). The electrocatalysts are generally developed keeping in mind the better oxygen reduction reaction (ORR) as oxygen reduction kinetics at cathode side is equally important like an anode electrooxidation kinetics to achieve better performance of the fuel cell. The fast reduction kinetic of ORR in alkaline media made it more suitable to use oxygen as oxidant in DSBFC (Huang et al. 2023). Hydrogen peroxide (H_2O_2) is also one of the oxidants that are widely used in fuel cell (Gouda et al. 2021, Yin et al. 2022, Rathore and Pramanik 2016). One of the main advantages of using H_2O_2 in DSBFC is that it shows a high theoretical open circuit voltage (2.11 V) at 25 ^oC (Gouda et al. 2021). Additionally, H_2O_2 has high volumetric density as it is liquid at room temperature (Luo et al. 2008). Due to the liquid nature of H_2O_2, the handling, storage and transportation is easy as compared to oxygen. The activation energy barrier is lower of H_2O_2 is lower than oxygen (Ma et al. 2010). Moreover, the liquid nature of hydrogen peroxide, it prevents alkali buildup in cathode pores and carbonate fouling in direct borohydride fuel cell (Choudhury et al. 2005). However, direct hydrogen peroxide (H_2O_2) reduction on common electrocatalysts such as platinum and palladium is frequently accompanied by oxygen gas generation from its decomposition (Kjeang et al. 2007). There is a need for the development suitable cathode material for the reduction of H_2O_2 without decomposition. The other oxidants that are used as an alternative to above oxidants are vanadium redox species (Roznyatovskaya et al. 2020), permanganate (Choban et al. 2004) and hypochlorite (Kjeang et al. 2008, Martins et al. 2018), which were used mainly in microfluidic fuel cell (MFC). The advantages of using vanadium redox species are the open circuit voltage may reach to 1.7 V, it is highly soluble due to which there is closer migration to electrode resulting in more unused species and it is able to react with carbon electrode without a metal electrocatalyst (Tanvee et al. 2021). However, vanadium redox species are of high cost and has low energy density (Doetsch et al. 2022). In some studies, $KMNO_4$ (You et al. 2006) and hypochlorite (Kjeang et al. 2008, Cardenas-Valencia et al. 2007) are also used as oxidant at cathode of fuel cell. The permanganate is a powerful oxidant that allows for high current densities and high positive reduction potential (You et al. 2006). However, it is reported that the precipitation of manganese dioxide from permanganate can clog the porous structure of the electrocatalyst layer

(Licht 1999). Thus, permanganate as an oxidant should be avoided in a fuel cell with a porous electrode surface. On the other hand, hypochlorite does not produce any precipitate and has demonstrated safe electrochemical properties as an oxidant in a microfluidic fuel cell cathode using platinum and palladium or iridium electrocatalysts (Kjeang et al. 2008). The hypochlorite as an oxidant demonstrates many advantages such as (i) relatively high standard reduction potential and rapid kinetics, (ii) high solubility in aqueous media, (iii) highly soluble reduction product (chloride) and (iv) no gaseous decomposition reactions take place when hypochlorite is used as oxidant in an alkaline medium (Cardenas-Valencia et al. 2007). Furthermore, hypochlorite solution is widely used as household bleach. The sodium hypochlorite bleach is regarded as relatively safe and inexpensive. In view of these, sodium hypochlorite could be used as an oxidant as it fits all the requirements for fuel cell using liquid fuel at anode side with high energy density. Furthermore, sodium chloride obtained as the product is common and non-toxic in nature (Equation 2.4). The cathode reaction of sodium hypochlorite is given by the following equation (Equation 2.4) (Kjeang et al. 2008):

$$\mathrm{ClO^- + H_2O + 2e^- \leftrightharpoons Cl^- + 2OH^-} \tag{2.4}$$

So far, the very limited study for the hypochlorite as an oxidant in the fuel cell is found in the open literature. Panjiara et al. 2022 studied microfluidic fuel cell (MFC) using $Ca(OCl)_2$ as cathode oxidant. The maximum power density obtained was 3.43 mW/cm^2 using 1.5 M calcium hypochlorite mixed with air as oxidant and 1 M glycerol as fuel mixed in 1 M KOH. The anode and cathode electrocatalysts used were Pd-Ni/C (1 mg/cm^2) and Pt/C (1 mg/cm^2) at a cell temperature of 35 °C. Kjeang et al. 2008 studied on formate and sodium hypochlorite based MFC and obtained a maximum power density of 52 mW/cm^2 at room temperature. The fuel used was 1.2 M formate and 0.67 M sodium hypochlorite as oxidants. The electrocatalysts used were palladium (Pd) and gold (Au) at the anode and cathode, respectively. Similarly, Martins et al. 2018 and Guima et al. 2020 studied on the MFC using sodium hypochlorite as an oxidant.

It is clear from the thorough literature review that only limited study has been performed on hypochlorite as an oxidant and that too in the membrane less microfluidic fuel cells (MFC) (Panjiara et al. 2022, Kjeang et al. 2008, Martins et al. 2018 and Guima et al. 2020). Only a few studies have been published on calcium hypochlorite as an oxidant in microbial fuel cells (Jadhav et al. 2014, Momoh 2011). Although, some studies on hypochlorite as oxidant is found in open literature for the MFC and microbial fuel cell, no such studies are found for the conventional fuel cell using solid membrane electrolyte like proton exchange membrane fuel cell (PEMFC) (Atak et al. 2023), direct methanol fuel cell (DMFC) (Vecchio et al. 2023), direct ethanol fuel cell (DEFC) (Choudhary and Pramanik 2020b) direct borohydride fuel cell (DBFC) (Hosseini et al. 2021) etc. where hypochlorite is used as oxidant. In view of these, oxygen was selected as oxidant for the DSBFC and sodium hypochlorite was also studied for the comparison of performance with oxygen as oxidant in DSBFC.

2.2.3.3 Electrochemical Characterizations

As already discussed in **section 2.2.3.1** (page no. 44), the platinum electrocatalyst is used in the present thesis for the electrochemical reduction of oxygen and sodium hypochlorite at the cathode side. The electrochemical reduction of oxygen in an alkaline medium on Pt electrocatalyst is widely studied. It is well known that electrochemical reduction of oxygen in an alkaline medium may proceed either by a single step four electron route or by two steps two electron mechanism routes as presented in the following Equation 2.5, 2.6 and 2.7 (Rathoure and Pramanik 2016):

Single step four electron mechanism:

$$\mathrm{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-} \tag{2.5}$$

Two step two electron mechanism:

$$\mathrm{O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-} \tag{2.6}$$

$$\mathrm{HO_2^- + H_2O + 2e^- \rightarrow 3OH^-} \tag{2.7}$$

Rathoure and Pramanik 2016 studied the oxygen reduction reaction on Pt electrocatalyst in alkaline medium. They reported that ORR mechanism proceeds through two step two-electron pathways. The reduction peaks were obtained at around -0.4 V and around -0.8 V in the backward scan of CV curve as shown in **Figure 2.10**. Jin et al. 2010 also studied ORR of Pt electrocatalyst in varying concentrations of NaOH solution. It was observed that the higher concentration of NaOH oxygen reduction peak shift in a more negative direction, which may be due to the increase in overpotential of the ORR (Jin at al. 2010). The electrochemical characterization of sodium hypochlorite as an oxidant is not widely developed as in the case of ORR. Although, it was used as an oxidant in many membraneless microfluidic fuel cell, redox-flow batteries and microbial fuel cell (Kjeang et al. 2007, Martins et al. 2018, Jadhav et al. 2014). However, in the study conducted by Martins et al. 2018, cyclic voltammetry of Pt/C electrocatalyst in sodium hypochlorite (bleach) mixed in KOH solution was performed. It was seen that the reduction peak in the backward scan was obtained at a potential around 0.2 V and that corresponds to the reduction of hypochlorite in KOH solution.

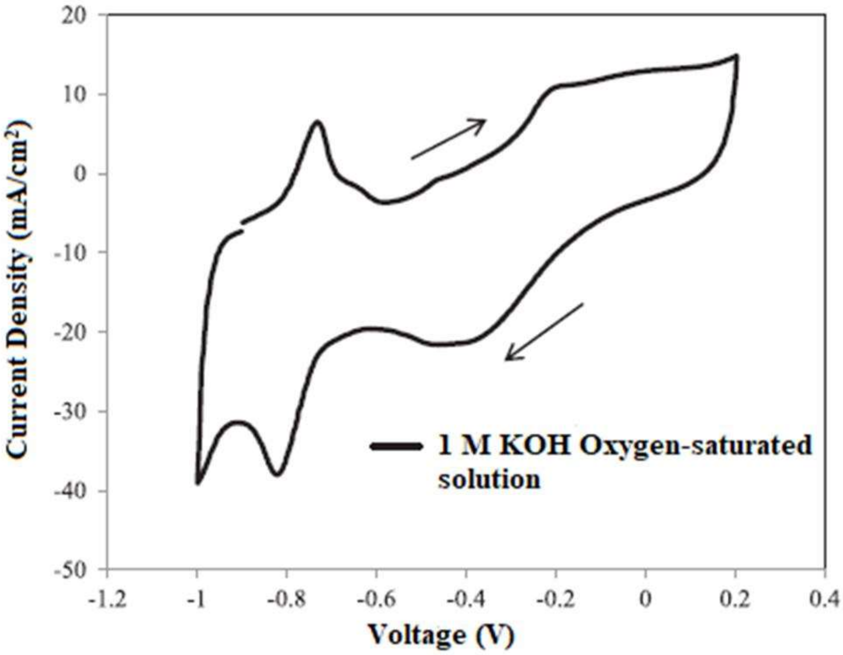


Figure 2.10 Cyclic voltammetry of Pt(40 wt. %)/C_{HSA} at a 1 mg/cm^2 loading was done in oxygen saturated 1 M NaOH solution at scan rate of 10 mV/s (Rathoure and Pramanik 2016).

2.2.4 The performance of alkaline membrane electrolyte in DSBFC

A thorough literature review on the performance of alkaline membrane electrolytes in direct sodium borohydride fuel cell (DSBFC) is reported in the current section. It is seen from open literature that very scanty research work is available on the synthesis of the alkaline membrane electrolyte for DSBFC application. As already discussed, that the costly Nafion® modified with NaOH modified membrane was widely used in DSBFC as a cation exchange membrane electrolyte (Ko et al. 2022, Ertürk et al. 2022, Wang et al. 2020). Huang et al. 2013 developed alkali doped pristine PVA/carbon nanotube composite membrane for the application in $NaBH_4$ based DBFC. The maximum power density of 92 mW/cm^2 was obtained for 1 M $NaBH_4$ mixed in 4 M NaOH as fuel at the cell temperature of 30 ºC. The catalysts used were Pt-Ru/C and Pt/C for the anode and cathode, respectively. The multiwalled CNTs used were first functionalized with PVA and then it was used for the preparation of PVA/CNT composite membrane electrolyte by solution casting method. The route for preparing PVA/CNT composite membrane is relatively complex and the cost of multiwalled CNTs is also high. Akay et al. 2018 investigated on alkaline NaOH doped pristine polybenzimidazole (PBI) membrane electrolyte for DSBFC and a maximum power density of 36.1 mW/cm^2 at 80 ^{o}C temperature was obtained. The catalyst used was Pt/C for both the anode and cathode side. It should be noted that the obtained power density is quite low and PBI material is relatively expensive. Qin et al. 2017 synthesized NaOH doped PVA membrane electrolyte modified by CoOOH for DSBFC and reported a power density of 144 mW/cm^2 at the cell temperature of 30 ^{o}C. The functionalization of PVA by CoOOH improves ionic conductivity. The electrocatalysts used were (Co(OH)$_2$-PPy-BP with very high loading of 5 mg/cm^2 at the anode and same electrocatalyst with high loading of 3 mg/cm^2 at the cathode. Wang et al. 2023 synthesized pristine Poly(isatin-piperidinium-terphenyl) anion exchange membranes by superacid catalyzed Friedel-Crafts alkylation reaction for the direct sodium borohydride fuel cell. The maximum power density of 75.5 mW/cm^2 was reported at the cell temperature of 20 ^{o}C. The electrocatalyst used was platinum foil (Gaossunion, China) of 0.25 cm^2 surface area at both the anode and cathode electrodes. The fuel used was 1 M $NaBH_4$ in 4 M NaOH and the oxidant supplied was 5 M H_2O_2 in 1.5 M HCl solution. The stringent procedure was adopted to synthesize the membrane electrolyte and a moderate maximum power density (75.5 mW/cm^2) was reported. It was also observed that the DSBFC was operated at very low cell temperature of 20 ^{o}C. The feasibility of the synthesized membrane electrolyte at higher temperature is not reported.

Some crosslinked membrane electrolytes are also synthesized and reported in open literature for the DSBFC. Zhang et al. 2020a synthesized photo-cross-linked by UV lamp poly(N-allylisatin biphenyl)-co-poly(alkylene biphenyl)s (PIB-co-PAB) as an anion exchange membrane electrolyte for DSBFC. The fuel and oxidant used were 1 M $NaBH_4$ mixed with 4 M NaOH at anode and 5 M H_2O_2 mixed in 1.5 M HCl at cathode, respevtively. The catalyst at the anode used was platinum foil of 0.25 cm^2 of active surface area, (Gaossunion, China), while the catalyst at the cathode used was platinum foil of 1 cm^2. The maximum power density of 76.1 mW/cm^2 at room temperature was reported. Th membrane electrolyte was prepared by super-acid catalyst polycondensation method followed by cyclo-quaternisation and photocrosslinking. The method of preparation of PIB-co-PAB membrane electrolyte is relatively complex and the performance of the synthesized membrane electrolyte in DSBFC in terms of power density is not tested at higher temperature. Yang et al. 2008c prepared a PVA/hydroxyapatite (HAP) composite membrane by the chemical crosslinking method using glutaraldehyde as crosslinking agent for DBFC application. The maximum power density of 45 mW/cm^2 was obtained when 1 M KBH_4 as fuel mixed with 4 M KOH was used at anode side and air as oxidant at cathode side at ambient conditions i.e., 1 atm pressure and 25 ^{o}C temperature. The power density obtained was quite low. The chemical crosslinking agent glutaraldehyde is expensive and not environmentally friendly. **Table 2.2** shows the performance of various types of alkaline membrane electrolytes used in direct sodium borohydride fuel cells.

Table 2.2 Performance of alkaline membrane electrolyte in DSBFC.

Membrane electrolyte Types	**Ionic Conductivity** (Scm^{-1})	**Fuel, Oxidants and Cell Temperature**	**Electrocatalysts used**	**Maximum Power Density** (mW/cm^2)	**References**
PVA/HAP	0.0442 Temperature: 30 °C	**Fuel**: 1 M $NaBH_4$ in 4 M NaOH; **Oxidant:** Air; **Temperature**: 25 °C	**Anode:** Pt-Ru/Ni foam **Cathode:** MnO_2/C	45	Yang et al. 2008c
PVA/CNT	0.066 Temperature: 30 °C	**Fuel:** 1 M $NaBH_4$ + 4 M NaOH (130 ml/min); **Oxidant:** O_2 (100 ml/min); **Temperature**: 30 °C	**Anode:** Pt-Ru/C (Loading: 5 mg/cm^2) **Cathode:**Pt/C (Loading:5 mg/cm^2)	92	Huang et al. 2013
PBI-NaOH	0.005 Temperature: Room Temperature	**Fuel:** 4 wt% $NaBH_4$ + NaOH(5 ml/min); **Oxidant:** O_2 (300 ml/min); **Temperature**: 80 °C	**Anode: Pt/C** **(**Loading: 2 mg/cm^2); **Cathode: Pt/C** (Loading: 1 mg/cm^2)	38.5	Akay et al. 2018
PVA/CoOOH	0.032 Temperature: 30 °C	**Fuel:** 5 wt. % $NaBH_4$ + 10 wt. % NaOH (10 ml/min); **Oxidant:** O_2 (100 ml/min); **Temperature:** 30 °C	**Anode:** $Co(OH)_2$-PPy-BP) (Loading: 5 mg/cm^2); **Cathode:** ($Co(OH)_2$-PPy-BP) (Loading: 3 mg/cm^2)	144	Qin et al. 2017
Alkali-doped poly(diphenyletheroxadiazole)	0.017 Temperature: Not mentioned	**Fuel:** 1 M $NaBH_4$ + 3 M NaOH (0.5 ml/min); **Oxidant:** O_2; **Temperature:** 40 °C	**Anode: Pt/C** **(**Loading: 1 mg/cm^2); **Cathode: Pt/C** (Loading: 0.5 mg/cm^2)	146	Mai et al. 2011

The thorough literature reviews the alkaline membrane electrolyte for DSBFC reveals that very little work was done on the synthesis of PVA-based membrane electrolytes. It is already discussed that PVA has an excellent film-forming ability and low-cost polymer that can be utilized as a potential membrane electrolyte for the DSBFC. The addition of tetraethyl orthosilicate (TEOS) in the PVA membrane matrix makes the PVA membrane more suitable the DSBFC application. Kim et al. 2004 synthesized PVA/SiO_2 composite membrane crosslinked with sulfosuccinic acid (SSA) and studied its various properties for direct methanol fuel cell (DMFC) applications. Yang et al. 2011 synthesized PVA/SiO_2 membrane electrolyte crosslinked with glutaraldehyde for alkaline DMFC. Chaudhary et al. 2020 developed PVA-TEOS pristine membrane for pervaporation application but did not use it in fuel cell. Thus, it is clear from the detailed literature review that no such research work has been reported on synthesizing alkaline pristine PVA-TEOS membrane electrolyte. The properties of the PVA-TEOS membrane electrolyte can be further improved by crosslinking. The physical crosslinking by freeze-thaw method is excellent, simple and harmless crosslinking method as discussed earlier (page no. 30). A thorough literature review shows that no paper was reported on the synthesis of physically crosslinked PVA-TEOS membrane doped with NaOH and its subsequent use in fuel cell. It is also seen from the literature that the number of freeze-thaw cycles also improves the structure of the physically crosslinked PVA membrane (Hatakeyema et al. 2005, Ru-yin et al. 2008). However, no such studies of varying freeze-thaw cycles on PVA-TEOS membranes were reported in any open literature.

In view of this the detailed study on the synthesis of the NaOH doped pristine PVA-TEOS membrane electrolyte and physically crosslinked PVA-TEOS membrane electrolyte both are required along with the characterization followed by testing of the synthesized membrane electrolyte in the DSBFC. The performance of the DSBFC also depends on the various effective parameters of the cell and thus, the input cell parameter like fuel $NaBH_4$ concentration, oxidant types, electrocatalyst loading and cell temperature were also optimized in the present thesis work to highest power density using the synthesized PVA based alkaline membrane electrolyte doped with NaOH.

2.3 Objectives

The detailed literature shows that the synthesis of the low cost alkaline membrane electrolyte is essential for the DSBFC to develop a sustainable direct sodium borohydride fuel cell. It is also found from the thorough literature that PVA is the most suitable material for membrane electrolyte preparation and TEOS proved to be an excellent doping inorganic filler to improve the important properties of the PVA membrane. To further improve the properties of the PVA-TEOS membrane, physical crosslinking by freeze-thaw method was adopted which would enhance the performance of the PVA-TEOS membrane electrolyte in DSBFC. Thus, the detailed study of synthesis and characterization of the alkaline PVA-TEOS membrane electrolyte for application in DSBFC is very much essential. Towards the fulfillment of these requirements, the thesis has the following objectives:

1. Synthesis and characterization of NaOH-doped pristine PVA-TEOS and physically crosslinked membrane electrolytes for the application in direct sodium borohydride fuel cell (DSBFC).
2. Fabrication of Direct sodium borohydride fuel cell (DSBFC) experimental setup.
3. Development of anode and cathode followed by physical characterization through XRD, SEM and electrochemical characterization viz CV, CA.

4. Experimental study of DSBFC to optimize the various effective parameters like $NaBH_4$ fuel concentration, NaOH doping concentration, electrocatalyst loading, and temperature to achieve the highest cell performance in terms of power density.
5. Optimization of process parameters of physically cross-linked NaOH doped PVA-TEOS membrane electrolyte via Response Surface Methodology (RSM).
6. To study the stability test of PVA-TEOS based alkaline direct sodium borohydride fuel cell (DSBFC).

The next chapter (**Chapter 3**) describes the material required and method of the synthesis of the PVA-TEOS membrane electrolyte and direct sodium borohydride fuel cell. The various characterization methods, such as XRD, FT-IR, SEM, ionic conductivity measurement by EIS, ion exchange capacity, mechanical strength test, water uptake and NaOH uptake are discussed in detail. The procedure of electrochemical characterization of electrocatalysts in half-cell analysis using cyclic voltammetry is also discussed. The assembling and testing method of DSBFC using the synthesized PVA-TEOS membrane electrolyte is discussed in the next chapter i.e**., Chapter 3** Experimental.