# CHAPTER 2

# LITERATURE REVIEW AND OBJECTIVES

## 2.1 Literature review

Direct alcohol fuel cell (DAFC) consists of several components like electrocatalyst (anode and cathode), membrane electrolyte and current collectors. In this thesis, main work focuses on synthesis of membrane electrolyte material of alkaline type. In the following section direct alcohol fuel cell electrodes, different types of alkaline membrane electrolyte, membrane electrolyte characterization and their performances in the direct alcohol fuel cell are discussed using various section and subsection.

### 2.1.1 Direct alcohol fuel cell (DAFC) components

Important components of any DAFC are electrodes i.e., anode and cathode which are fabricated using active electrocatalyst and the other one is membrane electrolyte.

#### 2.1.1.1 Electrode materials

The electrodes are the most active component of the fuel cell where electrooxidation of fuel and reduction of oxidant takes place. Proper electrocatalyst selection depending upon the anode fuel and cathode oxidant are required for fabricating anode and cathode which will result in efficient cell performance. The types of anode and cathode electrocatalysts are discussed in the following section.

##### 2.1.1.1.1 Anode electrocatalysts

There are several electrocatalysts studied for the application in alkaline direct alcohol fuel cell based on methanol and ethanol. Primarily the materials are of metallic origin which

include platinum (Pt) (Manoharan and Prabhuram 2001, Tripkovic et al., 2001, Liu et al., 2006 and Aarnio et al., 2013), gold (Au) (Tremiliosi-Filho et al., 1998, Lima et al., 2008, Kwon et al., 2011 and Geraldes et al., 2013), palladium (Pd) (Manoharan and Prabhuram 2001, Coutanceu et al., 2006, Hu et al., 2008 and Bianchini et al., 2009), ruthenium (Ru) (Liu et al., 2006, Teng 2013, Leo et al., 2013 and Santos et al., 2017), nickel (Ni) (Motheo et al., 1994, Shafei 1999, Zhang et al., 2013 and Barbosa et al., 2015) and cobalt (Co) (Jafarian et al., 2003, Das et al., 2010 and Babu et al., 2017). Among all these materials, electrocatalyst based on platinum is the most widely used. Platinum based electrocatalyst available are either in single or binary and tertiary forms. Platinum, palladium, ruthenium and gold belong to the category of noble metals while non noble metals are nickel and cobalt. All these transition metals show excellent electrochemical activity when used as electrocatalysts (Liu et al., 2006, Teng 2013 and Leo et al., 2013). This activity is attributed to the unfilled d-orbital and unpaired d-orbital electrons due to which bonding with adsorbed species is facilitated. However, all the electrocatalysts do not show equal activity when tested for methanol and ethanol. The differences in activity are due to the variation in the number of unpaired d-electrons and their energy levels (Chen et al., 2019 and Greef et al., 1985). In alkaline fuel cells, alloys of platinum have been found to exhibit good electrocatalytic activity than single metal electrocatalysts. In addition, the alloying of platinum with other transition metals reduces cost significantly due to the use of lesser amount of noble metal in comparison to pure metal based electrocatalyst which is an important aspect for commercialization.

Lamy et al., 2001 studied the electrooxidation of methanol, ethanol and other aliphatic alcohols on unsupported platinum based electrocatalyst and found that the activity of ethanol is comparable to that of methanol using pure platinum as electrocatalyst. However, platinum based bimetallic electrocatalyst (Pt-X) where (X = Ru, Sn, Mo….) is

more suitable for alcohol electrooxidation. Gu et al., 2014 studied the electrooxidation of methanol on Pt-Ru nanocomposites supported on carbon and elucidated the effect of Ru nanocrystals surface structure on platinum's performance. Therein they found Pt-Ru nanospheres to be more active than simple Pt-Ru. It is also reported in the literature that the Pt-Ru/C and Pt-Sn/C are very active electrocatalysts for the electrooxidation of methanol and ethanol due to their bi-functional mechanism (Lamy et al., 2001, Lamy et al., 2004, Gu et al., 2014, Tripkovic et al., 2002 and Artyushkova et al., 2015).

Lai et al., 2010 studied electrooxidation of ethanol on unsupported platinum and gold electrodes in varying pH solutions (pH 1 to pH 13). The catalytic activity of gold was poor for ethanol at pH 1. However, the electrocatalytic activity increases at higher alkaline solutions. Similar observation has been reported by Tripkovic et al., 2002, where the electrooxidation of methanol was studied using Pt and Pt-Ru electrocatalyst supported on high surface area carbon in acidic and alkaline medium. It was observed that the electrode kinetics are significantly higher in alkaline medium than acidic medium. The kinetics of Pt was also found to be slightly lower than Pt-Ru/C. Although, methanol and ethanol electrooxidation on Pt-Ru/C anode electrocatalysts are found in open literature, very scanty literature is available on the electrooxidation of methanol-ethanol mixture using Pt/C, Pt-Ru/C and Pt-Sn/C in acidic medium (Leo et al., 2013 and Wongyao et al., 2011). Almost no such work on mixture of methanol-ethanol is available in alkaline medium using Pt/C and platinum based other bimetallic and trimetallic electrocatalyst.

The literature review suggests that the Pt-Ru/C is the widely used anode electrocatalyst for methanol and ethanol respectively (Lamy et al., 2001, Tripkovic et al., 2002, Manoharan and Prabhuram 2001 and Aarnio et al., 2013). Thus, in this thesis work commercial Pt-Ru/C was selected as anode electrocatalyst. The cathode electrocatalysts

selection is also a very crucial part for the fabrication of direct alcohol fuel cell. The cathode electrocatalysts using oxygen and air as oxidant are discussed in the following section.

#### 2.1.1.1.2 Cathode electrocatalysts

Primarily, oxygen is used as an oxidant for any fuel cell using alkaline electrolyte, except in some cases where hydrogen peroxide (An et al., 2014) and sodium hypochlorite (Kjeang et al., 2008) are also used as cathode oxidant. It is already well established that the oxygen reduction reaction (ORR) kinetics is superior in alkaline medium in comparison to acidic medium (Ge et al., 2015 and Couture et al., 2011). Single metal platinum supported on carbon (Pt/C) (Tse and Gewirth 2015, Yan et al., 2015, Deviprasad et al., 2014, Rizo et al., 2013 and Ong et al., 2013) has been an excellent choice for cathode electrocatalyst. Other noble metals, such as Pd/C (Yang et al., 1995 and Huang et al., 2018), Ag/C (Chatenet et al., 2002 and Guo et al., 2010) and Au/C (Prieto et al., 2003 and Quiano et al., 2012) have also been evaluated as cathode electrocatalyst for ORR. Among all these mentioned noble metals Pd/C showed promising results for ORR in alkaline medium (Nishanth et al., 2010 and Meng et al., 2015). However, Pd/C is less stable and shows lower electrocatalytic activity in comparison to Pt/C (Norskov et al., 2004). The Ag/C is reported to be stable; however, it shows less electrocatalytic activity than Pt/C (Erikson et al., 2019, Chao et al., 2016 and Demarconnay et al., 2004). In addition, Au/C is not considered to be a suitable choice for ORR due to its weak affinity between Au and $O_2$ or $OH^-$ (He and Cairns 2015, Zhang et al., 2014, Quiano et al., 2012 and Hvolbæk et al., 2007)

The non noble metal like iron (Fe), cobalt (Co) and Nickel (Ni) do not exhibit electrocatalytic activity for ORR in their metal crystals or nanoparticles form due to

strong reactivity or affinities with oxygen (He and Cairns 2015 and McQuarrie et al., 2011). In the specific study, a low cost cathode was fabricated using an alternative metal (Co, Fe) complex with polyacrylonitrile (PAN) macromolecules supported on high area carbon (Gupta et al., 1989). However, the oxygen reduction performance was excellent initially but highly unstable for long term application.

From the literature, it is clear that Pt/C is the widely used cathode electrocatalyst for oxygen reduction reaction in alkaline medium (Tse and Gewirth 2015, Yan et al., 2015, Deviprasad et al., 2014, Rizo et al., 2013 and Ong et al., 2013). Thus, commercial Pt/C was selected as cathode electrocatalyst. The electrocatalytical activity of anode and cathode is important to evaluate before its application in a single cell. The electrochemical analysis of anode and cathode are discussed in the following section.

#### 2.1.1.1.3 Electrochemical analysis of electrodes

The electrochemical methods are widely used to determine the electrochemical activity of electrodes as they are sensitive, selective, convenient and less expensive (Baghbamidi et al., 2013). Among all the electrochemical methods, cyclic voltammetry (CV) is the most common and widely used technique to examine electrooxidation and reduction processes of anode fuels and cathode oxidant on suitable electrocatalyst material. The CV technique also helps in assessing intermediates, poisoning species, reaction mechanism at fuel cell electrodes, combination of electrolyte-fuel mixtures and their concentration such that the redox reaction occurs at low overpotential (Pramanik and Rathoure 2016, Pramanik and Basu 2011, Han et al., 2012 and Wang, Macomber, et al., 2013). The electrochemical characterization of anode and cathode are discussed in the following section.

**2.1.1.1.3.1 Anode**

Table (2.1) shows the electrochemical methods employed for the electrooxidation study of methanol and ethanol at anode using pure platinum and its alloy based electrocatalysts. It is clearly seen from the literature that the most widely used technique is the cyclic voltammetry.

The electrooxidation studies of C1-C4 alcohols namely methanol, ethanol, propanol and butanol were carried out in alkaline medium using Pt (111) and stepped Pt (755) and Pt (332) (Tripkovic et al., 2001). Oxygen contains species such as reversible $OH_{ad}$, irreversible $OH_{ad}$ and PtO were proposed to play an important role in alcohol oxidation. The reaction mechanism proposed is given below:

$$R - COH + OH^- \leftrightarrow R - CO_{ad} + H_2O + e^- \quad (2.1)$$

$$OH^- \leftrightarrow OH_{ad} + e^- \quad (2.2)$$

$$R - CO_{ad} + OH_{ad} \rightarrow R - COOH \quad (2.3)$$

$$R - COOH + OH_{ad} \rightarrow R - COO^- + H_2O \quad (2.4)$$

It was discovered that ethanol electrooxidation is most favourable in comparison to the other three alcohols on the Pt (111) surface. The irreversible $OH_{ad}$ acted as a poison in the alcohol oxidation while the reversibly adsorbed $OH_{ad}$ species were the active intermediates.

**Table 2.1** Electrooxidation of methanol or ethanol at anode in alkaline condition and techniques used for analysis of the system.

| **References** | **Electrocatalyst** | **Fuel and Electrolyte** | **Subject of investigation/Major electrochemical investigation technique** | **Electrocatalyst and electrode preparation technique** | **Remarks** |
|---|---|---|---|---|---|
| Tripkovic et al., 2001 | Pt crystal | **Fuel:** Methanol, Ethanol, Propanol, Butanol **Electrolyte:** NaOH | Alcohol electrooxidation/Cyclic voltammetry | The single crystal surface was prepared by annealing in a hydrogen flame and cooling in a hydrogen stream. | The influence of oxygen containing species was investigated on lower aliphatic alcohols using pure platinum in alkaline medium. A dual path mechanism was proposed for alcohol oxidation based on existence of reversible $OH_{ad}$, irreversible $OH_{ad}$ and PtO species in the potential region relevant for alcohol oxidation. |

| References | Electrocatalyst | Fuel and Electrolyte | Subject of investigation/Major electrochemical investigation technique | Electrocatalyst and electrode preparation technique | Remarks |
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| Aarnio et al., 2013 | Pt/C<br>Pt-Ru/C | **Fuel:**<br>Methanol,<br>Ethanol,<br>Isopropanol<br>**Electrolyte:**<br>KOH | Alcohol electrooxidation /Cyclic voltammetry, Chronoamperometry | The electrocatalyst ink was dropped on the surface of glassy carbon electrode and dried for 12 h. | The correlation between electrochemical analysis and single cell results were investigated. The results of single cell using ethanol were best correlated with chronoamperometry. Higher current densities using Pt-Ru/C was observed in comparison to Pt/C. |
| Manoharan and Prabhuram 2001 | Pd<br>Pt<br>Pt-Ru | **Fuel:**<br>Methanol<br>**Electrolyte:**<br>KOH | Methanol electrooxidation/Cyclic voltammetry | Porous and unsupported Pd, Pt, Pt-Ru electrocatalyst were prepared using $NaBH_4$ reduction method. The electrodes were prepared by compaction method. | It was concluded from the detailed cyclic voltammetry studies that the use of porous electrodes may reduce the formation of poisoning species. |

| References | Electrocatalyst | Fuel and Electrolyte | Subject of investigation/Major electrochemical investigation technique | Electrocatalyst and electrode preparation technique | Remarks |
|---|---|---|---|---|---|
| Santos et al., 2017 | Pt/C<br>Pt-Ru/C | **Fuel:** Methanol **Electrolyte:** KOH | Methanol electrooxidation /Cyclic voltammetry/ Chronoamperometry | The Pt/C and Pt-Ru/C electrocatalyst were synthesized using $NaBH_4$ reduction method. The electrodes were prepared by thin porous coating technique | Cyclic voltammetry and chronoamperometry studies showed that PtRu/C (50:50) had superior performance for methanol oxidation, compared to Pt/C. The reason could be associated with the occurrence of the bifunctional mechanism and electronic effect. |
| Kashyout et al., 2011 | Pt/C<br>Pt-Ru/C | **Fuel:** Methanol **Electrolyte:** KOH | Methanol electrooxidation /Cyclic voltammetry/ Chronoamperometry | The electrocatalyst was prepared by simple impregnation reduction method. The working electrode prepared by coating the glass carbon disc with the electrocatalyst ink | The reaction time of electrocatalyst preparation influences the electrocatalytic activity despite having same crystal structure. Among all the electrocatalyst Pt-Ru/C showed higher electrocatalytic activity for methanol electrooxidation. |

| References | Electrocatalyst | Fuel and Electrolyte | Subject of investigation/Major electrochemical investigation technique | Electrocatalyst and electrode preparation technique | Remarks |
|---|---|---|---|---|---|
| Mudrinic et al.,2013 | Pt/C<br>Pt/C/Nafion<br>Pt/C/Zeolite 13X | **Fuel:** Methanol<br>**Electrolyte:** KOH | Methanol electrooxidation/Cyclic voltammetry | The electrocatalyst was prepared by impregnation/decomposition procedure. The working electrode was prepared by adding droplets of electrocatalyst ink on the surface of glassy carbon rotating disc electrode. | The electrooxidation study of methanol using bare Pt electrode, the Pt/Nafion electrode and Pt/Zeolite 13X electrode was conducted in alkaline medium. The dual path mechanism of methanol oxidation with formation of formate ions were found for all types of electrode. |

The mechanism for electrooxidation of ethanol as proposed by Ksar et al., 2009 is given through Equations (2.5) to (2.8). It is seen that at anode side ethanol is oxidized to acetate ions.

$$C_2H_5OH + 3OH^- \leftrightarrow CH_3CO_{ad} + 3H_2O + 3e^- \quad (2.5)$$

$$OH^- \leftrightarrow OH_{ad} + e^- \quad (2.6)$$

$$CH_3CO_{ad} + OH_{ad} \rightarrow CH_3COOH \quad (2.7)$$

$$CH_3COOH + OH_{ad} \rightarrow CH_3COO^- + H_2O \quad (2.8)$$

It is seen from the literature that similar to acetate formation as observed for ethanol electrooxidation, the methanol electrooxidation reaction follows the following reaction (Equation (2.9)) to generate formate ions (Pandey and Lakshminarayanan 2009). It is also seen from the Equation (2.9) that the overall electrooxidation reaction of methanol results in four electrons and a single water molecule.

$$CH_3OH + 5OH^- \leftrightarrow HCOO^- + 4H_2O + 4e^- \quad (2.9)$$

Aarnio et al., 2013 found promising results on electrooxidation of methanol, ethanol and propanol using Pt/C and Pt-Ru/C in alkaline medium on the basis of cyclic voltammetry results (Fig 2.1). They argued that for proper use of electrocatalyst, better alkaline membrane and ionomer is required. Methanol oxidation yields maximum current density using platinum as it is a simple molecule. However, enhanced oxidation current densities were obtained using Pt-Ru for all the fuels specially ethanol. It may be due to enhanced reaction kinetics using bimetallic catalyst.

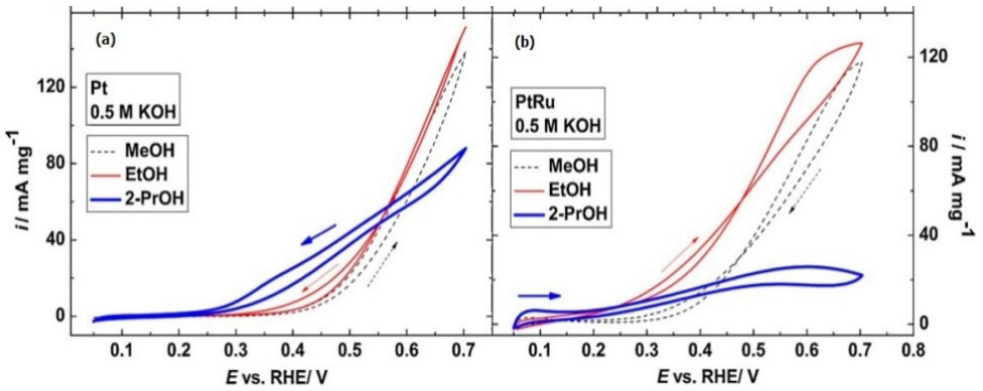


**Figure 2.1** Cyclic voltammograms for 1 M methanol, ethanol and isopropanol oxidation on Pt/C and Pt-Ru/C nanocatalyst in 0.5 M KOH. Scan rate: 10 mV/s (Aarnio et al., 2013).

Porous unsupported Pt, Pd and Pt-Ru electrocatalyst were prepared and extensively studied by Manoharan and Prabhuram 2001, using cyclic voltammetry. The CV of Pt using 6 M KOH with different methanol concentration showed that during the forward scan the methanol electrooxidation reaction (MOR) starts at 0.18 V for all combinations. The forward peak at 0.7 V were obtained for 1 M methanol mixed with 6 M KOH. A PtO layer is formed at around 0.8 V with lower activity suppressing the further electrooxidation of methanol. A second peak is also observed at the backward scan due to electrooxidation of weakly bonded CHO residues formed in the forward scan. The oxidation increases with increase in methanol concentration up to 3 M. However, the formation of PtO is not reduced. Methanol concentration of 6 M yields a featureless curve and this was due to the complete electrooxidation of methanol at this concentration (Manoharan and Prabhuram 2001). For higher concentration i.e., 9 M and 11 M methanol featureless curve were obtained with decreased current density. Comparing the CV using smooth Pt electrodes it was argued that the oxidation of intermediates species does not take smoothly on smooth platinum. It may be due to lower population of active sites at smooth electrodes in comparison to porous electrode. Using Pd instead of Pt similar observations were made with PdO as the poisoning species. Taking the study

forward with Pt-Ru, it is found that the active oxygen atoms are supplied by both Pt and Ru**.** Similar observations were made with respect to methanol concentration. A featureless polarization curve is obtained at higher methanol concentration.

Santos et al., 2017 prepared Pt-Ru electrocatalyst by $NaBH_4$ reduction method for studying the electrochemical behavior of methanol in acidic and alkaline condition. The Pt-Ru (50:50) electrocatalyst showed excellent performance for methanol electrooxidation in acidic and alkaline medium as shown by chronoamperometry and cyclic voltammetry studies. However, the current values were higher for alkaline media in comparison to acidic medium. The results were also validated using single cell studies. The reason was attributed due to bifunctional mechanism and electronic effect. Methanol adsorption occurs on active platinum sites whereas ruthenium provides oxygenated species.

**2.1.1.1.3.2 Cathode**

The oxygen reduction reaction (ORR) generally proceeds by two pathways in alkaline medium (Ortiz and Gautier 2003). The single step 4 electron pathway (Equation (2.10)) for direct oxygen reduction reaction is given below:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad (2.10)$$

The alternative two electron pathway also called as 2 + 2 electron pathway (Equation (2.11) and (2.12)) is shown below:

$$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^- \quad (2.11)$$

$$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^- \quad (2.12)$$

Where, Equation (2.11) shows the oxygen reduction to peroxide ($HO_2^-$) ions followed by reduction of $HO_2^-$ to $OH^-$ ions (Equation (2.12)).

Table (2.2) shows the electrochemical methods employed for oxygen reduction reaction at cathode using pure platinum and its alloys based electrocatalyst. Yan et al., 2015 used

the cyclic voltammetry technique to determine the electroreduction behaviour of $O_2$ on Pt electrode in KOH solution. For comparison purpose cyclic voltammetry in $N_2$ saturated solution was also performed (Figure 2.2). The presence of oxygen greatly influence the electroreduction behavior at Pt electrode surface with a significant increase in reduction current.

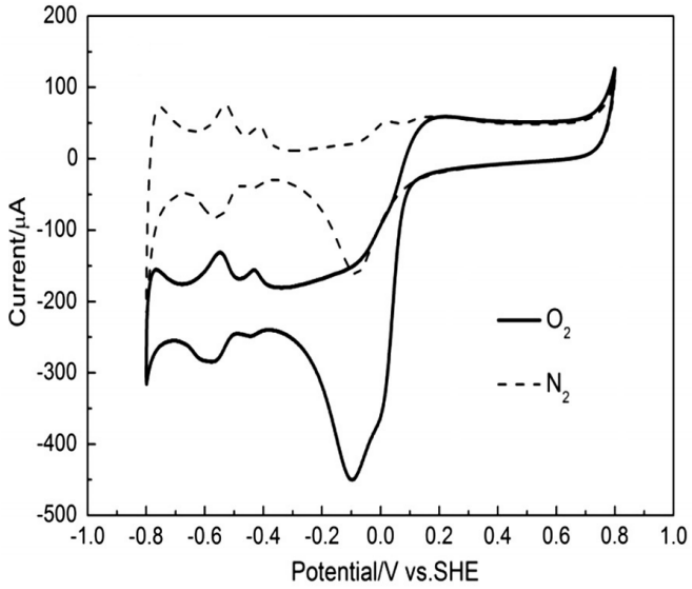


**Figure 2.2** The CV curves of ORR on Pt wire electrode in 1 M KOH solutions saturated with nitrogen and oxygen at temperature of 25 $^{o}$C. Scan rate: 40 mV/s (Yan et al., 2015).

Markovic et al., 1996, carried out oxygen reduction studies on platinum in alkaline medium. The study was focused on the role of $OH_{ad}$ species in ORR. In alkaline medium the $OH_{ad}$ simply comes from the KOH adsorption. The cyclic voltammetry using rotating disk electrode was used to evaluate the ORR. The order of activity increased in the sequence (100) < (110) < (111); for platinum (hkl) in a KOH solution of 0.1 M. The difference in activity is mainly due to the structure sensitiveness of hydroxyl anion ($OH^-$) on platinum surface.

**Table 2.2** Oxygen reduction at cathode in alkaline condition and techniques used for analysis of the system.

| References | Electrocatalyst | Oxidant and Electrolyte | Subject of investigation/Major electrochemical investigation technique | Electrocatalyst and electrode preparation technique | Remarks |
|---|---|---|---|---|---|
| Yan et al., 2015 | Pt wire electrode | **Oxidant:** Oxygen **Electrolyte:** KOH | Oxygen electroreduction/Cyclic voltammetry | The commercial Pt wire were polished with metallographic sandpaper and alumina powder to get smooth surface. | The presence of oxygen greatly influence the electroreduction behavior at Pt electrode surface with a significant increase in reduction current when compared to $N_2$ saturated solution. |
| Rizo et al., 2013 | Pt disk | **Oxidant:** Oxygen **Electrolyte:** NaOH | Oxygen electroreduction/Cyclic voltammetry | Platinum single crystals beads were prepared from small beads (2 mm) by melting and slow crystallization. The working electrode was prepared by annealing and cooling in hydrogen. | The effect of different surfaces on ORR was studied. The results show that Pt (111) electrode has the highest electrocatalytic activity among all the studied surface. |

| References | Electrocatalyst | Oxidant and Electrolyte | Subject of investigation/Major electrochemical investigation technique | Electrocatalyst and electrode preparation technique | Remarks |
|---|---|---|---|---|---|
| Demarconnay et al., 2004 | Ag/C<br>Pt/C | **Oxidant:** Oxygen **Electrolyte:** NaOH | Oxygen electroreduction/ Cyclic voltammetry | The electrocatalyst were prepared using colloidal precursor method. The working electrode was prepared by depositing the electrocatalyst ink through a syringe onto a glassy carbon substrate. | The mechanism of ORR at Ag/C is similar to Pt/C at high potentials. However, the electroactivity, measured in terms of exchange current density of the Pt/C was 10 times higher than Ag/C. |
| Tammeveski et al., 1997 | Pt film | **Oxidant:** Oxygen **Electrolyte:** NaOH | Oxygen electroreduction/Cyclic voltammetry | Thin platinum films were formed by electron beam evaporation onto glassy carbon substrate and used as working electrode. | The kinetic parameters of ORR were determined for Pt films over 1 to 50 nm thickness. The thickness of films only slightly influenced the ORR kinetics. |

| References | Electrocatalyst | Oxidant and Electrolyte | Subject of investigation/Major electrochemical investigation technique | Electrocatalyst and electrode preparation technique | Remarks |
|---|---|---|---|---|---|
| Markovic et al., 1996 | Pt crystal | **Oxidant:** Oxygen **Electrolyte:** NaOH | Oxygen electroreduction /Cyclic voltammetry/ Rotating disk electrode | The cylindrical single Pt crystal was prepared by flame annealing and cooling in hydrogen. The crystal samples were then mounted into a rotating ring-disk arbor to get the working electrode. | The study was focused on the role of $OH_{ad}$ species in ORR. The order of activity increased in the sequence (100) < (110) < (111); for platinum (hkl) in a KOH solution of 0.1 M. These differences are due to the structure sensitivity of hydroxyl anion ($OH^-$) adsorption on Pt (hkl) and its inhibiting (site blocking) effect on oxygen kinetics. |
| Lee et al., 1996 | Pt/C Ag/C | **Oxidant:** Oxygen **Electrolyte:** NaOH | Oxygen electroreduction /Cyclic voltammetry | The electrocatalyst was prepared by colloidal precursor method. The electrocatalyst layer and Toray carbon paper was hot pressed to make the working electrode. | The electrocatalytic activity of Pt/C and Ag/C in terms of the time required to reach the equilibrium electrode potential was compared. The early saturation achieved by Pt/C indicates good electroactivity than Ag/C. |

The adsorbed hydroxyl anion ($OH^-$) also has blocking effects of active sites for oxygen and peroxide. The effect of platinum thickness (1 - 50 nm) on ORR was studied by Tammeveski et al., 1997. The electrochemical studies were performed using rotating disk electrode and cyclic voltammetry in a 0.1 M KOH solution. They did not observe any significant change in ORR mechanism for films of different thickness. However, slight effect on kinetics was observed due to differential absorption pattern of KOH. The effect of surface structure of Pt/C on ORR kinetics in alkaline medium was studied by Rizo et al., 2013 using rotating disk electrode/cyclic voltammetry. It was observed that The $OH^-$ adsorption strength depends on the surface structure of Pt/C instead of pH and Pt (111) was found to be the most active surface for ORR in alkaline medium. The lower electroactivity for other surfaces was attributed to the stronger $OH^-$ adsorption.

Thus, it is clear from the literature review that cyclic voltammetry has been widely used as an electrochemical technique to evaluate the electrocatalytic activity of anode electrocatalyst (Santos et al., 2017, Aarnio et al., 2013, Tripkovic et al., 2001 and Manoharan and Prabhuram 2001) and cathode electrocatalyst (Rizo et al., 2013, Ong et al., 2013, Markovic et al., 1996 and Tammeveski et al., 1997). Thus, in this thesis work, cyclic voltammetry has been adopted as a technique to study the electrochemical activity of anode and cathode electrocatalyst. It is also seen from the literature that the efficient operation of a single cell also depends on the proper selection of alkaline electrolyte. The different types of alkaline electrolyte are discussed in the following section.

#### 2.1.1.2 Types of electrolyte

The widely used alkaline electrolyte in fuel cell is liquid KOH due to its lower ohmic overpotential than NaOH (Couture et al., 2011 and Santos et al., 2013). It has already been discussed in the previous section that alkaline medium in fuel cell is advantageous

than acidic medium (Lai et al., 2010 and Kwon et al., 2011) in many respects like the problem of fuel crossover is reduced due to counter flow of fuel and anion (Gupta and Pramanik 2019a). Nevertheless, fuel electrooxidation and oxygen reduction is enhanced in alkaline medium. The electrolytes used in the alkaline direct alcohol fuel cells are either in liquid or solid form which are discussed in detail in the following section.

#### 2.1.1.2.1 Alkaline liquid electrolyte

The alkaline fuel cell (AFC) was operated using liquid KOH as electrolyte at the beginning of fuel cell research (Al-Saleh et al., 1994, Verma 2000, and Verma and Basu 2005). They played a major role in powering successful missions of Gemini and Apollo spacecraft (Wang, Qiao, et al., 2013). It was the Apollo mission which landed man to the moon for the first time in human history. Al Saleh et al., 1994 conducted studies to evaluate the effect of $CO_2$ in $H_2$ on Ni/PTFE anode and Ag/PTFE cathode using 25 % KOH solution as alkaline liquid electrolyte. The ionic concentration polarization was observed to increase for the anode. In case of Ag/PTFE cathode no effect was observed at low levels of $CO_2$ (0.03 %). However, at higher levels of $CO_2$ (1 %) a decrease in electrode current density with time was observed. The performance of methanol fuel cell was studied by Verma 2000 using 6 N KOH solution as alkaline liquid electrolyte. The anode and cathode were fabricated using Fe (iii) and Ag (i) supported on graphite, respectively. The catalytic efficiency of methanol electrooxidation was found to be 78 %. A detailed study was conducted by Verma and Basu 2005 on the performance of AFC using methanol, ethanol and sodium borohydride using KOH as electrolyte. The anode and cathode were fabricated using Pt/C and $MnO_2$/C, respectively. The cell performance was highest for 3 M KOH and 2 M fuel. However, the cell performance decreased with

increase in KOH concentration beyond 3 M due to activation and concentration overpotential.

However, further commercialization could not happen due to many intrinsic problems. As discussed earlier (page no.4 - 5) problem of carbonate formation (Ong et al., 2017), leakage problem and high resistance (Velisala et al., 2015) reduces the cell performance. In view of all these problems, liquid alkaline electrolyte has been replaced by solid state alkaline membrane which conducts $OH^-$ ions and simultaneously separates the anode and cathode compartments (Zhang and Chen 2011, Agel et al., 2001 and Xu et al., 2005).

#### 2.1.1.2.2 Alkaline solid electrolyte

Solid state alkaline membrane offers many advantages in comparison to liquid electrolytes. They have improved water management, reduced crossover problem, low resistance to ion transport across the membrane and enhanced oxygen reduction kinetics in alkaline medium at the low temperature (Couture et al., 2011). The $OH^-$ ion conductivity is provided to the membrane in various ways viz, by doping the membrane in KOH solution (Gupta and Pramanik 2019b and Fu et al., 2010), by mixing KOH with the membrane solution (Lewandowski et al., 2000) and by attaching cationic groups to the membrane backbone which can exchange $OH^-$ ions (Couture et al., 2011).

The conduction mechanism of $OH^-$ ions through the membrane has been proposed in line with that of proton conduction in acidic membranes. Although, the anion conductivity is lower than proton, it follows the same pattern as proton conduction. Fig (2.3) shows the conduction mechanism as modeled by Grew and Chiu, 2010.

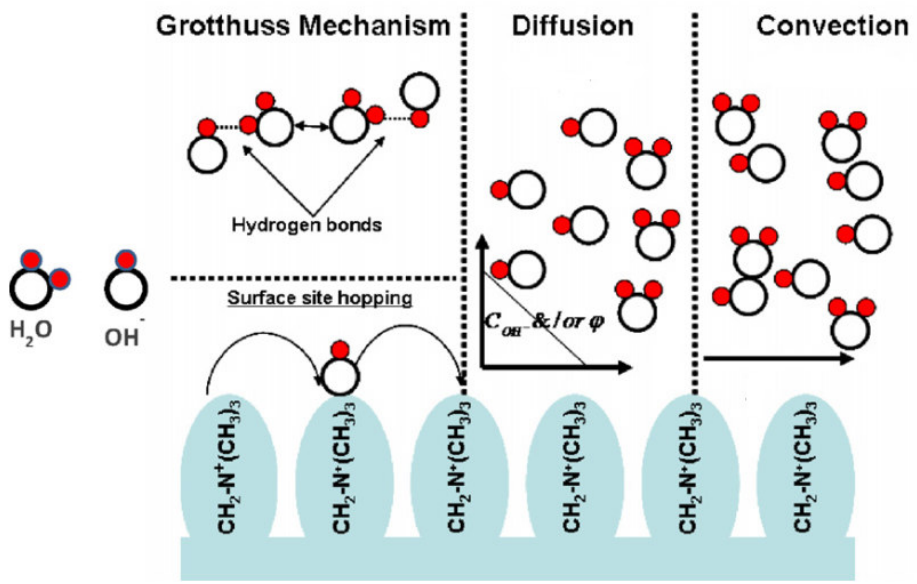


**Figure 2.3** Possible transport mechanism of $OH^-$ ions in alkaline membrane (Grew and Chiu, 2010)

The main conduction mechanism of $OH^-$ ions is the grothhus mechanism which in the combination of other mass transport phenomenon namely diffusion, migration and convection (Dominik 2006, Paddison 2002 and Choi 2005). Primarily, in the grothhus mechanism OH- ions are transferred by making and breaking of hydrogen bonds along the chain of water molecules. Thus, the proper hydration is required for better membrane conductivity. The concentration or potential gradient is responsible for diffusive conduction. It is well known phenomenon for fully hydrated membrane that the water molecules are dragged by the moving $OH^-$ ions and thus, creating a convective flow of water molecules in the membrane matrix (Karimi and Li 2005 and Basu et al., 2008). The surface site hopping is a secondary transport mechanism and occurs only in quaternary ammonium functionalized membranes (Varcoe 2007 and Hibbs et al., 2008).

The membranes to be used in direct alcohol fuel cell are selected very judiciously based on certain parameters. Some important parameters of membranes are cost, chemical stability, film forming ability, extent of hydrophilicity and crosslinking feasibility.

Additional factors like environment friendly, biodegradable and nontoxic could also be selected (Maiti et al., 2012).

Till date, the researchers have explored and developed many electrolyte materials to be used as solid alkaline membrane in low temperature fuel cells. These membranes are broadly classified as ion solvating polymers, hybrid membranes, alkoxysilane, interpenetrating polymer networks and homogenous membranes (Merle et al., 2011 and Maiti et al., 2012). The literature reported polymeric materials like polychloropropene, polyethylene oxide, polybenzimidazole (PBI), polyvinyl alcohol (PVA), chitosan (CS) and polyepicholrhydrine (PECH) are widely used for synthesis of solid alkaline membrane. The chemical structure of the polymer materials are presented in Fig (2.4).

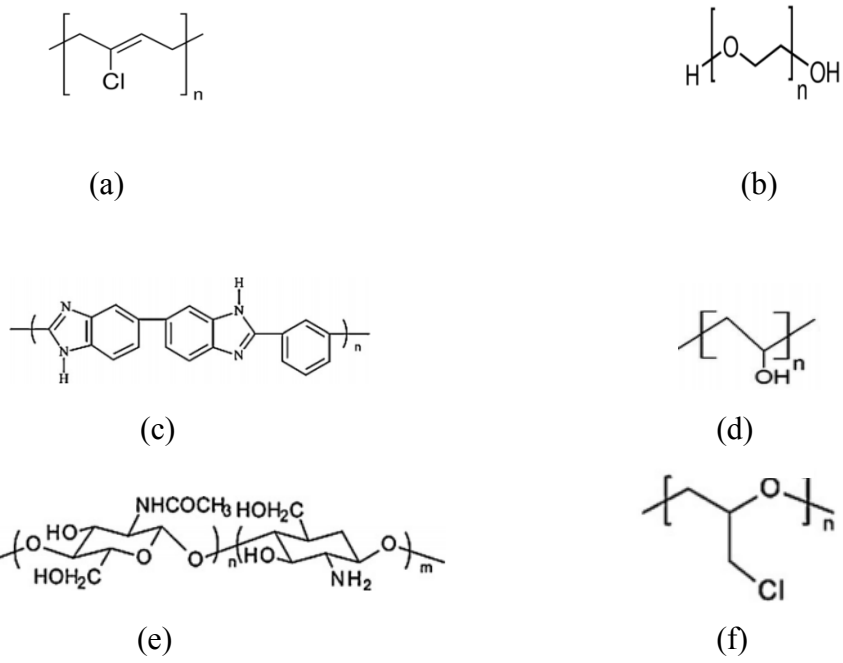


**Figure 2.4** Some important polymers for membrane electrolyte synthesis (a) Polychloropropene (b) Polyethylene oxide (c) Polybenzimidazole (PBI) (d) Polyvinyl alcohol (PVA) (e) Chitosan (CS) and (f) Polyepichlorhydrine (PECH).

Among them polymeric membranes, polyhydroxy polymer polyvinyl alcohol (PVA), has evoked special interest among scientists due to its availability, easy manufacturing, low cost, and environmentally friendly properties (Wu et al., 2010 and Xu et al.,2013). In addition, it has good film-forming ability, hydrophilic properties, chemical stability, and a large density of chemical functions, which renders easy crosslinking by irradiation, chemical, thermal, and physical treatment methods (Merle et al., 2012, Fu et al., 2010 and Mokhtar et al., 2016). The chemical stability of a PVA based membrane is recognized as a key factor that affects fuel cell performances, especially in an alkaline medium and high KOH concentration. Thus, in the present study PVA was selected to synthesize the membrane electrolyte using different types of crosslinking methods followed by KOH doping to make the membrane alkaline.

The polymeric membranes are synthesized by different techniques for low temperature use, e.g., solution casting (Wu et al., 2010 and Xu et al., 2013), phase inversion (Drioli and Giorno 2009) and sol-gel process (Wu et al., 2009 and Kickelbick 2003) followed by crosslinking to improve the stability of the membrane. In some research the membrane electrolytes have been synthesized without crosslinking. However, these membranes suffer from stability problem when operated for long time (Herranz et al., 2018). The synthesized membrane without or with crosslinking are impregnated by KOH immersing in KOH solution of different concentration for $OH^-$ conduction. There are many studies so far have been reported in open literature on PVA based alkaline membrane without crosslinking followed by KOH impregnation and some of them are PVA-KOH-$H_2O$ (Lewandowski et al., 2000), PVA-glass fiber cloth mat composite (Yang and Lin 2002), PVA-$TiO_2$ composite (Wu et al., 2008), PVA-poly (epichlorohydrin) blend membranes (Yang et al., 2003) and PVA-polybenzimidazole (PBI) blend membranes (Herranz et al., 2018). Among all these membranes, only some were tested in different types of cell to

evaluate the membrane performance (Wu et al., 2008, Yang et al., 2003 and Herranz et al., 2018). Wu et al., 2008 and Yang et al., 2003 studied the synthesized membranes in Zn–Ni and Zn–air battery, respectively. Wu et al., 2008 did not report any information on membrane durability when tested in Zn–Ni battery. However, Yang et al., 2003 mentioned that the synthesized membrane is mechanically and chemical stable. Herranz et al., 2018 reported that the membrane was unstable when tested in alkaline direct ethanol fuel cell (ADEFC) due to no crosslinking.

The crosslinking of the synthesized membranes are generally done by two ways (i) physical crosslinking and (ii) chemical crosslinking. The physical crosslinked membranes are formed primarily due to reversible interactions within the molecules (Voorhaar and Hoogenboom 2016) like hydrogen bonding, entanglements, hydrophobic /hydrophilic interactions (Berger et al., 2004 and Kuo 2001). The important advantage offered by physical crosslinking is its safety and environment friendliness as no chemical crosslinking agents are used in this method. Till date, only a few works have been carried out on physical crosslinking of PVA-based alkaline membrane using freeze-thaw method (Zugic et al., 2013 and Gupta et al., 2018). The physical crosslinked PVA membranes were tested in hydrogen fuel cell (Zugic et al., 2013) and direct methanol fuel cell (DMFC) (Gupta et al., 2018). Although the membrane synthesized by physical crosslinking is cheaper (Gupta and Pramanik 2018), the chemical crosslinking has been preferred over physical crosslinking as it gives better membrane quality in terms of chemical and thermal stability. The hydroxyl ion conductivity is also better when KOH is doped within the membrane frame-work/structure (Maiti et al., 2012).

The chemical crosslinked membranes are formed due to covalent bond along the polymer chains. The linkages are strong and permanent in comparison to physical crosslinked membranes. So far, many chemical crosslinking agents like glutaraldehyde (Fu et al.,

2010, Choudhary et al.,2009, Diaz et al.,2017 and Yang and Chiu 2012), formaldehyde (Tripathi et al., 2010), poly (ethylene glycol) diglycidyl ether (PEGDE) (Merle et al., 2012), and poly(GMA-co-γ-MPS) (Wu et a., 2010) have been used to synthesize PVA based alkaline membrane. Among all crosslinking agents, glutaraldehyde (GA) has been widely used by the researchers in the membrane synthesis due to its fast crosslinking and the control over the crosslinking process (Philipp and Hsu, 1979). In this context, glutaraldehyde was selected as a crosslinking agent for the synthesis of PVA-GA chemical crosslinked membrane doped with KOH for the use in direct alcohol fuel cell in the present study. The crosslinking mechanism of PVA with glutaraldehyde is shown in Fig (2.5).

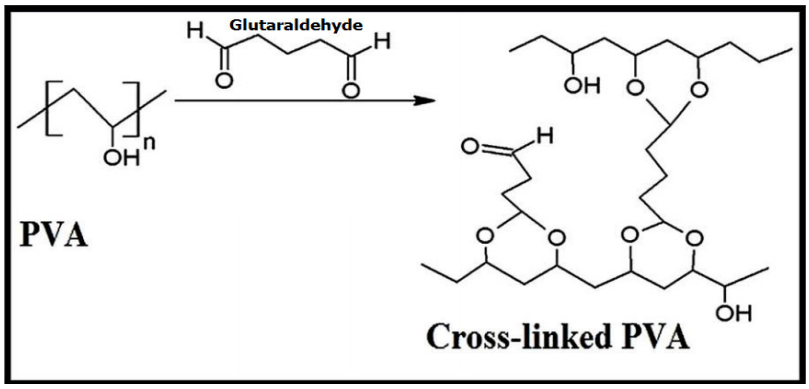


**Figure 2.5** The crosslinking mechanism of PVA with glutaraldehyde (Rudra et al., 2015).

The crosslinking agents improved the conductivity and mechanical stability of the synthesized membranes (Merle et al., 2012) in comparison to the membranes synthesized by physical crosslinked or without crosslinking. In addition, the membranes exhibited good chemical and thermal stability at higher alkalinity and different temperatures (Fu et al., 2010). In some studies, the mechanical stability of the PVA-PBI (Diaz et al., 2017) and PVA/chitosan (Yang and Chiu 2012) membranes was also improved due to blending. However, all the synthesized membranes were used for various applications such as

alkaline hydrogen fuel cell (Merle et al., 2012), dialysis (Wu et a., 2010), direct borohydride fuel cell (Choudhary et al., 2009), electrolysis (Diaz et al., 2017), and DMFC (Tripathi et al., 2010, Fu et al., 2010 and Yang and Chiu 2012 ) except ADEFC. The above literature review shows that the PVA based chemical crosslinked alkaline membranes have not been studied using lower aliphatic alcohols mainly methanol, ethanol and their mixture as a fuel in a single cell and thus, research work is necessary using the above fuels and their different combination.

The proper characterization of the synthesized alkaline membrane electrolyte is essential to evaluate the optimum properties of the electrolyte membrane which could be selected for application in a single cell. The techniques used for the characterization of synthesized alkaline membrane electrolyte are discussed in the following section.

#### 2.1.1.2.3 Membrane electrolyte characterization

The characterization of synthesized physical and chemical crosslinked membrane electrolytes are crucial for proper selection of membrane. The various techniques of membrane characterization have been extensively studied and discussed below.

##### 2.1.1.2.3.1 Water uptake

Proper hydration of alkaline membrane is very important for its efficient performance. Higher water uptake assists in higher conductivity for low temperature operation of alkaline fuel cell. However, excess water uptake may result in unwanted dimensional changes and a decrease in mechanical properties of membrane (Merle et al., 2012, Fu et al., 2010 and Herranz et al., 2018). Higher water uptake may hinder in MEA fabrication and also disrupt proper contact between electrodes and membrane. The water uptake of pristine PVA membrane is high due to its high hydrophilicity. However, the water uptake

is reduced by crosslinking and blending (Merle et al., 2012). Merle et al., 2012 synthesized membrane from PVA, KOH and PEGDE blend. The role of PEGDE was as a crosslinker and KOH as electrolyte for ionic conductivity. They argued that higher water uptake may induce swelling and dilute the ionic groups thereby reducing the durability and ionic conductivity. They observed a high water uptake of 62 wt % for pristine PVA membrane and the uptake reduced to 45 wt % for crosslinked PVA membrane. No change in water uptake and pH was observed after immersion in KOH solution indicating zero leaching of KOH from the membrane. The water uptake of crosslinked PVA membrane was found to be lower than that of commercial Tokuyama (A201) membrane (55 wt %)

In the case of PVA membrane doped with 4 M KOH, water uptake of 39.4 wt % was observed by Fu et al., 2010. The water uptake of Nafion® was lower than PVA membrane at 34 wt %. The PVA-PBI blend membranes showed a decrease in water uptake in comparison to pure PBI membrane. As the percentage of PVA in the blend was gradually increased (8:1 PVA: PB1) the water uptake approached similar to that of PBI (85 wt %) (Herranz et al., 2018).

**2.1.1.2.3.2 Conductivity**

Ionic conductivity of alkaline membrane is generally lower than the acidic membrane due to the greater size of hydroxide ($OH^-$) than proton ($H^+$) ion (Pan et al., 2011). To provide ionic conductivity in alkaline membrane the membranes are either doped with KOH or mixed with KOH. The most widely used technique to determine the ionic conductivity is electrochemical impedance spectroscopy (EIS). Ionic conductivity is directly correlated to the alkaline uptake and it strongly depends on alkaline doping concentration. The ionic conductivity in membrane is attributed to the alkali doped free volumes (An et al., 2012). A general trend observed is that peak conductivity is reported for a particular doping

concentration beyond which the conductivity decreases. An et al., 2012 has explained this phenomenon using theory of electrophoresis. According to this theory with increase in alkali concentration the viscosity decreases causing impedance to flow of ions, with reduced ionic velocity the ionic mobility is also reduced consequently ionic conductivity decreases (An et al., 2012). They reported an optimum NaOH concentration of 5 M for alkaline membrane. Lewandowski et al., 2000 did initial work on synthesis and characterization of uncrosslinked PVA membrane doped with KOH. The membrane was synthesized by dissolving PVA and KOH solution simultaneously. A maximum ionic conductivity of 9.2 x $10^{-4}$ S/cm was observed for PVA-KOH-$H_2O$ mixture in ratio of 42.2 : 29.9 : 27.9. The conductivity of membrane was stable for a period of 2 years.

The conductivity values of KOH doped PVA membrane with and without glass fiber mat was determined by Yang 2002, and only slight difference was observed. Increase in conductivity values with increase in temperature was also reported. The conductivity reported was of 0.0471 x $10^{-2}$ S/cm. Fu et al., 2010 did preliminary study on ionic conductivity of uncrosslinked KOH doped PVA membrane. They reported an optimum KOH value of 4 M corresponding to which the ionic conductivity was 4.73 × $10^{-4}$ S/cm. The conductivity got reduced at higher KOH doping.

#### 2.1.1.2.3.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR is a versatile tool to determine the functional groups present in a material. Almost all study on membrane development and characterization employ FTIR analysis to ascertain the functional groups and determine changes for various modifications of membrane. Herranz et al., 2018 conducted FTIR studies on synthesized PVA-PBI blend membranes to determine the possible interaction between PVA and PBI and identify functional groups present in the membrane structure. The characteristics peak of PBI

disappears in PVA-PBI blend membranes. The presence of "free KOH" inside the membrane was confirmed by the characteristics signal at around 1400 $cm^{-1}$. Rudra et al., 2015 studied the FTIR characteristics of pristine and glutaraldehyde crosslinked PVA membrane. The characteristics peak at around 3350 $cm^{-1}$ is attributed to the -OH stretching of strong hydrogen bonding in the PVA membrane. Carbonyl and acetal linkages peak were observed in crosslinked membranes at 1723 $cm^{-1}$ and 1087 $cm^{-1}$, respectively. The peaks for above groups shifted to higher frequency with increasing glutaraldehyde concentration. Reductions in peak intensities were observed at around 3350 $cm^{-1}$ indicative of crosslinking. The crosslinking reduces the concentration of -OH groups.

#### 2.1.1.2.3.4 X-ray diffraction (XRD)

The X-ray diffraction experiment is performed to evaluate the crystallinity of the synthesized membrane. PVA membrane is a semi crystalline membrane (Wu et al., 2008, Fu et al., 2010 and Rudra et al., 2015). Fu et al., 2010, studied the XRD patterns for KOH doped PVA membrane and pristine PVA membrane. Two characteristics peak were observed at a 2θ angle of 19°–20°and 39°–40°. The peak intensity at 2θ angles of 19°–20° decreased for KOH doped PVA membrane compared to pristine PVA membrane. This observation indicated that the amorphous domain was augmented by KOH doping. The presence of amorphous region plays an important role in ionic conductivity (Rudra et al., 2015 and Fu et al., 2010). It is reported in literature that KOH acts as a plasticizer making the membrane more flexible and amorphous (Yang 2006). Single diffraction peak at 2θ angles of 19.9° was observed due to 101 crystal planes for glutaraldehyde crosslinked PVA membrane (Rudra et al., 2015). The characteristic decrease in peak

height was observed due to crosslinking enhancing the semi crystalline nature of PVA membrane. The amorphousness increased with increase in crosslinking density.

#### 2.1.1.2.3.5 Mechanical properties

The sufficient mechanical strength of the synthesized membrane is required to use it for long time and bear the stress when hot pressing to fabricate membrane electrode assembly (MEA) and single cell assembly. The mechanical properties depend on various factors like water uptake, KOH uptake, crosslinking types, membrane structure etc. An et al., 2012 studied the mechanical properties of three types of membrane namely alkaline membrane (Tokuyama), Nafion® membrane and polybenzimidazole membrane. The tensile strength of alkaline membrane was found to be highest than the other two types of membrane. The KOH doped PVA with glass fiber exhibited good tensile strength but with lower elongation-at-break compared to pristine PVA membrane (Yang, 2002). The improved mechanical stability was due to the incorporation of glass fiber mat. The mechanical properties of PVA-PBI blend membranes were reduced after doping with KOH. However, the values were sufficient to be used in alkaline fuel cell (Herranz et al., 2018).

The tensile strength at elongation-at-break was observed for pristine and glutaraldehyde crosslinked PVA membrane by Rudra et al., 2015. The pristine PVA membrane showed a tensile strength of 20 MPa. The tensile strength was found to increase with crosslinking of the membrane. Maximum tensile strength of 30 MPa was observed for PVA membrane with 32 % crosslink density. The formation of crosslinked networks and decrease in polymer mobility caused increase in tensile strength.

#### 2.1.1.2.3.6 Scanning electron microscopy (SEM)

The surface morphology and pores are visualized by performing SEM analysis of membrane electrolytes. Properly synthesized membranes must have dense and compact structure with pores distribution. The pores and microchannels are important for imparting ionic conductivity and movement of ions and water molecules. The pores and microchannels are generally formed due to crosslinking of the polymer chains resulting in three-dimensional network structure (Ahmad et al., 2012). A "pan cake" shaped surface morphology with pores of dimension 0.1- 0.2 μm was observed by Yang 2002, for KOH doped PVA membrane composite with glass fiber mat. The surface morphology of PVA-PBI blend membranes with and without KOH doping was observed by Herranz et al., 2018. A homogenous surface was observed for undoped membrane while the circular islands were observed for doped membrane. The KOH doping removed the superficial PVA from PVA -PBI blend membrane. The morphological study of pristine and KOH doped PVA membrane by Fu et al., 2010 showed homogenous and dense membrane structure at a magnification of 2000X. They did not observe any membrane degradation or holes before and after KOH doping. The KOH particles were visible as dot at a magnification of 40,000X but no cracks were observed. A drastic surface roughness was observed in KOH doped PEGDE crosslinked PVA membrane by Merle et al.,2012 compared to pristine PVA membrane. They also observed reduction in graininess of membrane with increasing crosslinker concentration. The denseness of membrane prevented leaching of KOH from the membrane matrix. The cross sectional SEM images were also captured to confirm the dense property of membrane. Along with confirmation of denseness, pores were also observed for crosslinked PVA membrane. Similar observations were made by Rudra et al., 2015, for PVA membranes crosslinked with

glutaraldehyde. The porosity decreased with increasing glutaraldehyde concentration owing to reduction in free volume of the membrane.

### 2.1.2 Performance of membrane electrolyte in single cell

The majority of work done using PVA membrane is limited to synthesis and characterization of membrane. Only a few research works has been performed on single cell using synthesized membrane without crosslinking/pristine with a anode fed ethanol mixed with KOH electrolyte. Herranz et al., fabricated PVA and polybenzimidazole (PBI) blend membranes without any crosslinking agents and evaluated its performance in alkaline direct ethanol fuel cell. Table (2.3) shows the process parameters and cell performance data. The conductivity was in the range of $10^{-2}$ S/cm after doping in 6 M KOH solution. They obtained a maximum power density of 76 mW/cm$^2$ at a temperature of 90 $^{o}$C. However, the membrane deteriorated after short time due to no crosslinking and proved to be a very unstable.

**Table 2.3** Single cell study using PVA based alkaline membrane without crosslinking/pristine.

| **References** | **Membrane Types** | **Process Parameters** | **Cell Performance** |
|---|---|---|---|
| Herranz et al., (2018) | PVA-PBI | Cell temperature: 90 $^{o}$C<br>Fuel: 2 M Ethanol +2 M KOH<br>Oxidant: Oxygen<br>Anode: Pt-Ru/C<br>Loading: 1.33 mg/cm$^2$<br>Cathode: Pt/C<br>Loading: 1 mg/cm$^2$ | Power density:76 mW/cm$^2$<br>OCV: 0.65 V |

As the membranes without crosslinking are not stable enough for long time operation (Herranz et al., 2018), thus many efforts have been made to synthesize crosslinked PVA membranes, which may be manufactured by physical or chemical crosslinking method. Till date, very scanty works have been reported on physical crosslinking of PVA based alkaline membrane using freeze-thaw method (Zugic et al., 2013). The physical crosslinked PVA membranes were tested only in hydrogen fuel cell. Table (2.4) shows the data related to process parameters and cell performance using hydrogen as fuel for the physical crosslinked PVA membrane. It is clear from the above literature review that research work in a single DAFC using physical crosslinked membrane as solid electrolyte is required.

**Table 2.4** Single cell study using physical crosslinked PVA based alkaline membrane.

| **References** | **Membrane Types** | **Process Parameters** | **Cell Performance** |
|---|---|---|---|
| Zugic et al., (2013) | PVA-KOH | Cell temperature: 25 $^{o}$C<br>Fuel: Hydrogen<br>Oxidant: Oxygen<br>Anode: Pt/C<br>Loading: 0.2 mg/cm$^2$<br>Cathode: Pt/C<br>Loading: 0.2 mg/cm$^2$ | Power density: 350 mW/cm$^2$<br>OCV: 0.98 V |

Although, the membrane synthesized by physical crossslinking is cheaper (Gupta and Pramanik 2018), the chemical crosslinking has been preferred over physical crosslinking as it gives better membrane quality in terms of chemical and thermal stability. The

hydroxyl ion conductivity is also better when KOH is doped within the membrane framework/structure (Maiti et al., 2012).

As mentioned earlier that the chemical crosslinking of the PVA membrane gives better membrane quality in terms of chemical and thermal stability with higher hydroxyl ion conductivity when KOH is doped in it. Table (2.5) shows the list of work done using chemical crosslinked PVA membrane. The process parameters and cell performance data is also shown in Table (2.5). Merle et al., 2012, reported easy and cheap process for fabrication of PVA based KOH doped alkaline membrane which was crosslinked using Poly (ethylene glycol) diglycidyl ether (PEGDE) to improve conductivity and mechanical stability. Single cell study was conducted using commercially available electrodes anode and cathode both made of Pt/C at a very high loading of 4 mg/cm$^2$ using $H_2$ as fuel and $O_2$ as the oxidant. The maximum power density was 72 mW/cm$^2$. However, optimization of cell and membrane parameters was not performed. Fu et al., 2010, synthesized transparent, stable and active PVA membranes using glutaraldehyde of 10 mass % as a crosslinking agent by impregnation of KOH. They conducted a detailed stability test in high KOH solution at a very high temperature (80 $^oC$), which was lacking at their time. The membrane exhibited good stability at higher alkalinity at high temperatures. The performance of the synthesized membrane was evaluated in a methanol fuel cell using Pt/C as both anode and cathode, with loading of 1 mg/cm$^2$ and 2 M methanol mixed with 2 M KOH electrolyte. The maximum power density of 10.21 mW/cm$^2$ was obtained at a cell temperature of 90 $^oC$. Choudhary et al., 2009, reported the use of PVA hydrogel membrane for direct borohydride fuel cell and acidified $H_2O_2$ as the oxidant. Glutaraldehyde was used as a crosslinker. The maximum power density of 40 mW/cm$^2$ was reported. However, a detailed study of the operating conditions was missing. In another attempt, Yang et al., 2008 synthesized PVA/$TiO_2$ composite polymer by simple

solution casting method and chemical crosslinking using glutaraldehyde. Single cell studies were also conducted using anode Pt-Ru/C and cathode air-breathing $MnO_2$ with

**Table 2.5** Single cell study using chemical crosslinked PVA based alkaline membrane.

| **References** | **Membrane Types** | **Process Parameters** | **Cell Performance** |
|---|---|---|---|
| Cornejo et al., (2017) | A201 (Tokuyama commercial membrane) | Cell temperature: 60 $^oC$<br>Fuel :1M EtOH+1M KOH<br>Oxidant: Oxygen<br>Anode: Pt-Cu/C<br>Loading: 1 $mg/cm^2$<br>Cathode: Pt/C<br>Loading: 1 $mg/cm^2$ | Power density: 15.2 $mW/cm^2$<br>OCV: 0.82 V |
| Yang (2007) | PVA-GA-$TiO_2$ | Cell temperature: 25 $^oC$<br>Fuel: 2 M MeOH + 2 M KOH<br>Oxidant: Air<br>Anode: Pt-Ru/C<br>Loading: 4 $mg/cm^2$<br>Cathode: $MnO_2$<br>Loading: 3.63 $mg/cm^2$ | Power density: 3.86 $mW/cm^2$<br>OCV: 0.77 V |
| Fu et al., (2010) | PVA-GA | Cell temperature: 60 $^oC$<br>Fuel: 2 M MeOH + 2 M KOH<br>Oxidant: Oxygen<br>Anode: Pt/C<br>Loading: 1 $mg/cm^2$<br>Cathode: Pt/C<br>Loading: 1 $mg/cm^2$ | Power density: 6.04 $mW/cm^2$<br>OCV: 0.91 V |

| **References** | **Membrane Types** | **Process Parameters** | **Cell Performance** |
|---|---|---|---|
| Yang et al., (2008) | PVA-GA-$TiO_2$ | Cell temperature: 25 $^oC$<br>Fuel: 2 M EtOH + 4 M KOH<br>Oxidant: Air<br>Anode: Pt-Ru/C<br>Loading : 3.6 mg/$cm^2$<br>Cathode: $MnO_2$<br>Loading : Not available | Power density:8 mW/$cm^2$<br>OCV: 0.85 V |
| Yang et al., (2008) | PVA-GA-HAP | Cell temperature: 25 $^oC$<br>Fuel: 2 M MeOH + 8 M KOH<br>Oxidant: Air<br>Anode: Pt-Ru/C<br>Loading: 4 mg/$cm^2$<br>Cathode: $MnO_2$<br>Loading : 3.63 mg/$cm^2$ | Power density:10.59 mW/$cm^2$<br>OCV: 0.77 V |
| Yang et al., (2014) | PVA-GA-SA | Cell temperature: 30 $^oC$<br>Fuel: 2 M MeOH + 2 M KOH<br>Oxidant: Oxygen<br>Anode: Pt-Ru/C<br>Loading: 6 mg/$cm^2$<br>Cathode: Pt/C<br>Loading : 5 mg/$cm^2$ | Power density:20.7 mW/$cm^2$<br>OCV: 0.67 V |

methanol as fuel. The maximum power density of 7.54 mW/cm$^2$ at a temperature of 60 $^o$C was observed. The PVA/chitosan blend membranes were also synthesized by direct solution casting method and characterized by Yang and Chiu 2012, for the use in a direct methanol fuel cell.

To increase the conductivity and reduce high water uptake the blend membrane was crosslinked using 2.5 wt % glutaraldehyde solution. The maximum power density of 29.8 mW/cm$^2$ was achieved at a temperature of 50 $^o$C for methanol fuel. However, a high loading of anode Pt-Ru/C (6 mg/cm$^2$) and cathode of Pt/C (5 mg/cm$^2$) were used.

It is clear from the above exhaustive literature that many research works on PVA based alkaline membrane have been studied either by physical crosslinking or chemical crosslinking for fuel cell applications. However, no detailed study on direct alcohol fuel cell has been carried out using PVA based alkaline membrane crosslinked by glutaraldehyde. In addition, detail study on chemical crosslinking of PVA membrane by glutaraldehyde and thorough characterization of the membrane are not reported in the published literature till date. Thus, in this study, a detailed investigation have been reported on synthesized PVA membrane crosslinked with glutaraldehyde (GA) solution of different weight percent followed by membrane characterization and application in a single alkaline direct alcohol fuel cell (ADAFC). The ionic conductivity of PVA membrane doped with various KOH concentrations was determined using electrochemical impedance spectroscopy (EIS). The synthesized membrane was further tested in a single cell set up to get the optimum condition of different parameters e.g., alcohol concentration, KOH concentration, anode and cathode electrocatalyst loading, and cell temperature to achieve maximum cell performance in terms of OCV, current density, and power density.

## 2.2 Objectives

The detailed literature review reveals that development work on alkaline membrane-based fuel cell using methanol, ethanol and their mixture as fuel is required as half-cell and single cell studies show promising results in terms of power density and cell voltage. A detailed study is required to completely understand the effect of various parameters on membrane synthesis, and single cell performance using PVA based alkaline membrane. Towards the fulfilling of these requirements, the thesis has following objectives:

1. To synthesize PVA based alkaline membranes using physical crosslinking and chemical crosslinking methods.
2. To study various physicochemical properties viz., Water uptake, KOH uptake, surface morphology, mechanical properties, infrared spectroscopy and XRD analyses.
3. To determine the ionic conductivity of the synthesized membranes using electrochemical impedance spectroscopy.
4. To fabricate the anode and cathode for electrochemical study of the electrodes using cyclic voltammetry analysis to understand the electrooxidation and reduction mechanism.
5. To study the performance of synthesized membrane electrolyte in a single cell setup using different parameters, e.g., the doping concentration of KOH in membrane, the concentration of fuel, the concentration of electrolyte, electrocatalysts loading, the different types of electrocatalyst at anode, temperature, oxidant at the cathode (air/oxygen) and types of membrane such that the maximum power density is obtained.
6. To study the stability test of PVA based alkaline direct alcohol fuel cell.

The next chapter describes the experimental detail related to the development of PVA based alkaline membrane fuel cell using methanol, ethanol and their mixture as fuel, anode and cathode preparation and properties, half-cell analysis through cyclic voltammetry, single cell performance and stability test of the single cell.