Development of high temperature composite membranes for Direct Methanol Fuel Cell (DMFC)

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CERTIFICATE

This is to certify that the dissertation work entitled —**Development of high temperature composite membranes for Direct Methanol Fuel Cell (DMFC)**, which is being submitted by **Ms. PAGIDI ARUNA** (Roll No. 714147), is a bonafide work submitted to the Department of Chemical Engineering, National Institute of Technology, Warangal in partial fulfillment of the requirement for the award of the degree of **Doctor of Philosophy in Chemical Engineering.**

To the best of our knowledge, the work incorporated in this thesis has not been submitted elsewhere for the award of any degree.

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This thesis dedicated to my Parents,

Who always supported me, whatever path I took.

DECLARATION

This is to certify that the work presented in the thesis entitled "**Development of high temperature composite membranes for Direct Methanol Fuel Cell (DMFC)**" is a bonafide work done by me under the supervision of **Dr. Murali Mohan Seepana** and was not submitted elsewhere for the award of any degree.

I declare that this written submission represents my ideas in my own words and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea / data / fact / source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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ABSTRACT

The sustainable generation of green energy is one of the crucial challenges fronting the fast-paced development of socio-economic improvement. Fuel cells (FC) are non-polluting, energy efficient, consistent and silent systems. Fuel cells are the favorable renewable energy source compared to solar and wind energy. As long as fuel supplied, these devices are capable of producing a stable and constant energy. Direct methanol fuel cell (DMFC) has derived from polymer electrolyte membrane fuel cell (PEMFC) where gaseous hydrogen has replaced by the aqueous methanol in anodic electrochemical reaction. DMFCs are considered as one of the promising green technologies for generating energy for portable applications includes mobile phones, camera, and laptop. They have drawn wide attention of researchers due to their high energy density, long life cycles and compactness in cell design. Proton exchange membrane (PEM) plays a key role in DMFC. Nafion is the most widely used membrane but it is limited by its high methanol permeability, high cost and sensitivity towards temperature. Therefore, worldwide researchers are attempting to find alternative membrane. The organic-inorganic based hybrid membranes suggested in the literature revealed that there is a good interaction between organic polymer and inorganic materials which improves the mechanical and thermal properties of membranes along with improving proton conductivity. Therefore, present work aimed to develop a suitable and economically viable composite membrane for DMFC.

The PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE composite membrane were synthesized by adopting the hybrid method of pore infiltration, and layer by layer coating followed by heat treatment at 60ºC. The inorganic zirconium phosphate (ZrP) and polyvinyl alcohol (PVA) sol was infiltrated and layered over chemically treated 0.22 μm pore size and 45 μm thick chemically treated hydrophilic polytetrafluoroethylene (PTFE) film to obtain the PTFE-ZrP-PVA composite membrane. The wt% of ZrP and PVA in the sol were optimized with respect to methanol permeability and proton conductivity of the membrane. The top view of the membrane surface morphology was observed by using SEM and EDX, which revealed the presence of 31.9% zirconium and 26.44% phosphate in the synthesized membrane. The membrane top layer functional groups were analyzed by FT-IR, and the spectra confirmed the incidence of functional groups related to ZrP and PVA. Thermal stability of the membrane was analyzed using TGA-DTA and it was found that the membrane is stable up to 140℃. The membrane was mechanically stable with a mechanical strength of 44 MPa. The membrane possessed proton conductivity of 28.1 mS cm^{-1} and low methanol permeability (14.5×10^{-7} cm^2

s^{-1}) at 80℃. The composite membranes and Nafion117 were tested in single DMFC with 2M methanol at anode side and oxygen of 100% relative humidity at cathode side. The obtained polarization curves were compared in the higher temperature range. The open circuit voltage (OCV) of DMFC with PTFE-ZrP-PVA membrane is increased from 0.652 V to 0.725 V and peak power density increased substantially from 25.39 to 39.8051 mW cm^{-2}, with increase in temperature from 40°C to 80°C. Even though, the membrane has performed better than some of the composite membranes reported in the literature, the values were low compared to that of Nafion 117(49.51 mW cm^{-2}).

The silica immobilized PWA and PVA sol infiltrated and layered over the chemically modified PTFE support to synthesize the (Si-PWA)-PVA/PTFE composite membrane. The composition of the top layer was optimized to be 0.3M PWA: 0.2M TEOS: 0.15PVA concerning to proton-conductivity and methanol permeability of the membrane. Surface morphological studies and elemental analysis were carried out by using SEM-EDX. The FT-IR and XRD analysis had confirmed the intercalation of sol with PTFE. Thermal deformation of the membrane was studied by TGA and found to be stable up to 180˚C. Ion exchange capacity and water uptake were determined to be 2.38 meq per gram and 21.7% respectively. The synthesized membrane has exhibited maximum proton conductivity of 41.2 mS cm^{-1} at 100˚C. The membrane has significantly lower methanol permeability of 3.2×10^{-7} cm^2 s^{-1} compared to that of Nafion117 (7.9×10^{-7} cm^2 s^{-1}) at 28°C and the same trend was observed at 40, 60, and 80°C. Low methanol permeability and increased proton conductivity at higher temperature makes the membrane workable in high-temperature DMFC. The (Si-PWA)-PVA/PTFE composite membrane has shown superior properties than the other reported composite membranes and the near peak power density compared to Nafion 117 (i.e. 49.51 mW cm^{-2}).

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Symbols

H^+	Proton
e^-	Electron
M	Methanol concentration
˚C	Degree Celsius
g	grams
%	Percentage
μm	Units of Thickness
nm	Units of Thickness
RH	Relative Humidity
MPa	Unit of tensile strength
vol%	Volume percentage
wt %	Weight percentage
W_{wet}	Weight of wet membrane
W_{dry}	Weight of dry membrane
M_{NaOH}	Molarity of NaOH
V_{NaOH}	Volume of NaOH
V_B	Solution volume in compartment ‘B’ (cm^3)
I	The membrane thickness (cm).
A	Active membrane area (cm^2)
C_A	The concentration of methanol in the compartment ‘A’
$C^0{}_B$	The initial concentration of the methanol of compartment ‘B’
$C^t{}_B$	The concentration of methanol at time ‘t’ in the compartment ‘B’
P	Permeability of the methanol solution (cm^2/sec)
t	Time (sec)

R_m	Resistance of the membrane in ohms (Ω)

Abbreviations

DOE	*Department of Energy*
DMFC	Direct methanol fuel cell
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PEM	Proton Exchange Membrane
GDL	Gas Diffusion Layer
Pt-Ru	Platinum-Ruthenium
PtRu/C	Platinum Ruthenium on porous carbon paper
Pt/C	Platinum on porous carbon paper
GDE	Gas Diffusion Electrodes
MEA	Membrane Electrode Assembly
CO	Carbon monoxide
CO_2	Carbon dioxide
O_2	Oxygen
H_2	Hydrogen
rpm	Revolutions per minute
PTFE	Polytetrafluoroethylene
ZrP	Zirconium phosphate
PVA	Polyvinyl Alcohol
PWA	Phosphotungstic acid
TEOS	Tetraethyl Orthosilicate
H_2O_2	Hydrogen Peroxide
HCl	Hydrochloric acid
DDW	Double Distilled water

LBL	Layer by Layer
SEM	Scanning Electron Microscope
HR-SEM	High Resolution Scanning Electron Microscope
EDX	Energy-Dispersive X-ray spectroscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-Ray Diffraction
WU	Water Uptake
IEC	Ion exchange capacity
TGA-DTA	Thermal gravimetric analysis - Differential thermal analysis
EIS	Electrochemical Impedance Spectroscopy
OCV	Open Circuit Voltage
V	Voltage
R	Resistance (Ω)

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 Importance of fuel cells in electrical energy generation

The energy retreat is one of the crucial challenges fronting the fast-paced development of socio-economic improvement. The energy deficit, pollution, and global warming are the main alarming issues needs immediate solutions (Fanchi and Fanchi 2016). Development in green technologies towards the energy generation are required for avoiding negative impacts on the environment. The united states *department of energy* (DOE) has strategic planning to meet the global demand for portable applications using fuel cells (<250 W) by 2020 (Fanchi and Fanchi 2016; Radenahmad et al. 2016). Fuel cells (FC) are non-polluting, energy efficient, consistent and silent systems. Fuel cells are the favorable renewable energy source compared to solar and wind energy (Williams 1994). As long as fuel supplied, these devices are capable of producing a stable and constant energy.

Direct methanol fuel cell (DMFC) has derived from polymer electrolyte membrane fuel cell (PEMFC) where gaseous hydrogen has been replaced by the aqueous methanol in anodic electrochemical reaction. The DMFC is capable alternative power source for portable energy devices over the batteries by overcoming storage and transmission losses (Kamarudin and Hashim 2012). However, the factors like cost and low efficiency of DMFC are majorly impeding the commercialization (Kamarudin, Achmad, and Daud 2009).Thus various methods are studied to increase the power density and lower the initial and operating cost of DMFC's.

1.2 Main categories of fuel cells

The researchers have developed and demonstrated many verities of fuel cells. They are majorly categorized into four classes based on the type of electrolyte that can be employed in fuel cell (Larminie, Dicks, and McDonald 2003). Because the employed electrolyte determines the nature of half-cell reactions, required catalysts, operating temperature, and fuel required (Lucia 2014; Steele and Heinzel 2011; Carrette, Friedrich, and Stimming 2000). The main categories of fuel cell include (i) Alkaline fuel cell (AFC) (ii) Polymer electrolyte membrane fuel cell (PEMFC) (iii) Phosphoric acid fuel cell (PAFC) (iv) Molten carbonate fuel cell (MCFC) and (v) Solid oxide fuel cell (SOFC). Introduction of direct methanol fuel cell (DMFC)

Most advanced and well-known fuel cells technology fall in the category of PEMFC, which are powered by hydrogen. However, the handling of gaseous hydrogen is the one the prime challenges in commercialization of PEMFC. The higher energy density liquid methanol (4820 Wh/L) which contains more hydrogen (99 g) than liquid hydrogen (71 g) has chosen to be a fuel in the PEMFC technology to address the challenge (Piela and Zelenay 2004). This sub category of PEMFC is named as the direct methanol fuel cell (DMFC). An improved attention towards methanol-based fuel cells are due to ease of production from renewable sources like biomass (pyrolysis of timber, i.e. wood alcohol) are more environmentally friendly, biodegradable, easily available, relatively cheap and having good electrochemical activity (Liu et al. 2011; Haile 2003).

Direct methanol fuel cells (DMFCs) are one of the most promising alternative power-delivery fuel cells due to their environmental friendliness, high energy density, small fuel cartridge, instant recharging, simple structure, ease of storage and transport. DMFC is an emerging technology as a portable power source for numerous kinds of mobile electronics because they can use methanol directly without additional equipment for the reforming step to hydrogen gas (Carrette, Friedrich, and Stimming 2000).

Working principle of DMFC

The inputs to the DMFC is diluted methanol solution at anode side and air (or oxygen) at cathode side and outputs are electrons, water and carbon dioxide (CO_2) as showed in Figure 1.1 (Billings and Saathoff 2004).

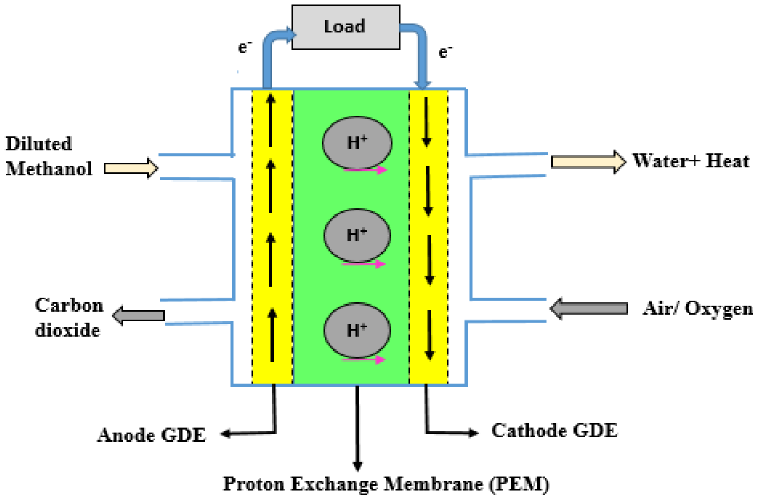

Figure 1.1. Direct Methanol Fuel Cell (DMFC)

The operating principle of DMFC involves a diluted methanol fuel passed through an anodic chamber where platinum ruthenium on porous carbon (PtRu/C) is generally employed as anode (Lee, Lalk, and Appleby 1998; Wang et al. 2003). The half-cell reaction that occurs at anode side, where its splits methanol in to protons (H^+), electrons (e^-) and carbon dioxide (CO_2), is showed in equation (1)

Anodic reaction (Oxidation): 0.03 V

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^- \qquad (1)$$

ΔH = 130.72 kJ/mol

The released electrons from the anode side flow through an outer circuit traveling towards the cathode. The platinum on porous carbon (Pt/C) is a standard cathode in DMFC. Similar to the electron flow, the proton and solvated water diffuses through the permeable membrane to the cathode side.

Simultaneously an oxidant usually humidified oxygen/air is sent through cathode side, which combines with protons and electrons (Vielstich 2003). The half-cell reaction that occurs on the cathode side, showed in equation (2),

Cathodic reaction (Reduction): 1.22 V

$$3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O \qquad (2)$$

ΔH = -857. 49 kJ/mol

Correspondingly, overall DMFC reaction, showed in equation (3),

Overall reaction: 1.19 V

$$CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O \qquad (3)$$

ΔH =-726.77 kJ/mol

1.4 Technical challenges

The methanol is a prevalent energy source, which has potential to replace ethanol and other hydrocarbons (Kamarudin and Hashim 2012). Many firms are producing the DMFC for the portable devices like laptops and mobile phones (Han and Park 2002). However, there are few impeding factors in commercialization of DMFC. The following are the main challenges, which trigger the button of continuous research for improved DMFC (Shrivastava, Thombre, and Chadge 2016; Munjewar, Thombre, and Mallick 2017; Zainoodin et al. 2014 ; Chetty et al. 2010; Moulijn et al. 2008)

(i) Catalyst loading and influence on half-cell reactions
(ii) MEA degradation
(iii) Temperature of the cell
(iv) Concentration of methanol
(v) Methanol crossover

Globally, many researchers are striving continuously to address the above challenges in DMFC. The development of suitable high temperature membranes with less price and good performance is required for commercial DMFC. In order to overcome the limitations of Nafion membrane, polymeric modification with composite materials are mentioned. The composite materials appear to perform well at high humidification as a substitute for Nafion, suggesting a motivating area for development.

1.5 Membranes for DMFC application

The function of membrane is to provide good proton transport while at the same time acts as an insulating barrier between the two electrodes. It separates the fuel (methanol) and oxidant gases (oxygen/air) in the anode and cathode compartments of the DMFC. As the membrane plays vital role, it should possess good proton conductivity, low methanol permeability, thermal and chemical stability (Synder, Ratner, and Shriver 2002).Considering the great variety of materials used for the synthesis of membranes in DMFC applications, classified based on ionomers, materials and preparation methods (Kreuer 1996). The state-of-the-art commercially available Nafion® membrane is being widely used for DMFC because of its proton conductivity and stability at low to moderate temperatures (Liu et al. 2011). Nevertheless, it is limited by high methanol crossover ($>10^{-7}$ cm^{-2}/sec) (Parthiban et al. 2016) and high price (\$2000-2500 m^{-2}) (Devrim et al. 2012). The methanol cross over through the membrane leads to poor cell performance and also deactivates the cathode catalyst causing in more efficiency losses and declines the cell potential (Moulijn et al. 2008; Zhou et al. 2014).

1.6 Scope for development of membranes for high temperature DMFC

Nafion and other perfluorinated PEMs have been widely used because of their excellent proton conductivity and electrochemical stability due to the PTFE backbone. However, they are expensive, not durable, especially under cycling voltage, humidity, and freezing and thawing conditions, unstable at temperatures over 100 ºC. It effectively conducts protons only when they imbibe sufficient water, which limits operating temperatures of PEMFC and DMFCs to around 80 ºC. On the other hand, fuel cell temperature above 100 ºC is a highly desirable goal. As the operation of fuel cells at higher temperature, increases electrochemical kinetics, improves CO tolerance, facilitates heat rejection and reduces the problems associated with water management.

The evaporation of water is the main challenge for high temperature proton exchange membranes (PEMs) which resultants loss in performance. Using of ionic liquid as charge carrier instead of water could be a possible solution. Composite membranes are synthesized by using organic support and organic/inorganic fillers. Polymers are sensitive to humidity and shows drop in proton conductivity at low humidity. There are several reporting in the literature to increase tolerance to higher temperature and reduced humidification of the composite membranes (Hoshino et al. 2016). Clays, various hygroscopic oxides and zeolites were been envisaged as fillers to increase the hydrophilicity of PEMs (Zhang and Shen 2012). On the other hand, fuel crossover from anode to cathode also becomes a serious problem in a liquid-type fuel cell (Branco et al. 2016).

The composite membranes have been explored as an alternative with low methanol cross over, high thermal and mechanical stability for DMFC application. These hybrid membranes are classified into two types based on the type of chemical bonds establishes between inorganic and organic phases. Type I, weak bonds with weak electrostatic interactions between organic and inorganic components. Type II, it consists of strong covalent bonds with organic and inorganic components (Hattori et al. 2015).Natural polymers like chitosan modified with zeolites or polyacrylic acid were reported as methanol barriers without negotiating their proton conductivity (Kundu et al. 2007). However, these membranes do not find suitable for DMFC applications due to swelling in an aqueous medium. Synthetic inorganic fillers like metal oxides (TiO_2 and ZrO_2), inorganic nanotubes ($Na_2Ti_3O_7$), silica, zirconium phosphate and inorganic-inorganic materials like silica modified with heteropolyacids (HPAs) used as PEM for DMFC applications (Pandey, Mir, and Shukla 2014;Yang et al. 2001;Chien et al. 2013).

Extensive studies were reported to develop a suitable membrane for DMFC either by modifying the Nafion or by developing new membranes altogether. Modification of Nafion by grafting, pore-filling, interpolymerization, and surface treatment reduces the methanol permeability, but results in a significant loss of proton conductivity. In addition, these modifications increase the cost of the Nafion membrane. In recent years there is extensive research to develop new membranes for DMFC; these include sulfonated polybenzimidazoles, sulfonated polyimide, sulfonated polysulfone and sulfonated poly(phenylene oxide)(Pandey et al. 2014). For reducing the methanol cross over of the membrane, composite membranes were synthesized by adding inorganic fillers such as inorganic oxide such as silica, zirconium phosphate, PVA and SPEEK (Pandey, Mir, and Shukla 2014;Yang et al. 2001;Chien et al. 2013; Jin et al. 1985) Thus, present work is aimed to synthesize a suitable economical membrane, which can sustain at elevated temperatures with low methanol permeability.

1.7 Motivation

The current DMFC membranes having limitations in terms of cost and performance. Huang et al., mentioned the synthesis of Nafion/PTFE/silicate composite membrane. It’s having high current density but exhibited low voltage (Huang et al., 2006). Lin et al., were prepared Nafion/PTFE membrane using pore impregnation method, its exhibited low methanol permeability compared to Nafion 112 and 117 (Lin et al., 2005).

There have been extensive research efforts to find alternative membranes, which are stable at higher temperature. In fact, a desirable PEM must not only be highly proton conductive under hot and dry conditions, it should be thin for low resistance and high protonic conductivity, compliant to make a good contact with electrodes but rigid enough to provide support to the membrane electrode assembly (MEA). It should be thermally and dimensionally stable, impervious to gaseous or liquid fuels, as well as to electrons, with a low electro-osmotic drag, and mechanically strong enough to last several years. This is a tall order indeed, and it is small wonder that success at finding alternates to Nafion has been limited despite a very large-scale research effort.

The main challenges for current DMFC membranes, includes low proton conductivity, high methanol permeability and high cost. The usage of readily available low-cost inorganic ion-exchangers like ZrP and PWA can reduce the cost of the membrane without comprising, the performance of the membrane. The hydrated ZrP was proven its capability as a proton exchanger in membrane synthesis due to its high IEC (6.64 meq g^{-1}) and ZrP contributes proton conduction through proton of phosphate moiety ranges from 10^{-2} to 10^{-3} S cm^{-1} based on composition and ZrP was thermally stable up to 450° C (Clearfield, 1988). The inorganic ion-exchanger, phosphotungstic acid (PWA) is an effective proton conductor and provides added proton exchangeable sites to improve transport capacity of protons due to its kegging structure (Keggin, 1933). These ion-exchangers are chemically and thermally stable (Mikhailenko et al., 2001;Branco et al., 2016; Kim et al., 2015). The operation at elevated temperatures (100-160℃), would significantly improve its performance of DMFC because of following reasons (Kumar et al. 2009).

(i) Increasing the electrode reaction kinetics (ORR)
(ii) Making the water management and heat subtraction
(iii) Enhancing the electrocatalyst CO tolerance, and
(iv) Lowering the expensive platinum (Pt) metal catalyst requirement

With addition of small quantity of PVA can inhibit the methanol cross over (Sahu et al., 2008). The ion-exchange layer has to be laid on porous support which gives structural stability of the membrane. Polytetrafluoroethylene (PTFE) is one the materials which can increase the mechanical strength of the membrane (Liu et al., 2006). Xing et al. also reported a PTFE based composite membrane that provided good mechanical stability at high temperature with low swelling ratio(Xing et al., 2011). Hence in this work, PTFE film was selected as support for providing mechanical strength and structural stability, ZrP and PWA were selected as cation-exchangers and PVA was selected as methanol permeability inhibitor. The PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE composite membranes were synthesized and performance curves of high temperature DMFC were reported.

1.8 Thesis layout

The entire thesis is organized into seven chapters including the current part as chapter 1, which comprises the brief introduction part of the fuel cell, main categories of fuel cells, introduction to DMFC, the scope for development of membranes for high temperature DMFCs and representing thesis layout.

Chapter 2 provides a detailed review of literature which is relevant to the fuel cell, the role of membranes in DMFC, review on composite membranes in DMFCs along with research gaps and the objectives of the overall study presented in this chapter.

Chapter 3 gives a deep insight into experimental studies and characterization of DMFCs membranes, the methods approached for the synthesis of composite membranes. The detailed characterization procedures of PTFE based composite membranes are explained along with testing of single cell DMFC.

Chapter 4 provides detailed discussions of membrane characterization results and single cell DMFC testing results. The highly stable PTFE-ZrP-PVA composite membrane was characterized in terms of hydrophilicity of PTFE film, surface morphology, thermal stability, mechanical strength, water uptake, proton conductivity, methanol permeability studies have been elaborated with significance to the DMFC performance is discussed.

Chapter 5 gives the detailed discussion on the synthesis of (Si-PWA)-PVA/PTFE composite membrane PEM with characterizations like contact angle, functional group analysis, surface morphology, thermal, mechanical stability, proton conductivity, methanol permeability and DMFC studies are discussed.

Chapter 6 provides the conclusion drawn from the present research work.

Chapter 7 describes the challenges that are faced while carrying out the present work and scope for future work.

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CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

This chapter gives a comprehensive literature review on high temperature composite membranes for direct methanol fuel cell (DMFC). The detailed synthesis methods, along with various membranes with intensive details on the importance of membrane properties in measuring the complete performance of DMFC have been reported.

2.1 Types of fuel cells

The electrochemical devices which convert chemical energy of fuel to electricity directly are fuel cells (Radenahmad et al. 2016; Wong et al. 2019; Sharaf and Orhan 2014). Fuel cells are categorized according to the type of electrolytes used, based on operating temperature and applications are showed in figure 2.1.

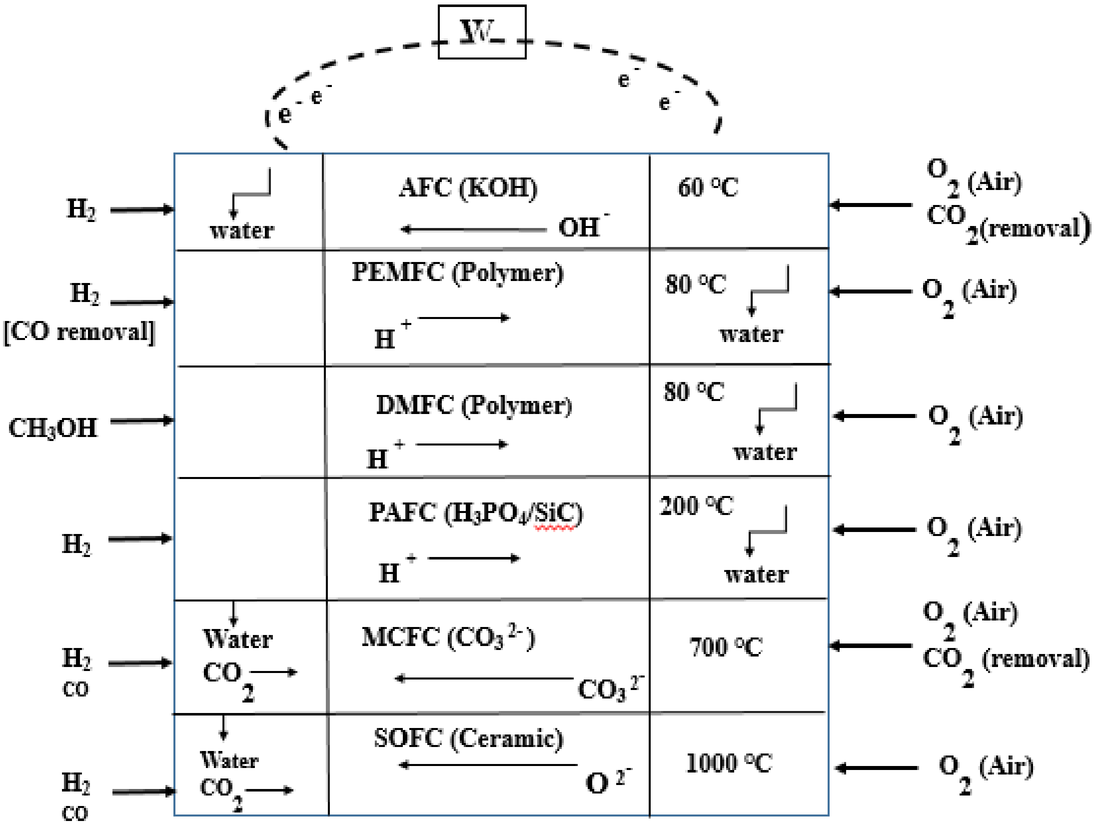

Figure 2.1 Types of fuel cells, electrolytes and operating temperatures

Table 2.1- Fuel cells and applications

Type	**Temperature (˚C)**	**Electrolyte**	**Efficiency (%)**	**Advantages**	**Limitations**	**Applications**	**References**
Polymer electrolyte membrane fuel cell (PEMFC)	30-80	Proton exchange membrane (PEM)	40 - 60	Compact design, Quick startup, low temperature, and long life of the operation	Price of catalyst, complex management of heat and water	Transportation, stationary and Portable	(Abdul Rasheed et al. 2017; Valdés-López et al. 2020)
Direct methanol fuel cell (DMFC)	30-100	Proton exchange membrane (PEM)	35 - 60	Compact size, no compressor and methanol feed	Less efficiency and complex structure	Mobile, stationary and Portable	(Kamarudin, Achmad, and Daud 2009)
Alkaline fuel cell (AFC)	90 -230	Alkaline solution	60-70	Nontoxic electrolyte, less operating cost, fast cathode kinetic and	More sensitive towards the impurities like hydrogen and	Mobile, space and military	(Wang et al. 2017)

				tremendous gas separator	oxygen, bigger in size		
Phosphoric acid fuel cell (PAFC)	150- 220	Phosphoric acid solution	35- 45	Carbon monoxide (CO) tolerance to impurities	Less efficiency, limited life and high catalyst price.	İntermediate to large scale power stations	(Spainhour 2014)
Molten carbonate fuel cell (MCFC)	600-700	Molten carbonate salt electrolyte	45-55	Flexible fuel with good efficiency	Long start-up, limited life, more heat leads to corrosion	Large capacity power stations	(Raza et al. 2020; Mehmeti et al. 2016)
Solid oxide fuel cell (SOFC)	650 – 1000	Ceramic ion conducting electrolyte	55-65	High efficiency and natural gas used as fuel	High heat due to high operating temperature, extensive start-up and short lifespan	İntermediate to large scale power stations	(da Silva and de Souza 2017)

They can also be divided into low temperature fuel cells (<100°C), intermediate temperature fuel cells (100-500 ° C) and high temperature fuel cells (>500°C) and (Mekhilef, Saidur, and Safari 2012;Spiegel 2007). The classification of fuel cells and applications are mentioned in Table 2.1.

2.2 Direct methanol fuel cell (DMFC)

DMFC technology has become widely accepted as a viable fuel cell technology as a subcategory of PEMFC. DMFC has been proved its capability in powering cars, mobile phones, laptops and computers (Kamarudin et al. 2009; Chen et al. 2007). The liquid methanol is directly fed into as fuel in DMFC, without generating the hydrogen fuel separately. The hydrogen as gaseous fuel has limitations of storage and handling. The liquid methanol as hydrogen carrier overcomes the limitation of hydrogen fuelled PEMFC. Methanol is a low-cost liquid, has high energy density, easy to store, biodegradable and can be easily generated from sources like coal, natural gas, and biomass.

2.2.1 Components of DMFC

A DMFC is composed of two end-plates, two current collectors, anode gas diffusion electrode (AGDE), cathode gas diffusion electrode (CGDE) and the membrane. The make of AGDE, CGDE and membrane together has named as membrane electrode assembly (MEA), which is treated as the heart of the DMFC cell (Kamarudin and Hashim 2012;Shrivastava, Thombre, and Chadge 2016;Munjewar, Thombre, and Mallick 2017). In general, platinum ruthenium on carbon (PtRu/C) was used as anode catalyst and platinum on carbon (Pt/C) used as a cathode catalyst. The gas diffusion layer (GDL) with coated designated catalyst ink is called a gas diffusion electrode (GDE). The assembly of DMFC with all the components is shown in figure 2.2.

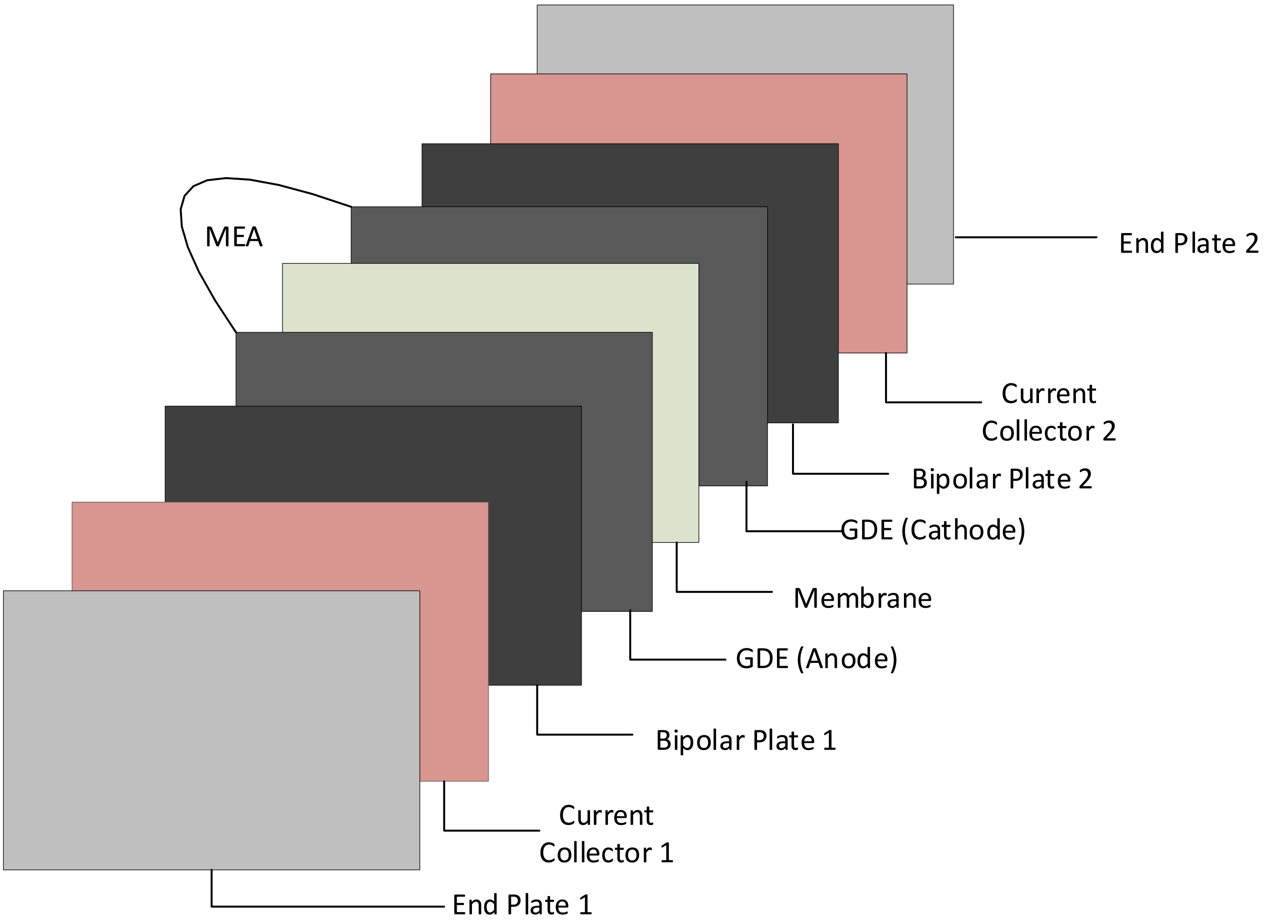

Figure 2.2 Fuel cell components

Electrodes: The carbon electrode particles (30 microns) are coated with nanosized platinum (Pt) or platinum-ruthenium (Pt-Ru) catalysts particles with the help of adhesive ionomeric material. It is layered on the support of 100-300 μm thick backing layer of carbon cloth or porous carbon paper. The nanometer scale of catalyst particles maximizes the catalyst surface area and enhance the three-phase interface between reactants, catalyst and the electrolyte. The classification of catalysts shown in Table 2.2. Generally, Pt-Ru and Pt catalysts are used on anode and cathode sides respectively in DMFC (Munjewar et al. 2017).

Table 2.2 Classification of catalyst

Catalyst	**Sub-classification**	**Material**
Anode catalyst	Platinum alloy catalyst	**Binary catalyst:** Pt-Ru, Pt-Mo, Pt-Co, Pt-Ni, Pd-Fe, Pt-Pb
		Ternary catalyst: Pt-Ru-Fe, Pt-Ru-Ni, Pt-Ru-Co, Pt-Ru-Mo, Pt-Ni-Cr, Pt-Co-Cr
		Quaternary Catalyst: Pt-Ru-Li-Ni
	Non-platinum catalyst	WC, W2C, MoCo, TiO_2, Ni-MnO, Fe-MnOx, Pd-Ni
Cathode catalyst	Platinum alloy catalyst	Pt, Pt-Ru, Pt-Fe, Pt-Ni, Pd-Pt
	Non-platinum catalyst	Pd-CO, Pd-Se

Gas diffusion layer (GDL): The GDLs, one next to the anode catalyst layer (CL) and the other next to the cathode CL, are usually made of 100–300 µm thick porous carbon cloth or carbon paper. The role of anode and cathode GDL is to provide a porous surface for uniform distribution of the reactants, and electron conduction towards the current collector (Shrivastava et al. 2016). In order to promote the transport between the catalyst layer and the electrolyte, a porous hydrophobic GDL is used. The GDE is obtained by coating liquid catalyst ink and heat treatment for solvent evaporation. The membrane, cathode GDE and anode GDE are hot pressed together to attain the membrane electrode assembly (MEA).

Bipolar plates**:** Bipolar plates provides structural stability to the cell and the flow fields distribute the fuels evenly over the active area of the MEA. The graphite is preferable material for making of bipolar plates but some other materials are also explored to decrease the weight and increase the durability of the DMFC cell. The studies on flow channels configuration also attempted to optimize the reaction kinetics and improve the cell efficiency. They also need to remove the water produced at the cathode effectively (Davies et al. 2000; Iranzo et al. 2020,Alias et al. 2020).

Current collector: DMFC consists of two current collectors one at cathode side and other at anode side (Kamarudin and Hashim 2012;Iranzo et al. 2020). Anode current collector (ACC) and cathode current collector (CCC) are required to complete the circuit between the two electrodes and carry the electrical charge to the system. The current collector is generally a stainless steel or copper plate.

Gaskets: Gaskets are placed between MEAs and graphite plates to prevent gas leakage and also the direct contact between electrolyte and the bipolar plate. They also prevent the electrical contact between plates in the fuel cell. The pressure required to prevent the leak between the layers depends on the gasket material and design (Barbir 2008). The commonly used seal materials are silicone, Teflon and other thermal plastics (Li et al. 2017;Iranzo et al. 2020). It provides excellent heat resistance, offers superior chemical resistance to many chemicals such as acids and also fuels.

Membrane: The membrane must be highly ion-conductive, have low fuel crossover, low electronic conductivity and be chemically stable, mechanically durable and cost-effective (Azad et al. 2014; Yamasaki, Koizumi, and Maekawa 2014;Fergus et al. 2016;Kamaruddin et al. 2013). Moreover, other properties such as water management and the ability to fabricate high performance membrane electrode assembly (MEA) are also important for an effective operating fuel cell system.

2.3 Role of membrane in DMFC

The membrane provides the proton transport, electrical insulation between the electrodes and prevents the cross mixing of the fuel as illustrated in figure 2.3. The ideal membrane for DMFC must provide high proton conductivity, good chemical resistance, good thermal stability, and low methanol cross over.

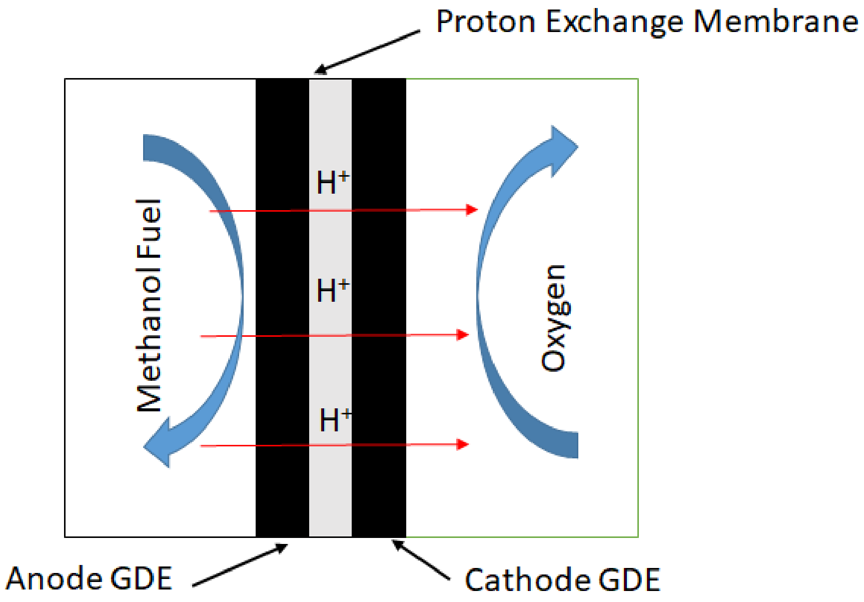

Figure 2.3 Role of the membrane

The high temperature operation of the fuel cell is being prevented by three main barriers (Yuan et al. 2014;Junoh et al. 2020).

1. Loss of hydration of the proton exchange membrane (PEM) and increase in PEM resistance.
2. PEM degradation of the polymer chains above 120 °C.
3. Absence of intermediate proton conductors in the temperature range of 100–400 ℃ with a unique proton ‘solvating’ species supporting conduction in the regime.

The factor that has the greatest influence on the conductivity of PEMs is the degree of hydration. Hence, the design parameters for elevated temperature PEMs, it is essential to have a fundamental understanding of water and proton transport mechanisms.

Elevated operational temperature for DMFCs is essential due to improved reaction kinetics at the electrodes, increased carbon monoxide (CO) tolerance, simplified heating and humidification management at these temperatures. As conventional membrane materials for DMFCs require operating temperatures of around 80°C and full humidification, it follows that the membrane must be modified if the fuel cell is to be operated above this temperature. Research in elevated operating temperature systems has recently focused on a temperature range of 90–120°C. The operation of the DMFCs in this temperature range is more attractive to get the increased efficiency (Baglio et al. 2005). .

On the other hand, fuel crossover from anode to cathode also becomes a serious problem in the liquid-type fuel cells. Fuel crossover can substantially reduce the overall cell performance due to the low fuel utilization, deterioration of cathode catalytic activity, reduction of cell potential and increase of heat generation. In fact, Nafion is the benchmark by which all new materials are compared but it's having some limitations. Expensive Nafion membranes conduct protons only in the presence of water content in the membrane which restricts the fuel cell operating temperature to be about 80 °C without pressurization, causing low fuel cell performance due to slow electrode kinetics and limited CO tolerance. Therefore, to accomplish the commercialization of DMFCs, it is essential to develop novel PEMs for elevated temperature systems.

According to literature, membranes can be either inorganic or organic. PEMs with low methanol permeation may allow the use of fuels with high methanol concentration and thereby increase the energy density, which is particularly attractive for portable electronic applications. Furthermore, the cost of existing membranes is one of the key issues influencing the cost of the fuel cell system. To achieve high efficiency in DMFCs, the following membrane properties are required:

i. Chemical and electrochemical stability under operating conditions;
ii. Mechanical strength and stability;
iii. Compatibility with and good adhesion to the components of the DMFC;
iv. Extremely low crossover to the reactants (H_2, methanol and O_2) to maximize coulombic efficiency;
v. High electrolyte transport to maintain uniform electrolyte content and to prevent local drying;
vi. High proton conductivity to support high currents with minimal resistive losses and zero electronic conductivity;
vii. Production costs are compatible with the intended application.

Many membranes have been developed, and many membranes are under ongoing research. The comprehensive literature on DMFC membranes shown in Figure 2.4 and explained in detail.

2.4 DMFC Membranes

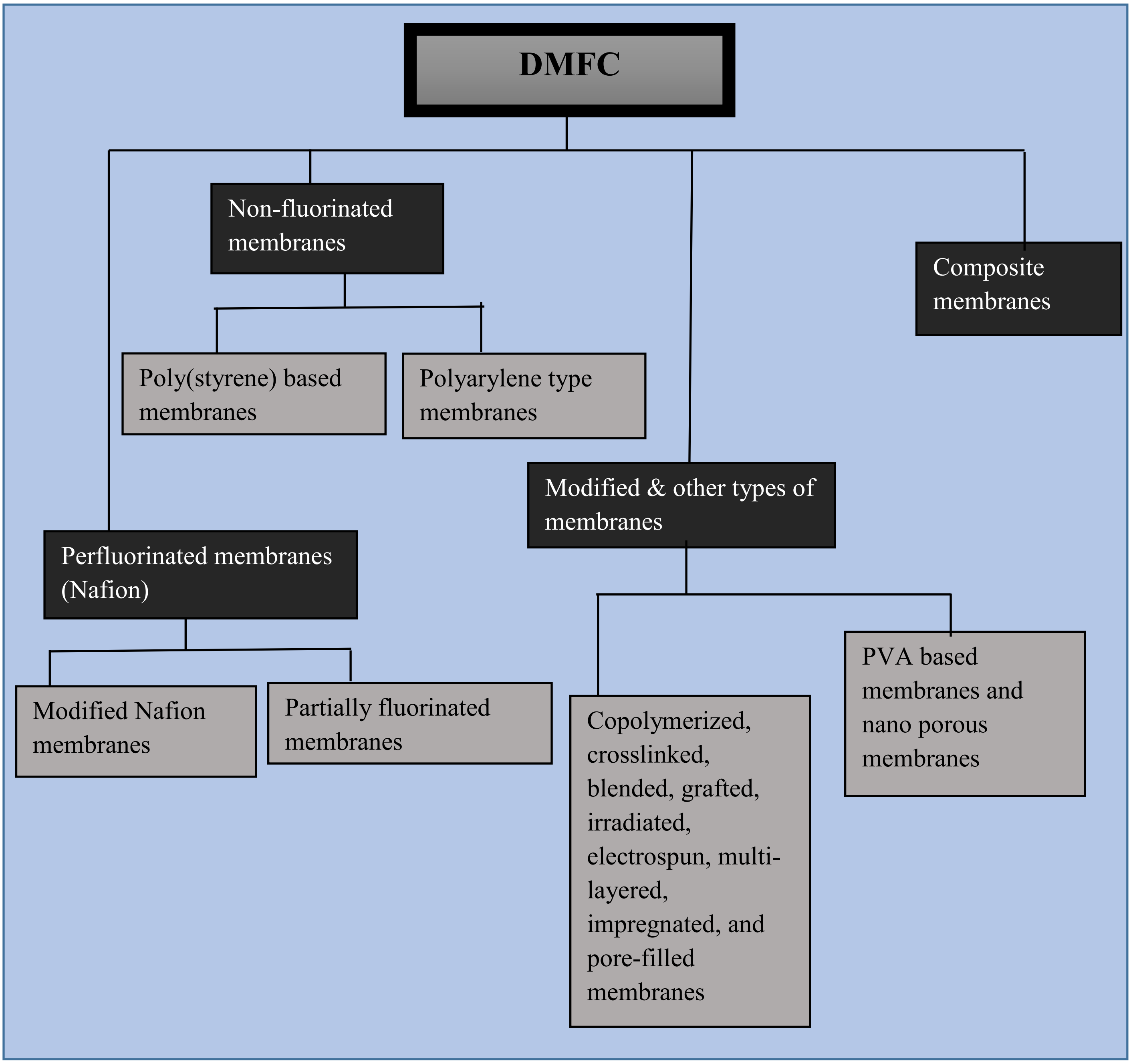

Figure 2.4 Classification of membranes

2.4.1 Perflourinated membranes

The perflourinated membranes such as Nafion® series membranes are predominantly used as PEMs in DMFCs. Nafion consists of polytetrafluroethylene (PTFE) as a backbone with sulphonated functional groups all over the structure. The uniform membranes proved to be good proton conducting membranes (PEMs) because of their high electronegative C-F bond and less polarization ability. The sulfonic group ($-CF_2SO_3H$) promotes the proton conductivity and chemical stability. PTFE back bone provides the thermal stability. These features makes these PEMs' suitable for PEMFC, DMFC applications (Lufrano et al. 2013; Branco et al. 2016; Awang et al. 2015). The hydrophilic channels provide the path for proton conduction but these channels also allow the methanol in DMFC. The high methanol permeability of Nafion ($>10^{-6}$ $cm^2 sec^{-1}$) is the major limitation. The high price (2473 $\$/m^2$) and reduction of DMFC efficiency over 80°C also limits the membrane. The research has been focused to overcome these limitations and many alternatives have been explored.

Partially fluorinated membranes

Partially fluorinated membranes which display the Nafion like structure with low methanol cross over in DMFC. Fluorinated polymers exhibit good thermal and chemical stability which make the membranes suitable for DMFC (Awang et al. 2015).The performance of the partially fluorinated polymer membrane improves by the adding of pendant structural sulfonic acid groups (Arnett et al. 2007; Kim et al. 2009) reported that poly(arylene ether)s with pendant sulfonic acid groups exhibited nanosized phase separation, high proton conductivity even at low humidity, excellent mechanical properties, and low gas permeability. Grafted ionomer membranes based on poly (vinylidene fluoride) (PVDF) have been established by Lehtinen et al,(Lehtinen et al. 1998). The Ballard corporation has established most of the partially fluorinated PEMs which consist of phosphonates (Wei, Stone, and Steck 1995), β-trifluorostyrene, sulfonated (Wei et al. 1995), polymerisates of unmodified and α, β, β-trifluorostyrene modified with radicals R. This partially fluorinated sulfonated copolymer-based membranes exhibited better and durable DMFC performances than Nafion 112 membrane, because of less methanol permeability. Unfortunately, these have limited stability in water and prone to dissolve (Livingston, Kamath, and Corley 1956).

Modified Nafion membranes

Some of the researchers have modified Nafion membrane using organic-inorganic materials to reduce methanol permeability. Penner and martin synthesized the first composite fluorinated membranes by the impregnation method of Gore-Tex with Nafion (Penner and Martin 1985). Kolde et al. has used the Gore-select membranes in fuel cell applications (Kolde et al. 1995). They observed that these membranes possess good mechanical strength in both swollen and un-swollen state.

Nafion–inorganic membranes

The performance of composite fluorinated membranes can be improved with the addition of inorganic materials or metal oxides such as zeolite, TiO_2 and SiO_2 to maintain water content for high temperature applications (Zheng et al. 2018;Rodgers, Shi, and Holdcroft 2008; Thiam et al. 2013). Silica (SiO_2), titania (TiO_2), zirconia (ZrO_2) are the most widely used metal oxides ion-exchangers for DMFC (Li and Nogami 2002). Silica is inexpensive strengthening inorganic material, environmentally friendly and easily available compared to Nafion membrane.

Nafion/SiO_2: Silica synthesized through hydrolysis and polycondensation in acidic or basic medium, with various precursors like tetraethyl orthosilicate (TEOS), alkoxy silanes, fumed silica and sodium metasilicate (Mishra, Kim, and Lee 2014). The silica has been used as inorganic filler because of its high-water retention capacity and it can able to hold water molecules at high temperature with low relative humidity (RH) conditions which promotes the proton conduction. Arico et al., consider silica for DMFC applications, which has showed remarkable changes in acid-base and surface properties of modified Nafion like water uptake and water adsorption density(Arico et al. 2004). Lufrano et al and Dresch, has reported the Nafion-silica based membranes, synthesized using sol-gel and recasting method(Lufrano et al. 2013; Dresch et al. 2013). Kim et al., mentioned that Nafion–silica membranes synthesized using layered techniques gave good performance compared to Nafion alone (Kim et al. 2004). Huang et al., and Dimitrova et al., also prepared Nafion-silica for DEFC and DMFC at high temperature(L.-N. Huang et al. 2006;Dimitrova et al. 2002).They observed that high proton conductivity and high water retention capacity but still having liquid permeability.

***Nafion/TiO_2*:** Baglio et al., Barbora et al., and Cele et al., mentioned the synthesis of Nafion/TiO_2 for DMFC applications(Baglio et al. 2004;Barbora, Acharya, and Verma 2009; Cele, Sinha Ray, and Sikhwivhilu 2012). Barbora et al., mentioned that with 5 wt% TiO_2 was identified to have the lowest alcohol permeability with high proton conductivity(Barbora et al. 2009). Cele et al., mentioned that, 0.5 wt% of titania nanotubes showed proton conductivity of 7.2×10^{-2} S cm^{-1} at 26 °C and 100% relative humidity(Cele et al. 2012).Baglio et al., mentioned that Nafion//TiO_2 for high temperature applications(Baglio et al. 2004). However, the information about particle size and degree of crystallinity were not provided.

***Nafion-ZrP*:** Yang et al., Arbizzani et al., Hou et al., Bauer et al., Arbizzani et al., Bauer et al., and Casciola et al., synthesized Nafion/ZrP for high temperature DMFC(Yang et al. 2001;Arbizzani et al. 2010;Hou et al. 2008;Bauer and Willert-Porada 2004;Casciola et al. 2009). Literature shows, with the addition of ZrP methanol permeability reduced without effecting the proton conductivity. Yang et al., Nafion/ZrP reported for high temperature DMFC(Yang et al. 2001). Hou et al, tested for high methanol concentrations like 5M and 10M with temperature 75℃(Hou et al. 2008). Arbizzani et al., mentioned Nafion/ZrP with varying ZrP loading 1–6 wt% using casting method(Arbizzani et al. 2010). With increasing ZrP loading the power density of composite membrane reduced. The doped ZrP improved the thermal stability of the membrane and reduced the methanol crossover but the tensile strength and the chemical stability was a bit lower than Nafion-117.

***Nafion/Zeolite*:** Zeolites are a class of crystalline aluminosilicates, which form a framework of SiO_2 and AlO_4 tetrahedra and contain exchangeable cations on the extra-framework to maintain the electrical neutrality. For zeolites at 100% relative humidity, the higher temperature of the higher ion conductivity is up to 100˚C (McKeen, Yan, and Davis 2008;Peighambardoust et al. 2010). Above this value, the conductivity of zeolites is strongly influenced by the amount of adsorbed water (Kornatowski 2005; Ng and Mintova 2008). It exhibited low proton conductivity of 1.86×10^{-5} S cm^{-1} at room temperature and 100% RH after 24 hours in the cell. This value is similar to that obtained by Chen et al.(Chen et al. 2007), 7.148×10^{-5} S cm^{-1}, for the same conditions Sancho et al.,(Sancho, Soler, and Pina 2007). Zeolite based membranes showed poor mechanical properties and comparatively less proton conductivity with that of per-fluorinated membranes.

Nafion–organic membranes

The Nafion-organic membranes are reported with different polymeric matrices like PVDF, PTFE, poly (propylene) (PP), poly(ether sulfone) (PES), PVA.

Nafion/PTFE: PTFE having high mechanical strength in the range of 20−30 MPa and low density of 2.2 gcm^{-3} and could be used under 300 °C for a long period. The thin porous PTFE films were used as a support framework to enhance the mechanical strength (Zaidi et al. 2000). Along with crosslinking structure in PTFE support improves dimensional and chemical stability (Peighambardoust et al. 2010). Lin et al., were prepared Nafion/PTFE membrane using pore impregnation method (Lin et al. 2005). The addition of PTFE reduces the methanol permeability compared to Nafion 117 and Nafion 112.

Nafion/PVA**:** PVA is a biodegradable, inexpensive, easily available and also used in pervaporization process for separating alcohol from water. PVA based membranes, the proton conductivity will be induced due to the change in chemical structure. Proton conductivity of pure PVA was very low 10^{-7} S cm^{-1} (Deluca and Elabd 2006). Lin et al., successfully prepared Nafion/PVA membranes for DMFC application using electrospinning, impregnation and the solution casting method(**Lin and Wang 2014**). Molla et al., found that the composite Nafion/PVA gave a good performance with increase in membrane thickness as 19 and 47 µm(Mollá and Compañ 2011). PVA was one of the preferable material to reduce methanol permeability of the membrane (Jin et al. 1985).

Nafion/PBI**:** Wycisk et al., used PBI based membrane for DMFC applications (Wycisk et al. 2006). The reported mechanical strength of 160 MPa was very high compared to PTFE and PEEK (Zhang, Klein, and Friedrich 2002). They mentioned that the membrane gives a power density of nearly 40% greater than that of Nafion 117 in DMFC.

Nafion-inorganic-inorganic membranes

Nafion/silica/PWA**:** Heterotungstic acid (Phosphotungstic acid, PWA, $H_3PW_{12}O_{40}\cdot nH_2O$) and silicotungstic acid (SiWA, $H_4SiW_{12}O_{40}\cdot nH_2O$) provided a good mechanical strength (Mioč et al. 1997). Among various types of HPAs, PWA has gained interest in recent times due to its effective proton conductor (~0.1 S cm^{-1} at ambient temperature).

Xu et al., synthesized Nafion/silica/phosphotungstic acid membrane for low-temperature DMFC(Xu et al. 2005).They synthesized the membrane by sol-gel method using tetraethoxysilane (TEOS) used as a derived silica to immobilize the PWA. Staiti et al., also studied Nafion-silica membranes modified with heteropolyacids for high temperature DMFC applications(Staiti et al. 2001). With optimum silica loading improves the proton conductivity and reduce methanol permeability. The leaching problem of PWA resulted in poor life of the membrane.

***Nafion-Pd-SiO$_2$*:** Thiam et al., prepared Nafion/Pd-SiO$_2$ for DMFC applications(Thiam et al. 2013). These Pd-SiO$_2$ nanofibers were synthesized using electro-spinning method. Nafion/Pd-SiO$_2$ membranes synthesized using solution casting method to improve ion conduction and water uptake. They reported the highest proton conductivity, 0.1292 S/cm, and lowered the methanol permeability to 8.36×10^{-7} cm^2 s^{-1} compared to Nafion 117(12.8×10^{-7} cm^2 s^{-1}). At low methanol concentration, Nafion/Pd-SiO$_2$ membrane gave the same performance that of Nafion; at high methanol concentration Nafion membrane power output decreased by 43% while Nafion/Pd-SiO$_2$ membrane power output increased by 23%. But still the cost of the membrane of Nafion and Pd may be an issue.

***Nafion/CS-SiWA*:** Ni et al., prepared Nafion/CS-SiWA using Nafion 112 membrane with chitosan (CS) and silicotungstic acid (SiWA) as methanol barriers (Ni et al. 2011). This membrane synthesized using layer by layer (LBL) techniques. They mentioned that modified Nafion membranes had lower performances than pure Nafion membranes.

Nafion-organic-organic membranes

***PVDF-co-HFP/PBI*:** Liu et al., reported a review on PVDF polymers which have mechanical strength in the range of 50–80 MPa and density of 1.78 gcm^{-3}(Liu et al. 2011). Alwin et al., reported radio-chemically-pore-filled PVDF membranes have also been prepared for use in DMFCs (Alwin et al. 2010). Scott et al., mentioned the surface of PVDF has been modified with an electron-beam-irradiation technique and styrene grafted radio-chemically to improve the surface properties in DMFCs (Scott et al. 2000).

Wang et al., mentioned the poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-*co*-HFP)/polybenzimidazole (PBI) nanofiber (PVFP-BI) on Nafion support for DMFC applications (Wang and Lin 2014). Nanofibers of PVdF-*co*-HFP/PBI were prepared using electro-spinning method and composite membrane prepared using the impregnation method. Kumar et al., prepared crosslinked sulfonated polystyrene in a blend of PVdF-*co*-HFP/Nafion for DMFC via in situ polymerization technique (Kumar et al. 2014).This membrane showed high water uptake like Nafion. However, PVDF contains fluorine content but is limited to operating temperature range along with price of the materials.

Nafion-organic-inorganic membranes

***Nafion/PTFE/Silicate*:** Chen et al., prepared Nafion/polyaniline/silica membrane, but it has showed low power density of 8 mW cm^{-2} at 40 °C in a cell operating with 2 M methanol concentration and air (Chen et al. 2007). Huang et al., mentioned the synthesis of Nafion/PTFE/silicate composite membrane. The DMFC results showed that Nafion/PTFE/silicate membrane showed higher voltage than Nafion/PTFE membrane at low current density (L.-N. Huang et al. 2006). But at high current density Nafion/PTFE/silicate membrane had lower voltage than Nafion/PTFE due to high resistance of silicate.

***Nafion/PTFE/ZrP*:** The hydrated ZrP has proven its capability as a proton exchanger with high ion exchange capacity (IEC) (6.64 meq g^{-1}). ZrP contributes proton conduction through proton of phosphate moiety ranges from 10^{-2} to 10^{-3} S cm^{-1} based on composition and ZrP was thermally stable up to 450℃ (Clearfield 1988). Only few research papers have been reported on ZrP based ion-exchange membranes for DMFC. Chen et al., prepared ZrP hybridized Nafion/PTFE composite membrane for DMFC applications using two methods(Chen et al. 2008). The first method shows, impregnation of porous PTFE film into Nafion/$ZrOCl_2$ solution. And the second method shows Nafion/PTFE impregnated into $ZrOCl_2$ solution. The First method gave better DMFC performance compared to second method.

***Nafion/PBI-ZrP*:** ZrP material, reported a very high IEC (4–8 meqg^{-1}) for ZrP, but poor counter-ion transport number (< 0.85) (Alberti, Casciola, and Costantino 1983;Clearfield 1988). PBI material is having a low density as 1.3 gcm^{-3}. The PBI based polymers are preferred for high temperature DMFC applications due to its excellent thermal stability (up to 400 ° C). Ahmad et al., synthesized Nafion/polybenzidazole (PBI)-zirconium phosphate (ZrP) composite membrane by solution casting method(Ahmad et al. 2011). Nafion/PBI-ZrP membrane showed lower proton conductivity than that of Nafion 117 in DMFC.

2.4.2 Non-fluorinated membranes

The other kind of materials used for PEM preparation is non-fluorinated hydrocarbon polymers, which can be either aliphatic or aromatic polymers, with benzene ring or bulky pendent groups as polymeric support. The capable of processing, readily availability and structurally diversity of aromatic polymers most suitable in DMFC environment (Hodgdon Jr

1968).The, poly(ether sulfone)s (PES), polyimides (PI), polysulfones (PSU), poly(ether ketone)s and polybenzimidazoles (PBI) are some polyarylenes. J.K.Lee et al., reported two methods to improve the stability of the non-fluorinated membranes, i) Polymers and bulky groups are customized together in the backbone of aromatic polymer to improve the proton conductivity and ii) Modification of hydrocarbon polymer using incorporating aromatic hydrocarbon directly to polymeric backbone(Lee, Li, and Manthiram 2009).

Polystyrene based membranes

The sulfonated poly (styrene) (PS), poly (styrene sulfonic acid) (PSSA) and sulfonated poly (styrene) (SPS) and random styrene-based copolymers have been used as membrane materials for DMFCs (Carretta, Tricoli, and Picchioni 2000; Bae and Kim 2003;Jung et al. 2001).These PEMs have advantages like good conductivity, mechanical and thermal stability. The ion selectivity of these membranes is higher compared to that of SPEEK and SPEEKK membranes (Gil et al. 2004; Kobayashi et al. 1998;Li, Zhang, and Wang 2003;Liu et al. 2005).The both "carbon-chain" (Polystyrene co-polymer with ethylene and butylenes (PSEB) (Chirawithayaboon and Kiatkamjornwong 2004), Quaternized ammonium polyvinyl alcohol (QAPVA), quaternized chitosan (HACC) blended with QAPVA (Yang et al. 2016; Huang et al. 2006) and "hetero-chain" polymers (polyethers (PE), the copolymer of chlorohydrin and allyl glycidyl ether (PECH/AGH) (Zarrin 2015), containing groups of ammonium bases in the side chain have been applied. These membranes are prone to have high oxidative chemical degradation.

Polyarylene type membranes

These type of membranes shows high oxidative, mechanical and thermal stability (Walker et al. 1999). The low methanol cross over with acceptable proton conductivity have made these membranes as Nafion alternative (Lufrano et al. 2013). The sulfonated poly (aryl ether ketone)-based membranes, sulfonated poly(aryl ether sulfone)-based membranes, poly(imide)s, poly(phosphazene)s and polybenzimidazole-based membranes are some widely studied polyarylene type membranes (Genova-Dimitrova et al. 2001;Lufrano et al. 2000; Kerres, Cui, and Reichle 1996). Kerres et al. reported that the existence of inflexible and bulky aromatic groups in the polyaromatic membranes makes its thermally stable up to 200 ℃ (Kerres et al. 2002). The alternate hydrocarbon backbone-based polymers not only provide the potential for high temperature performance at low RH, but also promise a cost advantage.

Chang Liu et al. mentioned the synthesis of “the sulfonated poly (aryl ether ketone sulfone) membrane with comb-shaped structures for DMFC applications”. They reported sulfonated poly (aryl ether ketone sulfone) polymers (SPAEKS-PSA X) preparation by grafting with 1,3-propanesultone (PSA) to reduce methanol crossover and to improve proton conductivity (Liu et al. 2020). Vikrant Yadav et al. reported sulfonated poly(ether sulfone) based sulfonated molybdenum sulfide composite membranes for DMFC applications, with improved DMFC performance (Yadav, Rajput, and Kulshrestha 2020). Hu¨seyin Deligo¨z et al. mentioned the sulfonated polyimide ionomers preparation for fuel cell applications. Here they reported ion exchange capacity (IEC) as 0.20 to 0.67 meq g^{-1} but it showed low proton conductivity (Deligöz et al. 2008). Fengyan et al. mentioned the preparation of “polyphosphazene graft copolystyrenes with alkylsulfonate chains” (Fu et al. 2015). Here the sulfonated graft polymers and the cross-linker 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) (5 wt%) were dissolved in DMSO to give 10 w/v% solutions and by adding a drop of sulfonic acid, prepared by casting method. Mader and Benicewicz et al. reported the new type of sulfonated PBI based membrane preparation by using random copolymerisation (Mader and Benicewicz 2011). Disodium 4,6-bis(4-carboxyphenoxy) benzene-1,3-disulfonate, 4,4_-dicarboxydiphenyl ether and 3,3_-diaminobenzidine, on a block copolymer consisting of sulfonated and non-sulfonated PBI segments, to improve proton conductivity to 0.037 S cm^{-1} at 170 °C and 0 %RH.

2.4.3 Modified and other types of membranes

The over swelling of the membranes in DMFC makes methanol to permeate more than 40% and results in poor performance. The permeation of methanol can be impeded by coating of impermeable layer or impregnating inorganic fillers or any other modification techniques. The thoroughly reviewed important DMFC membrane modification techniques are presented below.

Modified membranes

Blended membranes: The blended membranes are similar to composite membranes. The inorganic filler is completely dissolved and the membrane is formed by physical dispersion of filler into the polymer matrix through solution blending and polymer solidification. Gnana kumar et al., mentioned polyvinylidene fluoride-hexafluoropropylenesilica sulfuric acid synthesized by direct blending method, exhibited high thermal stability- high ionic conductivity and low fuel permeability(Kumar, Nahm, and Elizabeth 2008). The SPEEK–PBI, SPEEK–polyetherimide, PVA and poly(styrene sulfonic acid-co-maleic acid), PVA and

Nafion, PVA and PSSA sulfonated poly(sulfone) (SPSU) and acid-doped PBI, and SPEEK/PES are some of the compatible blends that were reported in the recent work of Hazlina Junoh et al.,(Junoh et al. 2020) . Filler agglomeration is the main difficulty faced in the blending method which can be overcome by the modification of the surface of the inorganic particles (Pourzare, Mansourpanah, and Farhadi 2016).

Cross-linked and grafted membranes: The polymer-polymer cross linking activates the sulfonic acid groups and reduced methanol permeability of the membrane. Cross linking depends on two factors such as nature and concentration of the cross-linking agents, it affects the mechanism of the reaction. Cross-linked blend membranes were prepared from commercial arylene main-chain polymers of the poly(etherketone) and poly(ethersulfone) classes, modified with sulfonate groups, sulfinate cross-linking groups, and basic N-groups (Zhou, Kim, and Kim 2010;Zhang, Glüsen, and Garcia-Valls 2006). The brittleness of the membrane and low proton conductivity limits the applications in DMFC.

Recently, organo-functionalization of CNT was grafted on smectite clays (SWy) by catalytic chemical vapor deposition (CCVD) technique by Simari et al. and their composite membranes with Nafion® matrix exhibited proton conductivity of 7× 10^{-2} S cm^{-1} at 120 °C and low RH (Simari et al. 2016). Sasikala et al., mentioned, bentonite clay was also modified by grafting using silane into SPEEK to synthesize composite membrane for DMFC applications(Sasikala, Gopi, and Bhat 2016). This membrane exhibited about 140 mW cm^{-2} of power density in comparison with 71 mW cm^{-2} of pristine SPEEK membrane at 70℃ with low methanol permeability. But, incompatibility between membrane surface and binder resulting in detachment of the catalyst layer (Sasikala et al. 2016; Yang 2007).

Pore filling and infiltrated membranes: These membranes are developed to improve the DMFC performance by controlling the swelling and methanol permeation. The gel-type organic/inorganic polymer fills the pores of the porous substrate to form the membrane. The precursors of inorganic fillers, infiltrate into a swollen or hydrogel-like polymer matrix, and then the nanocomposite membranes are obtained through filler growth, removing the impurities, and polymer curing. Meanwhile, the isolation effect caused by the polymer network can hinder the undesirable agglomeration of nanoparticles and simultaneously lead to controlled particle size and uniform distribution. The strategy called the 'infiltration' reported by Klevin et al.,(Klein 1987).The precursor of the filler is swollen or nano-porous polymeric membrane formed through in-situ filler growth and polymer curing (Tripathi and Shahi 2011;Li et al. 2013).

The host membrane or substrate should have a higher mechanical strength in order to prevent swelling during the impregnation process. PTFE, alumina, porous silica, PVDF are some examples of porous substrates. The different techniques like dip coating, spin coating and screen printing may be applied to fill the pores of the substrate. Hybridizing pure Nafion membranes with ZrP had been reported by WG Grot and Rajendran et al., Yang et al., and Costamagna et al., Si et al.,and Jiang et al., prepared Nafion/PTFE/ZrP (NF–ZrP) composite membranes by impregnating sub μm porous PTFE film(Grot and Rajendran 1999) (Yang et al. 2001;Yang et al. 2004;Costamagna et al.2002; Si,Kunz, and Fenton 2004; Jiang, Kunz, and Fenton 2006). In which they mentioned, the modified Nafion membrane exhibited good fuel cell performance at 120℃. In 2008, J Choi et al., proposed nanofiber-based composites for the first time(Choi et al. 2008). A nanofiber enhanced Nafion membrane was prepared with impregnation of UV-curable Norland Optical Adhesive (NOA) 63 for use as an ion-exchange membrane. Y Li et al., mentioned the preparation of Nafion-impregnated multi-layer PVDF fiber membranes(Li et al. 2019). They observed, comparison with membranes of pure Nafion, the PVDF fiber mats greatly enhanced the membrane's thermal and oxidation stabilities, suppressed swelling ratios and water uptake, and increase fuel cell performance with high methanol concentration of 10M.

Multi-layered membranes: The selection of materials and methods for synthesizing the membrane determines the performance of the membrane. These can be categorized as a subset of composite membranes. Each layer of multiple layers can keep unique characteristics to control the methanol cross over, proton conductivity, mechanical strength, thermal stability and water retention etc. Hasani-Sadrabadi et al., reported, a triple layer nanofiber PEM based Nafion for DMFC application, this membrane has exhibited methanol permeability as 1.36×10^{-6} cm^2 sec^{-1} than that of Nafion 2.00×10^{-6} cm^2 sec^{-1} (Hasani-Sadrabadi et al. 2011). Kamiya et al., reported the multilayer PEM as poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP) layer and a mono [poly(propylene oxide) methacrylate] phosphate ester (PPHP) layer membrane synthesized using solution-casting method followed by hot-pressing technique (Kamiya et al. 2010).This membrane, exhibited 13% lower methanol permeability as 2.97×10^{-7} cm^2 sec^{-1} than that of SPPBP. The proton conductivity of the multi-layered composite PEMs was lower than that of pure SPSu and Nafion. Furthermore, the conductivity of composite membranes decreased as the content of SiO_2 increased.

Xie et al., reported the synthesis of SPEEK/mesoporous benzene-silica, with high water retention capacity, with low methanol permeability as ($3.0\text{-}5.0\times10^{-7}cm^2s^{-1}$) along with improved proton conductivity (Xie, Cho, and Kim 2011). KS et al., mentioned the synthesis of SPEEK/dihydrogen imidazole-modified silica membrane, using a solvent casting technique(Roelofs, Hirth, and Schiestel 2011). They observed reduced alcohol permeability along with proton conductivity, due to increased loading of silica. Yang et al., mentioned PVA/SiO_2 by solution casting method, in which they reported increased ionic conductivity, with reduced methanol permeability ($8.81\times10^{-7}cm^2s^{-1}$) along with high selectivity ratio(Yang, Li, and Liou 2011). Y.P.Ying et al.,and Jung et al., mentioned the synthesis of mesoporous silica electrolyte/phosphotungstic acid prepared by gel-casting technique, they reported, that the casted membrane exhibited a better proton conduction pathway, it results in maximum power density as 101 mW cm^{-2} at 150℃ without humidification(Ying, Kamarudin, and Masdar 2018; Jung et al. 2001). However, the proton conductivity value was said to be considerably low (12 mS cm^{-1}) for these membranes when compared to the prerequisite value (> 0.05 S cm^{-1}). This phenomenon occurs as a result of the dense membrane structure which restricts the proton transportation across the membrane. The tight structure allows the blocking of methanol permeation; however, the proton also finds it quite difficult to pass through.

Irradiated membranes**:** The irradiation technique has been used to induce a strong chemical linkage between the membranes and electrolyte solution. It is enormously adopted for its simplicity, composition controllability, and the absence of film processability. The radiated electron beam makes the changes in hydrophilic polymer chains and forms a barrier layer that has an advantage in membrane performance (Nasef et al. 2006).The structure of the membranes are semi-crystalline and followed the sulfonation step further decreases it's crystallinity and absorbs more water (Rao et al. 2019). Gnana kumar et al., prepared PVdF-HFP–tin oxide composite membrane synthesized for DMFC applications(Kumar et al. 2008). Though the hydrophobic PVdF-HFP polymer does not swell in methanol, the high sulfonation degree given via the irradiation grafting leads to some intrinsic defects such as excessive swelling, physical infertility, high fuel permeability, and lower thermal stability etc. These limitations, reduced with the addition of tin oxide nanofiller with the help of the irradiation grafted method.

Electrospun membranes**:** The morphology and parameters of the membrane are fully dependent on the electrospun nanofibers by electrospinning technique. These are fully exfoliated type and possesses good proton conductivity. Awang et al., who produced electrospun SPEEK/Cloisite15Afi nanofiber for DMFC applications(Awang et al. 2017). In their study, they observed that the value for proton conductivity was 12 mS cm^{-1}. However, optimal nonofiber structure depends on various parameters like voltage, needle distance, and polymer solution concentration which is a tedious job to control.

Copolymerization: Copolymerization process is two types, graft copolymerization and radiation-induced graft copolymerization (Nasef and Hegazy 2004). In principle, copolymerization is a process in which sides chain are covalently attached to the main chain of a polymer backbone to form the branched copolymer. The extent of polymerization is called the degree of grafting (grafting yield) which is gravimetrically determined as the percentage increase in mass. Both the backbone and side-chain grafts can be either homopolymer or copolymer. Graft copolymerization takes place as a result of the formation of active cites on the polymer backbone. The active sites may be free radicals or ionic chemical groups, which initiate the polymerization reaction. Other methods, radiation-induced graft copolymerization of polar monomers onto polymer films. Radiation-induced graft copolymerization of different polar monomers onto various polymer films and their potential applications have not been reported. Radiation-induced graft copolymerization started in 1950s and continued to be a subject of intensive research to obtain modified materials for various applications (Chapiro 1967; Dole 1983). Radiation-induced graft copolymerization has been found to possess the potential to simplify the whole treatment process, leaves no detrimental residue and reduces the cost of production. This method is an economical technique for the preparation of various types of membranes, due to simple preparation procedure and easy control of membrane properties (Gupta and Scherer 1994; Nasef and PENYELIDIKAN 2009). This technique shows a superior advantage where the difficulty of shaping the graft copolymer into thin foil of uniform thickness (Hegazy et al. 1999). This adversely affects the morphology of membrane and prone to variation in the membrane properties.

Other type of membranes

Acidic sulfonated polymers such as (sPBEK, sPPESK, sPPENK) with basic polyetherimide (PEI), showed a good thermo stability, good oxidative and hydrolysis resistance, good resistance to swelling along with high proton conductivity (Wang et al. 2014). The extent of doping material is defined as phosphoric acid mole percent per repeating unit of the polymer. But limitations of these materials are, strong sensitivity to the doping level of the complex and temperature.

Jiang et al., reported SPEEK membrane for DMFC applications, synthesized by sulfonation of PEEK polymer(Jiang, Zhao, and Manthiram 2013). It clearly says, that how a structure of membrane helps in proton conduction in porous structure and dense structure. Aricó et al., mentioned that membrane thickness could affect the proton conductivity along with methanol permeability(Aricò et al. 2015). IIbeygi et al., reported SPEEK based nanocomposite membranes for DMFC application(Ilbeygi et al. 2013). In this study, they reported methanol permeability as 0.52×10^{-6} cm^2 sec^{-1} compared to Nafion 117(4.29×10^{-8} cm^2 sec^{-1}) at 60℃. But still it's having high methanol permeability along with high price (Xing et al. 2005).

PVA based membranes were developed to reduce methanol permeability in DMFC applications. Polyvinyl alcohol (PVA) is biodegradable, inexpensive, easily available and also used in pervaporization process for separating alcohol from water (Maiti et al. 2012). Proton conductivity of pure PVA was very low 10^{-7} S/cm (Deluca and Elabd 2006). In literature, it was mentioned that PVA is used as a modifier to inhibit the methanol cross over (Pan et al. 2011;Lo et al. 2013). It is also preferred due to its high mechanical strength (in the range of 80–100 MPa) and a low density of 1.19–1.31 g cm^{-3}. Cross-linking of PVA material can be done in various processes such as heat treatment, irradiation, freezing and chemical treatment. The hydrophilic nature of the membrane promotes proton conductivity by water assistant vehicle mechanism (Ren, Chia, and Gao 2013). This also increases methanol fuel cross-over because water and methanol permeate through these membranes together leads to voltage loss and drop the efficiency of the DMFC (Lo et al. 2013;Yang et al. 2001).

Zhang et al., synthesized lignosulfonate (LS)s groups into polysulfone (PSU) polymer and found that a proper amount of modified LSs could enhance the water uptake of the membrane through influencing the surface mean pore size and membrane porosity(Zhang, Glüsen, and Garcia-Valls 2006). During this process, pores were blocked. Balsara and Beers et al., mentioned that, pore size increases the length domains of hydrophilic and hydrophobic regions also increased, which resulted in lower proton conductivity (Balsara and Beers 2011). Li, Xiao., mentioned, incorporated sandwiched membranes in their study on DMFC applications (Li, Xiao, et al. 2017). In this they mentioned, sulfonated holey graphene oxide (SHGO) was squeezed with sulfonated poly (ether ether ketone) (SPEEK), it has shown that high density of sulfonic groups allows for higher diffusivity of ions in the membrane. Yan et al.,found that the selectivity of graphene oxide (GO)'s crystalline structure repelled the methanol transport while allowing protons through the membrane (Yan et al. 2016). Thus, in order to improve the proton conductivity along with reduced methanol permeability, one should understand the transport properties of the ions within the pores. The reduced proton conductivity and increase in methanol permeability are said to be caused by the formation of cracks during the membrane fabrication process and the difference in the size of sandwich materials (Helen, Viswanathan, and Murthy 2007).

2.4.4 Composite membranes (Organic-Inorganic)

The composite membranes are attractive due to their physical and electro-chemical properties at low cost. The composite membranes, in general, comprise of the polymer matrix and inorganic/organic fillers which provides the flexibility to fine-tune membrane properties by modifying either of them. The polymer support provides the mechanical strength and filler provides the proton conductivity in DMFC. The synergic effect of composite enhances the thermal stability and lowers the methanol cross over at low cost (Shukla et al. 2019). The most commonly, poly (tetrafluoro ethylene) (PTFE), poly(vinylidenefluoride)(PVDF), poly(ethersulfone)(PES), and poly(propylene)(PP) are explored as polymer matrix materials (Zaidi et al. 2000). These have no role in promoting proton conductivity. These are used as fuel barriers and supporting the fillers. The micrometer to nanometer inorganic range inorganic fillers such as hygroscopic oxides (SiO_2, TiO_2, ZrO_2, Al_2O_3), zeolites, mineral acids (HCl, H_3PO_4), clays (montmorillonite), heteropoly acids and zirconium phosphates (ZrP) are generally used for composite membrane synthesis (Pandey, Seepana, and Shukla 2015). The membranes that are synthesized with inorganic materials having excellent potential to compare with the Nafion membrane and can be used at high temperature DMFC applications. The operation of DMFCs at higher temperatures increases electrochemical kinetics, improves CO tolerance, facilitates heat rejection and reduces the problems associated with water management (Yang et al. 2001; Chien et al. 2013).

PTFE is a hydrophobic material with high mechanical strength and is used for high temperature fuel cells. Xu et al., also reported polytetrafluoroethylene/zirconium/phosphate ($PTFE/ZrP_2O_7{\cdot}xHPO_3$) composite membranes for an intermediate temperature of 120 to 200°C (Xu 2013). They filled the $ZrP_2O_7{\cdot}xHPO_3$ sol as the proton conductor into a porous PTFE as the membrane-supporting structure. This membrane showed good proton conductivity as 0.1 S cm^{-1} and having low mechanical strength of 10.25 MPa. The crosslinking method in PTFE support improves dimensional and chemical stability (Peighambardoust et al. 2010). Wang et al., reported the PTFE/sSEBS composite membrane for the alcohol fuel cell(Wang et al. 2014). This PTFE/sSEBS membrane is synthesized by using pore filling. Where it's exhibited proton conductivity as 0.019 S cm^{-1} at 60℃, methanol permeability as 3.78×10^{-6} cm^{2} sec^{-1} and it's exhibited power density as 91.4 mW cm^{-2} was achieved at 70 °C with 0.5M methanol. Pore filled method helps to reduce swelling property and methanol permeability of the membrane.

Donnadio et al., reported a sulphonated poly(ether sulphone) (SPES) membrane with a 34% degree of sulphonation (DS), and zirconium phosphate (ZrP)as a filler material(Donnadio et al. 2012). In this study, they mentioned the proton conductivity as 4.5×10^{-2} S cm^{-1} at 100℃ with 90% RH. But SPES membrane showed lower proton conductivity compared to Nafion 117. Lu et al., mentioned the synthesis of porous PTFE support impregnated using poly(ethersulphone)-poly(vinylpyrrolidone) (PES/PVP) and doped further with phosphoric acid(Lu et al. 2014). Here they mentioned PES/PVP acts as hydrophilic phase on hydrophobic phase of PTFE support to improve proton conductivity. But this PES/PVP membrane is not labelled as a multilayer membrane, its a transitional study between composite and multilayer membranes. Alvarez, et al., mentioned the polyamidoamine dendrimers as fillers in the Nafion matrix to reduce methanol permeability(Alvarez et al. 2014). In this study, they revealed the methanol permeability of composite membranes is lower than that of recast Nafion in DMFC. Hsiu-Li-Lin et al., evaluated porous PTFE impregnated Nafion membranes for DMFC applications(Lin et al. 2005). They mentioned PTFE/Nafion membrane showed lower proton conductivity compared to Nafion series membranes, but polarization studies of DMFC improved, with impregnation of PTFE reduced the methanol permeability. Lin et al., mentioned the synthesis of PTFE film cross linked with PVA, impregnated into Nafion(Lin et al. 2010). They reported permeability of composite membrane is 3.47×10^{-6} cm^{2} sec^{-1} which is lower than that of Nafion (4.2×10^{-6} cm^{2} sec^{-1}). The conductivity of composite membrane exhibited low performance, but methanol permeability reduced with addition of PVA.

The membranes modified with inorganic fillers having excellent potential to compare with unfilled original membranes, based on their chemical and thermal stabilities. These original membranes used at intermediate temperatures, but the membranes modified with inorganic fillers are stable at high temperature applications, which is a vital significance for accomplishing the required DMFC performance (Gashoul, Parnian, and Rowshanzamir 2017;Sacca et al. 2006). Inorganic proton conductors such as silica, zirconium phosphate (ZrP), polyvinyl alcohol (PVA) and sulfonated polyether ether ketone (SPEEK) (Pandey, Mir, and Shukla 2014;Yang et al. 2001; Lo et al. 2013). The most of reported composite membranes are not competitive enough to compete with Nafion. The composite membranes can perform better if we can operate at moderate to higher temperatures in DMFC. The selection of the materials and synthesis method plays a very crucial role in synthesizing the composite membrane for high temperature DMFC.

2.5 Gaps identified in the literature

A detailed literature review on DMFC membranes revealed that the following have been identified as gaps in the literature as below:

1. Literature is very limited to high-temperature membranes for DMFC.
   Extensive studies were reported to develop a membrane for DMFC either by modifying the Nafion or by developing new membranes. Most of the polymer-based membranes are not capable enough to withstand the DMFC operation at elevated temperature and few composite membranes were under performed compared to Nafion in DMFC application. Hence there is huge scope for developing novel composite membranes.

2. Suitability of inexpensive composite membranes with inorganic ion-exchangers for DMFC not studied widely.
   Nafion 117 having limitations in terms of cost and methanol crossover. The modified Nafion membranes are showed promising results in DMFC. But, still they are expensive and difficult to control the properties while modification. As per literature, the inexpensive inorganic ion-exchangers like silica (SiO_2), titania (TiO_2), zirconia (ZrO_2) and phosphotungstic acid (PWA) can be explored to synthesize low cost composite membranes for DMFC.

3. Reported composite membranes have comparatively less performance than state of art Nafion®.

   To achieve high performance of DMFC, there is always a compromise between the proton conductivity and methanol permeability of the membrane. Composite membranes such as *PVDF-co-HFP/PBI*, SPEEK/PES, Polyarylene, SPEEK/mesoporous, PES/PVP and PTFE/sSEBS are reported and found to be not competitive enough to compete with Nafion.

2.6 Aim and objectives

Based on the identified gaps in the available information in the literature, the current investigations were formulated to study the effect of, inorganic ion exchangers on organic support.

Aim: To synthesize and characterize the high temperature composite membranes for DMFC application.

To achieve this aim, the following broad objectives are envisaged.

Objectives:

1. Selection, synthesis and characterization of inorganic ion-exchanger.
2. To synthesize composite membranes using organic porous support polytetrafluoroethylene (PTFE) and inorganic ion exchangers such as, zirconium phosphate (ZrP), and poly vinyl alcohol (PVA).
3. Characterization studies of PTFE-ZrP-PVA membranes using physico-chemical and electrochemical characterization of synthesized membranes.
4. To study the effect of incorporation of phosphotungstic acid (PWA), tetraethyl orthosilicate (TEOS) and poly vinyl alcohol (PVA) sol into polytetrafluoroethylene (PTFE) support.
5. Characterization studies of (Si-PWA)-PVA/PTFE membranes using physico-chemical and electrochemical characterization of synthesized membranes.
6. Studies on DMFC performance for the synthesized membranes and comparing with that of Nafion117.

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CHAPTER 3

EXPERIMENTAL STUDIES OF HIGH TEMPERATURE DMFC MEMBRANES

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This chapter describes the generalized synthesis procedure of the membranes, characterization and testing of single cell DMFC.

3.1 Synthesis of composite membrane

The generalized procedure was adopted for synthesizing the composite membrane and depicted in figure 3.1. The hybrid sol-gel membrane synthesis method mainly consists of pore impregnation, casting and heat treatment. The selection of the porous support is important. The suitable support for synthesizing the composite membrane has been chosen based on the literature (Wang et al. 2014; Zaidi et al. 2000). The support plays a crucial role in enhancing the mechanical and thermal stability of the composite membrane. The next important step is synthesis of a sol. The sol is usually synthesized by mixing of ion exchanger, binder and solvent. The selection of these materials depends on the application of the study**.** The preceding section explains the selected materials for synthesizing the sol and its suitability for the DMFC application. The sol was impregnated into the pores of the support, casted over the film and then heat treated to obtain the composite membrane.

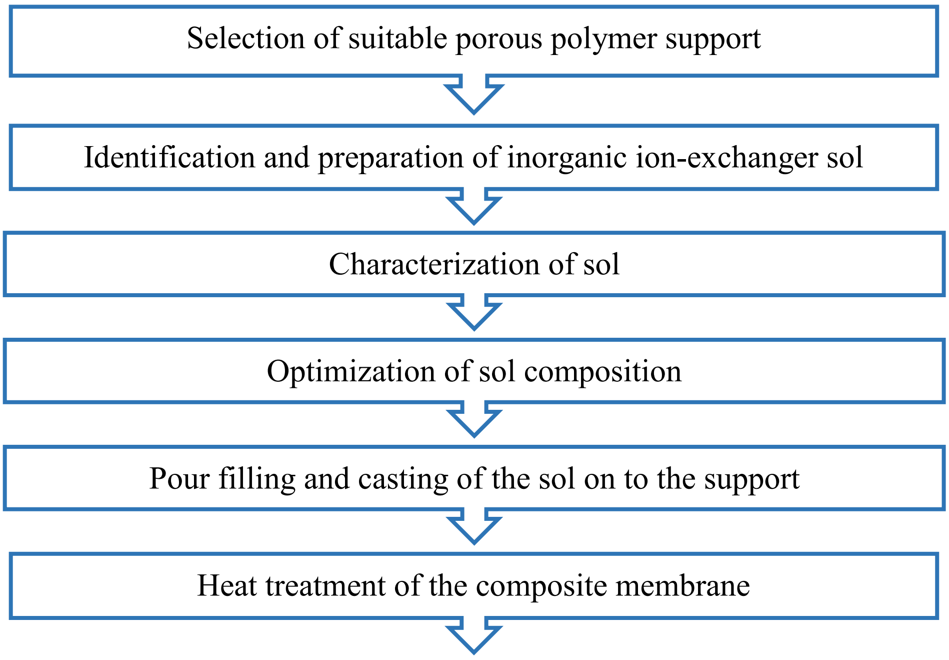

Figure 3.1 Generalized synthesis procedure for the synthesis of the composite membrane

The above procedure has been followed to synthesize the two suitable membranes namely PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE. The detailed synthesis procedure, characterizations and testing of the DMFC single cell are explained in the following section

3.2. Materials

The main chemicals used in synthesizing the composite membranes are summarized in table 3.1. The procured reagents are of analytical grade.

Table 3.1 Chemicals used in synthesizing the composite membranes

S.No.	**Name of the chemical**	**Make**
1	Polytetrafluoroethylene (PTFE) support (Pore size 0.22 µm, 45µm thickness	Merck India
2	Zirconium phosphate (ZrP)($ZrH_2O_8P_2$)	Sigma Aldrich, India
3	Poly vinyl alcohol (PVA)	HIMEDIA Pvt Ltd, India
4	Phosphotungstic acid (PWA, $H_3O_{40}PW_{12}.X\ H_2O$)	Merck India
5	Tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$)	Alfa Aesar India
6	Acrylic acid	Finar, India
7	Hydrogen peroxide (H_2O_2)	SDFCL Pvt Ltd, India
8	Methanol (CH_3OH, 99%)	Merck India
9	Ethanol (99.39%,)	Merck India
10	Hydrochloric acid (HCl)	SRL chemicals, India
11	Ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2·6H_2O$)	Merck India
12	Double distilled water	SOMA scientific & surgical, Hyderabad

3.3 Synthesis of PTFE-ZrP-PVA composite proton exchange membrane

The chemically treated PTFE film and ZrP-PVA sol are used together to obtain the PTFE-ZrP-PVA composite membrane.

3.3.1 Chemical treatment of PTFE support

The surface grafting is commonly used technique to modify the surface to improve the wettability of the polymeric membrane support. Common techniques like UV-irradiation, chemical treatment and plasma treatment are also used on the polymer surface. The choice of the specific graft polymerization technique depends on the desired characteristics after surface modification (Katoot 1999). Here, the PTFE was UV-irradiated with a chemical solution to obtain the modified polymeric surface. The surface properties tend to improve through covalent bonding by microwave irradiation with the chemical solution. In this process bulk structure of film is not significantly affected. However the film surface properties can be enhanced with surface modifiers in terms of hydrophilic nature (Ulbricht et al. 1996; Katoot 1999 ;Kochkodan and Hilal 2015).

The 90 mm diameter of polytetrafluoroethylene (PTFE) support film (pore size 0.22µm and 45µm thickness) was cleaned using pure ethanol solution to remove impurities present on the surface. The chemical solution is prepared by mixing 10ml of PVA (30 vol%), 10 ml of H_2O_2 (30 vol%) and 10 ml of (20 vol%) acrylic acid (Katoot 1999). PTFE film was immersed in a prepared composition solution for 5 minutes, and then subjected to microwave irradiation for 40-60 seconds (Katoot 1999). The treated PTFE film is then washed with DI water and dried in hot air oven at 50℃ for 30 minutes. The contact angle of both chemically treated and untreated PTFE film are checked for their hydrophilicity using contact angle analyzer (Goniometer, Model HO-IAD-CAM-01, Holmare Mechatronics- instruments, India).

3.3.2 Contact angle analysis

The contact angles of various test liquids (paraffin, ethylene glycol, formamide, and distilled water) on the films were measured using contact angle analyzer. The contact angle of the treated and untreated PTFE support was measured by the sessile drop (Gumı et al. 2003) method (Goniometer, Model HO-IAD-CAM-01, Holmare Mechatronics- instruments, India), to measure surface hydrophilic or hydrophobic properties of the film at ambient temperature. The static sessile drop method was employed by which the water droplet (Drop volume~3µl) was introduced by means of a syringe on the surface of the membranes to determine the average equilibrium water contact angle, as mentioned by (Marmur 1996). The mean of the left and right contact angles resulted in the equilibrium water contact angle and measurements were taken at three different locations to get the average equilibrium water contact angles of the respective membranes. Images of water droplets on the membrane surface were also captured by a computer-controlled video capture system. The variation in contact angle during the measurements was found to be within ±1.5°.

3.3.3 Synthesis of ZrP-PVA sol

The ZrP-PVA sol was synthesized by mixing of two solutions. Initially, 5 wt % of zirconium phosphate (ZrP) solution was prepared by vigorous stirring at 30℃ for 3 hours and 2 wt% of PVA solution was prepared separately by dissolving PVA in the cold water. Both the solutions were mixed together by stirring at the 500 rpm at 40℃ until the point of forming homogeneous sol. The sol was added with 2-3 drops of hydrochloric acid (HCl) in order to maintain acidic nature while stirring. In the later part, the ZrP composition was varied from 6 to 11 wt% and PVA composition was varied from 1-6 wt% to optimize the membrane properties.

3.3.4 Synthesize the membrane with ZrP-PVA sol and PTFE

The chemically treated PTFE support and ZrP-PVA sol were used to synthesize the PTFE-ZrP-PVA membrane. The hybrid synthesis procedure of pore infiltration/ impregnation and layer by layer (LBL) coating followed by heat-treatment was adopted for attaining the membrane. The treated PTFE support was immersed in the sol for 24 hours for pore infiltration and dried at 50°C. Further, 5 layers of the sol was coated on both sides by using a layer by layer method followed by heat-treatment at 60℃ for 12 hours. Finally, the synthesized composite membrane was immersed in an aqueous HCl solution (0.5M) for 1 day at 30℃. The resulting membrane was washed with DD water to remove traces of acid content present on the surface of the membrane.

3.4 Synthesis of (Si-PWA)-PVA/PTFE composite membrane

The chemically treated PTFE film (as reported in section 3.3.1) was used as polymer support and silica immobilized PWA-PVA was used as sol to obtain the (Si-PWA)-PVA/PTFE composite membrane.

3.4.1 Synthesis of (Si-PWA)-PVA sol

TEOS was used as a silica precursor and hydrolyzed in the presence of an acid catalyst (HCl). PWA was added to this silanol solution for immobilization. The resulting solution was mixed with the readily available low concentrated PVA solution and stirred for 1 hour at room temperature. In this process, the immobilized PWA is intercalated into the PVA chain. The detailed structural networking in the process of synthesizing (Si-PWA)-PVA sol was shown in figure 3.2 (Huang et al. 2010; Thanganathan 2011). The molar ratio of (PWA/TEOS) in the sol composition was varied from 0.5 to 2 and the composition of PVA was varied 0 to 0.2M. The sol composition was fine-tuned with respective to the optimized proton conductivity and methanol permeability.

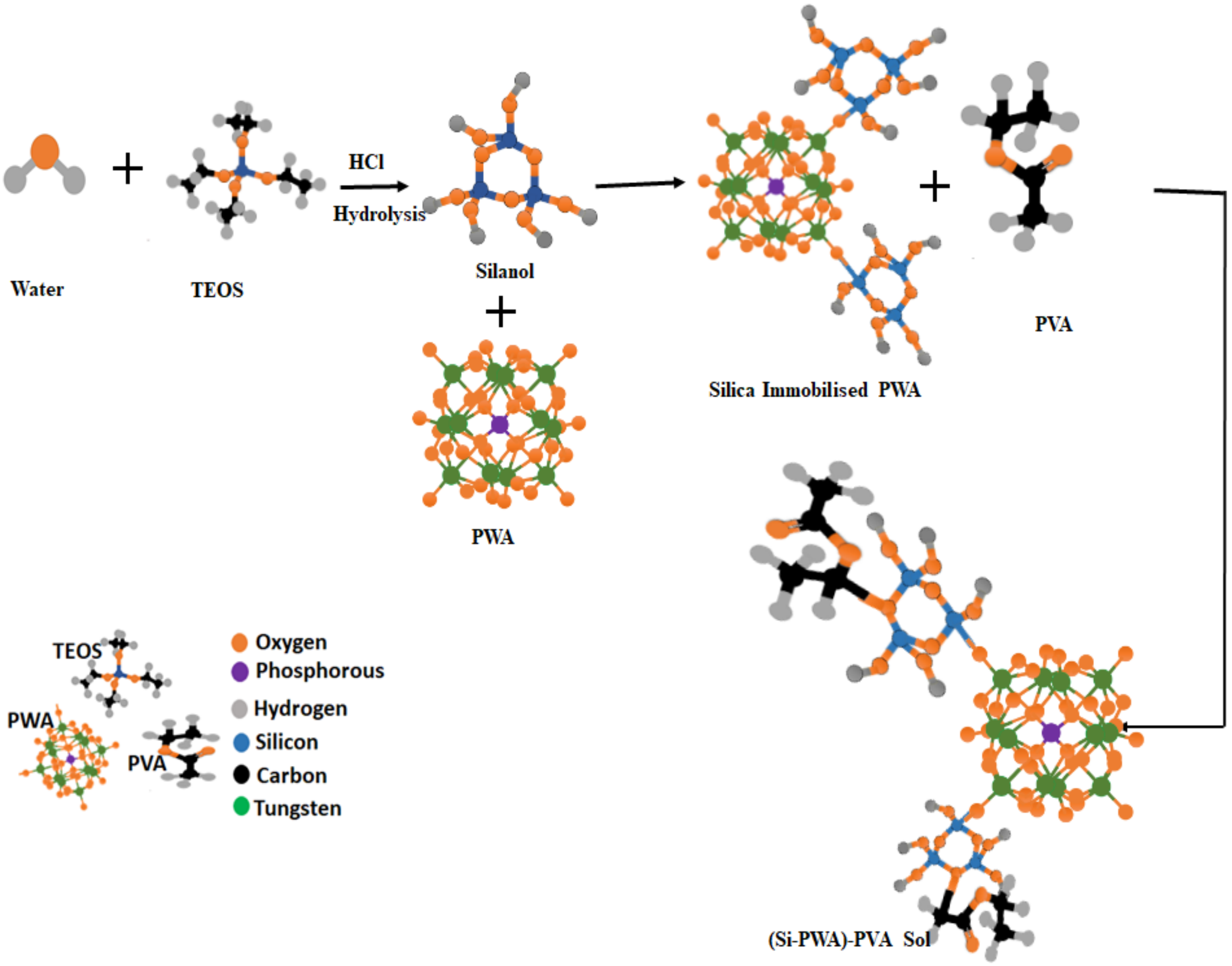

Figure 3.2 Structural networking of silica immobilized PWA-PVA sol formation

3.4.2 Synthesis of the membrane using optimized (Si-PWA)-PVA sol

The (Si-PWA)-PVA sol and modified PTFE supports were used for the synthesis of (Si-PWA)-PVA/PTFE composite membrane. The synthesis process consists of pore filling, LBL casting (Model: TC-71LC, Make: HED) and heat treatment. Initially, the hydrophilic PTFE film was dipped into the silica immobilized PWA-PVA sol for 24 hours, so that the pores of the support were filled by the sol. After that, the film was taken out and dried at 60ºC for removing unbound moisture. Further, three layers of the sol were cast over both surfaces of the film by the LBL method. And, it was subjected to heat treatment at 60ºC for 12 hours to obtain the (Si-PWA)-PVA/PTFE composite membrane.

3.5 Characterization of the membrane

The synthesized composite membranes were characterized for their physical, chemical and electrochemical properties. The performance of the single DMFC cell was measured with the composite membrane and it was compared with that of standard Nafion 117.

3.5.1 Scanning electron microscope (SEM)-Energy dispersive x-ray spectroscopy (EDX)

The SEM is capable of producing high-resolution images, which gives the morphology of a sample surface. In SEM, an electron beam with a spot size of a few nanometres is scanned over the sample. The surface morphology of samples was observed at various magnifications by using the SEM system (Model: VEGA3LMU, Make: TESCAN). The samples were dried at 60℃ for 3h to remove any moisture present on the surface and gold-sputtered to enhance the electrical conduction and frozen in a cryogenic environment. The SEM images were captured at 3-5 kX magnification for PTFE support and the membrane after incorporating the sol. The coverage of the top layer on the PTFE surface was studied.

The energy dispersive x-ray spectroscopy (EDX) is used for analyzing the elemental composition of the membranes. EDX relies on interactions between incident charged particles such as electrons and the sample. Simultaneously, EDX spectra of each sample was recorded just after the capture of the SEM image by using the same machine (Model: VEGA3LMU, Make: TESCAN). EDX analysis provides, the composition of impregnated particles onto the surface of PTFE film.

3.5.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy is a very commonly used method to recognize the molecular structures of organic compounds, mainly because it delivers a significant amount of information with ease. The existing bonds and functional groups in the polymer can be identified by comparing the absorption positions in the IR spectrum with the characteristic absorption regions.

Physicochemical interaction between PTFE film and sol particles observed and analyzed using FTIR (Perkin Elmer 100S) is shown in figure 3.3. The samples were prepared in a clean atmosphere. The PTFE support film and composite membrane film were separately loaded into the sample holder and the spectrums were recorded in the wavelength range from 500 cm^{-1} to 4000 cm^{-1} with an interval of 2 cm^{-1}. The functional groups present in the samples were analyzed and reported.

Figure 3.3 Fourier transform infrared spectroscopy (FTIR) set-up

3.5.3 X-ray diffraction (XRD)

XRD is a useful technique to describe the crystallinity of a material. In practice, the intensity of diffracted X-rays is recorded as a function of the angle, and the angles giving the intensity maxima are compared with a database containing the diffraction patterns of several structures.

The structural analysis of the powdered sol and composite membrane film has been carried out by using XRD (Make:PANalytical, Netherlands; Model:X'Pert) with CuKα radiation generated at 60 kV and 55 mA. The synthesized sol with PVA and without PVA were casted over the thin glass and dried at 60˚C for 3 hours. The samples were peeled off from the surface of the glass and grinded with mortar & pestle and these were subjected to powder XRD. The membrane samples were mounted on to the aluminium sample holder and subjected to film XRD. The XRD pattern was recorded with the diffraction angle (2θ) ranging from 10-60º with a scan rate of 1˚/min.

3.5.4 Mechanical strength

The mechanical strength of a material is the ability to withstand an applied stress at break point. The intensity of the internal forces is called stress, while deformation of the material is called strain. The stresses acting on the material cause deformation of the material. The applied stress may be tensile, compressive, or shear. Tensile stress is the stress state caused by an applied load that tends to elongate the material in the axis of the applied load, so the mechanical strength of membranes is showed as tensile strength. Most materials under a small stress showed elasticity which a material could return to its previous shape after stress is released, and this reversible deformation was called elastic deformation. The stress at break point of the material is the ultimate strength. The stress-strain behavior of a polymeric material depends on various parameters such as molecular characteristics, microstructure, strain-rate and temperature (Young and Lovell 2011).

The stress and strain analyzer (UTM -WDW-100S) was used to investigate the mechanical stability of the membrane at ambient temperature. The sample of 3×5 cm^2 was loaded to the sample holder and the experiment was conducted with 1 kN min^{-1} loading rate. The maximum withstandable load for the membrane sample was recorded. The mechanical strength of the sample was calculated by using equation (1). The procedure was repeated for 5 membrane samples and the average value is reported.

$$\text{Mechanical strength} = \frac{\text{Maximum load}}{\text{Cross−sectional area}} \times 100 \qquad (1)$$

3.5.5 Water uptake

The Water uptake (WU) is an important measurement, which exhibits the capability of an ion conductive electrolyte membrane to retain the water. The speed and extent of membrane water uptake depend on the membrane's viscoelastic mechanical properties, which are themselves dependent on membrane hydration, and increased hydration enhances the membrane ion conductivity and fuel cell performance (Malhotra and Datta 1997; Danks, Slade, and Varcoe 2003; Xiong et al. 2008).

Water uptake of the membranes is calculated by, immersing the samples of the membrane in DI water for 24 hours at room temperature, and then taken out from DI water and cleaned with tissue to remove moisture content and weighed, the water uptake is calculated by equation (2) (Basri, Ismail, and Aziz 2011). The above procedure is repeated thrice for the sample to check its repeatability

$$W\text{ater uptake }(\%) = \frac{(\mathrm{W_{wet}} - \mathrm{W_{dry}})}{\mathrm{W_{dry}}} \times 100 \qquad (2)$$

Where W_{dry} and W_{wet} are weights of dry and wet membrane samples.

3.5.6 Ion exchange capacity (IEC)

Ion exchange capacity (IEC) is a key property of an electrolyte membrane which determines how much ions can be exchanged per the weight of the membrane. The acid-base titration procedure was employed to determine the IEC of the cation exchange composite membrane (Kumar et al. 2014). Initially, the dry weight *(W_{dry})* of the composite membrane sample was measured. It was conditioned for 12h in 0.5 M HCl so that all ion-exchange sites are filled with a proton. The hydrated sample was washed by using DI water and it was immersed into 0.1M NaCl for 24 hours to replace protons (H^+) with sodium (Na^+) ions. The resulted acidic solution was back titrated against 0.5M NaOH solution (M_{NaOH} = 0.5M) and found the volume of NaOH *(V_{NaOH})* consumed to neutralize the acidic solution. The IEC value was calculated by using equation (3). The procedure is repeated for three regenerative cycles and the average value was reported.

$$\mathrm{IEC} = \frac{\mathrm{V_{NaOH} M_{NaOH}}}{\mathrm{W_{dry}}} \qquad (3)$$

Where, V_{NaOH} is volume of NaOH and M_{NaOH} are molarity of NaOH solution.

3.5.7 Thermal gravimetric analysis-differential thermal analysis (TGA-DTA)

TGA is a continuous process to study the thermal degradation of polymeric materials which involves the measurement of sample weight as the reaction temperature is changed by means of a programmed rate of heating. Mass is lost if the substance contains a volatile fraction. Thus, the sample weight decreases slowly as reaction begins, then decreases rapidly over a comparatively narrow temperature range, and finally levels off as the reactant becomes spent (Reich and Levi 1967). This study was carried out to compare the thermal decomposition and percentage weight losses in the respective temperature range. By incorporating heat-flow signals, DTA measurements were obtained during TGA at the same heating rate and under isothermal conditions. TGA-DTA analysis records endothermic/exothermic peaks against the respective % weight loss peaks of the samples.

The membrane samples were subjected to drying in an oven at 60℃ for about three hours to remove moisture content prior to the analysis. Later, 10-20 mg of the membrane sample was loaded into an alumina crucible, and analysis was performed. Thermal stability of the membranes was investigated in the range of 30-600˚C with a heating rate of 10℃ min^{-1} under the argon atmosphere by using TGA-DTA setup (TA Instruments NETZSCH STA 2500) interfaced to a computer as shown in figure 3.4. This study was carried out to determine the maximum withstandable temperature of the membrane.

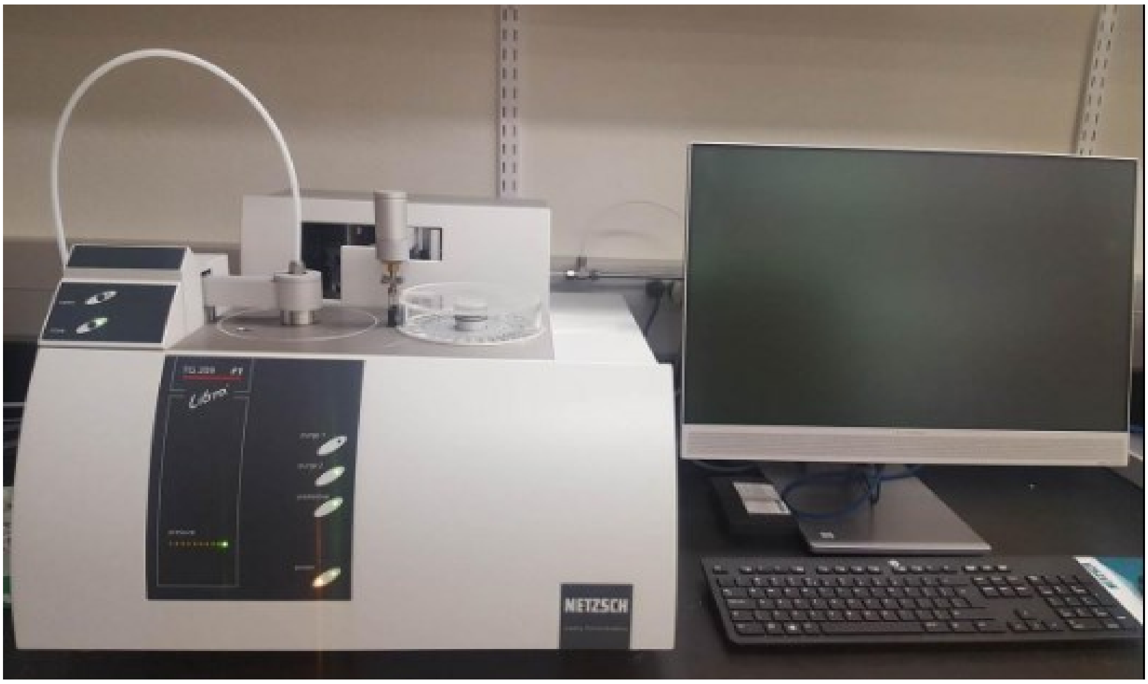

Figure 3.4 TGA-DTA set-up

3.5.8 Oxidative stability

The chemical stability of the membrane in the oxidative environment of the fuel cell was studied by using fenton's reagent (Asano et al. 2006). The ferrous ammonium sulphate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) was prepared by mixing 3 wt% H_2O_2 solution and 2 ppm $FeSO_4$ at 80 °C. The three membrane samples of 2×2 cm^2 size were dried at 60℃ in hot air oven to remove the moisture content and weighed for their initial weight. Each of three was immersed into the three different beakers which contain the fenton's reagent. The study was conducted for 24 hours and the weight of membrane samples was measured for every 6 hours. The overall average weight loss of the three membrane samples was calculated and compared with the Nafion 117.

3.5.9 Methanol permeability

Methanol permeability studies were conducted in the membrane separated two-compartment cell shown in figure 3.5. Where the two compartments have equal volumes of around 200ml. The conditioned membrane was sandwiched between the two compartments. One side of the compartment (B) was filled with DI water and 1M methanol solution on the other compartment (A). Solutions in both the compartments were stirred continuously for 12 hours to maintain the uniform composition in the compartments with help of magnetic stirrer at 500 rpm for 12 hours. Collected samples were analyzed by using UV–vis spectrometer (XD7500) at 270nm for every one hour with 10 ml of compartment B solution to find the methanol concentration (Duangkaew and Wootthikanokkhan 2008). Methanol permeability studies were conducted with varying temperatures of 40ºC, 60ºC, and 80ºC. Experimenters were repeated thrice to check for repeatedly of methanol permeability cm^2/sec). If 'A' is a methanol filled compartment and 'B' is the water filled compartment, the permeability of methanol is calculated by the following equation (5).

$$P = \frac{lV_B}{At} \ln \frac{(C^0{}_B - C_A)}{(C^t{}_B - C_A)} \tag{5}$$

Where P is the permeability of the methanol solution (cm^2/sec), V_B is solution volume in compartment 'B' (cm^3), A is active membrane area (cm^2) and l is the membrane thickness (cm). C_A is the concentration of methanol in the compartment 'A',$C_B{}^t$ is the concentration of methanol at time 't' in the compartment 'B', and $C_B{}^0$ is initial concentration of the methanol of compartment 'B'.

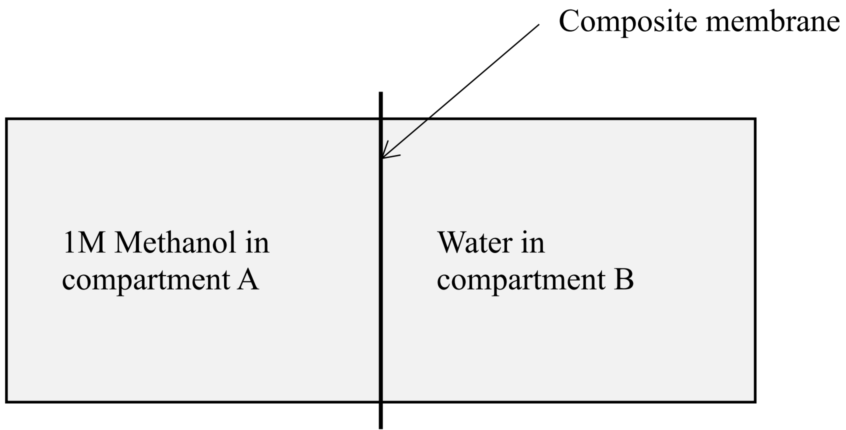

Figure 3.5. Schematic diagram of methanol permeability experimental set-up

3.5.10 Proton conductivity

In order to study the electrochemical performance of polymer electrolyte membranes, their capability to transfer the ions (protons or hydroxides) must be evaluated. In this respect, EIS is a well-known technique to measure and analyze the materials in which ionic conduction strongly predominates (Lee et al. 2005). The ion conductivity is generally obtained from the measurement of resistivity of the ion-conductive membrane against the flow of alternating current (AC). These measurements are carried out at different AC frequencies and, thus, the name impedance spectroscopy was later adopted (Park and Yoo 2003). The polarization, the distribution of chemical potential, and changes of electrode reaction should be considered in the measurement of resistivity with the current flow, which is classified into the two-probe and four-probe methods. The two-probe method is usually used to measure the resistivity of ion conductors with low resistance (Pandey, Mir, and Shukla 2014).

Membrane resistance (R_m) was measured by electrochemical impedance spectroscopy (EIS) two probe method (Metrohm Autolab PGSTAT204) in the frequency range of 1 mHz–1MHz with a voltage of 10mV. The membrane samples were kept in 0.5M HCl solution for 24 hours to attain equilibrium(Mikhailenko, Guiver, and Kaliaguine 2008; Falcão et al. 2017). Membrane samples were sandwiched between two compartment conductivity cell connected with Pt electrode and temperature of the cell and solution are maintained by heating elements connected to the temperature controller with humidity of 60%. The resistance of membrane (R_m) value used for calculating the proton conductivity by equation (4) (Lee et al. 2005;Mikhailenko et al. 2008).

$$\sigma = \frac{L}{R_m A} \tag{4}$$

Where, L is the thickness of membrane (cm), R_m is resistance of the membrane in ohms (Ω), A is the exposed area of membrane (cm^2) and σ is proton conductivity of membrane (Scm^{-1}).

3.6 Testing of single cell DMFC

Anode GDE of Pt-Ru/C with the loading of 4 mg cm^{-2} and cathode GDE of Pt/C with the loading of 2 mg cm^{-2} have been hot pressed along with synthesized composite membranes at 60℃ and 10 MPa pressure for 5 minutes to make MEA of 2.25 cm^2 active area. The anode side was fed with diluted methanol (2M) with a flow rate of 3 ml min^{-1} and 100% humid oxygen with a flow rate of 0.5 l/min was fed to the cathode side. Prior to testing MEAs were activated over a period of 12 hours with a constant load of 0.5V using 2M methanol solution. The optimum cell condition of 2M methanol in the anode compartment and 100% relative humidity in cathode the compartment was taken as the standard for single cell testing based on the literature (Junoh et al., 2020;Peighambardoust et al., 2010). The operating conditions of DMFC experimental study were summarized in table 3.2.

Table 3.2 Operating conditions in the present study

Parameters	**Units**	**Value**
Cell active area	cm^2	2.25
Anode GDE (Pt-Ru/C)	mg cm^{-2}	4
Cathode GDE (Pt/C)	mg cm^{-2}	2
Operating temperature	˚C	30-80 (ZrP membrane) & 30-120 (PWA membrane)
Anode methanol flow rate	ml min^{-1}	3
Cathode gas flow rate (Oxygen)	ml min^{-1}	500
Relative humidity (RH) of inlet gas, cathode	%	100
Anode methanol concentration	Molar	2

Single cell DMFC testing carried out with Nafion 117 and PTFE-ZrP-PVA composite membrane in the temperature range of 30-80°C as shown in figure 3.6.

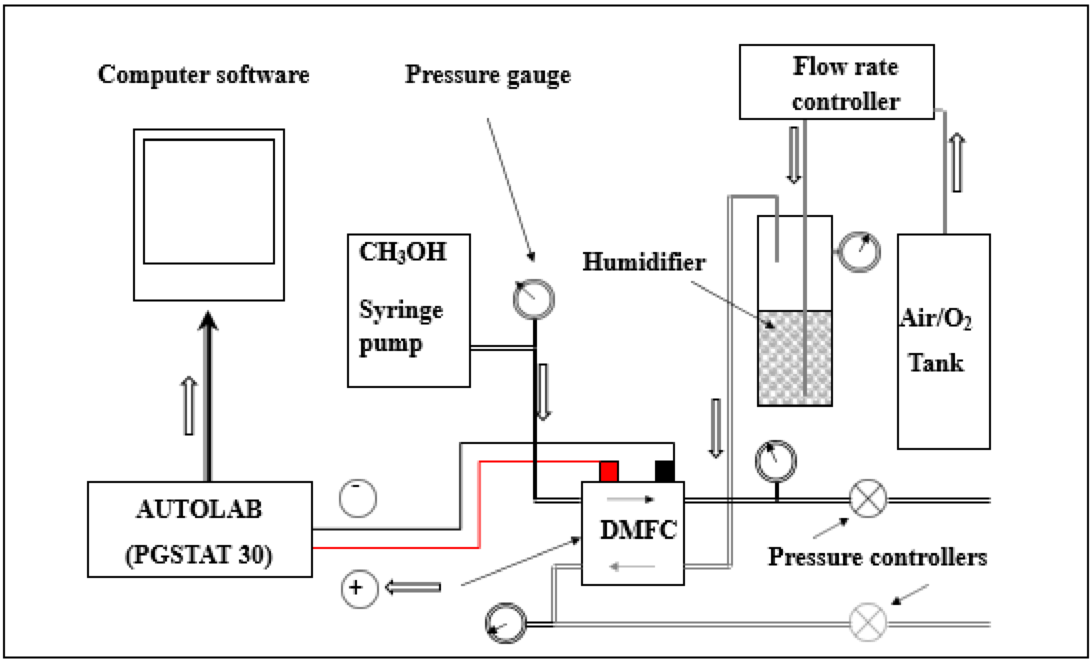

Figure 3.6 Laboratory experimental setup of fuel cell testation

The DMFC polarization curves were obtained with (Si-PWA)-PVA/PTFE composite membranes in the temperature range 30 °C - 120°C. The results of all three membranes and literature reported composite membranes were compared and concluded.

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CHAPTER 4

SYNTHESIS OF HIGHLY STABLE PTFE-ZrP-PVA COMPOSITE MEMBRANE

CHAPTER 4

SYNTHESIS OF HIGHLY STABLE PTFE-ZrP-PVA COMPOSITE MEMBRANE

The details of the experimentation are discussed in chapter 3. This chapter focuses on analyzing the results of synthesis and characterization of PTFE-ZrP-PVA composite membrane in the light of its' suitability for DMFC. The single cell DMFC performance results with the composite membrane and Nafion117 are also presented.

4.1 Introduction

The importance of synthesizing the composite membrane has been discussed in chapter 1. As it was described the composite membrane was synthesized with organic polymers and inorganic proton conductors such as inorganic oxide as silica, zirconium phosphate(ZrP), polyvinyl alcohol (PVA) and sulfonated polyether ether ketone (SPEEK) (Pandey et al. 2014;Yang et al. 2001;Chien et al. 2013;Jin et al. 1985). Based on recent reports, composite membranes prepared by impregnation method have advantages such as optimum thickness offers low proton resistance compared to Nafion series membranes (Kobayashi et al. 1998). Organic polymers such as poly (tetrafluoro ethylene)(PTFE), poly(vinylidenefluoride)(PVDF), poly(ethersulfone)(PES), and poly(propylene)(PP) were modified with inorganic ion exchangers (Zaidi et al. 2000). The hydrated ZrP has proven its capability as a proton exchanger in membrane synthesis due to its high ion exchange capacity (IEC) (6.64 meq g^{-1}) and ZrP contributes proton conduction through proton of phosphate moiety ranges from 10^{-2} to 10^{-3} S cm^{-1} based on composition and ZrP was thermally stable up to 450℃ (Clearfield 1988). Recent literature showed that PVA was one of preferable material to reduce methanol permeability of membrane ((Jin et al. 1985).

In this chapter, the PTFE-ZrP-PVA membrane was synthesized by using a hybrid method of pore infiltration followed by layer by layer (LBL) coating followed by the heat-treatment method. PVA was added to reduce the methanol permeability and membrane support was chemically treated to enhance the proton conductivity. Physical, thermal and electrochemical characterizations of synthesized PTFE-ZrP-PVA membrane investigated and compared with Nafion117 membrane. Methanol permeability and proton conductivity of synthesized PTFE-ZrP-PVA membrane were studied with respect to DMFC application. The single cell DMFC has been performed with the composite membrane and Nafion 117 and compared.

4.2 Experimental

The materials that were used, detailed procedure for synthesis of PTFE-ZrP-PVA composite membrane, sample preparation for characterizing, equipment that were used for characterizing, operating conditions of the equipment at the time of characterization and testing of single cell DMFC experimental procedure has been given in the chapter 3. The section 3.3, section 3.5 and section 3.6 describes the experimental part of synthesis, characterization studies and single DMFC testing respectively.

4.3 Results and discussion

4.3.1. PTFE-ZrP-PVA membrane synthesis

Hydrophilic nature of the support is an essential requirement for its wettability with methanol and proton conductivity. The PTFE support was treated as per the procedure given in the section 3.3.1 and it was examined for its contact angle with water. The contact angle reduced from 135° to 52.5° as shown in Figure 4.1. Reduced contact angle indicates the increased wettability and there by mobility of ions increasing which results in enhanced proton conductivity.

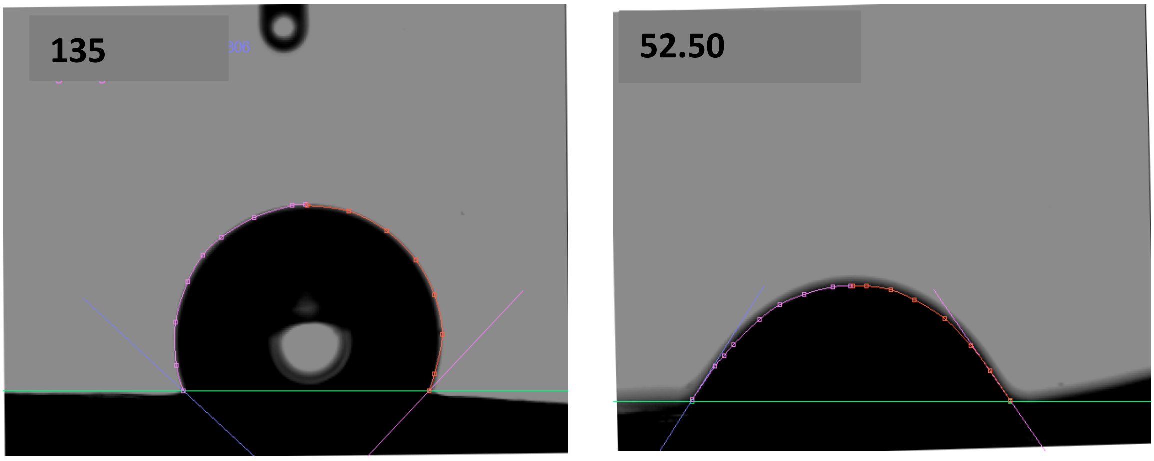

Figure 4.1 Contact angle measurement of PTFE support before and after chemical treatment

PTFE-ZrP-PVA membrane was successfully synthesized using treated and untreated support. Proton conductivity was measured for both membranes and the proton conductivity with untreated support was comparatively lower than (4.5×10^{-5} S cm^{-1}) the membrane with chemically treated support (3.8×10^{-3} S cm^{-1}).

ZrP imparts proton conductivity, PVA lowers the methanol permeability and PTFE support gives the mechanical strength to the membrane. The membrane was further characterized for its' physico-chemical, electro-chemical properties and suitability in the DMFC. The composition of ZrP and PVA in the sol was optimized based on the study showed in table 4.1. The optimum composition of 10 wt% of ZrP and 5wt% of PVA was selected, for synthesis of the membrane.

Table 4.1 Optimized sol studies of methanol permeability, proton conductivity for PTFE-ZrP-PVA membrane.

S. No	Membrane Description	Methanol permeability ($cm^2 s^{-1}$) at 25℃	Proton conductivity ($S cm^{-1}$) at 25℃
1	PTFE-10 wt% ZrP-1wt% PVA	14.8×10^{-7}	3.88×10^{-3}
2	PTFE-10 wt% ZrP-2wt% PVA	9.6×10^{-7}	4.15×10^{-3}
3	PTFE-10 wt% ZrP-3wt% PVA	7.4×10^{-7}	4.89×10^{-3}
4	PTFE-10 wt% ZrP-4wt% PVA	5.2×10^{-7}	5.02×10^{-3}
5	PTFE-10 wt% ZrP-5wt% PVA	**3.8×10^{-7}**	**5.3×10^{-3} (Optimized)**
6	PTFE-10 wt% ZrP-6wt% PVA	4.5×10^{-7}	4.7×10^{-3}
7	PTFE- 6 wt% ZrP-5wt% PVA	11.8×10^{-7}	1.2×10^{-3}
8	PTFE-7 wt% ZrP-5wt% PVA	9.2×10^{-7}	2.4×10^{-3}
9	PTFE-8 wt% ZrP-5wt% PVA	8.6×10^{-7}	3.3×10^{-3}
10	PTFE-9 wt% ZrP-5wt% PVA	6.2×10^{-7}	4.87×10^{-3}
11	PTFE-10 wt% ZrP-5wt% PVA	**3.8×10^{-7}**	**5.3×10^{-3} (Optimized)**
12	PTFE-11 wt% ZrP-5wt% PVA	4.4×10^{-7}	4.7×10^{-3}

4.3.2. Characterization of PTFE-ZrP-PVA membrane

HR-SEM and EDX: Surface morphology and elemental analysis of the synthesized membrane are mentioned in figure 4.2(a), 4.2 (b) and Figure 4.2(c) respectively. Figure 4.2(a) and (b) shows the surface images of PTFE support and PTFE-ZrP-PVA membrane respectively. The continuity of the top layer was observed on the support. This shows the uniform distribution of ZrP-PVA sol on the surface of the membrane. EDX analysis which was shown in Figure 4.2(c) gives the presence of all elements pertaining to the sol and membrane. It was observed that 31.9% Zirconium (Zr) and 26.44% Phosphate (P) were present by weight percentage (%). The details of the analysis are reported in table 4.2.

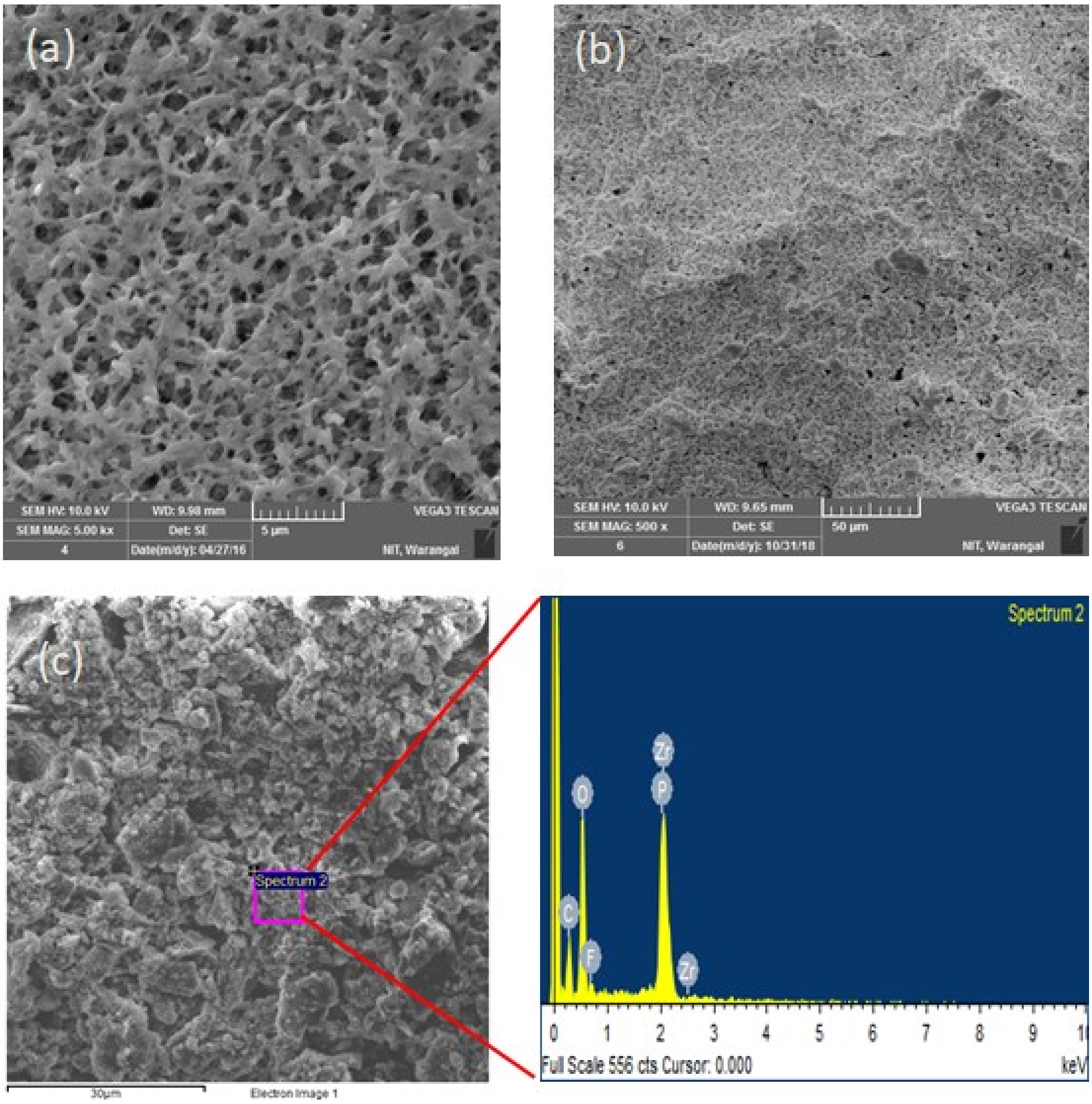

Figure 4.2. Surface morphology of **(a)** PTFE support **(b)** PTFE-ZrP-PVA membrane and **(c)** EDX image and spectrum of PTFE-ZrP-PVA membrane

Table 4.2 Composition of element analysis of top surface PTFE-ZrP-PVA Membrane

Element	**Weight percentage (%)**	**Atomic percentage (%)**
C	20.75	36.04
O	35.69	46.54
P	9.42	6.34
F	3.76	4.13
Zr	30.38	6.95

FT-IR: FT-IR spectrum of the synthesized membrane film and PTFE support film was recorded in the wavenumber range of 500-4000 cm^{-1}. It was shown in figure 4.3, the peaks which represent the functional groups of sol and PTFE support were observed at 3440, 2921, 1435, 1225, 1374 and 520 cm^{-1} (Okuhara, Mizuno, and Misono 1996).The broad peak observed at 3686 cm^{-1} due to O–H stretching of hydrogen bonding formed due to alcohol (PVA) molecules. Two C–F stretching vibrations at 1200 and 1225 cm^{-1} for PTFE backbone, peaks obtained at 1374 and 1435 cm^{-1} are because of P-OH stretching, peak at H-O-H stretching peak appeared at 1732 cm^{-1} and peak at 520 cm^{-1} is owing to Zr–O transmission (Rocchiccioli-Deltcheff, Thouvenot, and Franck 1976) and (Moosavi et al. 2009). The assigned peaks are summarized in the table 4.3. The presence of ZrP and PVA are reflected by spectra functional groups in the top layer of PTFE-ZrP-PVA membrane.

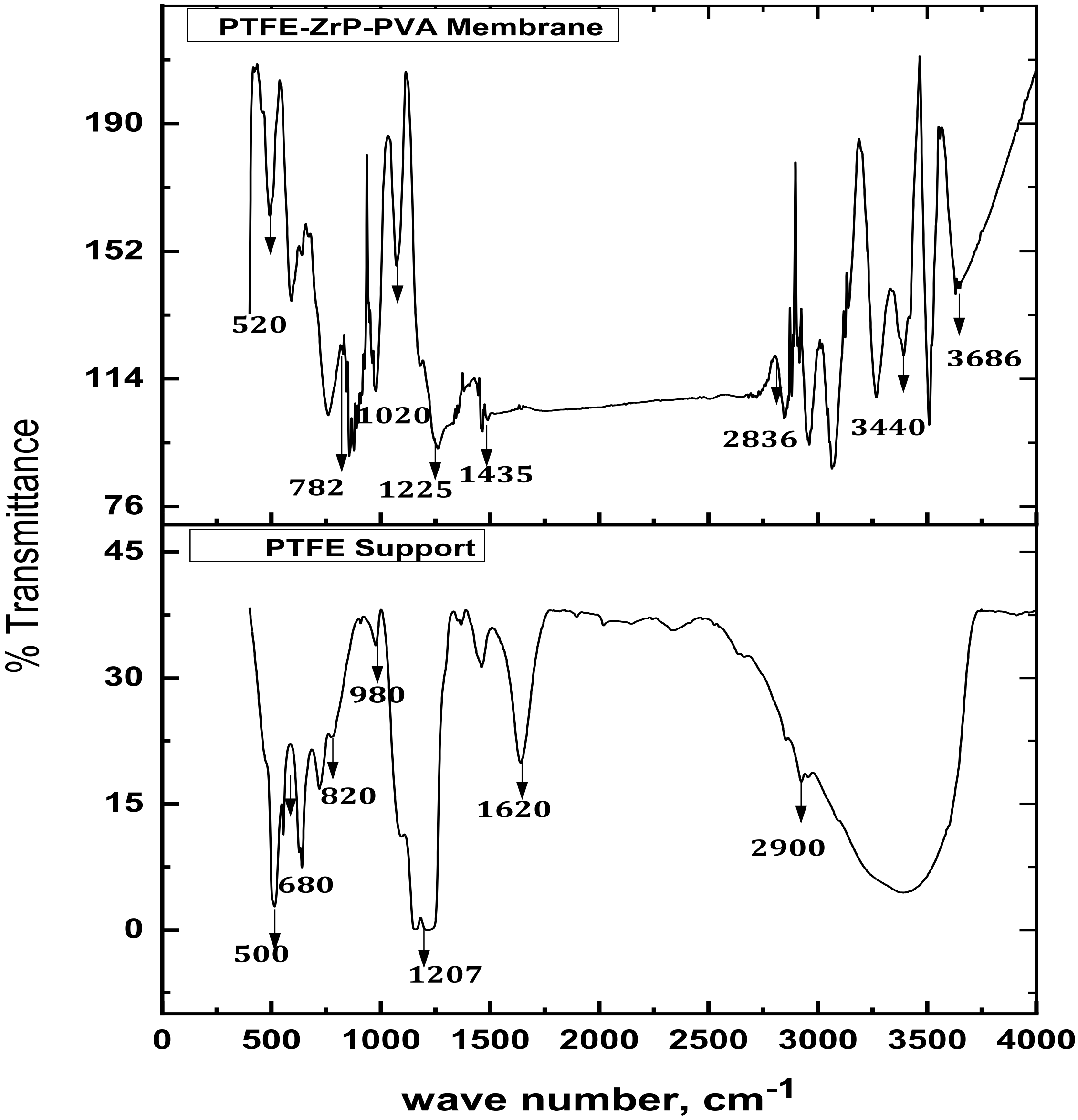

Figure 4.3. FTIR spectra of PTFE support and PTFE-ZrP-PVA membrane

Table 4.3 Summary of functional group identification

Frequency (cm^{-1})	Functional group Identification
500,520	Zr–O
680	=C–H bend structure
782,820	C-H stretch
980,1020	P-O_4 symmetric stretching
1207,1225	C–F stretching (PTFE)
1435	P-OH stretching
1620	H-O-H stretching
2836,2900	-CH_2 stretching
3440	O-H stretching
3686	Strong O–H stretch due to ZrP

TGA-DTA**:** Thermal deformation of the membrane was analyzed in temperature range of 0-600˚C with heating rate of 10˚C min^{-1}. The analysis part was divided into three stages as shown in Figure 4.4. Initial 8.5% weight loss was observed in stage I up to 150 ˚C on TGA curve and corresponding endo and exothermic peaks were observed on DTA curve, which shows the loss bound moisture and start of the transition point of PTFE support. There was no substantial weight loss (~7.5%) was observed in stage II. This may due to structural softening of PTFE support between its glass transition temperature (>140˚C) and melting point temperature (340 ˚C) and decomposition of PVA (Hassan and Peppas 2000). In stage III, the sudden decline in weight loss was observed, this may be due to melting of PTFE and oxidation of ZrP. Membrane is not workable after structural softening PTFE which happens to be in stage II. So, PTFE-ZrP-PVA membrane is thermally stable up to 140 ˚C.

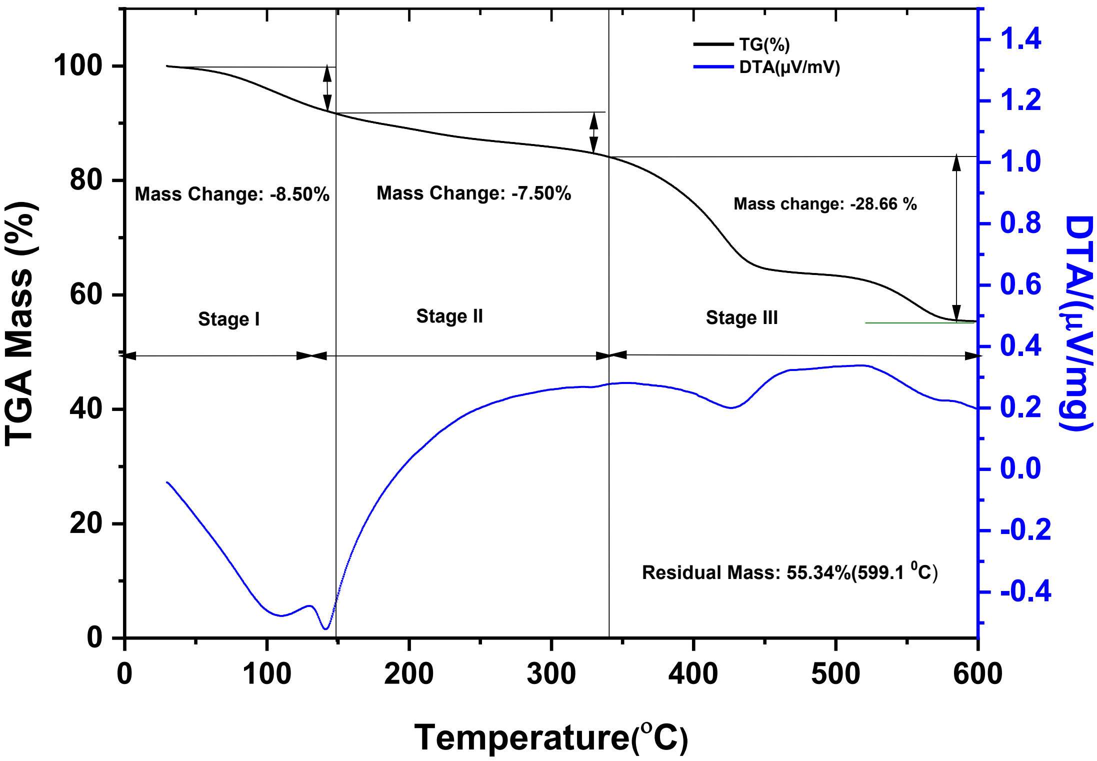

Figure 4.4. Thermal behaviour of PTFE-ZrP-PVA membrane

Mechanical (Tensile) strength: The stress-strain curves for PTFE support and PTFE-ZrP-PVA membranes are shown in figure 4.5. After chemical treatment hydrophilicity of PTFE support increased, due to hydrophilic nature, it absorbs more water molecules on to the surface. PTFE support is reinforced with infiltration of sol, LBL coating, and heat treatment. As ZrP and PVA weight % increases, mechanical (tensile) strength of membranes also increases as shown in table 4.4. It was observed that PTFE support (45µm) has a tensile strength of 30 MPa whereas the PTFE-ZrP-PVA membrane has 44 MPa. The membrane was mechanically strengthened by pore infiltration and LBL coating. This value is significantly higher than the Nafion 117 tensile strength (28 MPa) (Ding et al. 2007).

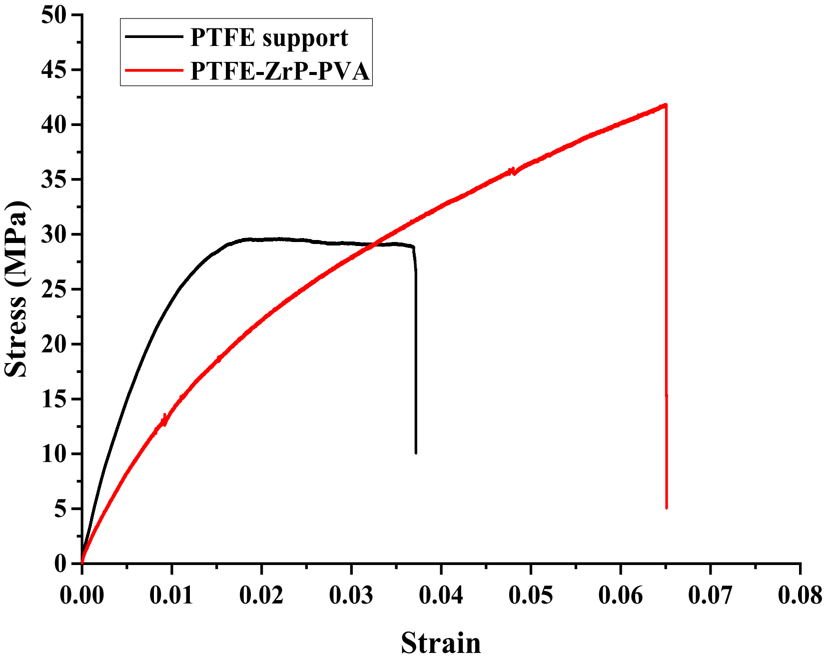

Figure 4.5. Stress-strain curves of PTFE support and PTFE-ZrP-PVA membrane

Water uptake: Water holding capacity of the membrane is an essential requirement for proton conductivity. Water uptake of PTFE-ZrP-PVA composite membrane is 30.65%, which is marginally higher than Nafion117 membrane (29.6%). The study was performed for optimizing the water uptake value with respect to composition and methanol permeability and shown in table 4.4. It was observed that water uptake is decreased with increasing wt% of PVA and water uptake was increased with increasing the wt% of zirconium phosphate in top layer composition. The hydroxyl O-H groups present in PVA molecules interacts with oxygen and hydroxyl groups in PTFE support, might form polar –polar interaction due to the mobility of PVA molecules are restricted and ZrP enhances water uptake characteristics, based on increasing weight % (Kreuer 1996) and (Vaivars et al. 2004). Hence, water uptake value was optimized at 15.2% with respect to composition and methanol permeability.

Ion exchange capacity (IEC): IEC value provides the information about the fixed charge density of ions present in, per gram of dry membrane. The increasing ion-exchangeable sites present in PTFE support due to increasing weight % of ZrP and PVA. IEC of the membrane was increased with increasing ZrP shown in table 4.4. The IEC of optimum composition PTFE-10wt%ZrP-5wt% PVA membrane was 1.28 meq per gram is higher than Nafion 117 i.e. 0.92 meq per gram.

Table 4.4 Ion exchange capacity, water uptake, methanol permeability and mechanical strength of PTFE-ZrP-PVA membranes at ambient temperature

S.No	Membrane Description	IEC (meq.g^{-1})	Water Uptake (%)	Methanol permeability (cm^2 s^{-1}) 25℃	Mechanical Strength (MPa)
1	PTFE-10 wt% ZrP-1wt% PVA	0.82	24.11	14.8×10^{-7}	34.2
2	PTFE-10 wt% ZrP-2wt% PVA	0.90	22.05	9.6×10^{-7}	36
3	PTFE-10 wt% ZrP-3wt% PVA	1.04	20.26	7.4×10^{-7}	39
4	PTFE-10 wt% ZrP-4wt% PVA	1.12	18.70	5.2×10^{-7}	41.8
5	PTFE-10 wt% ZrP-5wt% PVA	**1.28**	**15.62**	$\mathbf{3.8\times10^{-7}}$	**44**
6	PTFE-10 wt% ZrP-6wt% PVA	0.92	17.84	4.5×10^{-7}	45
7	PTFE-6 wt% ZrP-5wt% PVA	0.72	25.49	11.8×10^{-7}	38.2
8	PTFE-7 wt% ZrP-5wt% PVA	0.88	23.42	9.2×10^{-7}	39.8
9	PTFE-8 wt% ZrP-5wt% PVA	0.94	21.78	8.6×10^{-7}	41.2
10	PTFE-9 wt% ZrP-5wt% PVA	1.02	18.54	6.2×10^{-7}	42.8
11	PTFE-10 wt% ZrP-5wt% PVA	**1.28**	**15.62**	$\mathbf{3.8\times10^{-7}}$	**44**
12	PTFE- 11wt% ZrP-5wt% PVA	1.20	20.35	4.4×10^{-7}	44.8
13	Nafion 117	0.92	29.6	13.6×10^{-7}	28

Proton conductivity: The proton conductivity of PTFE-ZrP-PVA (55±2 μm) was measured by two probe impendence method by varying cell temperature from 25℃ to 80℃ with 1M methanol at 60% relative humidity. As it is shown in Figure 4.6, proton conductivity increased with increasing temperature. Proton conductivity at room temperature is 5.3 mS cm^{-1} and it was observed that the value more than doubled at 80˚C (28.1mS cm^{-1}) as illustrated in figure 4.6. Proton conductivity increases as mobility of ions increases at higher temperature range.

The proton conductivity value is compared with similar inorganic ion-exchanger based membranes (shown in table 4.5) and it was observed that the value obtained is comparable (Pandey, Seepana, and Shukla 2015) – (Gao et al. 2018). Nafion117 has high methanol permeability at higher temperatures than the current membrane (figure 4.7). Increased proton conductivity with minimal methanol permeability at higher temperatures makes the current membrane workable in DMFC.

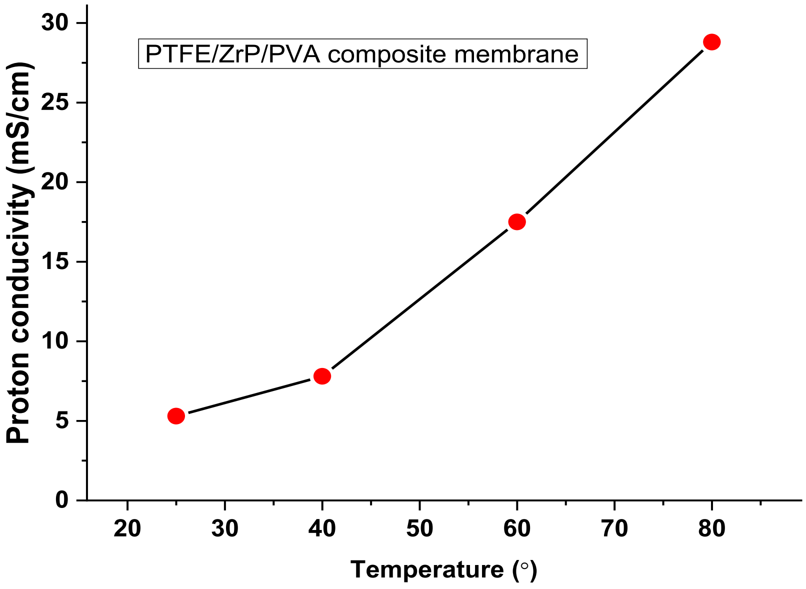

Figure 4.6. Proton conductivity of PTFE-ZrP-PVA membrane with change in temperature

Methanol permeability: Methanol fuel is lost because of permeation from the anode side to cathode side which in turn results in lower cell efficiency. Methanol permeability of PTFE-ZrP-PVA membrane and Nafion117 was compared in the temperature range of 30ºC-80ºC. It was observed that methanol permeability is increased with the temperature for both the membranes. At 40 ºC, the average value was 3.8×10^{-7} cm^2 s^{-1} which is considerably lower than that of Nafion117 (13.6×10^{-7} cm^2 s^{-1}).

Methanol permeability and proton conductivity value is comparable with similar inorganic ion-exchanger membranes shown in table 4.5 and obtained value comparable (Pandey et al. 2015)-(Gao et al. 2018). High methanol permeability of Nafion117 was observed at 80ºC, i.e. 41.32×10^{-7} cm^2s^{-1}. Whereas methanol permeability of PTFE-ZrP-PVA membrane is 14.5×10^{-7} cm^2s^{-1} which keeps the membrane workable in the DMFC application at higher temperatures. Methanol permeability values decrease with increasing PVA content in PTFE-ZrP-PVA membrane composition. As PVA weight % increases from 1 wt% to 6 wt% methanol permeability values are observed from 14.8×10^{-7} to 4.5×10^{-7} cm^2 s^{-1} are shown in table 4.2. This decreased permeability values with the addition of PVA molecules linked with high molecular weight ZrP. This PVA molecule forms a continuous network structure with ZrP molecules. So, the membrane has low methanol permeability with the increase of PVA content. Lower methanol permeability at higher temperature keeps the membrane workable in the high temperature DMFC application.

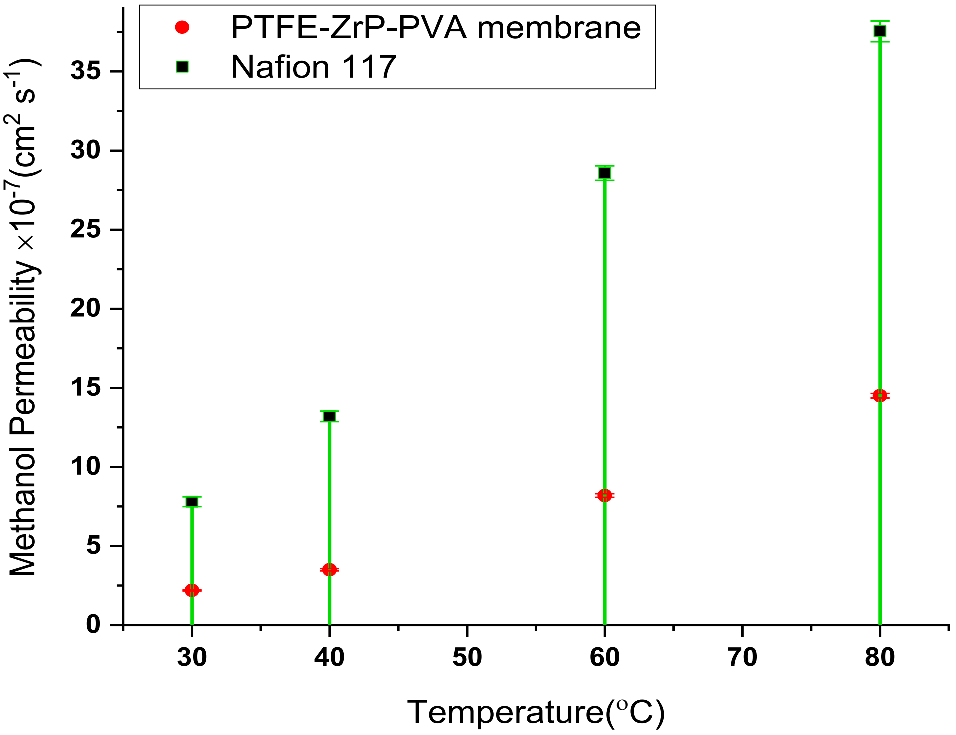

Figure 4.7. Effect of temperature on Methanol crossover of PTFE-ZrP-PVA membrane

Table 4.5 Comparison of IEC, methanol permeability and proton conductivity values with values reported in the literature for inorganic ion-exchanger based composite membranes

S. No	Membrane	IEC (meq.g^{-1})	Proton conductivity (S cm^{-1}) (25℃)	Methanol permeability (cm^{2} s^{-1}) 30℃	Reference
1	**PTFE-10 wt%ZrP-5wt%PVA**	**1.28**	**0.0053**	**3.8×10^{-7}**	**Present study**
2	PVDF/ZrP	0.76	0.0012	4.1×10^{-7}	(Pandey et al. 2015)-
3	QAPEI-PTFE composite membrane	0.08-0.14	0.0035		(Yan et al. 2013)
4	PTFE/sSEBS	-------	0.0032	21.2×10^{-7}	(Wang et al. 2014)
5	Sulfonated polystyrene/PTFE	-------	0.008	10×10^{-7}	(Shin et al. 2005)
6	PVA–ZrP–C$_{S2}$SWA	3.0	0.001-0.01	30×10^{-7}	(Helen, Viswanathan, and Murthy 2006)
7	PVA–ZrP–SWA (20%)	0.958	0.004	19×10^{-7}	(Helen, Viswanathan, and Murthy 2007)
8	PVA-ZW-20-Si	4.3	0.0073	25×10^{-7}	(Gao et al. 2016)
9	Nafion/Pd-SiO_2	0.86	0.1292	8.36×10^{-7}	(Thiam et al. 2013)
10	GO-mordenite/Nafion	0.85	0.0560	15×10^{-7}	(Prapainainar et al. 2019)
11	SPEEK/HPW@MSNs-0.5	1.35	0.0035	1.55×10^{-7}	(Gao et al. 2018)

Cost analysis of membrane: The cost of the membrane is one of the major impediments in commercialization of DMFC. The PTFE-ZrP-PVA membrane's cost was estimated by summing of each raw material cost in the process of synthesis while other is market price of Nafion117. As shown in figure 4.8, the cost of PTFE-ZrP-PVA membrane was compared with that of Nafion 117. the cost of PTFE-ZrP-PVA membrane is around 3-fold lower than that of Nafion 117. Therefore, it is economical to use the PTFE-ZrP-PVA membrane for DMFC.

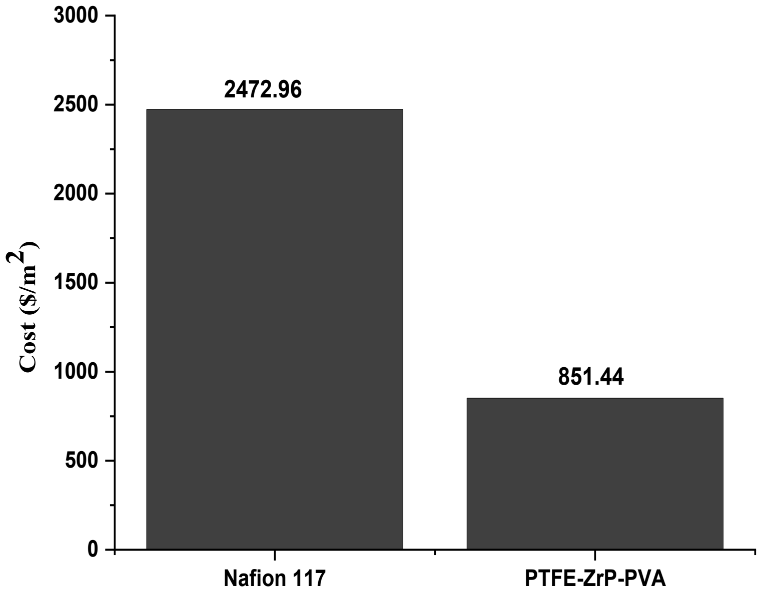

Figure 4.8 The cost comparison of Nafion 117 and PTFE-ZrP-PVA membrane

Single cell DMFC test: The testing of the DMFC was carried out as per the procedure described in the section 3.6. The experiment was carried out at standard condition like 2M methanol at anode side, 100% RH at cathode side and remaining parameters were set as shown in the table 3.2. The polarization curves of DMFC have been obtained in the temperature range of 30 – 80 °C with Nafion 117 and PTFE-ZrP-PVA composite membrane shown in figure 4.9 and figure 4.10.

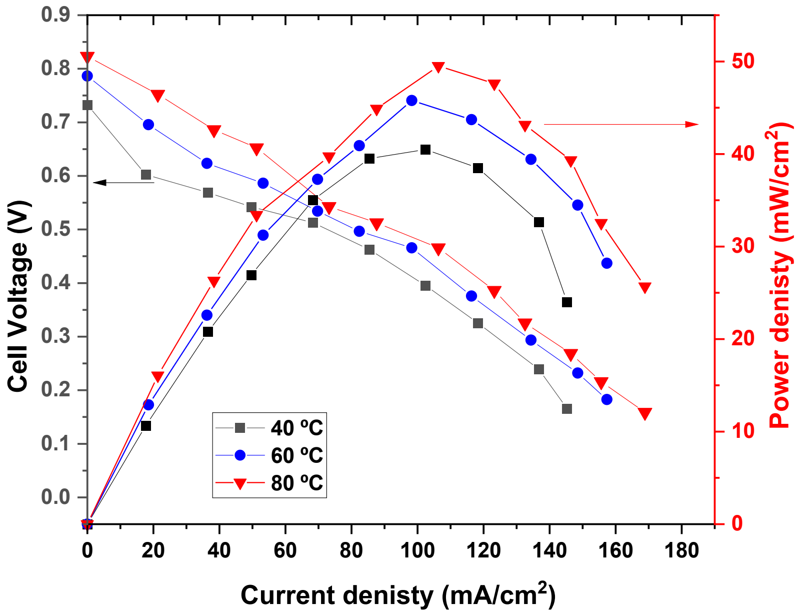

Figure 4.9 Effect of temperature on the DMFC single cell performance with Nafion 117

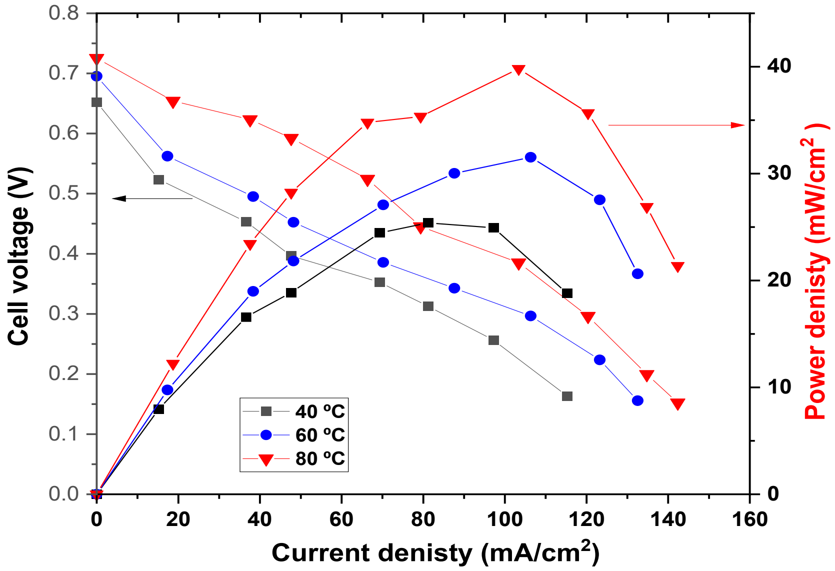

Figure 4.10 Effect of temperature on the DMFC single cell performance with PTFE-ZrP-PVA membrane

The open circuit voltage (OCV) of the DMFC with Nafion117 is increased from 0.733 to 0.823 V and peak power density is increased from 40.49 to 49.51 mW cm^{-2}, with increase in temperature from 40°C to 80°C (figure 4.9). Whereas OCV of DMFC with PTFE-ZrP-PVA membrane is increased from 0.652 V to 0.725 V and peak power density increased substantially from 25.39 to 39.8051 mW cm^{-2}, with increase in temperature from 40°C to 80°C (figure 4.10). This might be resulted from enhanced electrode kinetics (Chen, Ye, and Lin 2010). The current density of the cell is also increased from 145.26 to 168.86 mA cm^{-2} for the Nafion117 and from 115.23 to 142.36 mA cm^{-2} for PTFE-ZrP-PVA composite membrane with increase in temperature from 40°C to 80°C respectively. The performance of cell with the composite membrane is significantly improved at higher temperature range.

The cell voltage and power density were comparatively little lower with the PTFE-ZrP-PVA composite than Nafion 117 in the tested temperature range. The maximum peak power density was observed at 80°C for both Nafion 117 and PTFE-ZrP-PVA composite membrane. The peak power density of 49.5 mW cm^{-2} was observed at 0.46 V with Nafion 117 where as it was 39.9 mW cm^{-2} at 0.44 V for PTFE-ZrP-PVA membrane as shown figure 4.11.

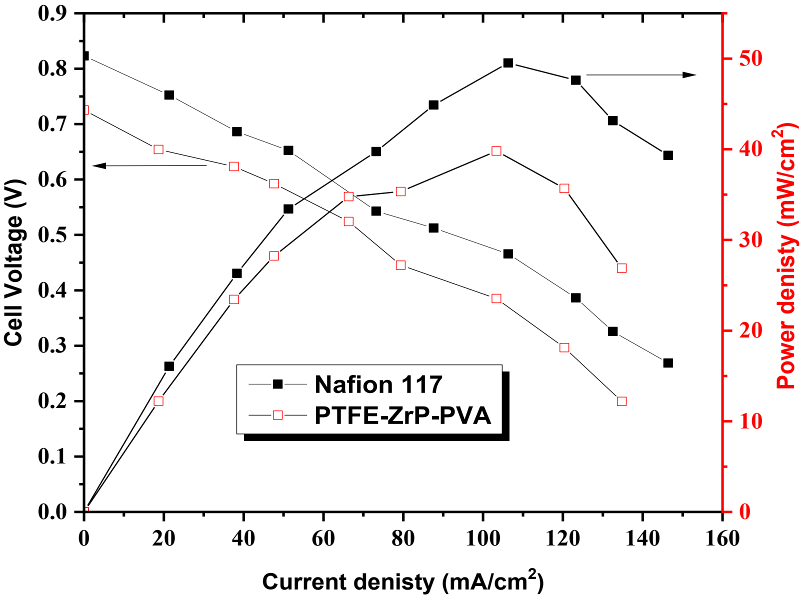

Figure 4.11 Performance of single cell DMFC with the synthesized PTFE-ZrP-PVA membrane and Nafion 117 at 80 °C

The synthesized composite membrane is performed poorly in the lower temperatures but its performance is competitive enough at higher temperature of 80°C. It can be related higher proton conductivity and low methanol permeability of the PTFE-ZrP-PVA composite membrane. The membrane has also shown comparable DMFC performance with other inorganic ion-exchanger based membrane reported in the literature (Helen et al. 2006; Helen et al. 2007; Pandey et al. 2015).

4.4 Conclusions

An asymmetric, inorganic-organic based PTFE-ZrP-PVA composite membrane was synthesized by a unique hybrid approach such as pore infiltration, layer by layer (LBL) coating and followed by heat-treatment at 60 ℃ using chemically treated PTFE support. The wettability of the PTFE support was improved by chemical treatment with PVA, H_2O_2 and acrylic acid solution. Surface morphology of ZrP-PVA sol on the PTFE support was observed in SEM images. Presence of ZrP and PVA was confirmed by EDX and functional groups confirmed the presence of ZrP and PVA using FT-IR analysis. The TGA-DTA analysis indicated that the membrane was thermally stable up to 140°C. The membrane has good mechanical stability with a tensile strength of 44 MPa. The membrane possessed fair proton conductivity of 28.1 mS cm^{-1} and low methanol permeability (14.5×10^{-7} cm^2 s^{-1}) at 80℃. Low methanol permeability at a higher temperature of the composite membrane, makes it workable in direct methanol fuel cell (DMFC). The membrane is economical compared to Nafion117. The composite membrane has exhibited competitive performance of DMFC single cell at 80℃ i.e. 39.9 mW cm^{-2} with 2M methanol anode side and 100% RH cathode side. It may be related higher proton conductivity and low methanol permeability of the PTFE-ZrP-PVA composite membrane at higher temperatures.

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CHAPTER 5

Synthesis of (Si-PWA)-PVA/PTFE high temperature proton conducting composite membrane

CHAPTER 5

Synthesis of (Si-PWA)-PVA/PTFE high temperature proton conducting composite membrane

The synthesis and characterization results of (Si-PWA)-PVA/PTFE composite membrane and DMFC single cell testing results are presented in this chapter. The performance of single cell DMFC with the (Si-PWA)-PVA/PTFE membrane has been compared with PTFE-ZrP-PVA membrane and Nafion117 which were reported in chapter 4.

5.1 Introduction

Even though PTFE-ZrP-PVA membrane was competitive with other composite membranes in the lite, but slightly underperformed compared to Nafion117. So, the (Si-PWA)-PVA/PTFE composite membrane was synthesized with objective of getting higher or comparative performance of DMFC. Selection of the materials for synthesizing the membrane has been carried-out based on literature. The inorganic ion exchanger, phosphotungstic acid (PWA) is an effective proton conductor, having excellent stability and provides added proton exchangeable sites to improve transport capacity of protons due to kegging structure (Keggin 1933). It has to be immobilized with silica due to its lone tendency to wash away in aqueous media. Additionally, hygroscopic oxide structure and high water retention capacity of silica provide good proton conduction even at higher temperatures (Mikhailenko et al. 2001;Branco et al. 2016; Kim, Jo, and Nam 2015). PVA was one of preferable material to reduce methanol permeability of membrane ((Jin et al. 1985). Therefore, present work was aimed to synthesize the highly stable and economical composite membrane by using the combination of silica immobilized PWA and PVA. The organic-inorganic based hybrid membranes suggested by Kim et al., revealed that good interaction between the organic polymer and inorganic materials improves the mechanical properties of membranes with good proton conductivity(Kim et al. 2009). The membranes that are synthesized with inorganic materials have excellent potential to compare with original membranes and can be used at high temperatures (Sacca et al. 2006;Gashoul, Parnian, and Rowshanzamir 2017; Salarizadeh et al. 2019).

In this work, the polytetrafluoroethylene (PTFE) film is used as support to hold the inorganic skin layer. The synthesis of (Si-PWA)-PVA/PTFE composite membrane was carried out by using the three-step method of pore infiltration, layer by layer (LBL) tape casting and heat treatment. The sol was synthesized using PWA, silica, and PVA. Physical, thermal and electrochemical characterizations of synthesized (Si-PWA)-PVA/PTFE composite membrane investigated and compared with Nafion117 membrane. The proton conductivity and methanol permeability were found out in the range of 28°C to 120˚C. The single cell DMFC testing has been performed with the composite membrane. The results were compared with PTFE-ZrP-PVA composite membrane and Nafion 117.

5.2 Experimental

The detailed experimental procedure for synthesizing the (Si-PWA)-PVA/PTFE composite membrane, characterization and testing of single cell DMFC was given the chapter 3, section 3.4, 3.5 and 3.6.

5.3. Results and discussion

5.3.1 Synthesis of (Si-PWA)-PVA/PTFE membrane

The wettability of the support is one of the essential properties to enhance the proton conductivity in aqueous DMFC application. The surface of PTFE film was modified by the following procedure outlined in the experimental part and wettability of the film was analyzed. The reduction in the contact angle from 136.5˚ to 51.8˚ was observed shown in figure 5.1. The succeeding enhancement in hydrophilicity of the film is due to hydroxyl (–OH) groups of PVA which are crosslinked with acrylic acid to decreases the surface roughness (Kanakasabai et al. 2011).

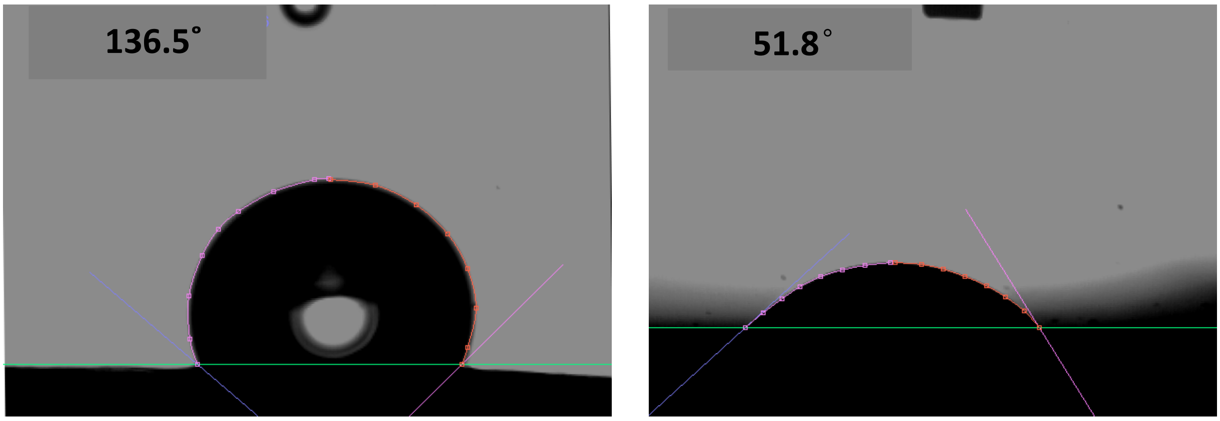

Figure 5.1. PTFE support film contact angle before and after surface modification

The sol was synthesized by mixing the different molar ratios of PWA, TEOS, and PVA as illustrated in the experimental section. The (Si-PWA)-PVA/PTFE membrane was obtained by using the method of pore filling and LBL casting. The thickness of the membrane was optimized concerning ion-exchange capacity (IEC) for the composition of 0.3M PWA, 0.2M TEOS, and 0.15M PVA. The thin layers of the sol were casted on both sides of 45μm thickness PTFE support initially and IEC value was measured for 47 μm thick composite membrane. The membrane thickness was varied from 47-62 μm. The IEC is increased linearly with increasing the membrane thickness up to 56μm. There was very little increase in IEC value up to 60 μm membrane thickness. Further increase of the membrane thickness has resulted in nearly constant IEC value (figure 5.2).

This might be resulted because of heterogeneity and hydrophilicity of the membrane (Inglezakis 2005; Khan et al. 2016; Mollá and Compañ 2011). The membrane thickness of 60 μm was taken as an optimum value for fine-tuning the composition of (Si-PWA) and PVA for the synthesis of the membrane. Silica immobilized PWA, (Si-PWA) provides the proton conductivity and PVA lowers the methanol permeability of the membrane.

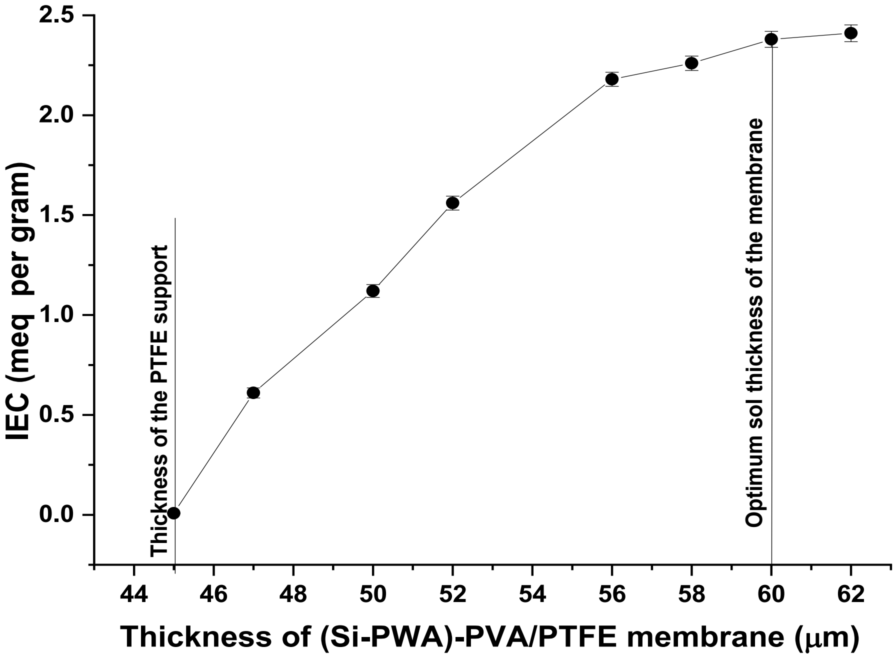

Figure 5.2. Optimization of the membrane thickness with respective to IEC

Hence, the composition of (Si-PWA) was optimized concerning proton conductivity and the PVA composition was optimized concerning the permeability of methanol. The detailed optimization study was presented in table 5.1 and table 5.2. The molar ratio of (PWA/TEOS) in the sol composition was varied from 0.5 to 2. The proton conductivity is increased with increasing the ratio of (PWA/TEOS) up to 1.5 (table 5.1). The (PWA/TEOS) ratio of 1.5 was used for the synthesis of the sol.

Table 5.1. Optimization of (PWA/TEOS) ratio of the sol at room temperature (~28°C)

Support	**PWA**	**TEOS**	**(PWA/TEOS) ratio of the sol**	**Proton conductivity of (Si-PWA)-PVA/PTFE membrane (S cm^{-1})**
PTFE	0.1M	0.2 M	0.5	2.63×10^{-3}
PTFE	0.2M	0.2 M	1.0	4.8×10^{-3}
PTFE	**0.3M**	**0.2 M**	**1.5**	**6.7×10^{-3} (Optimized)**
PTFE	0.4M	0.2 M	2.0	6.5×10^{-3}

The addition of PVA was fine-tuned for the optimized ratio of (PWA/TEOS) illustrated in table 5.2. The composition of PVA was varied from 0 to 0.2M and both the methanol permeability and proton conductivity were measured for each of varied value of PVA. The proton conductivity is affected because of crosslinking PVA with PWA. But without much compromise on proton conductivity, methanol permeability was appreciably lowered (3.2×10^{-7} cm^2 sec^{-1}) with the addition of 0.15M PVA to the sol. The optimal sol composition of 0.3M PWA: 0.2M TEOS: 0.15M PVA was used for the synthesis of 60 µm thick (Si-PWA)-PVA/PTFE composite membrane and subjected to physico and electrochemical characterization.

Table 5.2. Optimization of PVA composition of the sol at room temperature (~28°C)

Support	PWA	TEOS	PWA/TEOS ratio of sol	Addition PVA(M)	Proton conductivity (mS cm^{-1})	Methanol permeability (cm^2 s^{-1})
PTFE	0.3M	0.2M	1.5	0	6.7	9.8×10^{-7}
				0.05	6.62	8.2×10^{-7}
				0.1	6.47	5×10^{-7}
				0.15	**6.3**	**3.2×10^{-7} (Optimized)**
				0.2	5.96	3.58×10^{-7}

5.3.2. Characterization of (Si-PWA)-PVA/PTFE composite membrane

SEM-EDX: The composite membrane's surface morphological studies and elemental analysis were carried out by using SEM and EDX. The magnified SEM images of PTFE film and (Si-PWA)-PVA/PTFE composite membrane are shown in figure 5.3 (a) and figure 5.3(b) respectively. It was observed that the sol has fully covered the surface of PTFE support and the casted top layer was continuous and evenly distributed. The main elemental peaks of the sol and membrane include *C, O, Si, P, and W* were observed in the EDX spectrum [figure 5.3 (c)]. The result of the analysis was summarized in table 5.3.

Table 5.3. The % distribution of elements in EDX spectra

Element	Weight %	Atomic %
C	29.42	39.71
O	49.84	50.51
Si	1.89	1.09
P	16.13	8.44
W	2.72	0.25

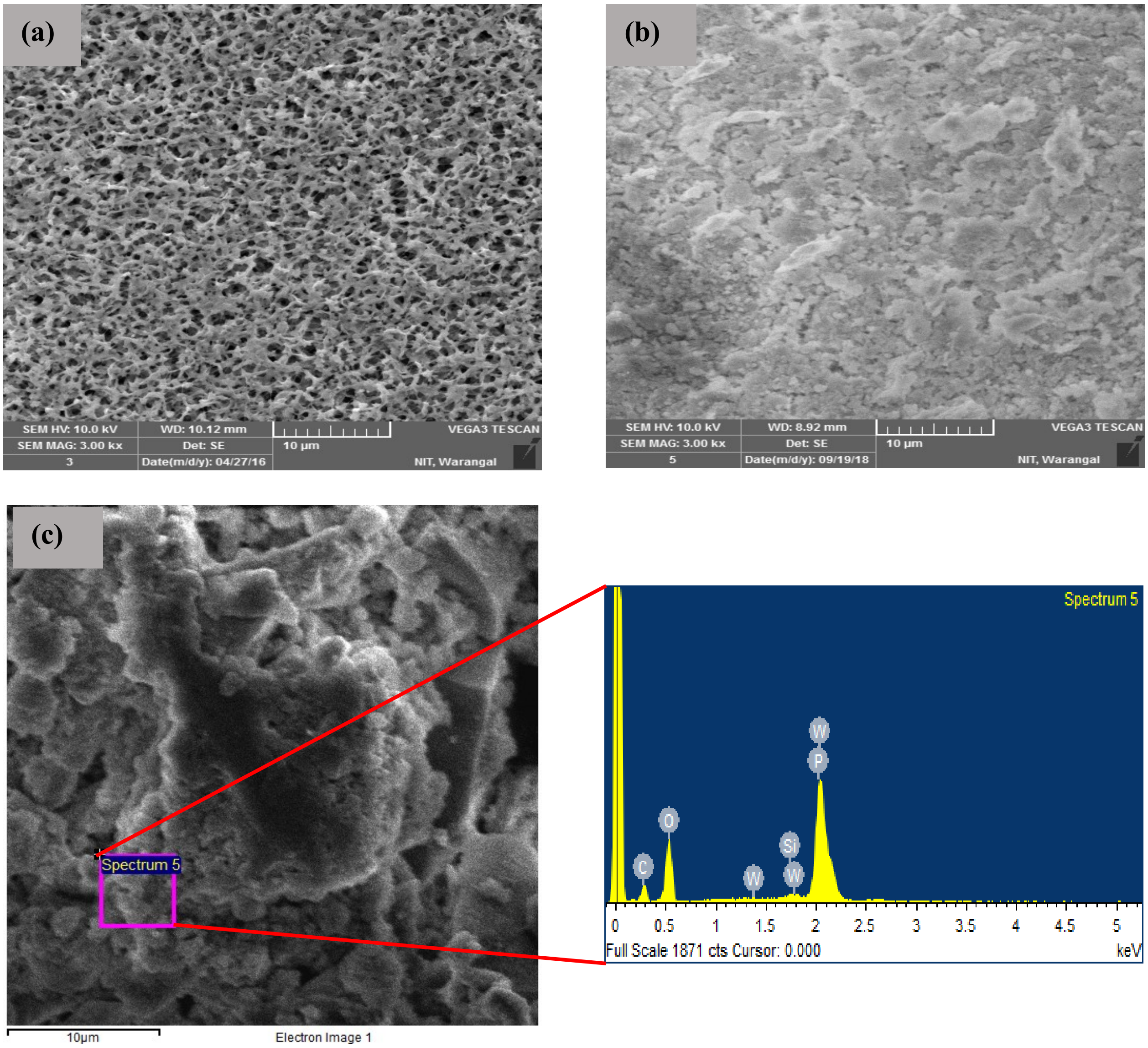

Figure 5.3. SEM images of (a) PTFE film (b) (Si-PWA)-PVA/ PTFE membrane (c) EDX spectroscopy for the membrane

FT-IR: Figure 5.4, shows the FT-IR spectrum of the synthesized membrane. The characteristic bonds of all the membrane compounds include PWA, TEOS, PVA and PTFE were observed at 520, 597, 798, 892, 981, 1078, 1082, 1136, 1147, 1237 and 1620 cm^{-1} (Dorschner, Lappan, and Lunkwitz 1998; Helen, Viswanathan, and Murthy 2006; Huang et al. 2010; Sutradhar et al. 2019; Thanganathan 2011; Xu et al. 2004). The functional groups of W–O–W corner-sharing, W–O–W edge-sharing, terminal W–O, P-O stretching is observed at 798, 892, 981 and 1082 cm^{-1} respectively and designate the presence of PWA. The characteristic bonds of Si–O stretching at 520 cm^{-1} and Si–O–Si stretching at 1078 cm^{-1} can be attributed to the interaction between the PWA and TEOS.

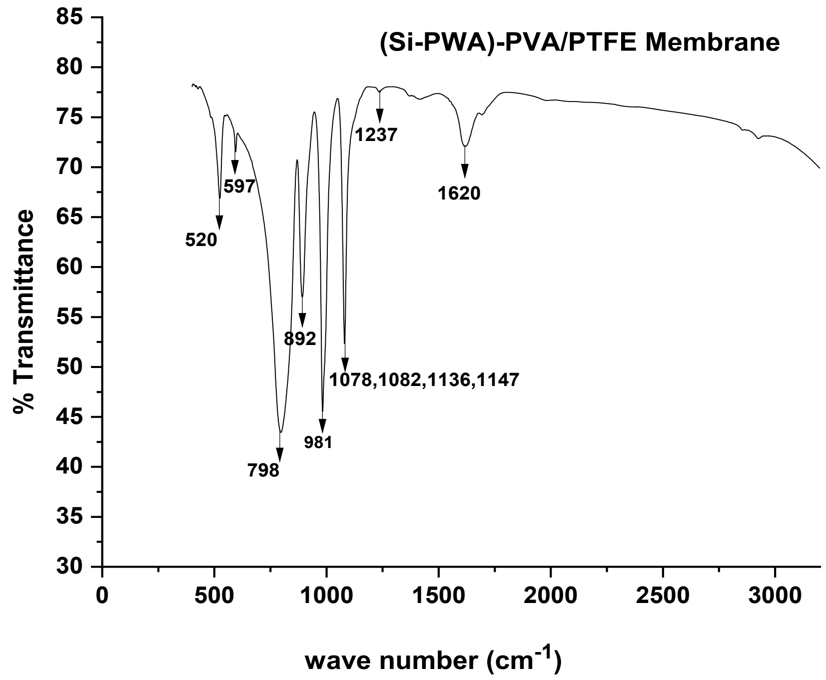

Figure 5.4. FTIR characterization of composite membrane

Table 5.4. The main functional bonds of PTFE support and (Si-PWA)-PVA/PTFE membrane

Vibration frequency (cm^{-1})	**Assigned functional group**
520	Si–O stretching (of TEOS)
597	– $(CH_2)_2$ stretching (of PVA)
798	W–O–W corner sharing (of PWA)
892	W–O–W edge sharing (of PWA)
981	terminal W–O (of PWA)
1078	Si–O–Si stretching (of TEOS)
1082	P–O stretching (of PWA)
1136	– C–OH, Si–O–C stretching (of PVA & TEOS)
1147	– CF_2 stretching symmetric (of PTFE)
1237	– CF_2 stretching asymmetric (of PTFE)
1620	– OH (increased hydrophilicity)

The presence of PVA in the membrane is confirmed by the functional groups of -$(CH_2)_2$ at 597 cm^{-1} and –C–OH at 1136 cm^{-1}. The bonds of –CF_2 stretching symmetric at 1147 cm^{-1} and –CF_2 stretching asymmetric at 1237 cm^{-1} are due to PTFE supprot. The – OH functional group at 1620 cm^{-1} indicates the water deformation and increased hydrophilicity which could enchance the proton conductivity (Caro, Lappan, and Lunkwitz 1999). The detailed study of characteristic bond assignment is presented in table 5.4.

X-RD: Figure 5.5 (a) shows the X-ray powder diffractograms of silica derived from TEOS, PVA, PWA, (Si-PWA) and (Si-PWA)-PVA. The semi-crystalline of PVA and amorphous silica can be observed in the 1 and 2 patterns of figure 5.5(a).

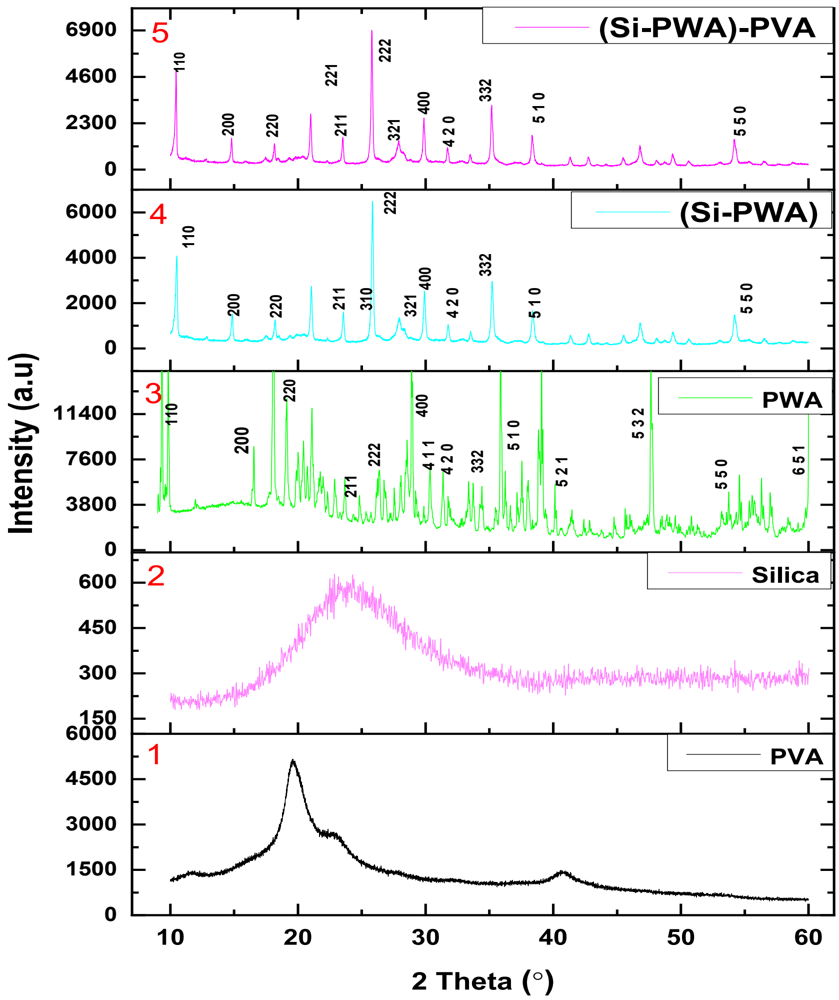

Figure 5.5 (a). XRD patterns of PVA, Silica, PWA, (Si-PWA) and (Si-PWA)-PVA

The high intensity crystalline peaks are observed in the pattern 3 and the peaks are in good agreement with standard spectrum (**JCPDS** no.: 75-2125, **space group**: 224) with lattice parameter of 12.14 (Kremenović et al. 2000, 2002). The crystalline peaks of PWA are broadened and observed slight shift towards right due to the interaction of PWA with amorphous silica shown in pattern 4 of figure 5.5(a). The semi-crystalline peaks were observed in the pattern 5 of figure 5.5 (a) with the addition of PVA to the (Si-PWA). The overlap of the peaks of all the components of the sol mixture indicates the compatibility and homogeneity among the components. The samples of PTFE support and the membrane were subjected to film XRD and of those XRD patterns along with powder sol are shown in figure 5.5(b). The semi-crystalline peaks of the (Si-PWA)-PVA sol and crystalline peaks of the PTFE film are complemented each other in the X-ray diffractograms of the composite membrane.

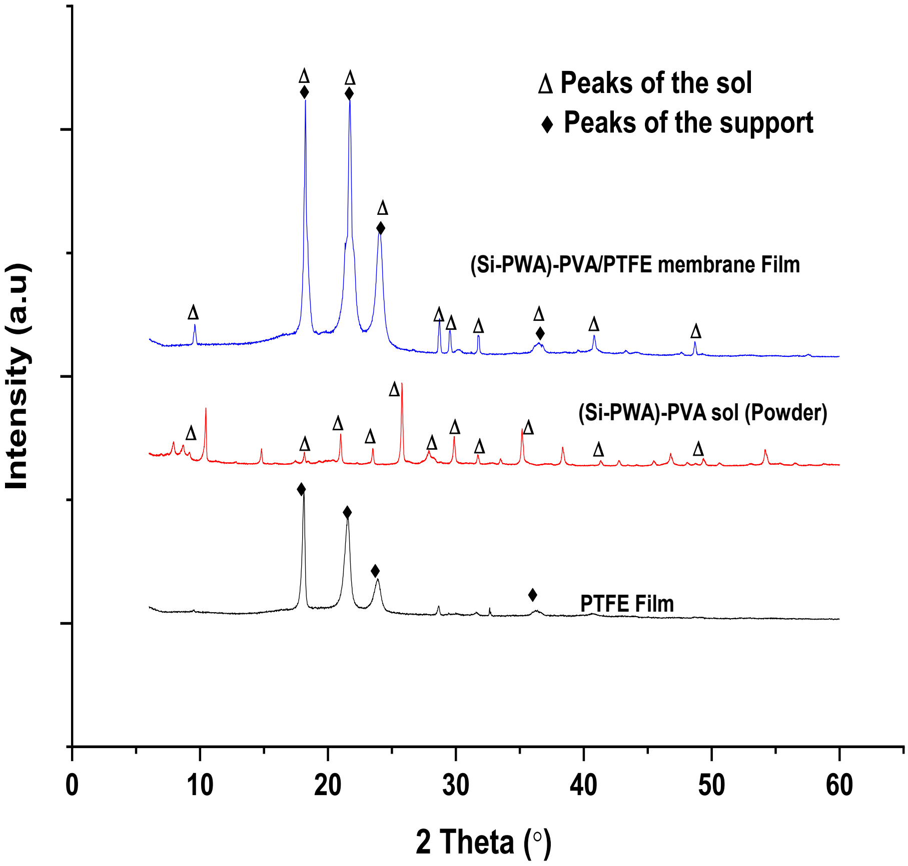

Figure 5.5(b). XRD spectra for (Si-PWA)-PVA/ PTFE membrane

Mechanical strength: The mechanical strength of the (Si-PWA)-PVA/ PTFE composite membrane and PTFE support are shown in the stress-strain diagram and those are compared with the mechanical strength of Nafion117 (figure 5.6). The horizontal reference line was drawn at 27 MPa to indicate the mechanical strength of Nafion117 (Zhang et al. 2019). The mechanical strength of PTFE support (29.5 MPa) is close to that of Nafion117 membrane. The PTFE support was further reinforced with pore-filling and LBL casting of the synthesized sol. The tensile strength of the synthesized composite membrane is 53.13MPa which is considerably higher than that of Nafion 117.

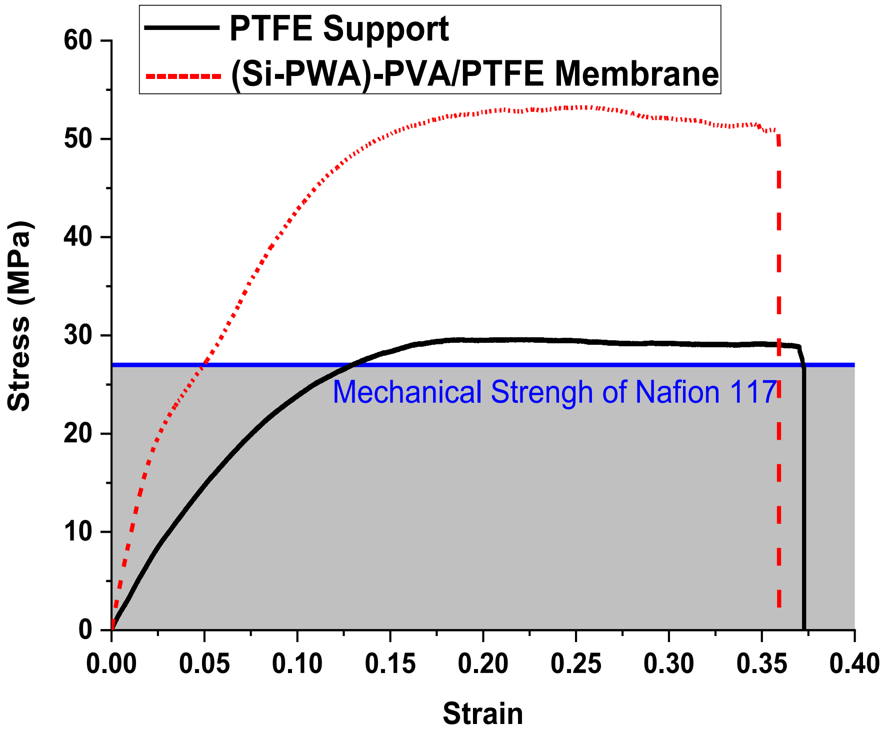

Figure 5.6. Mechanical strength of PTFE support and (Si-PWA)-PVA/ PTFE membrane

TGA-DTA: Thermogravimetric analysis and differential thermal analysis of the membrane was conducted in the temperature range of 30-500˚C with 10˚C min^{-1} heating rate. The TGA curve is divided into three parts for analysis (figure 5.7). The temperature ranges of part I, part II and part III are 30-180˚C, 181-370˚C, and 371-500˚C respectively.

The initial weight loss of ~ 4.1% and corresponding endothermic peak at 137˚C is observed in Part I up to 180˚C due to loss of bound water content. The second major weight loss ~11.56% in Part II up to 370˚C is associated with thermal decomposition of PVA, loss of crystalline water of (Si-PWA) and structural softening of PTFE (Guhan et al. 2009). The corresponding endothermic and exothermic peaks are witnessed in the DTA curve of the membrane. The sudden decline in the weight loss is observed in Part III can be attributed to the decomposition of PTFE and oxidation of PWA. The (Si-PWA)-PVA/ PTFE composite membrane is workable under 180˚C due to comprising of thermally stable Si, PVA, and PWA.

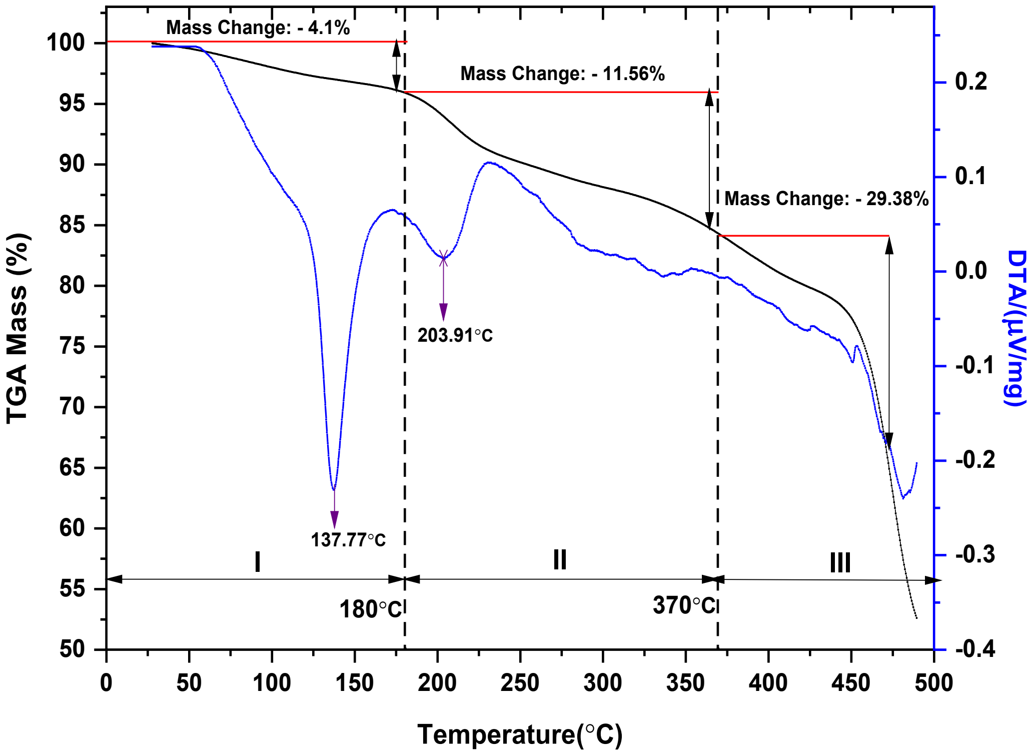

Figure 5.7. Thermal deformation of (Si-PWA)-PVA/ PTFE membrane

Oxidative stability: Oxidative stability of (Si-PWA)-PVA/PTFE and Nafion 117 membranes were determined by using Fenton's reagent. This test also represents resistance of membrane in oxidative reaction by radical spaces (HO. and OOH.) (Asano et al., 2006). The free radicals are generated through many initiation reactions, and they react with molecular oxygen (Li et al., 2018). For commercially available polymers, the thermal decomposition of hydroperoxides is considered of the utmost importance. •OH radicals are extremely reactive and can react with many organic compounds with encountered controlled rate constants.

The average % weight loss of the composite membrane over the 24 hours of study was found out to be 9.2 and it was 11.3 for Nafion117. The chemical stability of the composite membrane is slightly more and comparable with that of Nafion117 as showed in figure 5.8.

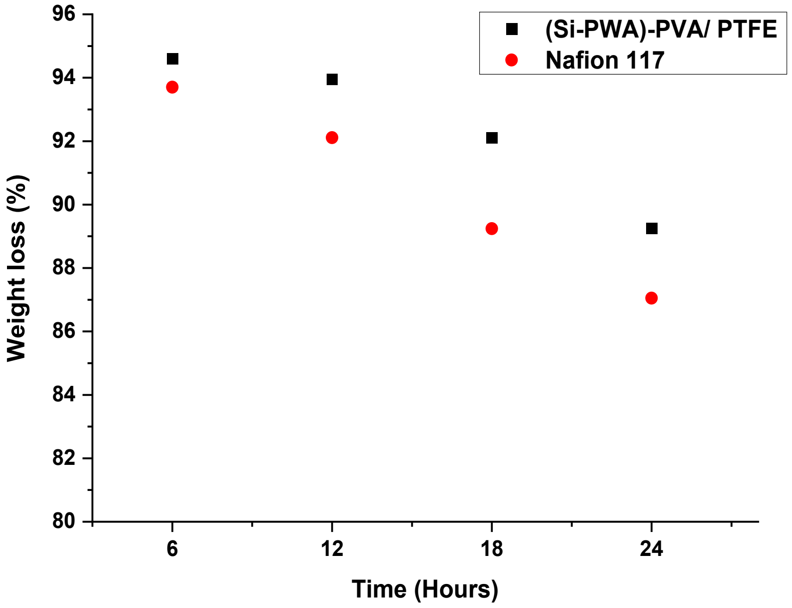

Figure 5.8. Oxidation stability of (Si-PWA)-PVA/PTFE and Nafion 177 membranes

IEC and water uptake: Ion exchange capacity and water uptake are essential for the membrane. Existence of water molecules inside the membrane significantly affects membrane properties. The proton conductivity is directly related to IEC and water uptake values. The enhanced proton conductivity could be observed with increased values of IEC and water uptake due to enhanced kinetics of ions in the water (Salarizadeh et al. 2019). The IEC and water uptake of the composite membrane was determined at room temperature by using the procedure given in the experimental section. The IEC of the membrane is 2.38 meq per gram which is more than double the value of Nafion 117 (~0.89 meq per gram).

The water retention capacity of the membrane was calculated as 21.7% which is close to literature reported water uptake value for Nafion 117 (Zawodzinski Jr et al. 1993). The determined values of IEC and water uptake for the composite membrane are in the range which suits in DMFC application.

***Proton conductivity*:** Proton conductivity plays an important role in DMFC efficiency. The proton conductivity of 60 µm thick (Si-PWA)-PVA/PTFE composite membrane was determined in the temperature range of 28˚C-120˚C. The figure 5.9 shows the increase in proton conductivity with increasing the temperature up to 100 ˚C and further showed a slight declining trend.

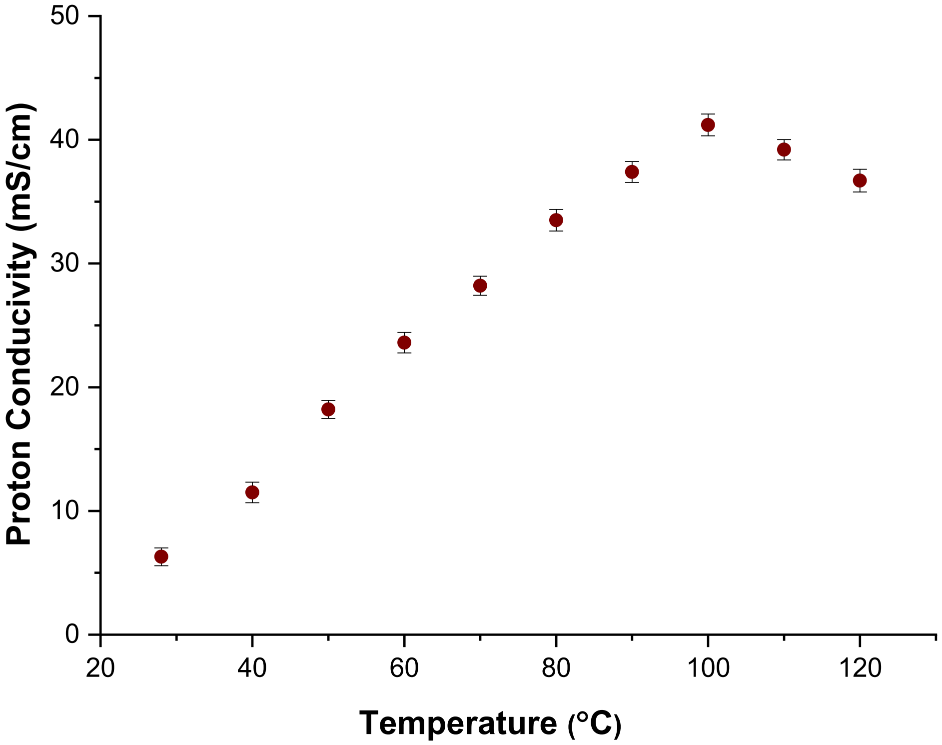

Figure 5.9. Proton conductivity of the composite membrane

This could be due to dehydration of the membrane at elevated temperatures (Helen et al. 2006; Kim et al. 2003). The determined proton conductivity at 28˚C is 6.3 mS cm^{-1} but it is almost 6.5 times increased (41.2 mS cm^{-1}) at 100˚C. The proton conductivity of the present membrane is comparable with that of similar literature reported membranes are shown in table 5.5. The DMFC cell can deliver satisfactory performance even at 120 ˚C since there is no significant drop in proton conductivity. The activation energy of the membrane was calculated by using Arrhenius-type law (Jiang et al. 2012) and it was found out to be 18.25 kJ/mol. It was well within in the range (14-60 kJ/mol) for proton exchange membrane reported (Jiang et al. 2012; Lu et al. 2011).

Methanol permeability: The methanol permeability is one of the foremost concerns in DMFC operation. The energy efficiency of the cell will be lowered due to loss of permeated fuel from anode to the cathode side. The methanol permeability of the (Si-PWA) -PVA/PTFE membrane was determined in between 28˚C and 120˚C [figure 5.10(a)] and compared with Nafion117 up to 80˚C [figure 5.10 (b)].

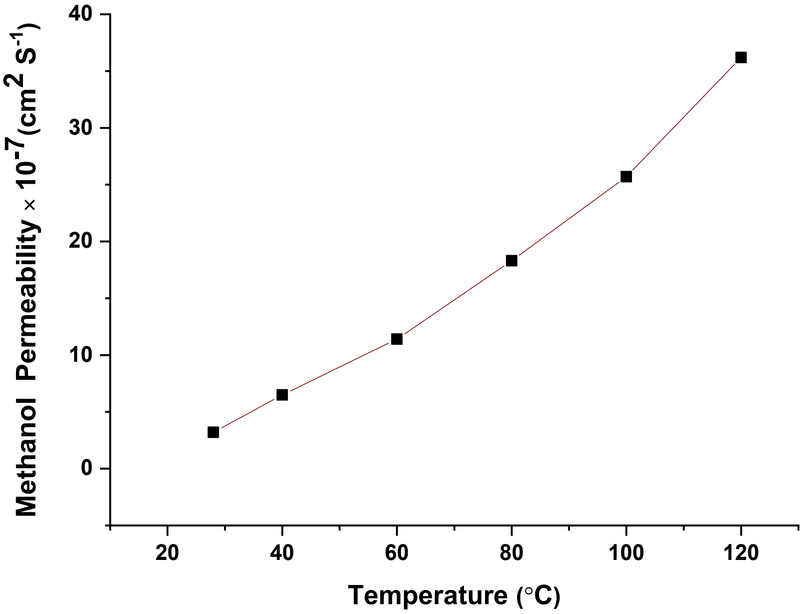

Figure 5.10 (a). Methanol Permeability of (Si-PWA)-PVA/PTFE composite membrane

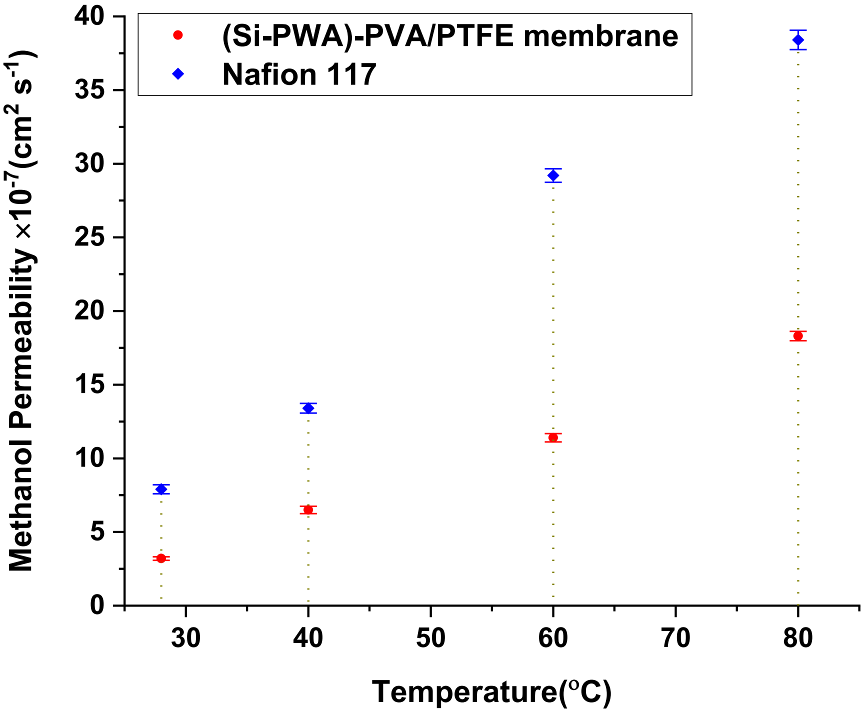

Figure 5.10(b). Comparison of methanol Permeability values of composite membrane and Nafion 117

The comparison of the methanol permeability values was restricted up to 80˚C due to the thermal instability of Nafion117. The methanol permeability of the membrane at room temperature is 3.2×10^{-7} cm^2 s^{-1} and it is lower or comparable to similar type of membranes reported in the literature (table 5.5). The values are considerably lesser than methanol permeability of Nafion 117 at all temperature of interest [figure 5.10 (b)]. The methanol permeability of Nafion 117 at 80˚C was comparable with that of the composite membrane at 120˚C. It shows that the (Si-PWA)-PVA/PTFE composite membrane is competent membrane with improved proton conductivity and low methanol permeability at elevated temperatures.

Table 5.5. Comparative study for methanol permeability and proton conductivity of composite membranes

S.No.	**Composite membrane**	**Methanol permeability (cm^2 s^{-1}) ~28˚C**	**Proton conductivity (mS cm^{-1}) ~28˚C**	**Reference**
1	***(Si-PWA)-PVA/PTFE***	***3.2×10^{-7}***	***6.3***	***Present study***
2	Si-PWA/PVDF	3.8×10^{-7}	4.3	(Pandey, Mir, and Shukla 2014a)
3	PTEF/sSEBS	21.2×10^{-7}	1.4	(Wang et al. 2014)
4	PVA/PWA	$10\text{-}40 \times 10^{-7}$	6	(Li, Xu, and Wang 2003)
5	$PVA_{80}/PES_{20}/PWA_{50}$	10×10^{-7}	7	(Madaeni, Amirinejad, and Amirinejad 2011)
6	PVA/SiO_2	8.81×10^{-7}	3.5	(Yang, Li, and Liou 2011)
7	PTFE-ZrP-PVA	3.8×10^{-7}	5.3	(Pagidi, Arthanareeswaran, and Seepana 2020)
8	Si-PWA-PVA	1.6×10^{-7}	7	(Pandey, Mir, and Shukla 2014b)

Cost analysis of synthesized membranes: The cost of the membrane is one of the major impediments in commercialization of DMFC. The PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE membrane's cost was estimated by summing of each raw material cost in the process of synthesis, while other is market price of Nafion 117. As shown in figure 5.11, the cost of PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE membrane is around 3-fold lower than that of Nafion 117. Therefore, it is economical to use both the synthesized membranes for DMFC application.

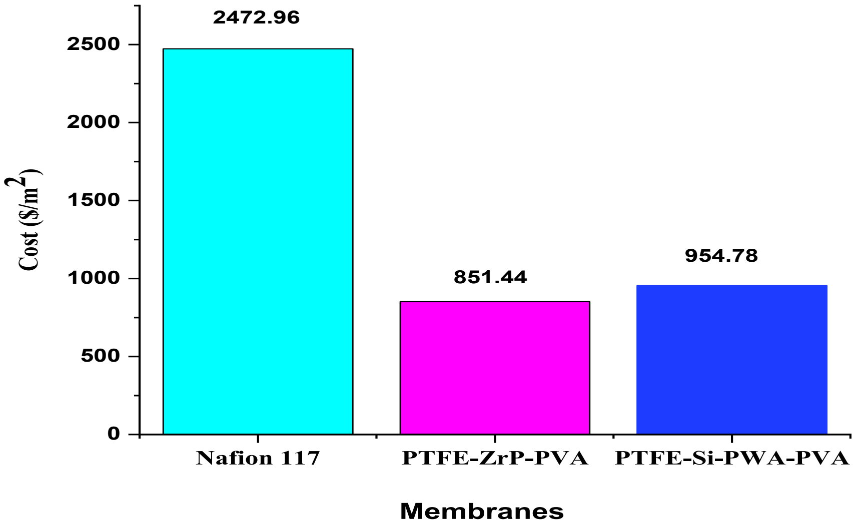

Figure 5.11 Cost comparison of Nafion 117 and synthesized composite membranes

Single cell DMFC performance: The present studies were carried out at constant conditions, keeping the methanol concentration fixed at 2 M with 100% relative humidity (RH) at cathode side, by varying operating temperatures from 30-120℃. The MEA preparation, single cell assembly and testing of DMFC studies were mentioned in Chapter 3.6 and the operating parameters were set as shown in the table 3.2. The polarization curves of DMFC have been obtained in the temperature range of 30 – 80 °C with Nafion 117 as showed in figure 5.12. The polarization curves of DMFC have been obtained in the temperature range of 30 – 120 °C for (Si-PWA)-PVA/PTFE composite membrane as showed in figure 5.13.

The open circuit voltage (OCV) of the DMFC with Nafion 117 is increased from 0.733 to 0.823 V and peak power density is increased from 40.49 to 49.51 mW cm^{-2}, with increase in temperature from 40°C to 80°C (figure 5.12). Whereas OCV of DMFC with (Si-PWA)-PVA/PTFE membrane is increased from 0.695 V to 0.782 V and peak power density increased substantially from 32.25 to 43.19 mW cm^{-2}, with increase in temperature from 40°C to 100°C (figure 5.13). This might be resulted from enhanced electrode kinetics (Chen, Ye, and Lin 2010). Further increase in cell temperature (120°C) resulted in slight decline of cell performance. This might be because of loss of bound moisture of the membrane at elevated temperature (Guhan et al. 2009) as showed in figure 5.13.

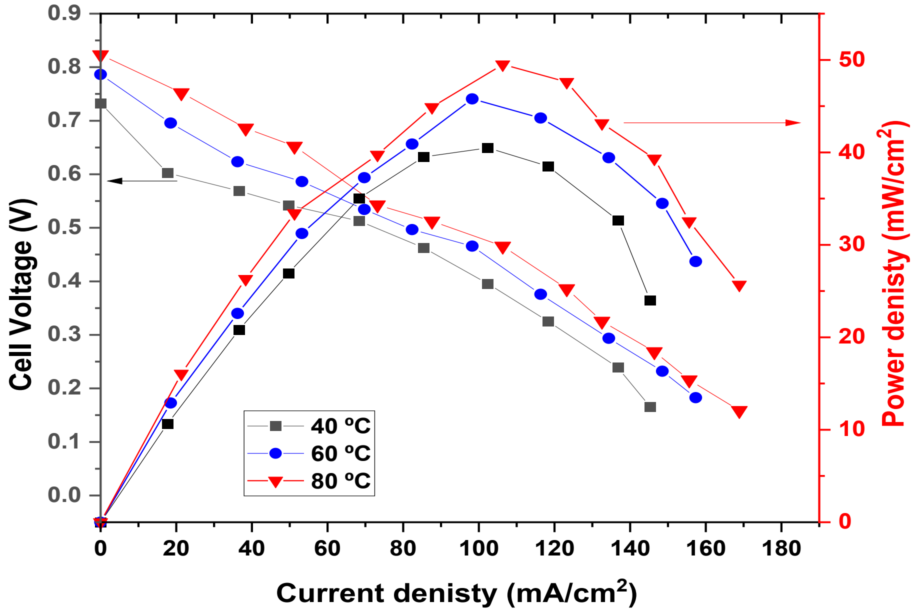

Figure 5.12 Effect of temperature on the DMFC single cell performance with Nafion 117

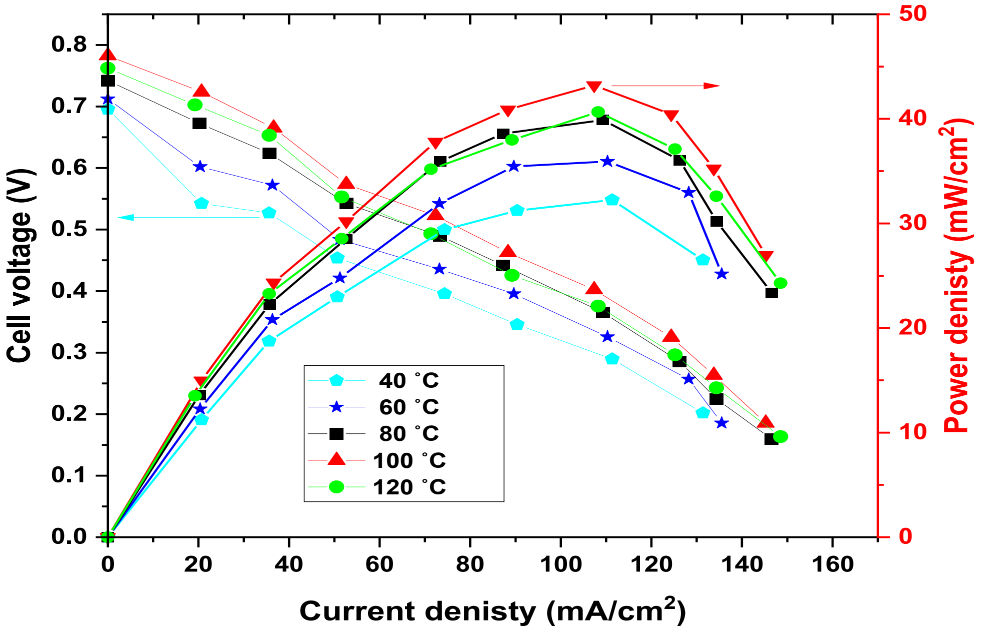

Figure 5.13 Effect of temperature on the DMFC single cell performance for the (Si-PWA)-PVA/PTFE membrane

The performance of the single cell DMFC with PTFE-ZrP-PVA, (Si-PWA)-PVA/PTFE composite membranes was compared with that of Nafion117 at higher temperature of 80℃ and

100°C respectively shown figure 5.14 and figure 5.15. The DMFC peak power density with PTFE-ZrP-PVA membrane is lower than Nafion 117 and (Si-PWA)-PVA/PTFE composite membrane as shown in figure 5.14.

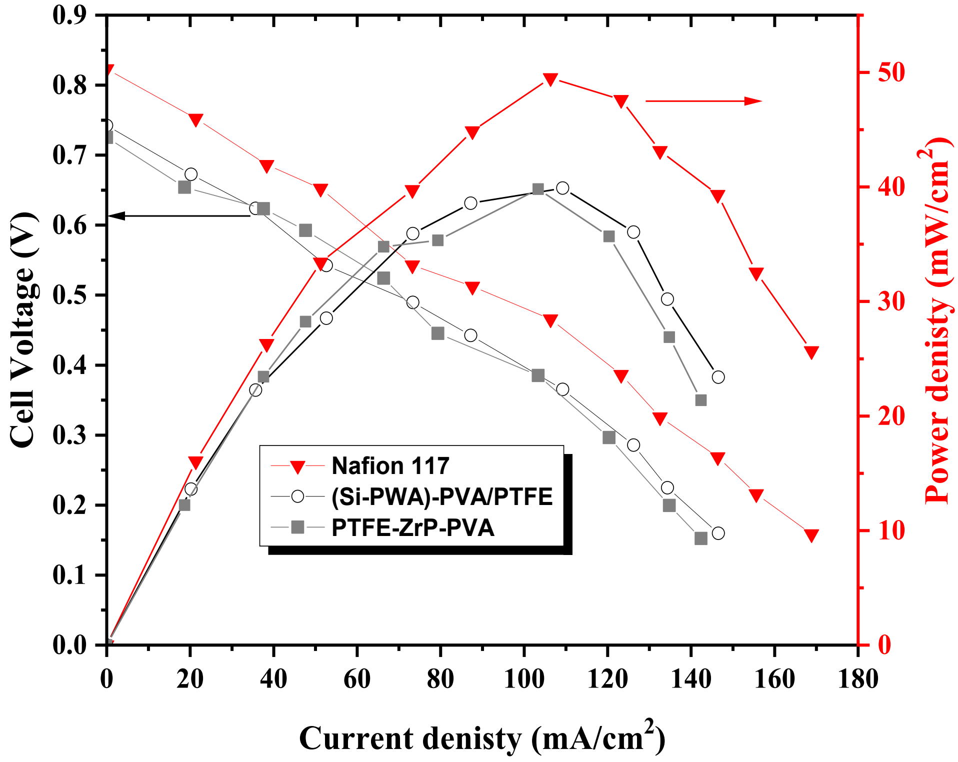

Figure 5.14 Comparison of DMFC performance with the PTFE-ZrP-PVA, (Si-PWA)-PVA/PTFE composite membranes and Nafion117 at 80 °C

The current density of the cell has increased substantially to a maximum value of 157.34 mA cm^{-2} (at 100°C) with the (Si-PWA)-PVA/PTFE composite membrane which is comparable with that of Nafion 117 (168.86 mA cm^{-2} at 80°C) as showed in figure 5.15. The (Si-PWA)-PVA/PTFE composite membrane is shown superior properties than the other reported composite membranes and near peak power density (i.e. 43.19 mW cm^{-2}) compared to Nafion 117. The DMFC results are compared and summarized in the table 5.4.

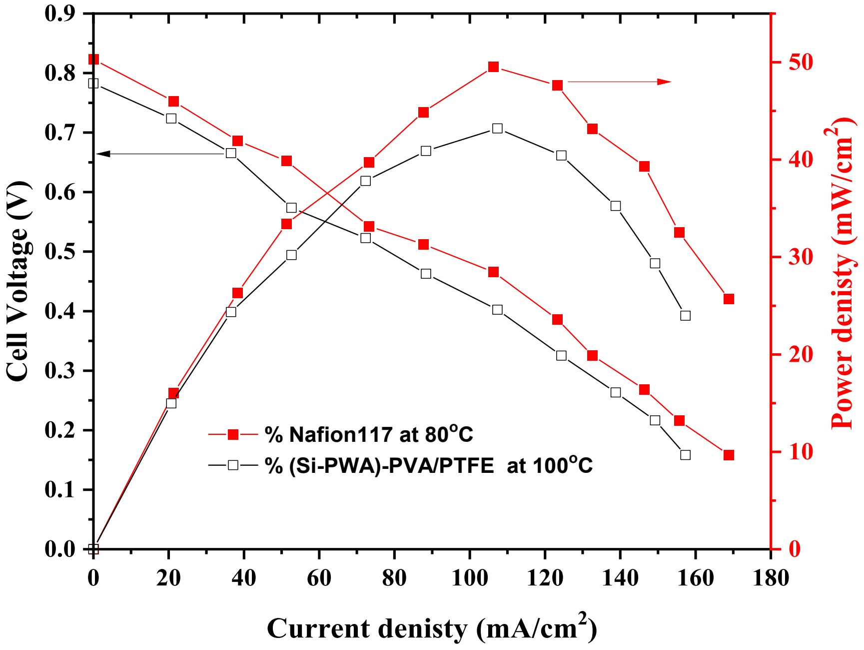

Figure 5.15 Polarization and power-density curves of the DMFC with the synthesized (Si-PWA)-PVA/PTFE membranes and Nafion 117 with 2M and 100%RH

Table 5.5 Comparative study for DMFC results of composite membranes

Membrane	**Methanol concentration (M)**	**Temperature (℃)**	**Relative humidity (RH) (%)**	**Current density (mA cm^{-2})**	**Maximum power density (mW cm^{-2})**	**Reference**
(Si-PWA)-PVA/PTFE	2	**100**	**100**	**107**	**43.19**	**Present study**
PTFE-ZrP-PVA	2	**80**	**100**	**103**	**39.8**	**Present study**
Nafion 117	2	**80**	**100**	**106.32**	**49.5**	**Present study**
Nafion 117	2	60	100	250	50	(Thiam et al. 2013)

PVA–ZrP–Cs$_1$SWA	4	30	60	4.8	2.02	(Helen et al. 2006)
PVA–ZrP–Cs$_2$SWA	4	30	60	11.09	5.07	(Helen, Viswanathan, and Murthy 2007)
ZrP/PVDF	2	30	60	52.73	50.9	(Pandey, Seepana, and Shukla 2015)

The improved performance at elevated temperatures can be related to higher proton conductivity and low methanol permeability of the PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE composite membrane. It is suggested that the (Si-PWA)-PVA/PTFE membrane is a promising alternative membrane for high temperature DMFC application.

5.4 Conclusion

The (Si-PWA)-PVA/PTFE composite membrane was developed by employing a pore-filling and LBL casting method for DMFC application at higher temperatures up to 120ºC. The hydrophilic nature of the PTFE support was enhanced by surface modification. The top layer thickness was optimized to be 60 µm and the composition of the sol was optimized as 0.3M PWA: 0.2M TEOS: 0.15M PVA. The morphological studies and elemental analysis were carried out by using SEM-EDX. The EDX spectrum has shown the incidence of all elements of the membrane. The interaction between the composition of the sol and support was analyzed by using FT-IR, and XRD. The interaction between PWA, TEOS, PVA and PTFE was observed by presence characteristic bonds of W–O–W corner-sharing, W-O-W edge-sharing, terminal W–O, Si–O–Si stretching, $-(CH_2)_2$ stretching and $-CF_2$ stretching symmetric. The broadened crystalline XRD peaks of PWA were noticed due to the presence of the amorphous phase of silica and PVA. The composite membrane was thermally stable up to 180˚C with aggregate weight loss of 4.1%. The customized (Si-PWA) - PVA/PTFE membrane shows higher IEC and water uptake values. The proton conductivity is increased with increasing temperature showed a maximum of 41.2mS cm^{-1} at 100˚C. The composite membrane has shown significantly low methanol permeability than that of Nafion117 in the temperature range of 28-120˚C. The membrane is economical compared to Nafion117. The open circuit voltage (OCV) of DMFC with (Si-PWA)-PVA/PTFE membrane is increased from 0.695 V to 0.782 V and peak power density increased substantially from 32.25 to 43.19 mW cm^{-2}, with increase in temperature from 40℃ to 100℃. The DMFC performance (Si-PWA)-PVA/PTFE composite membrane was shown superior properties than the other reported composite membranes and near peak power density (i.e. 43.19 mW cm^{-2}) compared to Nafion 117. The (Si-PWA)-PVA/PTFE membrane composite membrane has proven its suitability for DMFC at elevated temperatures.

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CHAPTER-6

CONCLUSION

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The PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE composite membranes were successfully synthesized for the DMFC application. The inorganic based PTFE-ZrP-PVA composite membranes was synthesized by a unique hybrid approach such as pore infiltration, and layer by layer (LBL) coating and followed by heat-treatment at 60℃. The wettability of the PTFE support was improved by chemical treatment using PVA, H_2O_2 and acrylic acid solution. Surface morphology of ZrP-PVA sol on the PTFE support was observed in SEM images. Presence of ZrP and PVA was confirmed by EDX and functional groups confirmed the presence of ZrP and PVA using FT-IR analysis. The TGA-DTA analysis indicated that the membrane was thermally stable up to 140°C. The membrane has good mechanical stability with a tensile strength of 44 MPa. The membrane possessed fair proton conductivity of 28.1 mS cm^{-1} and low methanol permeability (14.5×10^{-7} cm^2 s^{-1}) at 80°C. The membrane is economical compared to Nafion117. The composite membrane has exhibited competitive performance in DMFC single cell at 80°C i.e. 39.9 mW cm^{-2} with 2M methanol anode side and oxygen with 100% RH cathode side. It may be due to higher proton conductivity and low methanol permeability of the PTFE-ZrP-PVA composite membrane at higher temperatures.

The (Si-PWA)-PVA/PTFE composite membrane was developed by employing same method for DMFC application at higher temperatures up to 120ºC. The top layer thickness was optimized to be 60 μm and the composition of the sol was optimized as 0.3M PWA: 0.2M TEOS: 0.15M PVA with respective to proton conductivity and methanol permeability. The morphological studies and elemental analysis were carried out by using SEM-EDX. The EDX spectrum has shown the incidence of all elements of the membrane. The interaction between the composition of the sol and support was analyzed by using FT-IR, and XRD. The interaction between PWA, TEOS, PVA and PTFE was observed by the presence of characteristic bonds of W–O–W corner-sharing, W-O-W edge-sharing, terminal W–O, Si–O–Si stretching, $-(CH_2)_2$ stretching and $-CF_2$ stretching symmetric. The broadened crystalline XRD peaks of PWA were noticed due to the presence of the amorphous phase of silica and PVA. The composite membrane was thermally stable up to 180°C with aggregate weight loss of 4.1%. The customized (Si-PWA)-PVA/PTFE membrane shows higher IEC and water uptake values. The proton conductivity is increased with increasing temperature and showed a maximum of

41.2mS cm^{-1} at 100˚C. The composite membrane has shown significantly low methanol permeability than that of Nafion117 in the temperature range of 28-120˚C. The open circuit voltage (OCV) of DMFC with (Si-PWA)-PVA/PTFE membrane is increased from 0.695 V to 0.782 V and peak power density increased substantially from 32.25 to 43.19 mW cm^{-2}, with increase in temperature from 40℃ to 100℃. The DMFC performance (Si-PWA)-PVA/PTFE composite membrane was shown superior properties than the other reported composite membranes and near peak power density (i.e. 43.19 mW cm^{-2}) compared to Nafion 117(49.51 mW cm^{-2}).

The PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE composite membranes are economical and these possesses 2-3 folds low methanol permeability compared to that of Nafion 117.Low methanol permeability at a higher temperature of the composite membrane, makes it workable in direct methanol fuel cell (DMFC). The PTFE-ZrP-PVA composite membrane has underperformed with that of Nafion117 but (Si-PWA)-PVA/PTFE membrane has yielded comparable results at 100ºC. The (Si-PWA)-PVA/PTFE membrane composite membrane has proven its suitability for DMFC at elevated temperatures.

CHAPTER 7

SCOPE FOR FUTURE WORK

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This chapter describes the challenges that were faced while carrying out during research work and extending the work in the near future.

7.1 Challenges

The hydrophilicity is one of the important properties of the support. Low proton conductivity was observed with hydrophobic PTFE support and higher methanol permeability is expected with hydrophilic support. Hence, the optimal contact angle was adjusted with chemical treatment. Many membrane samples were synthesized and tested for proton conductivity and methanol permeability, as they are the basic properties of DMFC membranes. The composition of both the membranes was fine-tuned with respective to the above basic properties. Maintaining the humidity along with varied temperatures is one of the most difficult challenges that was faced while DMFC single cell testing.

7.2. Future Work

The composite membranes with optimized hydrophilicity can be tried to obtain the better DMFC performance. The present work was concentrated on asymmetric membranes, this work can be extended for symmetric composite membranes like PVA or SPEEK based membranes. The PTFE-ZrP-PVA and (Si-PWA)-PVA/PTFE membranes can be employed in DMFC stack for higher power generation. Experimental results can be modelled to get control over the operating parameters and optimize the performance of the fuel cell stack. As the synthesized membranes exhibited higher proton conductivity, having higher scope in other type fuel cells and flow batteries.

LIST OF ARTICLES PUBLISHED IN INTERNATIONAL JOURNALS

1. **Aruna Pagidi**, G.Arthanareeswaran, Murali Mohan Seepana, **"**Synthesis of highly stable PTFE-ZrP-PVA composite membrane for high-temperature Direct Methanol Fuel Cell" International journal of Hydrogen Energy, **Doi.org/10.1016/j.ijhydene.2019.04.164** **(*SCI:* Elsevier),** Impact factor:**4.939**

2. **Aruna Pagidi,** Murali Mohan Seepana, "Synthesis of (Si-PWA)-PVA/PTFE high temperature proton conducting composite membrane for DMFC", International journal of Hydrogen Energy, ***doi.org/10.1016/j.ijhydene.2020.02.113*** ***(SCI:*** **Elsevier),** Impact factor:**4.939**

3. **Aruna Pagidi,** Murali Mohan Seepana, "Application of composite membranes for high temperature DMFC studies", Manuscript is ready for communication.

4. **Aruna Pagidi,** Murali Mohan Seepana, "A review on composite membranes for DMFC application", Manuscript under preparation

LIST OF INTERNATIONAL CONFERENCES

1. **Aruna Pagidi,** G. Arthanareeswaranan**,** Murali Mohan Seepana "Purification and fouling studies of dairy effluent using SPEEK and bentonite based polymeric membranes", **INCEEE 2015**, 20-21 March, 2015 at NIT Warangal.

2. **Aruna Pagidi,** S. Murali Mohan, **"**Studies on Membranes for Direct Methanol Fuel Cell"**,** ICM 2015, 21-24 August 2015, Kochi, Kerala, India.

3. Murali M Seepana, Nitin T**, Aruna Pagidi,** "Simulation Study of Direct Methanol Fuel Cell for Optimizing the Cell Performance", **ICATI 2017,** 25-28 June 2017, Samui, Thailand.

4. **Aruna Pagidi**, Murali Mohan Seepana, "Synthesis And Characterization Of ZrP/PTFE Membrane For Energy Devices", **ICEE 2018,** March 9-10, 2018, NIT Calicut, Kerala, India.

5. **Aruna Pagidi,** S. Murali Mohan, "Synthesis of Sulfonated Polyether ether ketone (SPEEK) based composite membrane for DMFC", **INCEEE-2019**, 15-16 February, 2019 at NIT Warangal.

6. **Aruna Pagidi,** Murali Mohan Seepana," A review on composite membranes for DMFC application", **(IEEES-11),** July 14-18, 2019, Chennai, India

BIBLIOGRAPHY

Ms. Aruna Pagidi comes from Mancherial, Telangana. She attended the Osmania University, Hyderabad where she received her B.Tech degree in Chemical Engineering with distinction, in June 2012. She then went for advanced degrees, M.Tech, in Chemical Engineering with specialization in Chemical Engineering from National Institute of Technology, Trichy, with first class in June 2014. Then, she joined as a full-time PhD scholar in Department of Chemical Engineering from National Institute of Technology, Warangal, India for pursuing her Ph.D degree in December, 2014. Her research works focus on synthesis of composite membranes for high temperature DMFC applications. The development of composite membranes which are environmentally benign, cost effective, chemically and mechanically more stable at higher temperatures applications. She developed PTFE based composite membranes using various organic and inorganic ion exchangers for DMFC applications. Ms. Aruna Pagidi is submitting her Ph.D research work on Development of composite membranes for high temperature Direct Methanol Fuel Cell (DMFC) applications. She published her research findings in SCI Journals and has also presented research articles in International Conferences. Ms. Aruna Pagidi has strong desire and passion to continue her research works after Ph.D on various areas namely, synthesis of hybrid membranes, development of composite membranes for energy devices and waste water treatment.