

**THE REPUBLIC OF TURKEY
BAHÇEŞEHİR UNIVERSITY**

**SULFONATED POLY (VINYL ALCOHOL)-
MORDENITE MIXED MATRIX MEMBRANES FOR
DIRECT METHANOL FUEL CELLS**

Master's Thesis

JINAN NIJEM

ISTANBUL, 2016

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**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
ENERGY SYSTEMS OPERATION AND TECHNOLOGY**

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The thesis has been approved by the Graduate School of Natural And Applied
Sciences

Assoc. Prof. Nafiz ARICA
Graduate School Director
Signature

I certify that this thesis meets all the requirements as a thesis for the degree of Master
of Science.

Asst.Prof.Dr.Gürkan SOYKAN
Program Coordinator
Signature

This is to certify that we have read this thesis and we find it fully adequate in scope,
quality and content, as a thesis for the degree of Master of Science.

Jury Members

Signature

Asst. Prof. Dr. Fehmi Görkem ÜÇTUĞ

Asst. Prof. Dr. Gürkan SOYKAN

Prof. Dr. Ş. Birgül TANTEKİN ERSOLMAZ

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ABSTRACT

SULFONATED POLY (VINYL ALCOHOL)-MORDENITE MIXED MATRIX MEMBRANES FOR DIRECT METHANOL FUEL CELLS

Jinan Nijem

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Poly (vinyl alcohol) – mordenite (PVA-MOR) and a sulfonated poly (vinyl alcohol) – mordenite (SPVA-MOR) mixed matrix membranes were synthesized, characterized and compared for prospective direct methanol fuel cell use. SEM images showed a homogeneous distribution with no voids for both membranes. The methanol uptake was lower in the SPVA-MOR membrane which indicates lower methanol permeability. The water uptake was also lower in the SPVA-MOR membrane and this was linked to the blocking of the water adsorption sites in the membrane by the sulfonic acid groups. However the proton conductivity was higher for the SPVA-MOR membrane with a value of 0.052 S/cm which is 51 percent of that for Nafion membrane. This indicates that the sulfonation improved the proton conductivity in the SPVA-MOR membrane. The reason for this trend is thought to be relevant to the dominant of proton conductivity mechanism in membrane, which is more likely to be Grotthuss mechanism than the vehicular mechanism. Finally, an IEC value of 0.474 mequiv/g was obtained from the SPVA-MOR membrane which denote a low sulfonation degree in the membrane

Key words: Direct methanol fuel cell, Poly (vinyl alcohol), mordenite, mixed matrix membrane, Sulfonation

ÖZET

DOĞRUDAN METANOL YAKIT PİLLERİ İÇİN SÜLFONLU POLİVİNİLALKOL-MORDENİT MEMBRANLARIN GELİŞTİRİLMESİ VE KARAKTERİZASYONU

Jinan Nijem

Enerji Sistemleri İşletim ve Teknolojileri

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Doğrudan metanol yakıt pillerinde kullanılmak amacıyla polivinilalkol-mordenit (PVA-MOR) ve sülfonlu polivinilalkol-mordenit (SPVA-MOR) membranlar sentezlenmiş, karakterize edilmiş ve kıyaslanmıştır. Taramalı elektron mikroskobu analizlerinde membranların içindeki zeolite dağılımının homojen olduğu ve tanecikler arasında boşluklar olmadığı gözlemlenmiştir. SPVA-MOR membranların metanol emiliminin daha düşük olduğu gözlemlenmiş ve buradan yola çıkarak, bu membranların metanol geçirgenliklerinin de daha düşük olacağı sonucuna varılmıştır. SPVA-MOR membranlarda su emiliminin de daha düşük olduğu ölçülmüş, buna gerekçe olarak da membrane üzerinde suyun adsorbe olabileceği noktaların sülfonik asit grupları tarafından bloke edilmiş olması düşünülmüştür. Buna rağmen SPVA-MOR membranların proton iletkenliği 0.052 S/cm olarak ölçülmüştür ki bu değer PVA-MOR membranlara göre daha yüksek olup, Nafion ile ulaşılabilen değerlerin yaklaşık yüzde 51'i civarındadır. Bu sonuçlar bize sülfonlamanın proton iletkenliğini artırdığını göstermektedir. Bu durumun daha baskın proton iletkenlik mekanizmasının Grotthus mekanizması olması dolayısıyla gerçekleştiği düşünülmektedir.

Anahtar kelimeler: doğrudan metanol yakıt pili, polivinilalkol, mordenit, karışık matriksli membran, sülfonlama

CONTENTS

TABLES	viii
FIGURES	ix
ABBREVIATIONS	x
SYMBOLS	xii
1. INTRODUCTION	1
2. THEORETICAL BACKGROUND	4
2.1 DIRECT METHANOL FUEL CELL (DMFC)	4
2.2 DMFC COMPONENTS	4
2.2.1 Electrodes	4
2.2.2 Electrolyte	5
2.3 DMFC ADVANTAGES	6
2.4 DMFC OPERATION	7
2.4.1 Redox Reactions	7
2.4.2 The Role of Catalysts	8
2.4.3 Water Management	9
2.4.4 Protons transportation in the MEA	10
2.4.5 Voltage obtained in fuel cells	11
2.4.6 Efficiency of fuel cells	15
2.5 DMFC MEMBRANE	18
2.5.1 Nafion and Nafion Based Membranes	18
2.5.2 The use of Poly (vinyl alcohol) (PVA) polymers in membranes ..	20
2.5.3 The use of Zeolites in membranes	24

2.5.4 PVA- Mordenite mixed matrix membranes	27
3. METHODOLOGY.....	33
3.1 PVA- MORDENITE MEMBRANE FABRICATION.....	33
3.1.1 Materials used:	33
3.1.2 Synthesis of PVA- MOR membrane:	33
3.2 SULFONATED PVA-MORDENITE MEMBRANE FABRICATION... 34	
3.2.1 Materials used:	34
3.2.2 Synthesis of the membrane.....	34
3.3 STRUCTURAL ANALYSIS	35
3.4 SWELLING MEASUREMENTS:.....	36
3.5 ION EXCHANGE CAPACITY (IEC).....	37
3.6 PROTON CONDUCTIVITY	37
4. RESULTS AND DISCUSSION	41
4.1 STRUCTURAL ANALYSIS	41
4.2 SWELLING MEASUREMENTS	43
4.3 ION EXCHANGE CAPACITY	45
4.4 PROTON CONDUCTIVITY	45
5. CONCLUSION.....	48
REFERENCES.....	50

TABLES

Table 2.1: MEA Components and Their Tasks.....	6
Table 2.2: Properties of PVA Based Membranes.....	23
Table 2.3: The Properties of DMFCs Membranes Having Zeolite Fillers	27



FIGURES

Figure 1.1: Basic fuel cell operation.....	2
Figure 2.1: Schematic graph for a dual- layer GDL.....	5
Figure 2.2: Different Water Movements	10
Figure 2.3: Voltage-Current Relationship for a fuel cell at Low Temperature and Air Pressure.....	16
Figure 2.4: Effect of Methanol Crossover on DMFC Voltage	17
Figure 2.5: Nafion Structure.....	19
Figure 2.6: Different Coordinations of Zeolites Tetrahedral Frameworks.....	25
Figure 2.7: Pathways For Protons and Methanol	29
Figure 2.8: Potential Transport Mechanisms.....	30
Figure 2.9: Comparison of the ideal and the non-ideal	31
Figure 3.1: Schematic diagram for the sulfonation of the PVA matrix.....	34
Figure 3.2: Basic Construction of SEM	36
Figure 3.3: Nyquist Plot for Nafion 112.....	40
Figure 4.1: SEM Images for the surface of PVA-MOR membrane	41
Figure 4.2: SEM image for the PVA- mordenite.....	42
Figure 4.3: SEM images for the surface of SPVA-MOR membranes	43
Figure 4.4: Water and Methanol Uptake	44
Figure 4.5: Liquid uptake from another study	45
Figure 4.6: Comparison of Proton Conductivity Measurements for different membranes	46

ABBREVIATIONS

CL	:	Catalytic Layer
CNT	:	Carbon Nanotubes
DMFC	:	Direct Methanol Fuel Cell
GDL	:	Gas Diffusion Layer
g-GO	:	grafted graphene oxide
IEC	:	Ion Exchange Capacity
Im	:	imidazole amino acid
MEA	:	Membrane Electrode Assembly
MMMs	:	Mixed matrix membranes
MMT	:	Montmorillonite
MOR	:	Mordenite
MSA	:	Methane sulfonic acid
PEM	:	Polymer Electrolyte Membrane
PEMFC	:	Proton Exchange Membrane Fuel Cell
PMAV	:	Poly (Methacrylic acid-2-acrylamido-2-methyl-1-propanesulfonic acid-vinyltriethoxysilicone)
PSSA	:	Polystyrene sulfonic acid
PTFE	:	Polytetrafluoroethylene
PVA	:	Poly (Vinyl alcohol)
SEM	:	Scanning Electron Microscope
SPANi	:	Partially sulfonated polyaniline
SPEEK	:	Sulfonated poly ether ether ketone

SPVA : Sulfonated Poly (Vinyl alcohol)



SYMBOLS

Area	:	A
Current	:	I
Efficiency	:	η
Enthalpy	:	H
Entropy	:	S
Faraday's constant	:	F
Gibbs free energy	:	G
Impedance	:	Z
Internal energy	:	U
Methanol permeability	:	β
Molar gas constant	:	R
Number of electrons	:	n_e
Number of moles	:	n
Phase shift	:	θ
Potential difference	:	E
Pressure	:	P
Proton conductivity	:	σ
Resistance	:	r
Selectivity	:	α
Standard Energy	:	E°
Temperature	:	T
Thickness	:	L

Time : t
Volume : V
Work : W



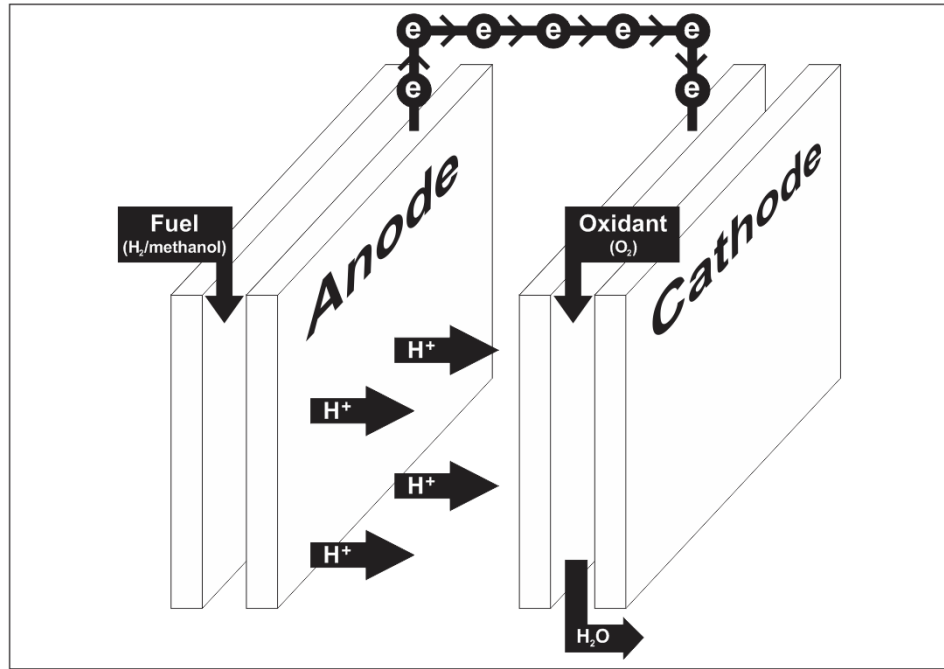
1. INTRODUCTION

During the last centuries the demand for conventional fossil fuels to be used in energy production has increased dramatically. In addition to its probability of depletion in the coming decades, the conventional fossil fuels have also become a source for many environmental problems. The increased amounts of greenhouse gases (especially CO₂) emitted have the main responsibility for the global warming issue. Moreover, hazardous chemicals (like CO, NO_x and SO_x) emitted cause many environmental problems like air pollution and acid rain. Therefore, many efforts were directed to find alternative, clean and sustainable sources of energy. One of those alternatives is fuel cells which has recently received much attention due to its high energy density and near zero emissions.

Fuel cell is an electrochemical device that generates energy continuously as long as electroactive chemicals are supplied. It resembles the batteries in the sense that it converts chemical energy into electrical energy however it differs from batteries because it does not need to be charged. The core components of fuel cells are an anode and a cathode which are called the electrodes, in addition to an electrolyte in between them. Oxidation and reduction reactions take place in the electrodes by means of catalysts. In the anode, an oxidation reaction occurs resulting in releasing electrons and charged ions. The electrons pass through an external circuit to produce current whereas the charged ions permeate through the electrolyte which is responsible for selective transport of the ions, acting as a barrier for electrons flow. After the charged ions reached the cathode, they meet the electrons and undergo reduction reaction (Üçtuğ 2008). See Figure 1.1.

There are various types of fuels that could be utilized in fuel cells. The hydrogen was the most common fuel used in fuel cells due to its high energy density. However, hydrogen is a hard fuel to be obtained and stored. Other than the hydrogen which is widely used, methanol as a liquid fuel has recently received a great deal of attention due to its promising characteristics in terms of production, storage and handling in addition to its very high specific energy (3800 kcal/L) compared to hydrogen (658 kcal/L) (Meenakshi et al. 2013).

Figure 1.1: Basic fuel cell operation



Lately, Direct Methanol Fuel Cell (DMFC) has become a possible attracting option due to their simple operation, high energy per unit volume, lightweight, compactness, and the ability for fast refueling. However, there are several challenges which should be overcome to be able to commercialize the DMFCs. This includes methanol crossover which permeates from the anode to the cathode while DMFC is operating, the relatively low kinetics in the anode, which decreases the power density, and the chemical stability which is not well achieved (Kim et al. 2015).

Most DMFCs is a type of Polymer Electrolyte Membrane (PEM) which employs a solid polymer membrane as an electrolyte (Üçtuğ 2008). In order for a material to be used as a membrane for DMFCs, it should have high proton conductivity, high electronic insulation, chemical and mechanical stability and prevent the crossover of methanol. Besides it should be cost effective and readily available (Maiti et al. 2012). The most known benchmark used for DMFC membranes is DuPont's Nafion®. This membrane provides excellent thermal and mechanical properties besides remarkably high protonic conductivity. However this membrane has the drawbacks of high cost, high methanol crossover, and loss of conductivity at high temperatures. These problems are still restricting the performance and applications of DMFCs. Because of these

reasons, much research is being directed towards proposing novel membranes which may overcome these problems (Yun et al. 2011; Tseng et al. 2011; Changkhamchom & Sirivat 2014; Bahavan Palani et al. 2014; Yoo et al. 2014).

Recently, Poly (vinyl alcohol) (PVA) based membranes have been widely used to prepare DMFCs membranes due to its high capacity to form films, inexpensive cost, its excellent capability to reduce methanol crossover, besides its good chemical and mechanical properties (Zhong et al. 2014). However, Pure PVA has a very low conductivity for protons ($\approx 0.014 \text{ S cm}^{-1}$) (Pivovar et al. 1999). Therefore, it is necessary for PVA to be modified in order to be used as a membrane in DMFCs.

In this work Both a PVA-mordenite and a sulfonated PVA – mordenite membrane will be synthesized characterized and compared.

Chapter 2 gives basic information about direct methanol fuel cells, their structure, advantages, operation and it focuses on the membrane of DMFCs. Chapter 3 explains the experimental procedure for synthesizing and characterizing PVA-mordenite membrane and sulfonated PVA-mordenite membrane. Chapter 4 gives the main results and the discussions of the results are presented in chapter 5. Finally, Chapter 6 is a conclusion.

2. THEORETICAL BACKGROUND

2.1 DIRECT METHANOL FUEL CELL (DMFC)

It is a type of fuel cells which uses methanol directly as a fuel. Like all types of fuel cells, DMFC is composed of two electrodes, anode and cathode, and an electrolyte. These components are called Membrane Electrode Assembly (MEA). The MEA is located between two current collector plates with flow field channels to feed the anode with fuel and the cathode with oxidant (Hoogers 2003). Each MEA forms a cell. However, the voltage which results from each fuel cell is quite small. Thus, several cells should be connected in series to produce a useful voltage. This collection of fuel cells in series is called a “Stack”. There are also other auxiliaries which could be also integrated in the system so that the system could operate in the desired way such as pumps, compressors, controllers, etc (Aricò et al. 2010; Larminie & Dicks 2003).

2.2 DMFC COMPONENTS

2.2.1 Electrodes

The electrode is the name given for the anode and the cathode. Each electrode is usually consisting of two layers:

i. The catalytic layer:

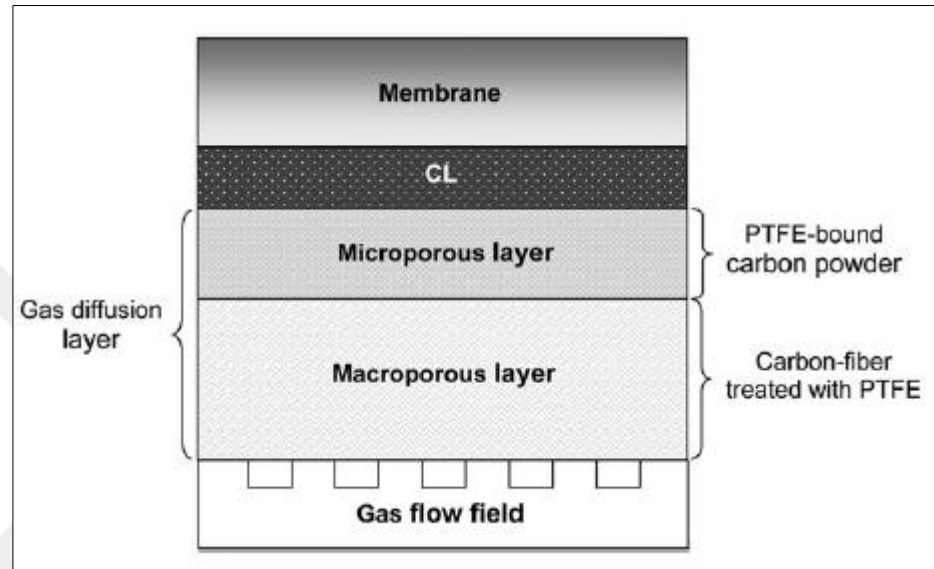
This layer consists of a very small catalyst particles formed on the surface of larger porous carbon ionomer particles. The catalysts presented are responsible for the motivation of the redox reactions on the electrodes (Aricò et al. 2010; Larminie & Dicks 2003).

One of the distinctive properties of this layer is having a dual electronic-ionic conductivity (Aricò et al. 2010). To elaborate, the ions generated by redox reactions on the electrodes should ionically transport to the electrolyte membrane. At the same time the electrons released from the reactions should transport electronically to the current collectors. Therefore, to be effectively utilized from the catalyst layer, it should form an active electrocatalyst site which is in contact with the reactants besides being connected electrically to the current collectors and ionically to the membrane (Üçtuğ 2008).

ii. The gas diffusion layer (GDL)

This layer is established between the gas flowing field and the catalyst layer. It consists of either a single layer from a macroporous substrate or dual- layer consists of a thin microporous carbon layer on a sheet of macroporous carbon cloth or carbon paper. Figure 2.1 shows the configuration of the dual- layer (Park et al. 2012).

Figure 2.1: Schematic graph for a dual- layer GDL.



Source: (Park et al. 2006)

This layer has many functions which could have effects on the catalyst utilization and on the efficiency of the fuel cell in general. It does not only allow the gas transport toward the catalyst layer but also forms a supportive layer to maintain the very thin catalyst layer. Moreover, it connects the ionomer and the current collector electrically and plays a major role in water management inside the membrane of the DMFC (Larminie & Dicks 2003; Park et al. 2012)

2.2.2 Electrolyte

The electrolyte in DMFC is usually a solid polymer membrane which is mainly responsible for the selective transportation of ions and at the same time, acting as a barrier for electron transportation.

The membrane of DMFC is discussed in more details in section 2.5

Table 2.1 summarizes the different tasks for each MEA component in DMFCs

Table 2.1: MEA Components and Their Tasks.

MEA Component	Task / Effect
Anode Diffusion Layer	Fuel supply and distribution Electron conduction
Anode Catalyst Layer	Heat removal from reaction zone Catalysis of anode reaction Proton conduction into membrane Electron conduction into substrate Water transport (membrane humidification)
Proton Exchange Membrane	Heat transport Proton conduction Water transport Electronic insulation
Cathode Catalyst Layer	Catalysis of cathode reaction Oxygen transport to reaction sites Proton conduction from membrane to reaction sites Electron conduction from substrate to reaction zone Water removal from reaction zone into substrate
Cathode Diffusion Layer	Heat generation / removal Oxidant supply and distribution (air / O ₂) Electron conduction towards reaction zone Heat removal Water transport (liquid / water)

Source: (Hoogers 2003)

2.3 DMFC ADVANTAGES

i. Superior specific energy density

Methanol has a high specific energy (6000 Wh/kg). This makes the devices which employ DMFCs lighter, more compact and could be used for long time before replacement. In addition to that, this makes the DMFCs suitable to be used in automotive applications (Hoogers 2003).

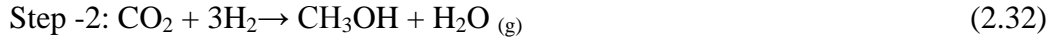
ii. Methanol is easy to produce

Methanol could be synthesized simply from hydrocarbons like natural gas. The most widely reactions used are: (Larminie & Dicks 2003)

Method 1



Method 2



iii. Ease of handling

DMFCs are easy to handle and transport. In addition to its simple design which contains no moving parts, the electrolyte of DMFCs is a solid membrane so once put in place; it does not redistribute, diffuse, or evaporate. Therefore the cell could operate steadily without intermitting or exposed to rapid load changes possibilities (Hoogers 2003).

iv. The possibility of instantaneous refueling

DMFC does not need to be charged like batteries. It is ready to operate once it is fed with the fuel and oxidant.

2.4 DMFC OPERATION

2.4.1 Redox Reactions

Redox reactions are chemical reactions during which the electrical charge of one or more atoms changes (Üçtuğ 2008). It consists of two complementary reactions: an oxidation reaction in which the atom loses electrons and a reduction reaction in which the atom gains electrons.

In the DMFC the oxidation reaction occurs in the anode with the existence of PtRu catalyst where the methanol is oxidized, resulting in releasing electrons and ions. On the other hand the reduction reaction occurs in the cathode with the aid of Pt catalyst during which the electrons and ions meet the oxidant and recombine forming water.

The oxidation and reduction reactions in DMFCs are given in the following reactions:

Anode:



Cathode:



The overall reaction:



2.4.2 The Role of Catalysts

Unlike the simplicity of the oxidation reaction of hydrogen which is used as a fuel in most types of fuel cells, methanol oxidation is much more complex. It involves the releasing of six electrons in step-wise process. Therefore, improving the anodic kinetics becomes an urgent need.

As with hydrogen fuel cells, platinum catalyst was used initially in the anode. However, this catalyst shows only poor performance. This is because a strongly bonded CO_{ads} creates a poisoning coat on the surface of the pure platinum. This layer should be oxidized to CO_2 so as to allow further electro sorption of methanol to occur. At potentials below 450 mV, this process is executed tardily so that the surface of pure platinum remains poisoned. To solve this problem, another noble metal was used as a catalyst along with the platinum. This shows significant improvement on the kinetics of the anode (Hamnett & Kennedy 1988; Hoogers 2003; Üçtuğ 2008). It is now well known that the standard binary metals used are a mixture of 50:50 platinum / ruthenium (PtRu). There are also other metals which could be used like SnRu, but still those metals show inferior performance when compared with PtRu (Cremers et al. 2005; Cheng et al. 2005).

At the cathode, the reduction of oxygen to water is the same in hydrogen and methanol fuel cells. This reaction is known to be the rate determining step in hydrogen fuel cells. However, in the case of methanol fuel cells this reaction is much simpler than the oxidation of methanol so the rate determining step in this kind of fuel cells becomes the oxidation reaction of methanol (Üçtuğ 2008). Usually, the platinum catalyst is used in

the cathode of DMFC just like hydrogen fuel cells. Some researchers suggest using non-platinum cathode catalyst so as to solve the problem of mixed potential problem caused by the oxidation of methanol crossed to the cathode (Aricò et al. 2010).

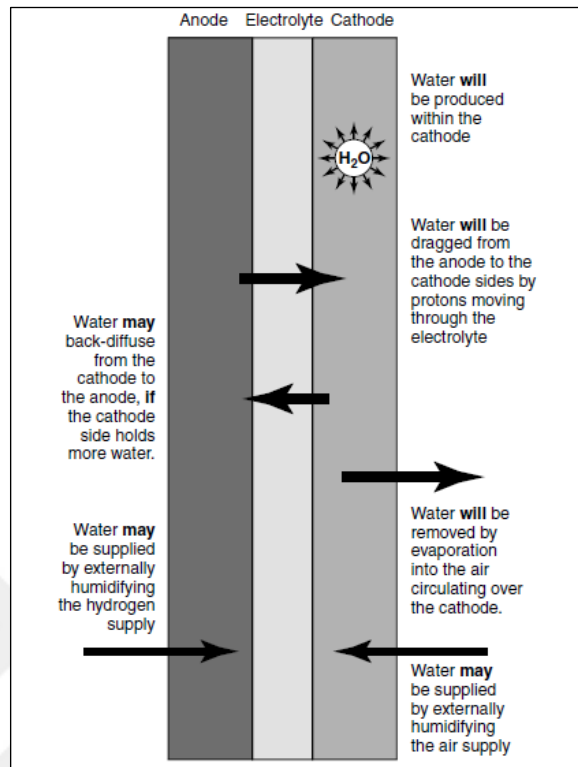
2.4.3 Water Management

Water management is an essential issue in DMFCs. Firstly, as it is shown in the anode reaction in 2.1 , in addition to the methanol ,water is also a requirement to undergo the oxidation reaction in the anode (Larminie & Dicks 2003). Secondly, the transportation of the protons through the membrane depends strongly on the presence of water inside the MEA. The proton's transportation in the MEA will be discussed later in section 2.4.4. Thus; the membrane should be hydrated sufficiently to achieve the highest amount of proton conductivity through the membrane. Furthermore, insufficient water content may cause the membrane and the catalyst layer to in contact to each other which results in an intense resistance between them. On the other hand, too much water may cause flooding in the electrodes and may block the pores in the electrodes and reduce the electrocatalyst sites. Therefore, the water content should be optimized (Larminie & Dicks 2003; Park et al. 2012).

In the ideal scenario, water is produced in large quantities in the cathode according to equation 2.2 and this water could diffuse from the cathode side to the anode side achieving the hydration needed in the cell. However things are not as simple as this. Firstly, water is susceptible to evaporate at high temperatures or when air passes over the cathode. So if the water evaporation rate exceeds the water formation rate, we will need to replenish the water inside the cell. Secondly, during the operation of the cell the protons moving from anode to cathode may pull water molecules with them. This may lead to a phenomenon called “*electro-osmotic drag*” which causes drying in the anode while the cathode is well hydrated (Hoogers 2003; Larminie & Dicks 2003).

Figure 2.2 below shows all the different water movements in the fuel cell.

Figure 2.2: Different Water Movements through the MEA.



Source: (Larminie & Dicks 2003)

2.4.4 Protons transportation in the MEA

The transportation of the protons through the membrane depends strongly on the presence of water inside the MEA as mentioned above.

Protons' transport through the membrane is done mainly using two mechanisms, the vehicle mechanism and Grotthuss mechanism which is also called "proton hopping" (Hoogers 2003).

In the vehicle mechanism the proton transports through the membrane by using a "vehicle". In this mechanism the proton attaches itself to a solvent like water which is the vehicle to form a hydronium ion like H_3O^+ , H_5O_2^+ , or H_9O_4^+ , which diffuses through the medium (Kim, J., Kim, B., Jung 2002; Agmon 1995; Kreuer 1996). In Grotthuss mechanism, protons hop from one water molecule to the other by continuously forming and breaking of hydrogen bonds. This mechanism is also called

“proton hopping” and it is responsible for approximately 90 percent of proton conductance in the membrane (Bockris, 1998). This is because the rate of proton transfer in Grotthuss mechanism is much higher than that in vehicular mechanism. In vehicular mechanism the rate of proton transfer depends on the rate of vehicular diffusion however in Grotthuss mechanism the rate of proton transfer is a function of the activation energy of proton transfer from one molecule to the other and because the free protons are short-lived this occurs spontaneously in a very short time (Li X., 2007).

2.4.5 Voltage obtained in fuel cells

To evaluate the performance of fuel cells we need to calculate the power output of them. To do that the voltage difference established on the opposite sides of the membrane at the end of the electrochemical reaction should be calculated. The fundamental equation which gives this value is called “Nernst Equation”. To reach this equation, we should begin first with the definition of Gibbs free energy (Laidler & Meiser 1999; Üçtuğ 2008).

Gibbs free energy (G) is defined as a thermodynamic potential which gives the useful work that the system can conduct in an isothermal and isobaric state. In fuel cells, this corresponds to the portion of the reaction enthalpy that can be converted to electricity (Dorf & Barbir 2005; Üçtuğ 2008). This could be written as the equation below:

$$G= H -TS \quad (2.4)$$

Where H is the enthalpy, T is the temperature and S is the entropy.

But

$$H= U + PV \quad (2.5)$$

Where U is the internal energy, P is the pressure and V is the volume. Then Gibbs free energy can be given as

$$G= U + PV -TS \quad (2.6)$$

For any change,

$$dG = dU + PdV + VdP - TdS - SdT \quad (2.7)$$

In isobaric ($dP=0$) and isothermal ($dT =0$) process this becomes:

$$dG = dU + PdV - TdS \quad (2.8)$$

Based on the first law of thermodynamics,

$$dU = dq + dw \quad (2.9)$$

where q is the heat and w is the work

For a process in which the system undergoes a volume change dV , the PV work is $-PdV$ and the total work thus

$$dw = dw_{pv} + dw_{non-pv} = -PdV + dw_{non-pv} \quad (2.10)$$

Then,

$$dG = dq + dw_{non-pv} - TdS \quad (2.11)$$

However, since the process is reversible, $dq = TdS$ Therefore,

$$dG = dw_{non-pv} \quad (2.12)$$

Or,

$$\Delta G = w_{non-pv} \text{ at constant T and P} \quad (2.13)$$

The electrochemical work done in the fuel cell is defined as the work done by the electrons which have the charge of $n_e F$ to move through a potential difference of E

$$W_{cell} = n_e F E \quad (2.14)$$

Where n_e is the number of electrons and F is the Faraday's constant which is equal to (96485 C/ mol). This value corresponds to the charge of the electrons times Avogadro's number.

So the Gibbs free energy in the fuel cell can be given as

$$\Delta G = - n_e F E \quad (2.15)$$

The potential difference in fuel cells depends on the standard electrode potentials, so we can define the standard Gibbs energy as:

$$\Delta G^\circ = - n_e F E^\circ \quad (2.16)$$

If we want to incorporate the effect of pressure onto Gibbs free energy and assume that the process is reversible (dQ cancels TdS) and the system is restricted to do only expansion work (dw cancels PdV) and the system is isothermal ($dT = 0$), then equation (2.7) will reduce to:

$$dG = VdP \quad (2.17)$$

Using the ideal gas law:

$$PV = nRT \quad (2.18)$$

Where P : Pressure, V : Volume, n : number of moles, R : molar gas constant and T : the temperature

Then,

$$dG = nRT \frac{dP}{P} \quad (2.19)$$

Taking the integral:

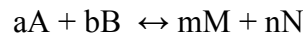
$$\int_1^2 dG = nRT \int_1^2 \frac{dP}{P} \quad (2.20)$$

This gives the Gibbs free energy for a change in Pressure while the Temperature is constant:

$$G_2 - G^\circ = nRT \ln\left(\frac{P_2}{P^\circ}\right) \quad (2.21)$$

$$G_2 = G^\circ + nRT \ln\left(\frac{P_2}{P_1}\right) \quad (2.22)$$

For a reaction with the following stoichiometric coefficients,



Equation (2.22) is substituted for each of the four terms, and then the four terms are collected together and simplified to get:

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_M^m P_N^n}{P_A^a P_B^b}\right) \quad (2.23)$$

The reaction quotient for the pressures is replaced by Q,

$$Q = \frac{P_M^m P_N^n}{P_A^a P_B^b} \quad (2.24)$$

Then, the expression is simplified into:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (2.25)$$

Finally, if we substitute (2.16) and (2.15) into (2.22)

Then we can get the “Nernst Equation” which is:

$$E = E^\circ - \frac{RT}{n_e F} \ln Q \quad (2.26)$$

(Hoogers 2003; Laidler & Meiser 1999; Üçtuğ 2008)

2.4.6 Efficiency of fuel cells

As it is mentioned in the previous section the Gibbs free energy in fuel cells is defined as the enthalpy of the reaction minus the irreversible losses that could be occurred because of entropy.

$$\Delta G = \Delta H - T\Delta S \quad (2.27)$$

The maximum Gibbs free energy could be obtained when $\Delta S = 0$ which means that the reaction is reversible and no losses are occurred.

So we can define the efficiency of the reaction as:

$$\eta = \Delta G / \Delta H \quad (2.28)$$

The Nernst Equation derived in the previous section shows that in any electrochemical reaction, the voltage which could be obtained is lower than the standard potential (E°) (Üçtuğ 2008).

DMFCs are known to have lower efficiencies than other types of fuel cells. This is mainly because of the slow anodic kinetics and the methanol crossover.

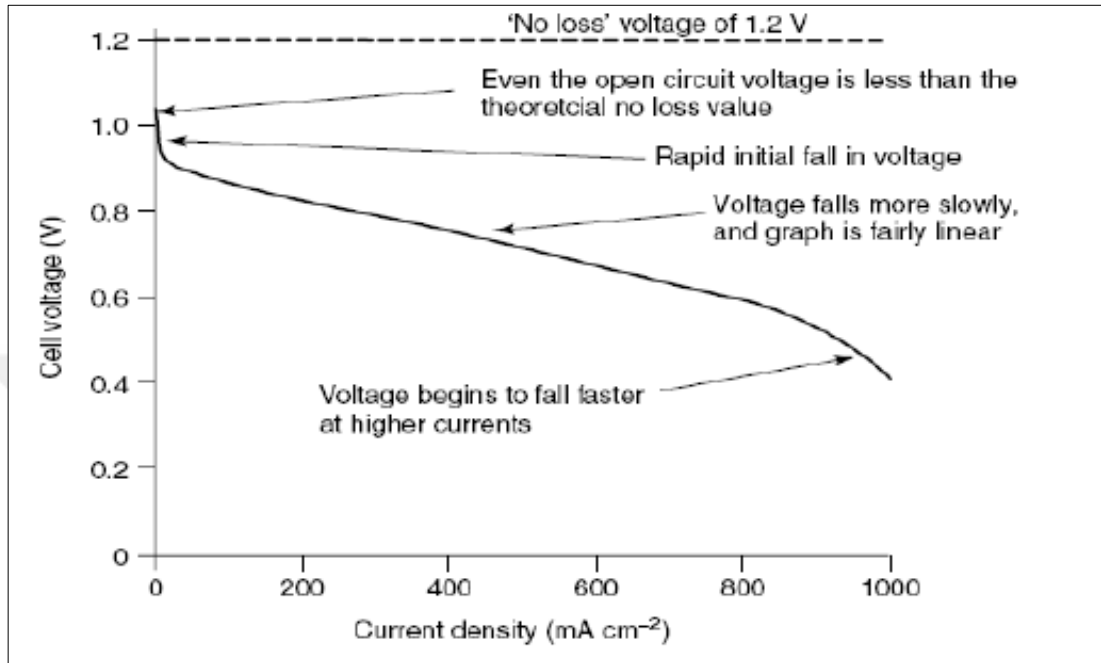
Figure 2.3 below shows the voltage losses as a function of current densities

There are different reasons which are responsible for the voltage losses in direct methanol fuel cells. The major reasons are (Larminie & Dicks 2003):

- i. **Activation Losses:** These losses take place at very low current densities because of the low rate of the reactions carried out in the electrodes. At that point the reverse reaction is taking place at the same rate of the forward reaction so a continual flow of electrons back and forth from and to the electrolyte is occurred. Therefore, an attribute of the generated voltage will be wasted in driving the chemical reaction that transports the electrons to or from the electrode. At high current densities, the surface of the electrode is more “active” so the current flow will be shifted in one particular direction and the performance will get better. To reduce this activation losses, some methods could be used such as increasing the cell temperature, using more active catalysts, increasing the roughness of the electrodes, increasing the

concentration of the reactants (especially the oxidant in the cathode side) and increasing the pressure.

Figure 2.3: Voltage-Current Relationship for a fuel cell at Low Temperature and Air Pressure



Source: (Larminie & Dicks 2003)

- ii. **Ohmic Losses:** This voltage drop occurs because of the electrical resistance through the material of the electrodes, current collectors, etc., as well as the resistance to ionic conduction through the electrolyte. This voltage drop is merely proportional to current density based on the equation:

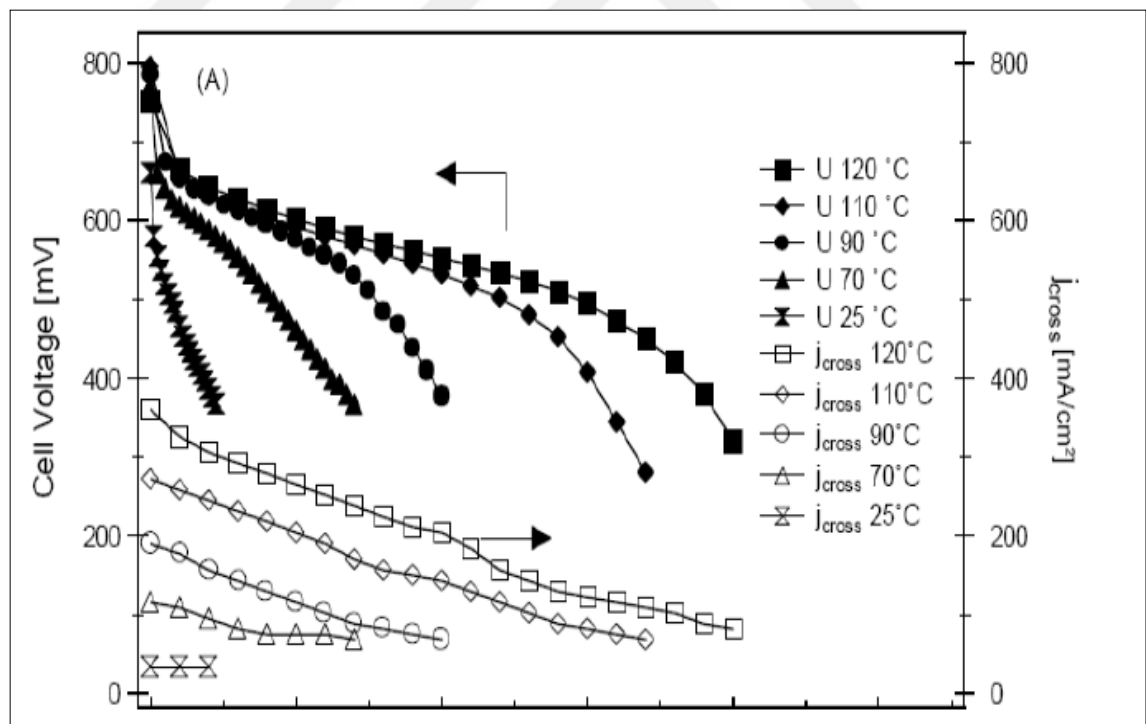
$$\text{Voltage} = \text{Current} \times \text{Resistance}$$

Therefore, this drop is highly linear. To reduce these internal resistances, proper design for the construction and the materials used in the electrodes, the electrolyte and other components should be taken into consideration.

- iii. **Mass Transport or Concentration Losses:** This source of losses outcome from the variation in the fuel concentration in the anode and the oxidant concentration in the cathode. These changes in concentrations will affect the pressure of the reactants and as it was shown in Nernst Equation, this change will affect the voltage.

iv. **Fuel Crossover and Internal Currents:** These losses occur due to the permeation of the fuel and to a lesser extent the electrons through the electrolyte from the anode to the cathode. The electrolyte should act as a barrier to methanol and electrons flow and at the same time should have high ionic conductivity. Fuel crossover does not only waste the fuel when methanol goes unreacted, but also it creates a reverse potential when methanol contacts the platinum sites on the cathode side, and undergoes oxidation reaction (Jung et al. 2006). To visualize the seriousness of this problem, Figure 2.4 below shows how much the performance of DMFC is affected by the methanol crossover. The black data points are the actual voltage values recorded during DMFC operation at different temperatures whereas the white data points represent the calculated voltage losses occurring as a result of methanol crossover. Based on this figure, it was noticed that at certain temperatures, almost 30-40 percent of the actual voltage is lost only because of methanol crossover (Üçtuğ 2008).

Figure 2.4: Effect of Methanol Crossover on DMFC Voltage



Source: (Friedrich et al. 2004)

To overcome this problem, the membrane of the fuel cell should be designed properly to have high proton conductivity and at the same time low methanol permeabilities and this is the main purpose of this study.

2.5 DMFC MEMBRANE

As it is mentioned before, DMFC employs a solid membrane as an electrolyte. This membrane should have high proton conductivity and at the same time should act as a barrier for methanol and electrons flow. A parameter called “selectivity” is usually used as a measure for the transport properties of fuel cell membranes. This parameter is defined as “*the ratio of proton conductivity to methanol permeability*”, as shown in the equation below:

$$\alpha = \frac{\sigma}{\beta} \quad (2.33)$$

Where α is the selectivity, σ is the proton conductivity and β is the methanol permeability. However, this parameter is deceiving sometimes. To elaborate, the membrane could have extremely high proton conductivity and high methanol permeability or it could have very low methanol permeability with poor proton conductivity. These cases could lead to high selectivity values however the actual DMFC performance will not be that good (Üçtuğ 2008).

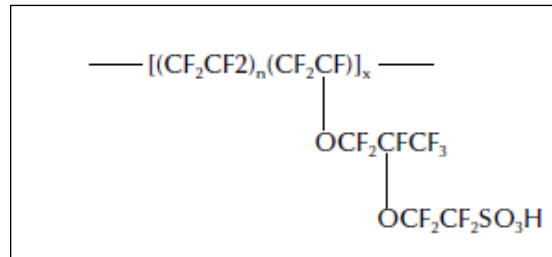
In addition to these properties, the membrane should have good thermal and mechanical properties and should be commercially available and inexpensive.

The most commercially trademark known is Nafion®. However, there are many efforts from the scientists to suggest novel membranes which could have high selectivity and could solve the problem of methanol cross over. In the following sections some of these efforts are reviewed.

2.5.1 Nafion and Nafion Based Membranes.

Until now, Nafion® membranes are the most trademarks used in DMFCs. This is because Nafion® membranes have a very high proton conductivity which is close to 0.1 S cm^{-1} (Libby et al. 2003). The molecular structure of Nafion membranes are shown in Figure 2.5.

Figure 2.5: Nafion Structure



Source: (Hoogers 2003)

The polymer used in Nafion® is polytetrafluoroethylene (PTFE) which has the trade name of Teflon®. This polymer forms the backbone of the membrane and it plays a role in water management as it is strongly hydrophobic. The polymer is sulfonated by a side chains ended with acid groups which is (SO_3^-). This group is ionically bonded to the hydrogen atom (SO_3H). This sulfonic acid groups gives the polymer its proton conducting characteristics.

However, Nafion membranes are firstly designed to be employed in other types of fuel cells which are “Proton Exchange Membrane Fuel Cells” (PEMFC). This type of fuel cells has the same structure of DMFCs but the only difference is that they employ the hydrogen as a fuel. Therefore, methanol crossover in Nafion® is quite high in DMFCs. It has values of the order $10^{-6} \text{ cm}^2 \text{ S}^{-1}$ where the exact values of the permeability depends on thickness. For example Nafion® 117, which is 175 μm thick, has a methanol permeability of $2.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Li et al. 2005).

Many efforts were carried to improve the performance of Nafion® by making modifications. (Cui et al. 2015) prepared a composite of Nafion® based membrane enhanced with ammonium-X zeolite fillers. Two different sized NH_4 -X zeolites were used: Nano (30-100 nm) and sub-micron (200-300 nm) with loadings of 5 wt percentage and 10 wt percentage. Both of the composite membranes showed a slightly higher proton conductivity and lower methanol permeability than pristine Nafion®. The submicron NH_4 -X zeolite/Nafion® composite membrane with 5 wt percentage loading showed the highest selectivity value ($37.4 \times 10^4 \text{ s.S.cm}^{-3}$) which is twofold increase than that of pristine Nafion®.

(Shen et al. 2015) synthesized a composite membrane of pillar [5] arene/Nafion composite membranes. The membrane exhibited superior properties over Nafion. Significant improvements on the proton conductivity and methanol permeability were observed resulting in a double increase in selectivity compared to Nafion. The highest proton conductivity and the lowest methanol permeability was observed in pillar [5] arene's (10 wt percentage) /Nafion composite membrane with values 0.145 S cm^{-1} and $2.43 \times 10^{-6} \text{ cm}^2/\text{s}$ respectively.

Another composite membrane based on Nafion was synthesized by (Asgari et al. 2013). The membrane consists of multi wall carbon nanotubes (CNT) functionalized by histidine, an imidazole amino acid (Im) and these (Im- CNTs) with a content of 0.5 wt percentage were dispersed in Nafion[®] solution. This membrane was synthesized, characterized, tested and compared to recast Nafion[®], Nafion[®] 117 and Nafion[®]/CNT-0.5 percentage. The new Nafion[®]/Im-CNT-0.5 percentage membrane shows significant improvements on the proton conductivity, methanol permeability and power density. It exhibits a methanol permeability of $9.84 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$ and a power density of 61 mW cm^{-2} .

(Dutta et al. 2014) enhanced the performance of Nafion by making a blend membrane consisting of Nafion and partially sulfonated polyaniline (SPANi). Increasing the content of SPANi in the blend membrane causes a decrease in both the methanol permeability and the proton conductivity. The optimized content which gives the best performance was obtained when using a content of 70:30 of Nafion to SPANi in the blend membrane giving selectivity values of $7.91 \times 10^4 \text{ S cm}^{-3}$ (at 20°C) and $1.97 \times 10^4 \text{ S cm}^{-3}$ (at 60°C) with proton conductivities of $7.21 \times 10^{-3} \text{ S cm}^{-1}$ (at 20°C) and $2.36 \times 10^{-2} \text{ S cm}^{-1}$ (at 60°C) and methanol permeabilities of $9.12 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$ (at 20°C) and $1.2 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$ (at 60°C). The maximum power density was obtained from this membrane at 60°C with a value of 25.76 mW cm^{-2} .

2.5.2 The use of Poly (vinyl alcohol) (PVA) polymers in membranes

There are a variety of commercial polymers available today. Poly (vinyl alcohol) (PVA) is one of the polymers which have been receiving increasing attention in DMFC application.

PVA is a scentless, transparent, white or cream colored grainy powder. Environmentally it is non-hazardous, biocompatible and biodegradable so it is an environmentally benign polymer. Commercially, it is not expensive and easily available. It has also good chemical and mechanical properties in addition to good film forming ability. These properties enable it to be widely used in several fields like medical, cosmetic, and packaging applications (Maiti et al. 2012).

PVA has specific properties which makes it suitable to be utilized in DMFC membranes. It is a highly hydrophilic polymer which dissolves in water and could react with different cross linking agents. Moreover, it has excellent insulation properties; its maximum electronic conductivity can reach a value of 10^{-10} S cm⁻¹. It also has high selectivity for water to alcohol, so it can efficiently constrict the methanol crossover. (Maiti et al. 2012) However, pure PVA have a very low protonic conductivity (≈ 0.014 S cm⁻¹) (Pivovar et al. 1999) .This is because PVA does not possess any negatively charged ions, such as, carboxylic and sulfonic acid groups (Boroglu et al. 2011). Therefore, to be used in DMFCs, it is necessary for the PVA to be modified so as to induce the protonic conductivities. To improve the properties of PVA polymer, the PVA could either form a composite membrane with other materials or could be modified in different ways such as (Maiti et al. 2012):

- i.** Copolymerization: By coupling a hydrophilic and a hydrophobic components and copolymerizing them.
- ii.** Cross linking: This could be done by various methods like freezing, annealing, irradiation and chemical treatment.
- iii.** Blending: The PVA could be mixed with a variety of sulfonating polymers.
- iv.** Acid- base

Table 2.2 gives examples of different PVA based membranes and their characterizations (Maiti et al. 2012).

(Bahavan Palani et al. 2014) prepared a composite membrane composed of PVA with montmorillonite (MMT). The conductivity values of the composite membranes were tested for different concentrations of the protonic MMT filler (H⁺MMT) and non protonic MMT filler (Na⁺MMT). Results show that the proton conductivity increases up to 10 wt percentage concentration of MMT filler in the case of (Na⁺MMT) while it

increases linearly with the increase of protonic MMT filler (H^+MMT). The maximum proton conductivity was obtained for the composite membrane of PVA (80) – H^+MMT (20) with a conductivity value of 0.9527S/cm at room temperature with 100 percent humidity. Other characterizations also show enhanced mechanical properties for the PVA with the addition of MMT filler.

(Zhong et al. 2014) synthesized a series of poly (vinyl alcohol) (PVA)-based organic-inorganic crosslinked membranes with PVA and poly (methacrylic acid-2-acrylamido-2-methyl-1-propanesulfonic acid-vinyltriethoxysilicone) (PMAV). The membrane has conductivities of the order of 10^{-2} S/cm which are comparable to that of Nafion[®] 117. The highest selectivity value was obtained from the membrane of 30 mass percentage of PMAV (PVA-PMAV 30) membrane which equals to (4.63×10^4) S/cm. This value represents more than twofold increment than that of Nafion[®] 117 membrane. The membrane also has excellent methanol barrier, good mechanical and thermal stability in addition to its low cost.

There are also people who used the sulfonated Poly (vinyl alcohol) (SPVA) to prepare their membranes. A cross-linked SPVA membranes were prepared by (Tseng et al. 2011), characterized and compared by Nafion 117 . The highest proton conductivity obtained equals to 0.218 S.cm^{-1} at 70°C which is 1.7 fold increases than Nafion 117 which showed a conductivity of 0.127 S.cm^{-1} at 70°C . All the cross-linked SPVA membranes show an extensively lower value for methanol permeability than that of Nafion 117.

(Yoo et al. 2014) prepared an organic/ inorganic composite membrane consists of SPVA mixed and crosslinked with different amounts of PVA- grafted graphene oxide (PVA-g-GO). The methanol permeabilities of the crosslinked SPVA/PVA-g-GO membrane ranged from 5.374×10^{-7} to $1.530 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ which were obviously lower than Nafion[®] ($2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The proton conductivities were also tested in this study. The composite membrane shows proton conductivities ranging from 0.041 to 0.0319 S/cm at 60°C . It was also shown in the study that the membranes utilizing SPVA have higher proton conductivity than other membranes which utilizes only PVA. This is because the sulfonic acid groups forms well-connected ionic channels, resulting in the enhanced transport of protons through the membrane.

Table 2.2: Properties of PVA Based Membranes

Membrane	Dry thickness (µm)	Conductivity (Scm ⁻¹)	IEC (M equiv g ⁻¹)	Water uptake (%)	Methanol permeability (Cm ² s ⁻¹ × 10 ⁻⁶)
PVA/SSA	100–150	0.001–0.01	0.5–2.24	10–80	0.1–1
PVA/ sPTA	100–150	0.024–0.035	3.4	–	<1.8
PVA/sulfo acetic acid/ polyacrylic acid	125	0.00057–0.00192	0.092–0.654	1.84–62.48	0.00266–0.346
Poly(vinyl alcohol-co-2-methyl-1-propanesulfonic acid)/ GA	–	0.216	–	–	0.1
PVA-co-PE/IDA/PA	–	0.01	–	–	–
KOH containing PVAHEMA-SiO ₂	–	0.11	–	–	–
PVA/PSSA_MA/F	–	0.053	0.6–0.72	–	0.34–0.5
PVA/PAA/ UV radiation/	–	0.312	–	–	–
PVA/gamma irradiation/KOH	100–400	0.00006–0.013	–	–	–
PVA/EPTMAC/GA	–	0.0027420.00734	–	–	1.0–4.1
PVP/PVA-PAMPS	100	0.088	1.63	–	0.61
PVA/PSSA_MA	100–150	0.001–0.044	0.73–1.22	22–85	0.241
PVA/PSSA_MA/Silica	–	0.01–0.026	–	–	0.46–1.2
PVA/SSA/GA	–	0.01–0.0526	0.576–2.676	–	0.14–2.9
PVA/p-sulfonate phenolic resin	300–400	0.012–0.197	0.28–2.66	49.85–366.2	0.1
PVA / Nafion	181–201	0.0009–0.02	0.09–0.91	13–43	0.31–0.65
PVA/ Nafion/Chitosan	–	0.01	–	41–95	1.0–2.2
Nafion/PI/PVA/TSPS	–	0.063–0.064	–	16.8–22.5	0.489–0.7
PVA/PI/TSGEPS	90	0.01–0.04	–	–	0.14–0.432
PVA/PSSA	110	0.17–0.246	1.58	–	–
PVA/PSSA	150	0.0013–0.0166	1.9–2.6	–	–
PVA/PSSA/MOR	160	–	2.68–3.32	–	–
PVA/SSA/PSSA_MA-semi interpenetrating network	100–120	0.006–0.0259	1.1–1.86	20–60	0.09–0.4
PVA/PSSA-MA/GA	100–150	0.1	3.4	–	0.253
PVA/PAMPS/OG	60–100	0.06–0.1	–	<90	1/3–1/5 of Nafion-117
PVA/PAMPS/PEGBCME/ semi-IPN	60–70	0.095	1.79	3 fold of Nafion	1/3 of Nafion
PVA/PVdF-HFP	160–190	0.085	–	–	–
PVA/SPEEK	–	–	0.47–0.72	–	3.5
PVA/SPEEK double layer	–	–	0.73–1.17	43–70	1.31
PVA/SSA/PVP	–	0.004–0.01	–	44–128	0.06–0.1
PVA/SA/GA	–	0.01	0.79	–	0.069
PVA/CS/GA	–	0.0099	0.62	–	0.094
PVA/APDPS/ Phosphonic acid	–	0.03–0.046	1.37–1.85	–	0.14–0.2
PVA/CS/ Organophospho-ric acids	107–110	0.02–0.03	0.75–1.33	52–79	0.23–0.42
PVA/KOH	80–100	0.002–0.004	–	36.1	–
PVA/PTSA	–	–	0.3–2.2	–	0.32
PVA/NH ₄ Br	–	0.005	–	–	–
PVA/ functionalized silica	200–300	0.03–0.2	–	–	–
PVA/ Phosphoric acid functionalized aminopropyl triethoxysilane	–	0.02–0.05	1.09–1.95	71–123	0.4–1.0
PVA/ AESP	200	0.03–0.07	1.21–1.76	55.6–80.9	0.2–0.6
PVA/TMAPS functionalized silica	20	0.031	–	–	–
PVA/Colloidal silica/ SSA	120	0.001	0.9–3.3	15–25	–
PVA/Phosphosilicate	80–200	0.02	–	–	–
PVA/FS/KOH	160–200	0.058–0.16	–	–	2.58–3.88
PVA/TiO ₂	100–200	0.0046–0.048	–	–	0.36
PVA/TiO ₂	100–300	0.005–0.012	–	83–95	–
PVA/HAP	100–300	0.025–0.044	–	45–60	–
PVA/PTA	150	0.03	–	–	–
PVA/PWA	80–100	0.006	–	–	0.1–0.4
PVA/PWA/SiO ₂	–	0.011–0.012	–	–	0.035–0.01
PVA/STA	90–110	0.0002–0.047	–	40	1.3
PVACO/PMA	90–110	0.000–0.002	–	–	1.5–3.9
PVA/Zirconium phosphate	–	0.01–0.03	3–3.2	140–260	2–3.5
PVA/MMT	100–300	0.0368	–	–	3–4
PVA/ntTiO ₂ /PSSA	100–200	0.001–0.002	–	–	0.3–0.8
PVA/ Organo clay/PSSA_MA	–	0.023	0.79–1.68	–	0.2
PVA/NCBC/Silica	–	0.019–0.053	1.4–1.73	–	0.2–1
PVA/sPOSS/EDTAD	–	0.042	0.3–0.8	130–135	0.18
PVA/SiO ₂ /SSA	–	0.001–0.01	0.2–1.1	45–60	0.01–0.1
P-PVA/PEG-SiO ₂	100	0.0017	–	–	–
PVA/PAA/Silica	–	0.001–0.01	0.46–1.58	30–55	0.01–0.1
PVA/SPEEK/PWA	–	0.001	1.3–3.6	–	–
PVA/SSA/ Sulfonated Benzene-silica Hybrid membrane	–	0.039	0.08–0.6	–	0.5

Source: (Maiti et al. 2012)

(Yun et al. 2011) also worked with SPVA. They prepared an organic/inorganic membrane consists of a crosslinked SPVA and sulfonated multi-walled carbon nanotubes nanocomposite membranes. The membrane shows excellent proton conductivities ranging from 0.032 to 0.075 S/cm as well as low methanol permeabilities ranging from 1.12×10^{-8} to $3.32 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 60°C.

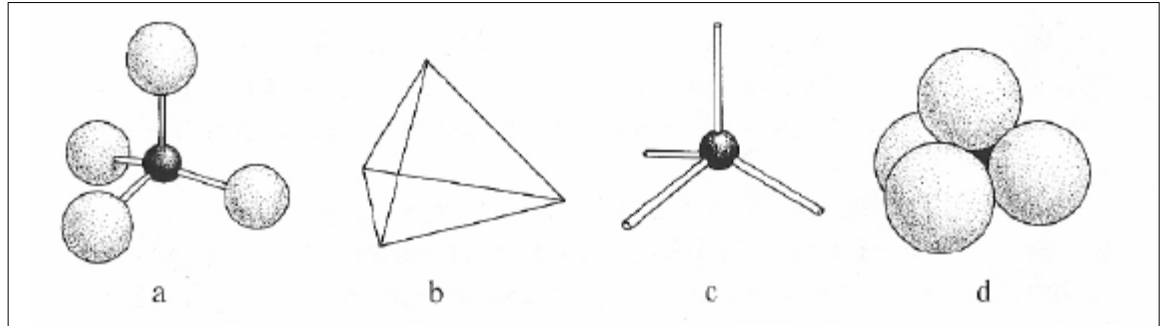
2.5.3 The use of Zeolites in membranes

Zeolites are very stable solids which have characteristics that enable them to tolerate different environmental conditions like high pressure and high temperatures. They have a high melting point temperature (over 1000°C) so they could endure high temperatures without being affected. In addition to that they do not oxidize in the air. These stable and unreactive features may raise questions about their usability, however what makes them interesting arises from their structure (Woodford 2009). Zeolites have a microporous crystalline structure which generally contains silicon (Si), aluminum (Al) and oxygen (O) in their framework and other molecules like cations, water... etc within the pores. They either could be found naturally as minerals, or synthesized (Breck 1974). Their structures are made up of 4-connected networks of atoms connected together like a tetrahedra, with oxygen atoms distributed at the corners and centered with a silicon atom (see Figure 2.6 below). The corners in the tetrahedra can link together to form various structures including linked cages, cavities or channels, which ranges approximately between 3 and 10 Å in diameter so as to permit tiny molecules to enter. Figure 2.6 shows different methods of representing the tetrahedral coordination of oxygen ions with aluminum and silicon.

The major structural formula of a zeolite can be written as: $M_x/n [(Al_2O_3)_x (SiO_2)_y] \cdot wH_2O$, where “M” is the cation which has a valence of “n”, and w is the number of tetrahedral in the unit cell. The portion included in the square brackets represents the framework composition (Breck 1974). The ratio of the Si/Al in this framework has a very important role in determining physical and chemical properties in the zeolite like ion exchange capacity, thermal stability and whether the surface selectivity of zeolite is hydrophilic or hydrophobic. Typically a zeolite with a 1-5 ratio of Si/Al is known to be hydrophilic while a zeolite with a ratio of 100 or above is considered hydrophobic. In general, the selectivity of the zeolite changes from hydrophilic to hydrophobic by

increasing the Si/Al ratio however it is not certain where the change occur (Libby et al. 2003).

Figure 2.6: Different Coordinations of Zeolites Tetrahedral Frameworks



Source: (Breck 1974)

Zeolites could be classified based on their pores sizes into small, medium and large pores. The number of tetrahedra surrounding the pore gives an indication of the pore size. Usually, pores enclosed by 8, 10 or 12 tetrahedra are considered as small, medium, or large pore zeolites respectively. There are also extra large pore zeolites with pores enclosed by 14 or more tetrahedral, but these are rarer. Typical examples of these classes are zeolite A (small pores of 0.41 nm diameter), ZSM-5 (medium pores of 0.53 nm) and the zeolites X or Y (large pores of .074 nm) (Cejka & van Bekkum 2005).

In this study the Zeolite that will be used is the mordenite .Mordenite is a natural zeolite with 10-membered rings and a main channel pore size of 0.7 nm (Libby et al. 2003). Its formula is $H_8[(AlO_2)_x (SiO_2)_{48-x}]$ (Üçtuğ 2008). As a zeolite, it has a remarkably high proton conductivity with a value of nearly 0.187 S cm⁻¹ (Pivovar et al. 1999). Like other zeolites, it can withstand high temperatures and remain stable at temperatures up to 800°C (Breck 1974). It has a low Si/Al ratio, typically 5, and so it is a strongly hydrophilic zeolite(Libby et al. 2003).

Zeolites are utilized in many applications like chemical separation, production and purification. And it is also used in fuel conversion and pollution remediation (KRESGE et al. 1992). They are also widely employed in fuel cells. They can serve as electrode and electrocatalyst besides using them in fuel conversion, reforming and storage (Yeung & Han 2014). In membranes, zeolites are widely used in synthesizing selective membranes. Their regular pore size enhances the selective separation based on molecular size and shape(Coronas & Santamaria 1999). In addition to that the separation

could be achieved based on preferential adsorption. In this case the passage of the molecules is hindered because of the robust adsorption of a component (Libby et al. 2003). However, it is not favored to synthesize membranes of pure zeolites. This is because pure zeolite membranes are so brittle and fragile and are known to be inhibited by defects (Berry et al. 2000) Besides being so expensive to manufacture (Caro et al. 2000).

There are many studies which investigated the incorporation of zeolites in membranes. (Yeung & Han 2014) reviews the papers which studies the use of zeolites in fuel cells including their use in membranes. Table 2.3 shows a summary for their use in membranes.

Recently, Composite membranes consisting of ZSM-5 embedded in sulfonated poly (ether ketone ether sulfone)(s-PEKES) were synthesized by (Changkhamchom & Sirivat 2014). The membranes vary in their zeolite content and their Si/Al ratio. The lowest methanol permeability is equal to $5.27 \times 10^{-8} \text{ cm}^2/\text{s}$ and it is obtained from the membrane which has a zeolite content of 10 percentage v/v while the highest proton conductivity was obtained from the membrane which has a zeolite content of 2 percentage v/v and it equals to $1.7 \times 10^{-7} \text{ S/cm}$. The later membrane also shows the highest selectivity among all with a selectivity value of $2.12 \times 10^{-5} \text{ s.S.cm}^{-3}$.

zeolite 4A incorporated to methane sulfonic acid (MSA)- sulfonated poly (ether ether ketone) (SPEEK) mixed matrix membranes were prepared, characterized and compared with Nafion 117,pristine SPEEK and SPEEK-MSA blend membranes by (Meenakshi et al. 2013). The zeolite4A-SPEEK-MSA mixed matrix membrane showed the lowest methanol permeability and the highest proton conductivity as well as the highest peak power density when compared with the other membranes. The highest peak power density was observed for the 4 wt percentage zeolite 4A-SPEEK-MSA (20 wt percentage) mixed matrix membrane with a value of 159 mW cm^{-2} .

An another very related study to this study was carried by (Bhat et al. 2009). He prepared a mordenite incorporated in PVA–polystyrene sulfonic acid (PSSA) blend membranes. The mordenite that is used in this study has a Si/Al ratio of 40. The membranes have 40 percent and 50 percent sulfonation degrees. The membranes were characterized and tested in DMFC. The 50 percent sulfonated PVA-PSSA blend membranes gives the higher proton conductivity owing to its larger content of the

sulfonation group and the existence of the mordenite in the membrane which enhances the proton conductivity. However, it was shown that a higher content of mordenite in the membrane (>10 wt percentage) may block the voids of the polymer matrix resulting in a disruption of the proton conduction path. This membrane also shows the highest peak power density with a value of 74 mW/cm³ at a load-current of 325 mA/cm². This value is slightly lower than the performance of Nafion-117 although the later have higher methanol permeability. That was explained because of the higher proton conductivity of Nafion-117.

Table 2.3: The Properties of DMFCs Membranes Having Zeolite Fillers

Membrane	Thickness (μm)	Operation temperature (K)	Conductivity (S cm ⁻¹)	Methanol permeability (cm ² s ⁻¹)	Test conditions of methanol permeation	MPD (mW cm ⁻²)
(A, mordenite, X, ZSM-5)/chitosan	50–90	RT	(1.7–2.2) × 10 ⁻² [after immersion in H ₂ SO ₄ for 24 h]	(6.24–12.2) × 10 ⁻⁷ (chitosan: 1.15 × 10 ⁻⁶)	5 mol L ⁻¹ methanol, RT	N
A/Nafion	N	308	(1.4–3.5) × 10 ⁻³ [in boric acid solution at pH 4.7]	(1.03–1.12) × 10 ⁻⁶ (Nafion 117: 7.4 × 10 ⁻⁶)	1 mol L ⁻¹ methanol, 308 K	N
Beta/chitosan	35–45	RT ^a	(1.10–1.55) × 10 ⁻² [10–50% RH]	(5.80–9.55) × 10 ⁻⁷ (chitosan: 1.17 × 10 ⁻⁶)	2 mol L ⁻¹ methanol, RT	N ^b
Beta/Nafion	175	353	(4.8–6.7) × 10 ⁻² [100% RH]	(3.63–5.86) × 10 ⁻⁶ (Nafion 117: 5.07 × 10 ⁻⁶)	8 vol. % methanol, 353 K	N
Beta/SPEEK	131–150	353, 393	N	–	–	285 (SPEEK: 180) [wet H ₂ , O ₂ at 393 K]
Beta/Nafion	151	343 K	8.8 × 10 ⁻²	1.40 × 10 ⁻⁶ (Nafion 115: 2.36 × 10 ⁻⁶)	8 vol. % methanol, RT	120 (Nafion 115: 62) [5 mol L ⁻¹ methanol, O ₂ at 343 K]
Chabazite (Clinoptilolite)/Nafion	70	363–413	N	N	N	350–370 (Nafion: 270) [1 mol L ⁻¹ methanol, O ₂ at 413 K]
Chabazite/Nafion	156	295, 333	4.08 × 10 ⁻² (295 K)	5.75 × 10 ⁻⁶ (333 K)	8 vol. % methanol, 333 K	N
Clinoptilolite/Nafion	N		4.89 × 10 ⁻² (295 K) [in 10 ⁻⁵ mol L ⁻¹ H ₂ SO ₄] (0.8–10) × 10 ⁻³	5.93 × 10 ⁻⁶ (333 K)	–	–
ETS-10/PVDF			(0.2–2) × 10 ⁻³	–	–	N
NaA/PVDF			(0.2–2) × 10 ⁻³	–	–	N
Umbite/PVDF			(0.2–2) × 10 ⁻⁴	–	–	N
Mordenite/PVDF			(1–6) × 10 ⁻⁵ [43–100% RH]	4.9 × 10 ⁻⁷	12 mol L ⁻¹ methanol, RT	N
Mordenite/chitosan	50–80	RT	N	–	–	–
Mordenite/PVA	100–300	RT	(1.3–3.0) × 10 ⁻² [after immersion in H ₂ SO ₄]	(3.13–11.3) × 10 ⁻⁸ (PVA: 3 × 10 ⁻⁷)	1 mol L ⁻¹ methanol, RT	N
Mordenite/PTEF	300–400	293–373	4 × 10 ⁻⁴ –10 ⁻² [RT]	N	N	4 [methanol, O ₂ at 343 K]
(X,Y, ZSM-5, mordenite, A)/PTFE	196–860	348–423	1.3 × 10 ⁻⁷ –2 × 10 ⁻³ [80% RH]	–	–	N
Y/chitosan	N	RT	(1.51–2.58) × 10 ⁻² [after immersion in H ₂ SO ₄ for 24 h]	9.04 × 10 ⁻⁷ (Nafion 117: 2.71 × 10 ⁻⁶)	5 mol L ⁻¹ methanol, RT	N
Y/SPEEK	100–220	293–413	(7.2–9.6) × 10 ⁻³	–	–	N
ZSM-5/Nafion	100–150	RT	(7–12) × 10 ⁻²	(1.0–1.6) × 10 ⁻⁶ (Nafion 115: 1.4 × 10 ⁻⁶)	16 wt.% methanol, RT	N
Fe-silicalite-1/Nafion	N	323	(0.13–34) × 10 ⁻³ [after immersion in H ₂ O for 48 h]	(0.04–7.3) × 10 ⁻⁷ (Nafion 115: 2.5 × 10 ⁻⁶)	1 mol L ⁻¹ methanol, 323 K	N
Zirconium phosphate/Nafion	165, 90	403	N	–	–	450 (165 μm), 680 (90 μm) (Nafion 115: 110) [wet H ₂ , O ₂ at 403 K]
SiO ₂ /SPEEK	29	328	N	610 g h ⁻¹ m ⁻²	20 wt.% methanol, 328 K	N
ZrO ₂ /SPEEK	24–73			70–480 g h ⁻¹ m ⁻² (SPEEK: 1300)	–	–
HPA/Nafion	N	393	1.5 × 10 ⁻² [35% RH]	–	–	N
SiO ₂ /PEG	N	308	10 ⁻³ –10 ⁻² [after immersion in H ₂ O]	(0.78–2.1) × 10 ⁻⁸ (Nafion 117: (7.5–2.3) × 10 ⁻⁶)	3 wt.% methanol, 308 K	N
TiO ₂ /Nafion	N	418	N	N	–	350 [2 mol L ⁻¹ methanol, O ₂ at 418 K]

Source: (Yeung & Han 2014)

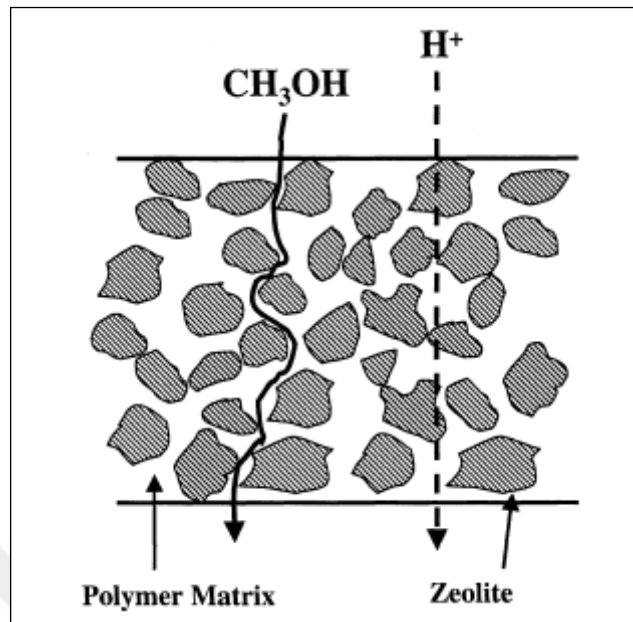
2.5.4 PVA- Mordenite mixed matrix membranes

Mixed matrix membranes (MMMs) are heterogeneous membranes typically consists of inorganic fillers like molecular sieves, zeolites, nano size particles... etc. embedded within polymeric organic materials. These types of membranes are known to be widely used in the field of gas separation (Sadeghi et al. 2015; Ahmed et al. 2010).

MMMs have the possibility to exhibit an improved selectivity when compared with the pure polymeric membranes due to the inherent superior separation characteristics of the inorganic particles (Sadeghi et al. 2015; Ahmed et al. 2010). Furthermore, these membranes are easier to process and manufacture than inorganic membranes. However, a proper selection of the materials is a necessity to succeed in challenging the traditional separation processes (Üçtuğ 2008). In this thesis, the polymer will be the PVA and the fillers are the mordenite particles. Both of these materials are discussed in the previous chapters.

In order to achieve a high selectivity, there should be two requirements. Firstly, the zeolites should be impermeable to methanol. As it is seen in figure 2.7, when the zeolite particles are impermeable to methanol, the protons will have shortened and straight path compared with methanol. To achieve this, the pore size of the mordenite should be bigger than H^+ ions and smaller than methanol molecules. H^+ ions are known to have a very small diameter; in the order of $10^{-15}m$ (Ramsden 2000). Mordenite has a main channel pore size of 0.7 nm (Libby et al. 2003), while methanol molecules has an approximate diameter of 0.252 nm (Bonn D., Wegdam G.H., Kellay H. 1992). Clearly, the diameter of mordenite is big enough to let the permeation of both H^+ and the methanol. As a result, it could be concluded that the mordenite is permeable to methanol. However, this is not the case. The PVA- mordenite membrane is a very hydrophilic membrane and so it would be very likely that the pores would be partially or completely blocked with water so that the passage of methanol will be hindered by the water molecules (Üçtuğ 2008).

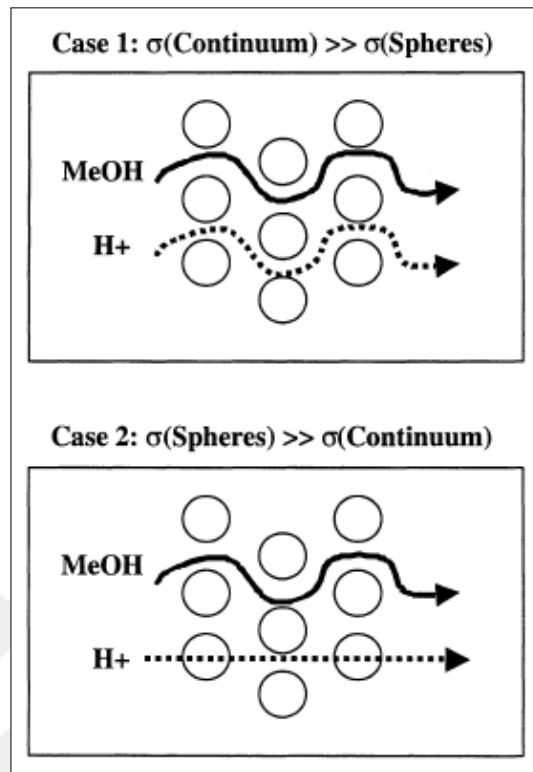
**Figure 2.7: Pathways For Protons and Methanol
in a Mixed Matrix Membrane**



Source: (Libby et al. 2003)

The second requirement to achieve a high selectivity in the membrane is that the relative speed of the proton transport in the zeolite spheres should be greater than the proton's speed in the continuous phase which is in our work the PVA. This could be more explained by figure 2.8. In case 1, the continuous phase has higher proton conductivity than the dispersed phase (spheres). As a result, protons and methanol will move in the same track through the dispersed phase. In case 2, the spheres have higher proton conductivity than the continuum. Thus the protons could move through both the continuous and the dispersed phases and have a direct and short pathway while methanol will travel around and between the spheres. In our case the continuous phase will be the PVA which has a conductivity of ($\approx 0.014 \text{ S cm}^{-1}$) while the spheres are the zeolite particles which has a conductivity value of ($\approx 0.187 \text{ S cm}^{-1}$) which is much greater than that for PVA (Pivovar et al. 1999). Therefore, it could be concluded that case 1 applies here and the membrane will have a high selectivity.

**Figure 2.8: Potential Transport Mechanisms
in a Mixed Matrix Membrane**

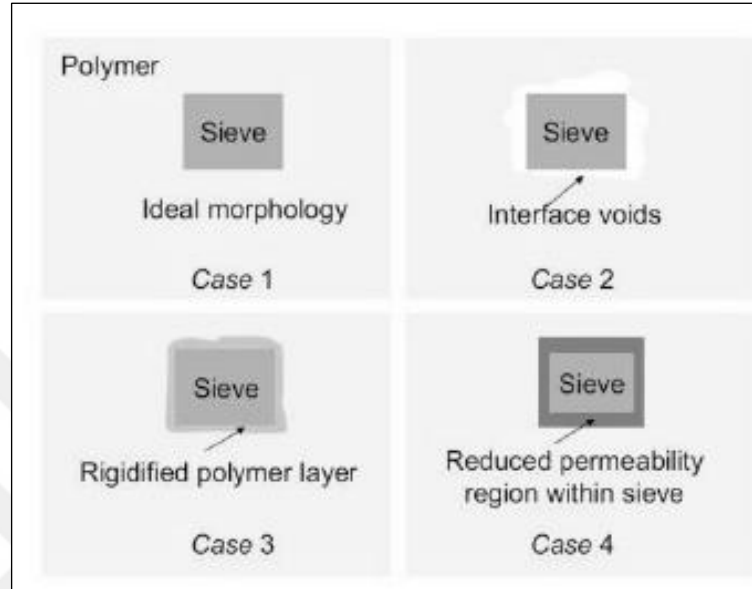


Source: (Libby et al. 2003)

It is also worth here to point for the defects which are widely spread in MMMs where a third phase is established in the membrane other than the polymer and the fillers. This phase may form because of the massive stress occurred during the solvent evaporation which may lead to a detaching between the polymer and the inorganic fillers resulting in the formation of an interfacial layer between them (Chung et al. 2007). Figure 2.9 gives an insight look at the sources for this phenomenon. Case 1 corresponds to the ideal case in MMMs where the fillers are tightly contacted to the polymer. Case 2 represents a filler encircled with an interface voids. Case 3; demonstrate a rigidified layer around the fillers. This layer sources from the polymer chain where they encounter an inhibited mobility compared with the rest polymer matrix. And finally case 4 illustrate a partially or entirely blockage for the pores of the fillers with the polymer chain (Chung et al. 2007). These defects could affect the proton conductivity as well as the selectivity in the membrane. There are some suggestions in the literature

to use a novel silane coupling agent around the zeolites so as to overcome those problems(Li et al. 2006).

Figure 2.9: Comparison of the ideal and the non-ideal morphologies in MMMs



Source:(Chung et al. 2007)

Libby et al. (2003) and Üçtuğ & Holmes (2011) have worked on PVA-MOR mixed matrix membranes. Before, (Libby et al. 2003) were the first who proposed the use of PVA- mordenite composite membrane. However, their study was concerned only about the characterization of the PVA-MOR membrane. They synthesized PVA – MOR membranes containing 50 percent and 60 percent mordenite by volume and subjected them to variable time heat treatments. They reported that the PVA- MOR with 50 percent mordenite membrane which heat- treated for 27 hour exhibit a 20 fold increment in selectivity greater than Nafion[®].

(Üçtuğ & Holmes 2011) characterized and tested the membrane in actual fuel cell and gave further information about the membrane performance. They prepared different membranes varying in the ratio of PVA to mordenite content. In addition to that they preserve the membranes in different environments. Some membranes were preserved in deionized water and others were preserved in sulfuric acid (H₂SO₄) and they study the effect of the storage environment on the performance of the membranes. The optimum performance was obtained from 60-40 wt percentage PVA-MOR membrane with

proton conductivity slightly lower than Nafion[®]-117 and at least two orders of magnitude less methanol permeability. However, when the membrane was tested in actual DMFC, it showed an inferior performance. This was linked to the loss of proton conductivity which occurred because of the drying in the fuel cell medium.

In this work an improvement on Libby et al. (2003) and Üçtuğ & Holmes (2011) membranes will be held by sulfonating the PVA and the new membrane will be compared to the PVA- mordenite mixed matrix membrane. It is expected that adding the SO₃H group will increase the protonic conductivity by supporting strong hydrogen bonding and thus increasing the transportation of protons by the Grotthuss mechanism.



3. METHODOLOGY

3.1 PVA- MORDENITE MEMBRANE FABRICATION

3.1.1 Materials used:

Poly (vinyl alcohol) of 98.0-98.8 percent hydrolyzed, with a molecular weight of approximately 146,000-186,000 which was provided by “Acros” was used. The mordenite was synthesized by Dr. Alper Sariođlan at TÜBİTAK Marmara Research Center. Deionized water is used as a solvent.

3.1.2 Synthesis of PVA- MOR membrane:

The procedure of (Libby et al. 2003) for membrane fabrication was followed. And the ratio of PVA- mordenite mixture used was 60-40 wt percentage PVA-Mordenite. This ratio is taken based on the optimization results of the study carried by (Üçtuğ 2008) which shows the best selectivity amongst different ratios.

The synthesis of the membranes was realized as follows: One gram of mordenite was dissolved via stirring in 5 ml of water for more than 18 hours until a homogeneous, white and a milky-looking suspension was obtained. Then the suspension was mixed 6 times (with 5 minute intervals) by using an ultrasonic bath. Every five minutes, the suspension was put on the regular stirrer for another five minutes. Thus the total time for mixing was 1 hour and the total time for ultrasonic mixing would correspond to 30 minutes. This is done to avoid the formation of high-temperature spots, which could occur during lengthened ultrasonic treatment (Kuijpers M.W.A 2004). Meanwhile, 1.5g of PVA was dissolved in 30 ml of water. The PVA powder was slowly added to cold water so as to avoid formation of lumps which is more susceptible to form at high temperatures (Silverson machines, Inc. [no date]). Once the powder is fully dispersed, the mixture was placed in an oil bath of 100°C and mixed for 1 hour. The PVA solution and the mordenite suspension were then mixed together for 4 hours at 60°C. Then the membrane was casted on a glass surface using film applicator device by setting the thickness at 750µm. The casted membrane was then dried in ambient air for approximately one week. After the membrane dried and peeled off the glass, the membrane was made insoluble by annealing it in an oven at 150°C for 24 hours. This

time of heat treatment was optimized by (Libby et al. 2003). The final membrane obtained had a brown color.

3.2 SULFONATED PVA-MORDENITE MEMBRANE FABRICATION

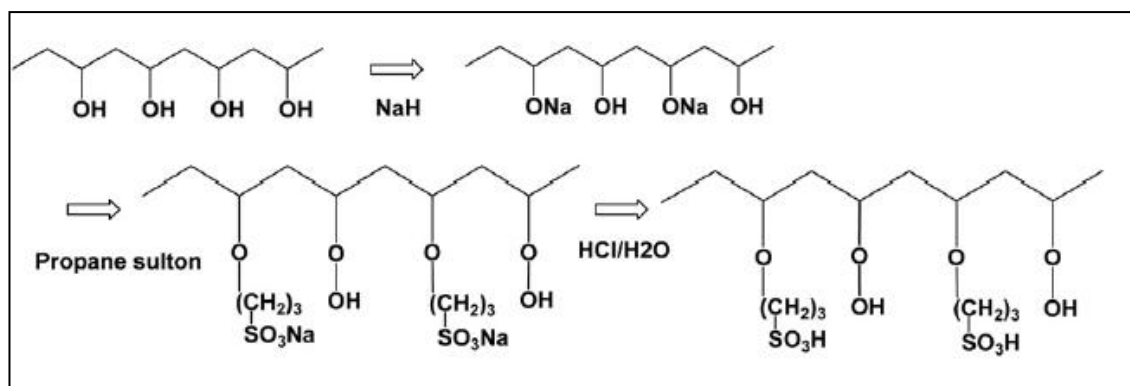
3.2.1 Materials used:

In order to prepare the SPVA powder, the same materials used in the synthesis of PVA-MOR membrane were also used here in addition to sodium hydride (NaH), propane sultone, ethanol and a 1 percent concentration of HCl in water mixture.

3.2.2 Synthesis of the membrane

The synthesis begins by sulfonating the PVA powder. Firstly, 1.5 grams of PVA were placed in 37.5 ml of ethanol. Then 0.72 grams of sodium hydride (NaH) were added to the PVA/ ethanol mixture slowly with continuous mechanical stirring. While mixing, 0.75 grams of propane sultone is then added drop wise to the mixture while stirring and the whole mixture was reacted at 80°C for 2-3 hours where the color of the PVA powder was turned into brown. After the reaction is completed, the PVA powder is filtered and immersed into the HCl/ water mixture and left overnight in order to replace the terminated Na with H. Then, the SPVA was filtered and washed with ethanol several times and put to dry in the oven at 50°C for 12h. Figure 3.1 shows a schematic diagram for the steps of sulfonating the PVA.

Figure 3.1: Schematic diagram for the sulfonation of the PVA matrix



Source: (Yun et al. 2011)

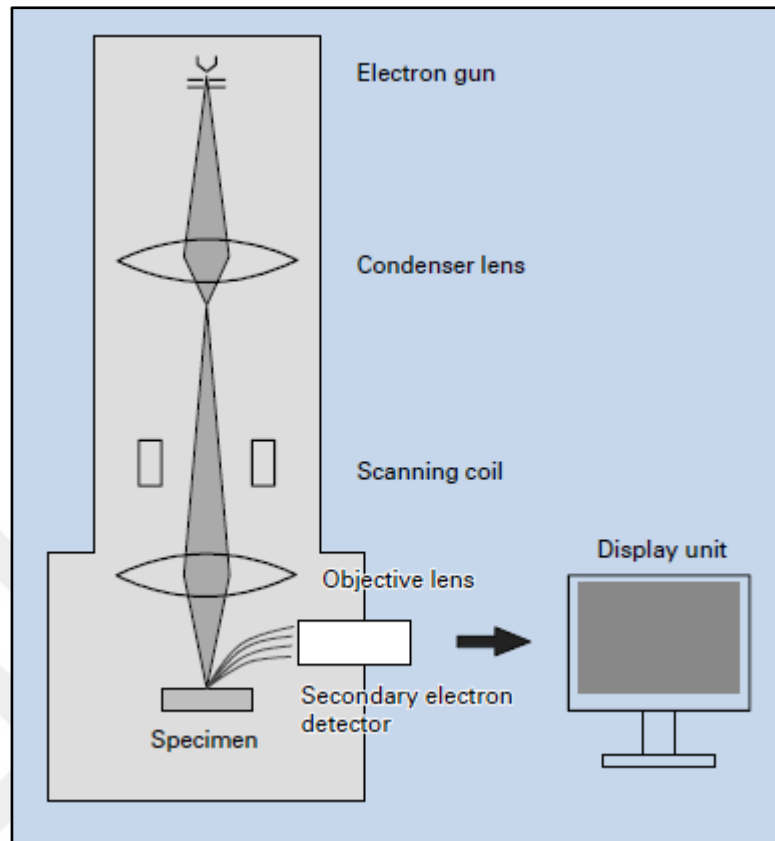
After Obtaining the SPVA, the SPVA- MOR membrane is synthesized using the same procedure used in synthesizing the PVA- MOR membrane.

3.3 STRUCTURAL ANALYSIS

Structural analysis is performed to confirm that the synthesized membranes have the proper morphology. In our membranes, the samples were observed to make sure that the zeolites are distributed homogeneously in the polymer matrix without voids.

Scanning Electron Microscope (SEM) was used to observe the surfaces of the membranes. This type of microscopes uses electron beams which interact with the surface of the specimen to produce an image for the topography of the surface. The electrons beams are generated in a system located at the top of the microscope called “Electron Gun”, which is composed of a cathode and an anode. A manipulation system consisting of electromagnetic lenses and coils placed in the microscope column are used to control size, shape and position of the electrons. An electrostatic field controls the electron motion in the gun while a magnetic field controls the electron’s motion throughout the rest of the SEM. When the “primary electrons” generated in the gun enters the specimen, it will travel some distance and hit an electron, nucleus, etc. and as a result it will scatter and continue in a new trajectory to produce “secondary electrons”. The scattering range of the electrons inside the specimen will differ depending on electron energy, atomic number of the elements making up the specimen and the density of the constituent atoms. A detector coated on the top with a scintillator with a high voltage of about 10 kV applied to it, will magnetically attract the emitted secondary electrons causing photons to be emitted. Those photons is directed into a photomultiplier which in turn amplify the original signal and results in a significant amplification for the electric signal. Then a display and a recording system will allow the visualization of the electronic signal and permits recording of the results using photographic or magnetic media. A vacuum system is required inside the apparatus so as the electrons do not scatter or disperse due to collisions with other molecules (Technology [no date]; Dunlap & Adaskaveg 1997). Fig (3.2) shows a schematic diagram of the basic construction of the SEM setup.

Figure 3.2: Basic Construction of SEM



Source: (Technology [no date])

3.4 SWELLING MEASUREMENTS:

In these measurements, the water and methanol uptake for the membranes were recorded. These measurements are important because they can give a general idea about the protonic conductivity and the methanol permeability of the membranes. As it was discussed in section 2.4.3 the presence of water inside the MEA may enhance the protonic conductivity in the membrane by the vehicle mechanism. On the other side, low values of methanol uptake give an indication that the membrane act as a good barrier for methanol and may reduce the methanol crossover.

In these measurements, the weight increase of the membranes samples after being conditioned in water or methanol is taken as a percentage of the original dry weight of the membranes samples.

Different samples from each membrane were cut and put in the desiccators for a few hours. Then the dry weights were recorded. Afterward, the samples were placed in deionised water or methanol for at least 72 hour. Later, each sample was taken, wiped from the surface moisture and the wet weights were recorded. Then the swelling ratio was calculated using the equation:

$$\text{Swelling ratio} = \frac{(\text{wet weight} - \text{dry weight})}{\text{dry weight}} \times 100\% \quad (3.1)$$

3.5 ION EXCHANGE CAPACITY (IEC)

This measurement is used to determine the total of exchangeable cations in the SPVA-MOR membranes and it gives an indication about the sulfonation degree achieved in those membranes where higher IEC value denotes higher sulfonation degree (Shen et al. 2015).

In this work, this value quantifies the number of milligram equivalents of ions (sulfonic acid groups) per 1g of the dry SPVA-MOR membrane (Meenakshi et al. 2013).

The simplest way to do this measurement is by using titration. Two samples of dry SPVA-MOR from two different membranes were first sunken in 1 molar solution of a NaCl for 24 hours so that the H⁺ ions could be replaced with Na⁺ ions. Then the solutions were titrated using 0.001 M NaOH solutions as a titrant and phenolphthalein as an indicator. Then the IEC value was calculated using equation (3.2)

$$\text{IEC} = \frac{\text{amount of NaOH consumed(ml)} \times \text{molarity of NaOH}}{\text{dry PVA-MOR membrane weight (g)}} \quad (3.2)$$

3.6 PROTON CONDUCTIVITY

Proton conductivity is one of the vital measurements for evaluating the potential membrane of the fuel cell. As it is mentioned before the most well-known membrane “Nafion” are known to have a very high proton conductivity of 0.1 S cm⁻¹ (Libby et al. 2003). The protonic conductivities of our novel membranes were measured to see if the new membrane could have good- enough proton conductivity values to compete with Nafion.

Alternating Current Impedance Spectroscopy was used for these measurements. This apparatus is used to characterize many of electrical properties of materials and their interfaces. It consists of cells having a pair of identical electrodes applied to the surfaces of a sample. The data are obtained by applying an electrical stimulus -which could be a known voltage or current- to the electrodes and detecting the response by looking at the resulting current or voltage (Barsoukov & Macdonald 2005).

The setup consists mainly of an electrochemical cell which include the system under investigation, a potentiostat or galvanostat which maintains the required conditions in the cell (Barsoukov & Macdonald 2005) and a frequency response analyzer (FRA) which is responsible for applying the sine wave and analyzing the response to determine the impedance (Metroham Autolab 2011).

The proton conductivity value of the membrane is generally obtained from the value of the impedance (Z) which is a measurement of resistivity of the membrane against the current flow. The value of the impedance can be calculated from Ohm's law as the ratio of the voltage (E) to the current (I) at a given frequency (ω).

$$Z(\omega) = \frac{E(\omega)}{I(\omega)} \quad (3.3)$$

Where,

$$E(\omega) = E_m \sin(\omega t) \quad (3.4)$$

E (ω) represents the monochromatic signal that is applied to the cell.

While

$$I(\omega) = I_m \sin(\omega t + \theta) \quad (3.5)$$

I (ω) represent the resulting steady state current.

In those equations, E_m , I_m , θ and t represent the maximum voltage, maximum current, phase shift and the time respectively.

When the phase shift (θ) = 0, the impedance is purely resistance.

In the Cartesian coordinate the impedance is represented by as a complex quantity that include a real part (resistance) and an imaginary part (reactance) with phase angle θ (Lee et al. 2005):

$$Z = \text{Re}(Z) + j \text{Im}(Z) \quad (3.6)$$

$$\text{Re}(Z) = Z' = |Z| \cos \theta \quad (3.7)$$

$$\text{Im}(Z) = Z'' = |Z| \sin \theta \quad (3.8)$$

$$\theta = \tan^{-1} \frac{Z''}{Z'} \quad (3.9)$$

$$|Z| = \sqrt{Z'^2 + Z''^2} \quad (3.10)$$

In Polar Coordinates, Z can be written as:

$$Z(\omega) = |Z| \exp(j\theta) \quad (3.11)$$

After measuring the impedance under a range of frequencies, a graph of Z' versus Z'' can be plotted. This graph is called “Nyquist Plot”.

Figure 3.3 shows a Nyquist plot for Nafion 112 in the frequency range of 100 kHz to 0.1 Hz.

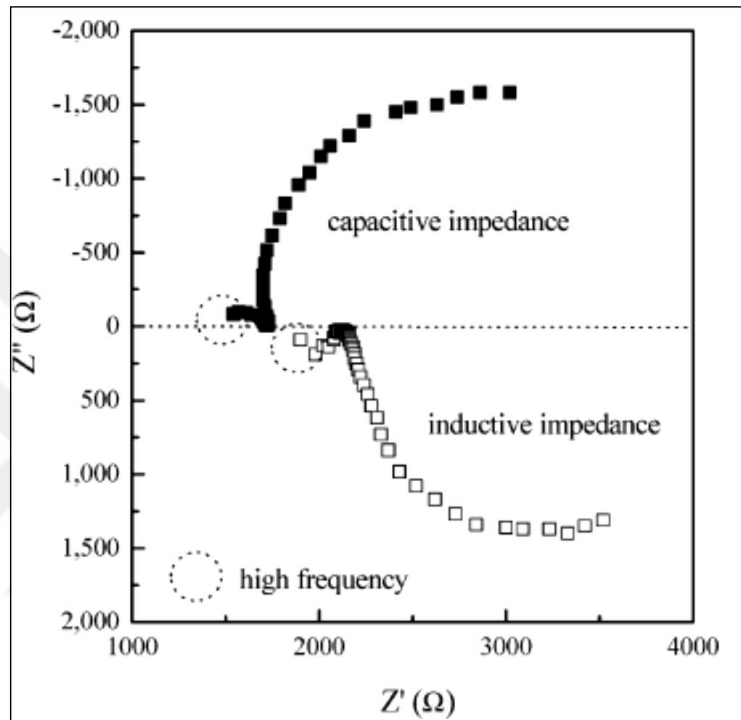
From the graph, one can determine the value of the resistance and then the conductivity per unit thickness can be calculated from the equation (Üçtuğ 2008):

$$\sigma = \frac{L}{rA} \quad (3.12)$$

Where σ is the membrane conductivity, L is the thickness of the membrane, R is the resistance and A is the cross sectional area of the membrane facing the current flow.

The proton conductivity measurements are done for samples from PVA-MOR and SPVA-MOR in addition to Nafion membrane samples to make a comparison. The measurements were realized by using a BT-512 BekkTech membrane testing system, at 80°C and 100 percent relative humidity. The measurements took 8 hours each. Samples were immersed and kept in deionized water for 12 hours prior to testing.

Figure 3.3: Nyquist Plot for Nafion 112



Source: (Lee et al. 2005)

4. RESULTS AND DISCUSSION

4.1 STRUCTURAL ANALYSIS

Figure 4.1 show the images taken by the SEM to the surfaces of the PVA- MOR membranes at different magnification factors.

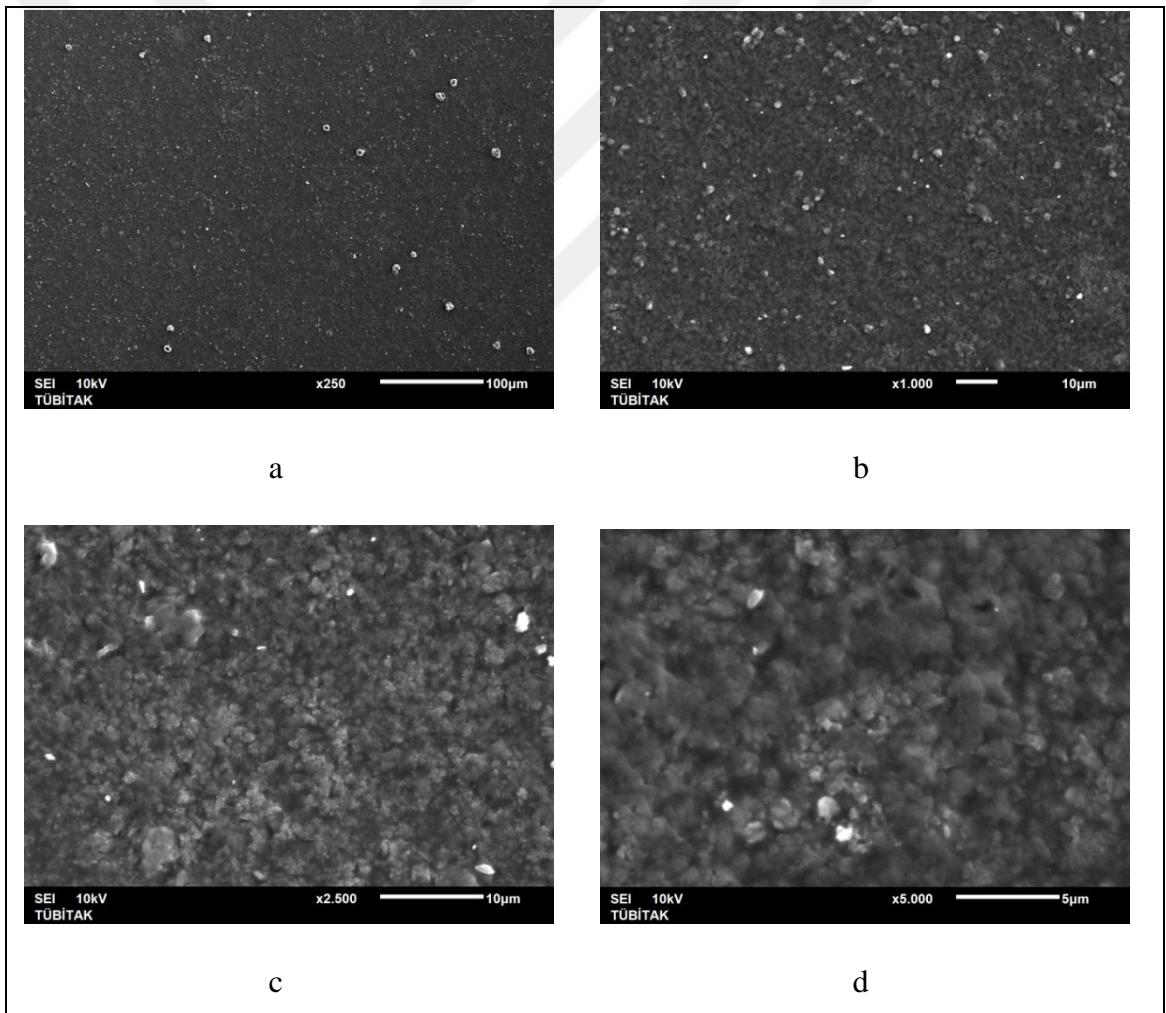
Figure 4.1: SEM Images for the surface of PVA-MOR membrane

4.1.a: PVA-MOR membrane magnified 250 times

4.1.b: PVA-MOR membrane magnified 1000 times

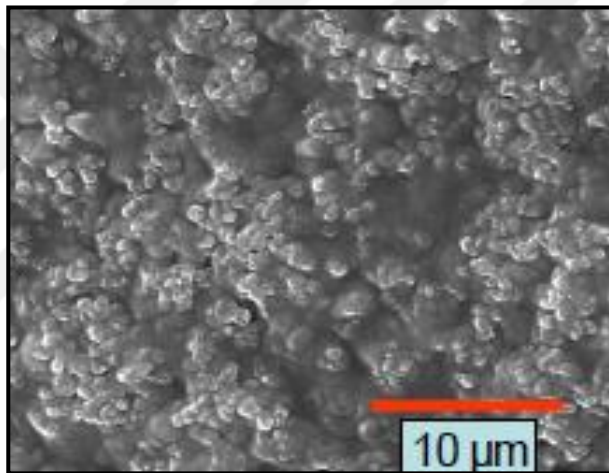
4.1.c: PVA- MOR membrane magnifies 2500 times

4.1.d: PVA-MOR membrane magnified 5000 times



In the images above, the mordenite particles appear as white spots surrounded by a black area which resembles the membrane matrix. After analyzing the photos, we could conclude that the mordenite seems to be distributed homogeneously in the membrane matrix of the PVA-MOR membranes and this is one of the things that we should confirm from the images as it is mentioned in section 3.3. In addition to that non-selective voids are not observed in the images and this is the second thing that we need to assert. Those images are also consistent with the images provided in the study of Üçtuğ (2008) . Figure 4.2 shows one of the images provided in the study of Üçtuğ for the PVA-MOR membrane

Figure 4.2: SEM image for the PVA- mordenite membrane magnified 5000 times



Source: (Üçtuğ 2008)

Figure 4.3 shows the images taken by the SEM to the surfaces of the SPVA- MOR membranes at different magnification factors. Image 4.3.b shows some clusters formed because of an agglomeration of mordenite particles. The homogeneous distributions of the mordenite in the membrane matrix are mostly clear in Image 4.3.d. And also in those photos the voids between the zeolite particles and the polymer matrix are not observed. Therefore, the morphology of the membrane tells that this membrane can successfully act as a mixed matrix membrane.

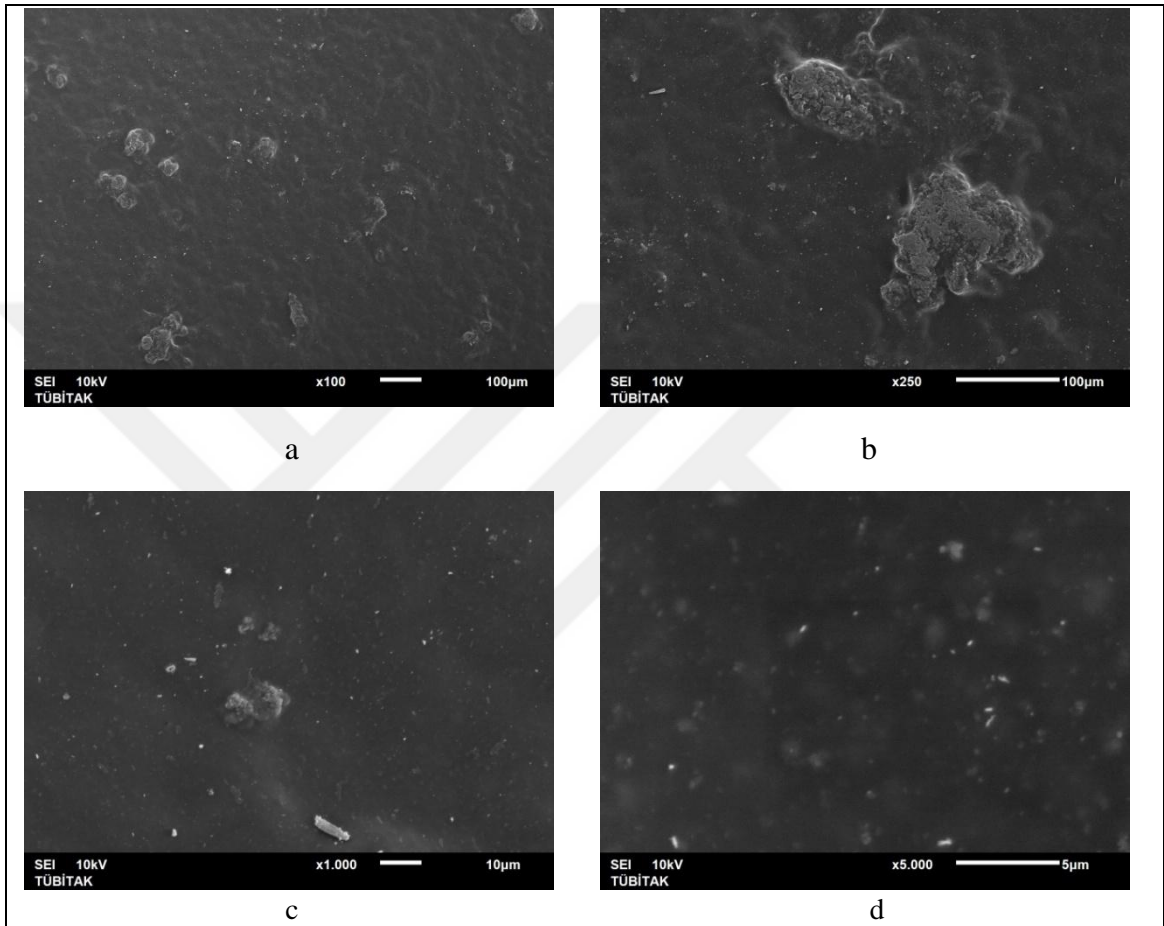
Figure 4.3: SEM images for the surface of SPVA-MOR membranes

4.3.a: SPVA-MOR membrane magnified 100 times

4.3.b: SPVA-MOR membrane magnified 250 times

4.3.c: SPVA- MOR membrane magnifies 1000 times

4.3.d: SPVA-MOR membrane magnified 5000 times



4.2 SWELLING MEASUREMENTS

The PVA- MOR membranes show an average water uptake of 30 percent while the SPVA-MOR membranes show an average of 22 percent. This decrease in the water swelling ratio for the SPVA-MOR could be explained because SO_3H groups and its interaction with the PVA may cause a blocking for some water absorption sites of the SPVA-MOR membranes. This in turn will result in decreasing the swelling ability of PVA in water.

In the case of methanol uptake, the decrease of the methanol uptake for the SPVA-MOR membranes is quite promising. The SPVA-MOR membranes indicate a methanol uptake of 10 percent in comparison with 13 percent for the PVA-MOR membranes. These values could tell us that the methanol crossover is expected to decrease in the SPVA-MOR membranes.

Figure 4.4 shows a comparison between the swelling measurements of PVA-MOR and the SPVA-MOR

Figure 4.4: Water and Methanol Uptake

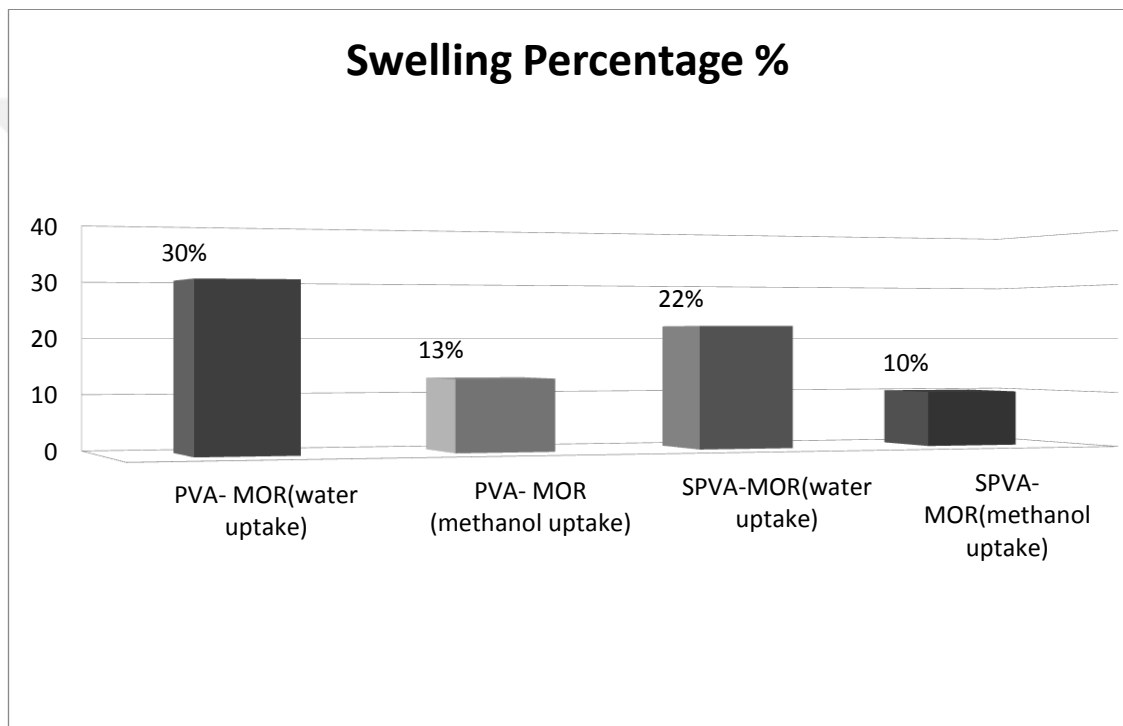
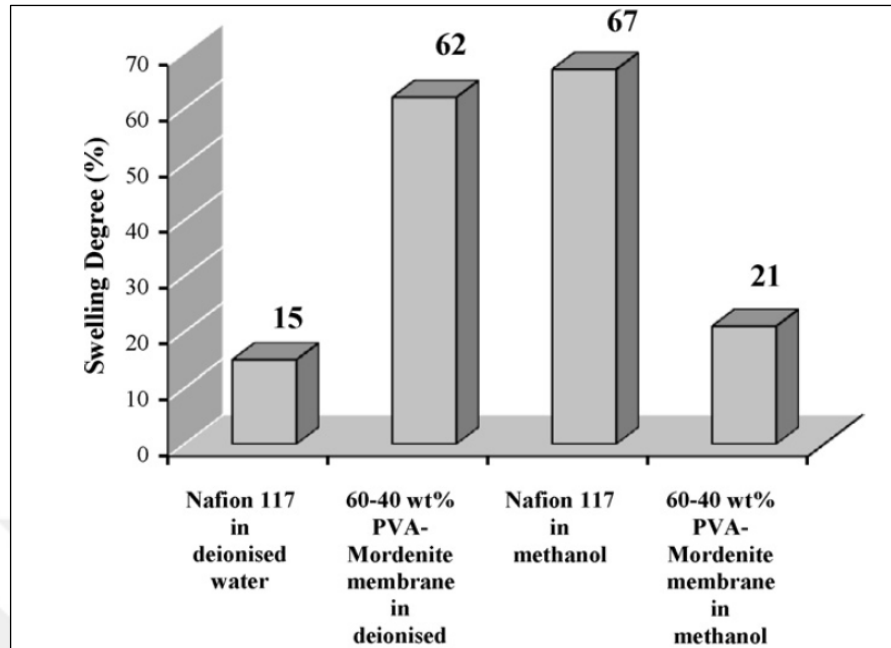


Figure 4.5 concludes the swelling measurements of Üçtuğ & Holmes (2011) study where they compare the water and the methanol uptake of the PVA-MOR with that of Nafion117. It is clear from the chart that the PVA-MOR membrane has an improved result regarding the methanol uptake which tells that the methanol crossover is expected to decrease in the case of the PVA-mordenite membrane. And as the methanol uptake of the SPVA-MOR membrane in this study shows lower value than that for the PVA-MOR, we can conclude that the SPVA-MOR membrane will have extremely lower value for the methanol permeability compared with Nafion.

Figure 4.5: Liquid uptake from another study



Source:(Üçtuğ & Holmes 2011)

4.3 ION EXCHANGE CAPACITY

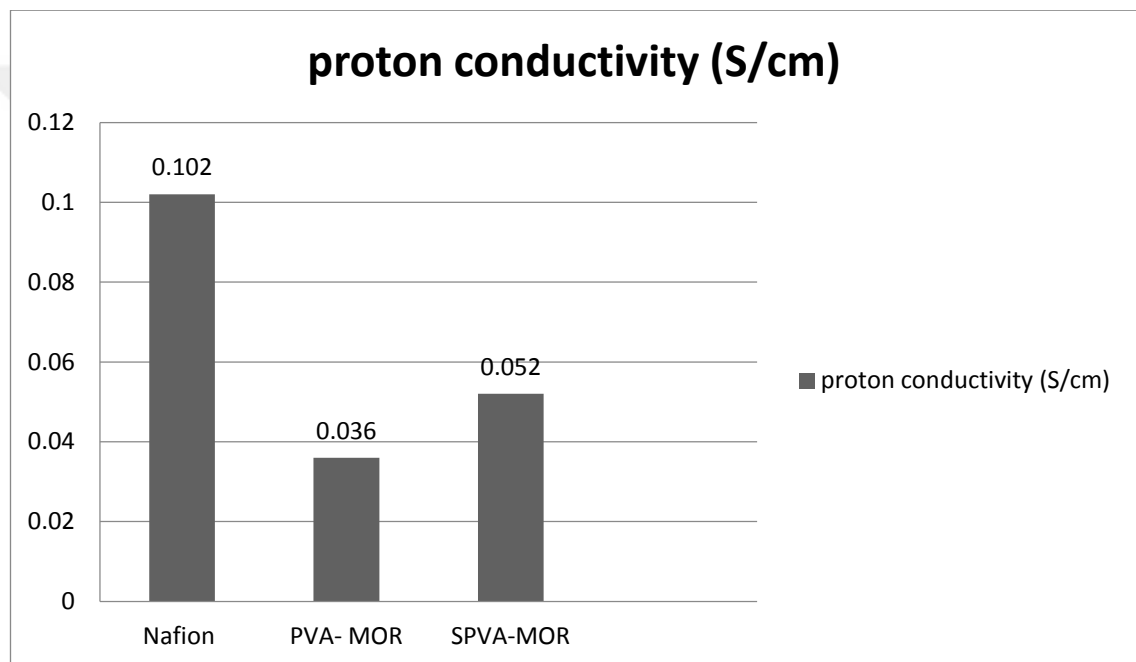
The SPVA-MOR membrane was found to have IEC value of 0.474 mequiv/g. Compared with the IEC values from the literature (Tseng et al. 2011; Yoo et al. 2014; Yun et al. 2011) for membranes containing sulfonated PVA polymer, The presence of sulfonic acid groups could be confirmed. In (Yun et al. 2011) the IEC values ranges between (0.7 - 2.25) mequiv/g. Approximately the same range was obtained from (Tseng et al. 2011) with a range between (0.8-2.4) mequiv/g. The most near IEC values to this study was obtained in (Yoo et al. 2014). In this study the IEC measurements were done to two groups of membranes. The first group contains sulfonated PVA and it exhibits IEC values ranges between (0.545-0.655) mequiv/g. The other group of membranes does not include sulfonated PVA and it shows IEC values ranges between (0.026-0.091) mequiv/g. Compared with the numbers given in the literature, it can be expected that the sulfonic acid groups are presented in the membrane but in low sulfonation degree.

4.4 PROTON CONDUCTIVITY

As it was mentioned before, the proton conductivity measurement was performed for samples from the PVA-MOR and the SPVA-MOR membranes in addition to samples

from Nafion membranes. The PVA-MOR and the SPVA-MOR samples were recorded to have proton conductivities of 0.036 S/cm and 0.052 S/cm, respectively; whereas Nafion was measured to have a proton conductivity of 0.102 S/cm which is consistent with the proton conductivity values for the Nafion given in the literature (Libby et al. 2003) . In addition to that, the proton conductivity value for the PVA-MOR membrane is just the same as the value obtained by Üçtuğ & Holmes (2011) for the 60-40 percentage wt PVA-MOR membrane preserved in deionized water. The results for proton conductivity measurements are concluded in Figure 4.6.

Figure 4.6: Comparison of Proton Conductivity Measurements for different membranes



From the results given above, it is clear that both of the PVA-MOR and the SPVA-MOR membranes showed proton conductivity results better than the proton conductivity value for the pure PVA which is known to have poor proton conductivity values of about 0.014 S/cm (Pivovar et al. 1999). This is without a doubt due to the presence of the mordenite which has a proton conductivity of about 0.187 S/cm (Pivovar et al. 1999) which increases the proton conductivity in the membranes.

More importantly in this study is the comparison between the proton conductivities between the PVA-MOR and the SPVA-MOR. As it was expected, the SPVA-MOR showed slightly higher proton conductivity than the PVA-MOR. This could be reasoned to the presence of the sulfonic acid group (SO₃H) which enables the protons

to form and break bonds with the ionically bonded hydrogen atom in its structure and so enhancing the proton transportation via the Grotthuss mechanism. It is also essential here to point that although the water uptake for the SPVA-MOR was lower than the PVA-MOR, this did not affect the proton conductivity. This is because the presence of water molecules increases the proton's transportation via the vehicular mechanism. However, as it was discussed in section 2.4.4, 90 percent of the proton transfer in the membrane is done by the Grotthuss mechanism which is expected to increase in the SPVA-MOR membranes.

Compared with the proton conductivity for the Nafion, the proton conductivity value for SPVA-MOR membrane has reached 51 percent of that for Nafion membrane. It is expected that this value could be increased when optimizing the sulfonation degree in the membrane. As it was shown in the IEC measurements, the SPVA-MOR membrane exhibits lower IEC value than the values given in the literature for sulfonated PVA membranes.

Other thing should be mentioned here is the effect of the interfacial layer between the zeolites particles and the polymer. As it was discussed in section 2.5.4 this layer may occur because of the rigidity of the polymer chain around the zeolites or the blockage of the zeolites' pores by those chains. Those defects have their drawbacks on the proton conductivity. Therefore, if the presence of those defects were confirmed, an increase on the proton conductivity is expected if we solve this problem. The observations of those defects may be done in future work.

5. CONCLUSION

The PVA-MOR membrane was previously studied by Libby et al (2003) and Üçtuğ & Holmes (2011). This membrane was found to have very low methanol permeability and a high selectivity. However, this membrane showed poor proton conductivities. In this study a sulfonic acid group was added to the PVA structure prior to the mixing with the mordenite. Both of the PVA-MOR and SPVA- MOR membranes were successfully synthesized, characterized and compared. The characterization of the membranes included SEM images, swelling measurements for water and methanol uptake and proton conductivity measurements. The SEM images gave an insight look at the morphology for the surface of the membranes. The images confirmed that the mixing was effective and the distribution of the mordenite particles in the PVA and the SPVA polymer was homogeneous in both membranes. In addition to that it asserts the absence of voids between the zeolite particles and the polymer. The swelling measurements due to methanol uptake gave a decrease in the swelling percentage for the SPVA-MOR. This result seems promising as it tells that this membrane is supposed to decrease the methanol crossover. The swelling measurements due to water uptake showed also a decrease in the swelling percentage for the SPVA-MOR. This was attributed to the presence of the sulfonic acid groups which may block the water adsorption sites in the membrane. Although the swelling measurements gave a lower swelling degree for the SPVA-MOR membrane, the proton conductivities for this membrane was on the contrary higher than that for the PVA-MOR membrane. The SPVA-MOR membrane showed a proton conductivity of 0.052 S/cm versus 0.036 S/cm for the PVA-MOR membrane. This is because the presence of water is responsible for the transportation of the protons via the vehicular mechanism while the sulfonic acid groups are known to enhance the proton transportation via the Grotthuss mechanism. However, the transportation of protons is known to occur 90 percent by the Grotthuss mechanism. Therefore, the water presence does not affect the proton conductivity value for the SPVA-MOR membrane. Finally, the SPVA-MOR membrane was measured to have an IEC value of 0.474 mequiv/g which indicates a low sulfonation degree in the membrane.

For future work the SPVA-MOR membrane could be synthesized with different sulfonation degrees and the proton conductivity could be optimized based on the sulfonation degree. Additionally, the methanol permeability could be measured and so the selectivity of the SPVA-MOR membranes could be calculated. More importantly, the membrane should be placed in an actual DMFC and the power output from the system should be measured and compared with the power output for Nafion Membrane.



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