Proton Exchange Membranes Prepared by Radiation Grafting of
N-Vinyl Imidazole/4-Vinyl Pyridine onto Poly (Ethylene-*co*-Tetrafluoroethylene) for High-
Temperature PEM Fuel Cells

by

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Naeimeh Rajabalizadeh Mojarrad

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ABSTARCT

The large contribution of fossil fuels emission to environmental pollution, as well as limited supplies, reveal the importance of alternative power sources. In this regard, fuel cells can be considered one the most favorable options for diverse applications. However, developing materials with properties that meet the requirements of fuel cell systems with high performance, reliable lifetimes and cost-effectiveness is still a challenging issue. Improvement of the membrane as the heart of the fuel cell is one of the growing research areas. Radiation-induced grafting methods have attracted extensive attention as a simple method for scaling up. The suitability of this method in terms of utilizing various combinations of base polymers and monomers results in the production of membranes with desired properties for numerous applications such as high-temperature PEM fuel cells.

In this study, 1-vinylimidazole (1-VIm) and 4-vinylpyridine (4VP) monomers have been utilized as monomers to graft onto ɣ-irradiated ethylene-*co*-tetrafluoroethylene (ETFE) films as the base polymer. Grafting reactions took place at 60°C for 24 h. The radiation grafted copolymer was subsequently doped with phosphoric acid to prepare new membranes for high-temperature operation. The effect of adding ferrous salt as an additive, utilizing various solvents during grafting and changing the monomer ratio on the grafting parameters was investigated. Properties of the resultant membranes were characterized via ex-situ ionic conductivity measurement at varying

temperature and humidity, thermal gravimetric analysis (TGA), and mechanical testing was completed using a universal test machine. The fuel cell performance measurements were conducted for the most promising membranes at various relative humidity and temperatures conditions. Additionally, the membranes with an ionic conductivity of 237 $mS.cm^{-1}$, prepared in the presence of salt with 36% GL at 110°C with 60% RH, exhibit the potential as promising membranes for high-temperature PEM fuel cell.

Yüksek Sıcaklıkta Çalışan PEM Yakıt Pilleri icin Proton Değşim Membranlarının N-Vinil Imidazol/4-Vinil Piridin Monomerlerinin Poli (Etilen-*co*-Tetrafluroetilen) üzerine Radvasyonla Aşılanması ile Üretimi

Naeimeh Rajabalizadeh Mojarrad

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ÖZET

Çevre kirliliğine yol açan ve sınırlı sayıda bulununan fosil yakıtlarından dolayı elektrik enerjisi üretmek için farklı alternatiflere yönelim önem arz etmektedir. Bu bakımdan, yakıt pilleri en elverişli enerji kaynağı olarak görülmektedir. Fakat yüksek performansa ve uzun ömre sahip düşük maliyetli yakıt pili malzemelerinin üretimi bu enerji kaynakları için sorun teşkil etmektedir. Yakıt pilinin önemli kısmı olan membran için geliştirme çalışmaları araştırmaya açık ve önemli bir konudur. Bu bağlamda yüksek miktarda üretim için kolay bir metot olan radyasyona bağlı aşılama metodu çok fazla dikkat çekmektedir. Bu metodun kolaylığının yanısıra, bu metotta baz polimerin ve monomerlerin değişik kombinasyonları PEM yakıt pili için istenilen özellikteki membran elde etmeyi sağlamaktadır ve bu durum PEM yakıt pilinin değişik alanlarda kullanımına imkan tanımaktadır. Bu yakıt pillerinin bir örneği de yüksek sıcaklıkla çalışan PEM yakıt pilleridir. Bu çalışmada ise, 1-vinilmidazol (1-Vlm) ve 4-vinilpiridin (4VP) monomerleri baz polimeri olarak kullanılan γ ile ışımınlanmış poli (etilen-co-tetrafloroetilen) filmleri üzerine aşılanmıştır. Aşılama reaksiyonu 60°C'de, 24 boyunca gerçekleştirilmiş ve sonrasında bu radyasyon ile aşılanmış kopolimere fosforik asit katılmıştır. Bu sayede üretilen membranlar yüksek sıcaklığa hazır hale gelmiştir. Bu çalışmada, demir esaslı tuzların reakiyon başlatıcı olarak etkisi, aşılama sırasında değişik solventlerin kullanımı ve monomer oranının değişiminin aşılama parametreleri üzerindeki etkisi araştırılmıştır. Sentezlenen membranların özellikleri, çeşitli sıcaklık ve nem değerlerinde

iyonik iletkenlik ölçümleri, termal gravimetri analizi, ve mekanik testler ile detaylı olaraak incelenmiştir. Sentezlenen membranlardan iletkenlik ve mekanik özellikler açısından üstün özellikli olanların, PEM yakıtpili şartlarında, çeşitli sıcaklık ve nem değerlerinde performansları incelenmiştir. 110°C'de ve % 60 RH'de, 237 mS.cm^{-1} değerine kadar iyonik iletkenlik gösterebilen, demir esasli tuz varlığında üretilen %36 aşılama derecesindeki membranlar, yüksek sıcaklıkla çalışan PEM yakıt pilleri için gelecek vaad eden membran olarak kullanılma potansiyeline sahiptirler.

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Abbreviations

1-VIm   : 1-vinylimidazole

4VP   : 4-vinylprydine

AAEM   : Anion exchange membrane

AD   : Acid doping

AFC   : Alkaline fuel cell

CL   : Catalyst layer

CHP   : Combined heat and power

ETFE   : Poly (Ethylene-*alt*-Tetrafluoroethylene)

GDL   : Gas diffusion layer

GL   : Graft level

HT   : High temperature

IPA   : Isopropanol

LT   : Low temperature

MCFC   : Molten carbonate fuel cell

MEA   : Membrane electrode assembly

PA   : Phosphoric acid

PAFC   : Phosphoric acid fuel cell

PBI   : Poly (benzimidazole)

PEM   : Polymer electrolyte membrane

RH   : Relative humidity

RIG   : Radiation-induced grafting

SOFC   : Solid oxide fuel cell

TGA   : Thermogravimetric analysis

THF   : Tetrahydrofuran

UTM   : Universal testing machine

Chapter 1. Introduction

The first chapter of this thesis includes a brief overview of developing fuel cell, from its invention around 160 years ago [1, 2], up to now. Furthermore, fundamentals, as well as several types of the fuel cells, specifically high-temperature polymer electrolyte (or proton exchange) membrane fuel cells (HT-PEM fuel cells), are introduced in detailed, in the following subsections. The focus of the present study is preparation proton conducting membranes for HT-PEM fuel cell applications.

1.1.   Invention of the Fuel Cell

The foundations for the fuel cell invention date back to the efforts of numerous scientists in the field of electrochemistry such as Sir Humphry Davy [3], who worked on the electrolysis of different compounds through the use of a voltaic pile [1]. However, the discovery of the basic fundamentals of fuel cells can be attributed to Michael Faraday, who contributed great deal to the study electrochemistry as well as electromagnetism [4]. William Robert Grove, one of Faraday's contemporaries, conducted numerous electrochemical cells which resulted in a considerable improvement of the voltage generated in the two-fluid voltaic batteries which were made by his peers, such as the well-known "Daniell Cell" that was designed by Frederik Daniell [1]. The further investigations of Sir W.R. Grove lead to

the breakthrough discovery of the initial "fuel cell" or rather "gas cell" in 1839. Grove is known as the father of fuel cell technology since he was the first to realize the possibility of producing electricity directly via an electrochemical reaction.

His primary apparatus consisted of a set of platinum electrodes, immersed in an acid bath and tubes containing H_2/O_2; these acted as the electrolyte and reactants, respectively Figure 1.1. [5] . He coined the term "voltaic gaseous battery" for his innovative invention.
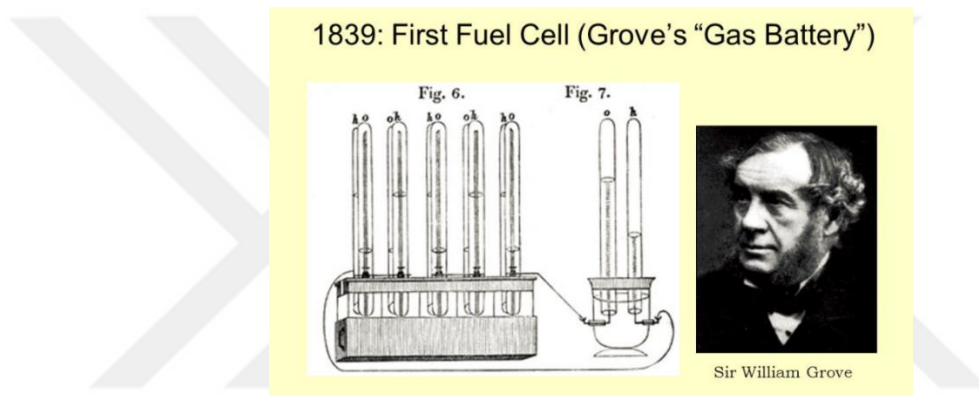
Figure 1.1. Schematic of Sir William Grove fuel cell [5]

Later, in 1889 Ludwig Mond and Charles Langer, the pioneering researchers of the fuel cell, used coal gas as inlet fuel to produce electrical current and named their system as a "fuel cell"[1]. The poising of the platinum electrode was the main barrier towards scaling up for their fuel cell system. In 1932 further studies of Bacon Frances, a British engineer resulted in the breakthrough discovery of the first alkaline fuel cell as well as a remarkable improvement of the previous fuel cells. NASA utilized the first practical fuel cell in the Gemini and Apollo spacecraft in 1960 [1, 6].

Table 1.1. Main milestones in history of fuel cells [6]

Year(s)	Milestone
1839	W.R. Grove and C.F. Schönbein separately demonstrate the principals of a hydrogen fuel cell
1889	L. Mond and C. Langer develop porous electrodes, identify carbon monoxide poisoning, and generate hydrogen from coal
1893	F.W. Ostwald describes the functions of different components and explains the fundamental electrochemistry of fuel cells
1896	W.W. Jacques builds the first fuel cell with a practical application
1933–1959	F.T. Bacon develops AFC technology
1937–1939	E. Baur and H. Preis develop SOFC technology
1950	Teflon is used with platinum/acid and carbon/alkaline fuel cells
1955–1958	T. Grubb and L. Niedrach develop PEMFC technology at General Electric
1958–1961	G.H.J. Broers and J.A.A. Ketelaar develop MCFC technology
1960	NASA uses AFC technology based on Bacon's work in its Apollo space program
1961	G.V. Elmore and H.A. Tanner experiment with and develop PAFC technology
1962–1966	The PEMFC developed by General Electric is used in NASA's Gemini space program
1968	DuPont introduces Nafion®
1992	Jet Propulsion Laboratory develops DMFC technology
1990s	Worldwide extensive research on all fuel cell types with a focus on PEMFCs
2000s	Early commercialization of fuel cells

1.2. Advantages of Fuel Cells

Comparing fuel cells in terms of efficiency, fuel flexibility and power density with batteries and combustion engines, with a limited lifetime and Carnot-limited procedure respectively reveals the significant advantages of fuel cells over them and makes it as the most promising green energy technology [7, 8]. From another point of view, this comparison figures out that they can be considered as the balance concepts, which possesses the advantages of both systems at the same time. Moreover, a negligible amount of vibration and noise during operation, quick start-up, infinitesimal emission and generation of water and recyclable heat as the only by-products of the process are the other brilliant aspects of this category [7]. According to the several above-mentioned worthwhile futures of fuel cells in addition to the human-being urgent need for a clean and renewable power planet for response to the rapid growth of population and industrialization, extensive attention and efforts have been focused on scaling up cost-effective and durable fuel cells as the potential alternative set-up with desired properties. Despite of the noticeable benefits, there are some difficulties for commercialization of fuel cell in a widespread manner due to non-solved issues relevant to the utilization of costly materials and insufficient lifetime. Stationary, portable, electronic and transportation application are the most common applications of fuel cells Figure 1.2. The

design characteristics of the fuel cell such as weight and shape are important parameters that associate with its relevant application.

Figure 1.2. Summary of fuel cell applications [6]

1.3. Fundamentals of Fuel Cell

The main principle in a fuel cell is the conversion of the stored chemical energy in inlet fuels to the electrical energy, through an electrochemical reaction [3]. In contrast to several stepped energy conversion process in conventional combustion systems, in fuel cell system as the same of batteries, conversion of chemical energy to electricity happens in a single step as shown in Figure 1.3 [9]. Therefore, fuel cells are considered as superior efficient systems without losses energy during different conversion steps. When using hydrogen fuel as inlet fuel and oxygen or air as the oxidant, each hydrogen molecule decomposes to two electrons and two protons in anode side, at same time the oxygen reduction reaction (ORR) occurs by separation of oxygen molecules to individual atoms at the cathode side. The produced electrons go through an external circuit and the resultant protons in anode through a proton conducting membrane, towards the cathode electrode. Combination of these species with single oxygen atoms leads to the formation of water. In other words, this reaction is the inverse reaction of electrolysis of water with aid of electricity. Additionally, the formation of water from its components is an exothermic reaction, so heat is the other by-product of this reaction.
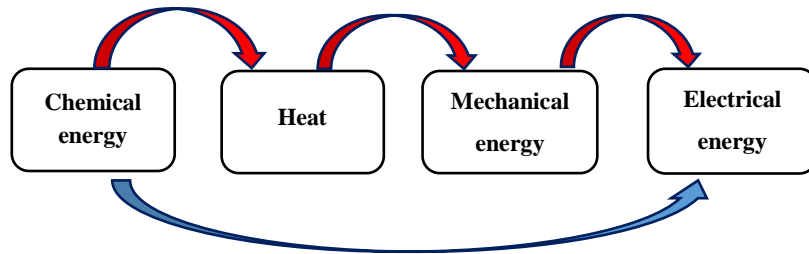
Fuel Cell

Figure 1.3. Comparison of the energy conversion procedure in a fuel cell and a combustion engine [9]

1.4. Components of Fuel Cell

A fuel cell system consists of several numbers of single cells to generate sufficient amount energy as Sir Grove Fuel Cell in which he connected several single cells in series. A single cell basically makes up of between two electrodes, an ionic conducting electrolyte (membrane), two gas diffusion layers (GDL) and bipolar plates and gas flow channels as represented in Figure 1.4 [7]. The membrane is sandwiched between the electrodes. Separation of anode side from the cathode side to avoid mixing of the fuel and oxidant directly, in addition, non-permeability for electrons, which means a selective transformation of various specious between anode and cathode are the most crucial roles of the membrane. Hence, an efficient selective permeability is the pivotal duty of a membrane. Each electrode have a catalyst layer (CL) and a gas diffusion layer (GDL).
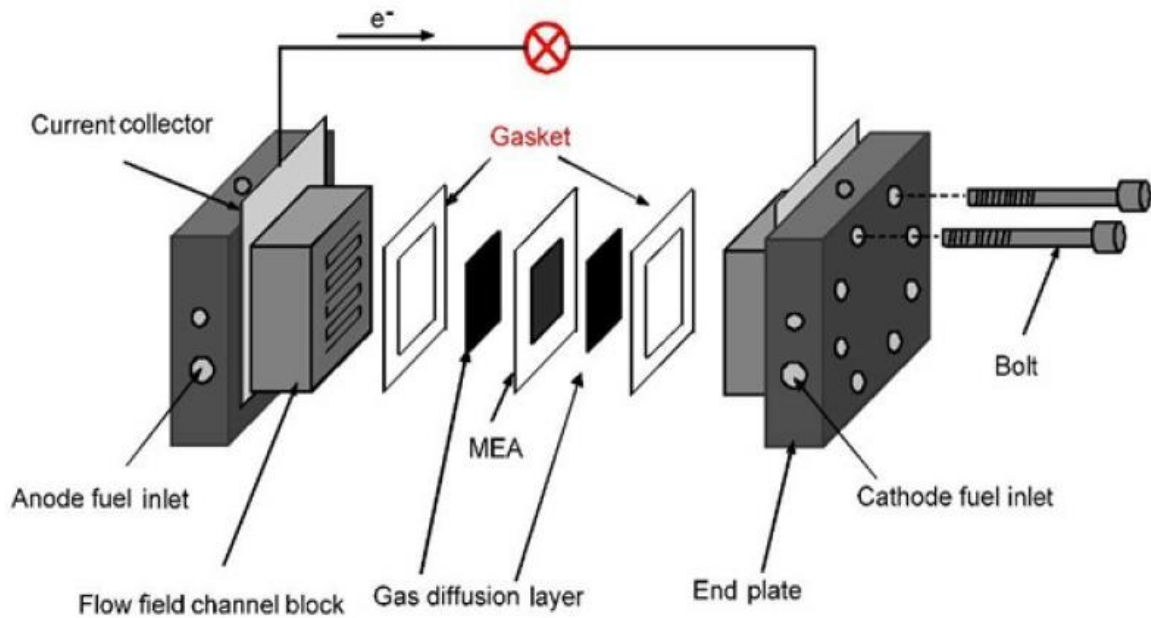
Figure 1.4. Schematic of membrane assembly [7]

The catalyst layer is where the reduction and oxidation reactions occur in anode side and cathode side respectively. The membrane electrode assembly (MEA), in the other words, the heart of a fuel cell, is referred to the abovementioned components as a whole that is governed the main procedures in the fuel cell. Fuel cells are mainly categorized according to their electrolyte nature, so their different operating conditions in terms of the inlet fuel/oxidant type and operating temperature, each category includes components with special characteristics to meet their requirements.

1.5. Types of Fuel Cells

Fuel cells are mainly categorized into five different categories based on their electrolyte type, however, their other properties such as operating temperature or kind of supplied fuels, have been used as well. Polymer Electrolyte Membrane Fuel Cell (PEM), Solid Oxide Fuel Cell (SOFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MOFC), and Alkaline Fuel Cell (AFC) are the common commercial fuel cells which are sorted by their operating temperature in Figure 1.5. [10].
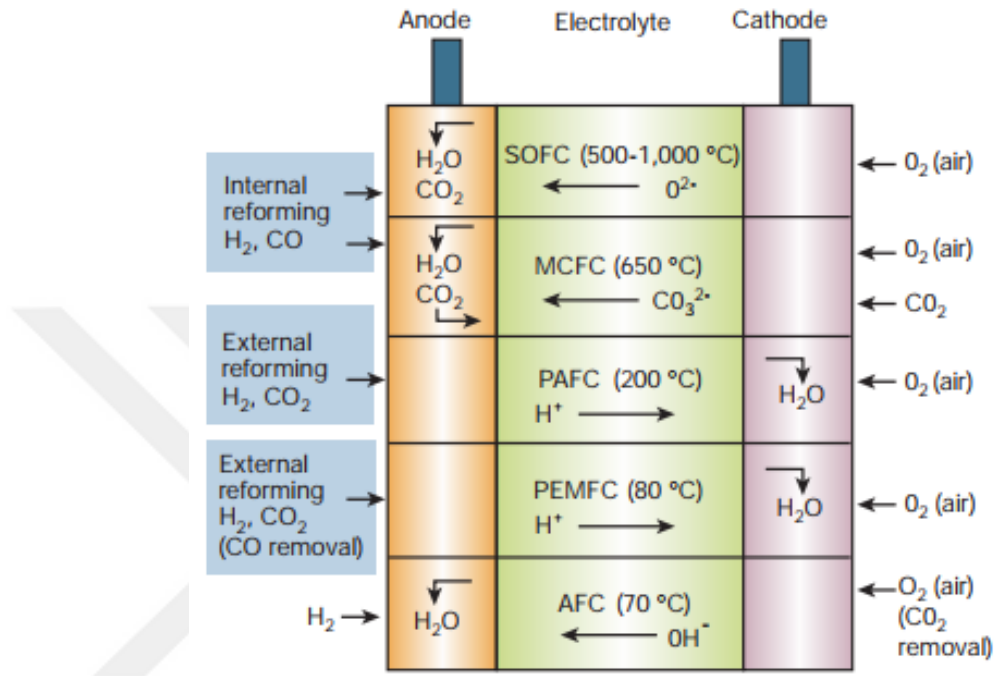
Figure 1.5. Different types of fuel cells [10]

Regardless of their differences in inlet fuel, electrolyte type or the other parameters, conversion of chemical energy directly to the electricity formation of water in anode or cathode, migration of ion species through membrane and electrons through an external circuit are the similarity aspects among these systems. A comprehensive summary of different kinds of fuel cells includes their operating temperature range, anode and cathode reactions, common applications, type of charge carrier and generated power is represented in Table 1.2. [2]. In addition to the single cell components, each type requires some manipulating systems based on the employed fuel and temperature range of cell [2].

Table 1.2. Different fuel cell types and their characteristics [2]

	AFC (Alkaline)	PEMFC (Polymer Electrolyte Membrane)	DMFC (Direct Methanol)	PAFC (Phosphoric Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
Operating temp. (°C)	<100	60–120	60–120	160–220	600–800	800–1000 low temperature (500–600) possible
Anode reaction	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode reaction	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$3/2 O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$
Applications	Transportation Space Military Energy storage systems			Combined heat and power for decentralised stationary power systems	Combined heat and power for stationary decentralised systems and for transportation (trains, boats, ...)	
Realised Power	Small plants 5–150kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small – medium sized plants 50kW – 11MW	Small power plants 100-kW- 2 MW	Small power plants 100–250kW
Charge Carrier in the Electrolyte	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

1.5.1. PEM Fuel Cells

Among existing types of fuel cells, polymer electrode membrane (PEM) fuel cells are regarded as the most promising category for various applications such as transportation, portable power generation and stationary. PEM fuel cells typically consist of:

1. Membrane: a very thin proton conducting layer (10-100 µm) as a solid electrolyte which separates the anode side from the cathode side [11]. Perfluorinated membranes are extensively utilized at PEM fuel cells such as Nafion®, Aciplex, and Flemion. High ionic conductivity, high selectivity to prevent crossover of fuel and oxidant, sufficient chemical stability and mechanical integrity are the most vital features for a membrane [11]. Developing tailor-made composite membranes with superior characteristics via several modification methods either in terms of the used materials, such as reinforcement of perfluorosulfonic membranes with PTFE, impregnation of membranes with selective materials or in terms of the fabrication techniques such as the-state-of-art radiation grafting method (RIG) and plasma polymerization method, have been studied extensively [2, 12-14].

2. Catalyst layer (CL): A thin carbon-based electrodes with Platinum (Pt) deposited particles where ORR and HOR take place. Pt is known as the best catalyst material according

to its high catalytic activity up to now. However, the limited reservoir, high sensitivity to CO contamination and particularly high cost of Pt are the major challenging points. In this regard remarkable number of studies for finding an alternative catalyst material, diminishing the loading amount, improvement of the surface area and dispersion of Pt particles via applying new techniques such as alloying, using high quality hybrid support material and state-of-the-art carbon-based materials (i.e. carbon nanotubes, carbon fibers) have been conducted [2, 15].

3. Gas diffusion layer (GDL): GDL is fabricated with common carbon-based materials, mainly carbon paper and carbon cloth, which is modified with a hydrophobic Teflon layer. GDL is considered as a porous (250-20 µm) multi-functional component and at the same time a support for the delicate membrane [16]. In some cases, GDL has a double layer form that is composed of a microporous layer (MPS) and a microporous layer for manipulating the capillary pressure. Transformation of reactant towards the catalyst layer, removing water from the system at cathode side and conducting the electrons to the external circuit take place through this component. The optimized pore size, water management as well as adequate electric conductivity are the most important issues associated with GDL layer [17]. High electrical conductivity, low diffusion resistance, and high corrosion resistivity are essential features for a reliable performance [18].
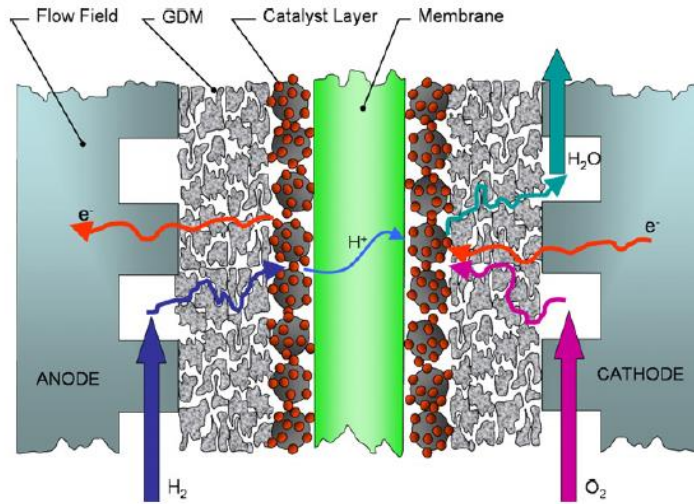
Figure 1.6. Components of a membrane electrode assembly [19]
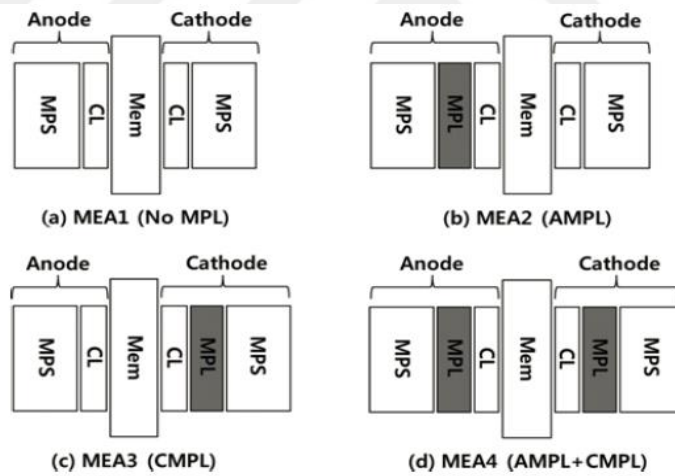
Figure 1.7. Four different designs of MEA in PEM fuel cell [20]

PEM fuel cells are classified in two types according to their operating temperature, Low-Temperature PEM fuel Cells (LT-PEM fuel cells) and High-Temperature PEM Fuel Cells (HT-PEM fuel cells) which operate below 100°C and up to200 °C respectively [3]. Hence, the nature of the used materials and designs of the MEA components to satisfy the operating conditions and requirements are necessary to be taken consideration.

1.5.1.1. Reactions in PEM Fuel Cells:

At the anode electrode hydrogen gas as the fuel is pumped into the system and each hydrogen molecule oxidizes in catalyst layer and splits into two protons and two electrons. This is called the hydrogen oxidation reaction (HOR). In addition, oxygen reduction reaction (ORR) is referred to the reaction that occurs in the cathode side since air or oxygen gas is fed to the system and the oxygen molecules are reduced to oxygen ions and react with protons and electrons that are transformed from anode to cathode [21]. Figure 1.8 shows the schematically the overall process that occurs in a PEM fuel cell.

Anode Reaction: $H_2 \rightarrow 2H^+ + 2e^-$ (1.1)

Cathode Reaction: $1/2\ O_2 + 2e^- + 2H^+ \rightarrow H_2O$ (1.2)

Overall Reaction: $H_2 + 1/2\ O_2 \rightarrow H_2O + heat$ (1.3)
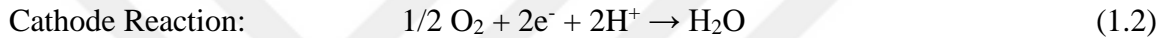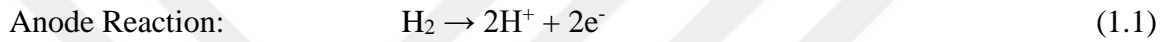
Figure 1.8. Schematic of a H_2/O_2 PEM fuel cell [2]

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1.5.1.2. Low-Temperature PEM Fuel Cells

Low-temperature fuel cells are considered as power generation systems, which operate below 100°C. They are well-known for their quick startup according to their operation at elevated current densities and low temperatures [9]. In the first generation of aforementioned fuel cell type, perfluorosulfonic acid-based membranes have been used widely [21]. Nafion® as the most well-known perfluorosulfonic acid-base membrane has been developed in the 1960s [11]. Up to 100 mS.cm^{-1} ionic conductivity of Nafion® in fully humidity condition, and its adequate chemical stability makes it as the most prominent choice for PEM fuel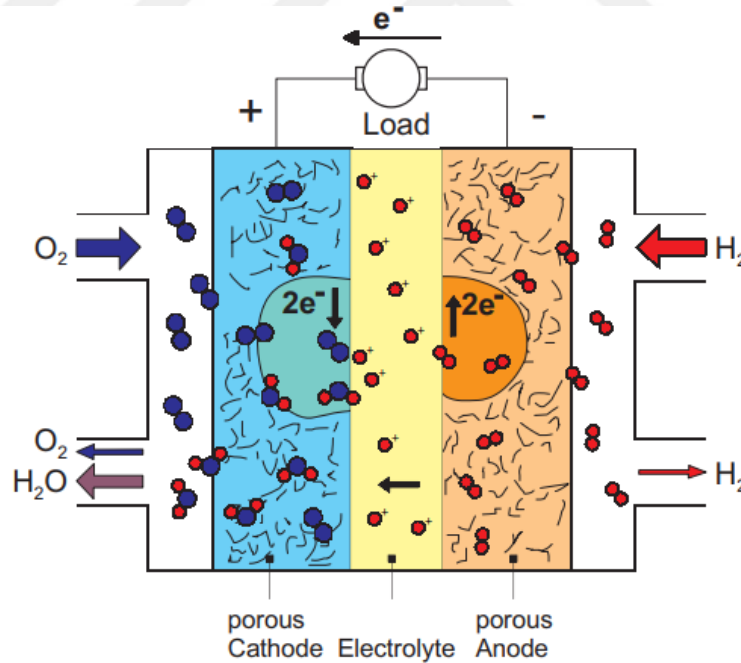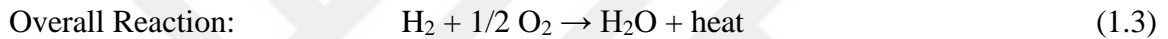 cells. Despite the numerous advantages of Nafion®, an extensive dependence of its ionic conductivity to water content, are making their application limited to the temperatures less than 100°C, also the complex and costly production procedure of Nafion® is another undesired feature for commercial purposes. In this regard, various investigations have been conducted to improve the existence membranes properties.

1.5.1.3. High-Temperature PEM Fuel Cells

High-temperature PEM fuel cells (HT-PEM fuel cell) have been attracted tremendous attention mostly due to their simple and compact structure. In this type, the water-based electrolyte material of LT-PEM fuel cell is replaced with a mineral-acid base membrane with the potential to resist up to 100-200°C temperature ranges [3, 22]. The most remarkable benefits of HT-PEM fuel cells over LT-PEM fuel cells are listed in the following subsection. Obtaining higher efficiency, elimination of the cooling system, the ability of the system to recycle the generated heat and elevated tolerance of CO are the major benefits of this category over LT-PEM fuel cells.

Advantages of the High-Temperature PEM Fuel Cells:

1. Improved reaction kinetics

Elevated operation temperature ranges provide the required activation energy for both oxidation and reduction reactions at the anode and cathode electrode respectively. Especially the enhancement of the ORR rate, which is about 10^5 orders of magnitude smaller than that

of HOR. This gives the opportunity to use alternative inexpensive catalyst particles than Pt in CL. Moreover, dwindling of the resistance for migration of various specious (gas, water and protons) towards anode to cathode or vice versa, leads to provide high proton conductivity and prevent the higher levels of voltage loss compared to LT-PEM fuel cells as well [21-23].

2. Increased catalyst contamination tolerance

In contrast to the LT-PEM fuel cells that even infinitesimal amount of CO (10 ppm) results in a remarkable decrease of catalyst activity, at temperatures above 150°C according to the Gibbs energy the absorbance of CO on the Pt particles of the electrode is not preferred as much as in lower temperature [23]. Therefore, elevated operation temperature ranges lead to lower sensitivity of the system to the impurities of the inlet fuel or in the other words lessen the poising of the active catalyst particles through the undesirable reactions [21, 22, 24].
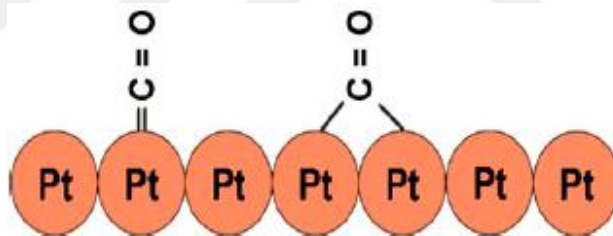
Figure 1.9. Schematic of the adsorption of CO on Pt particles [23]

Therefore, the possibility of utilizing lower amounts of costly Pt loadings in the electrodes of HT-PEM fuel cells, as well as no more need to pure hydrogen fuel cause to lessen the final cost of generated power due to the problematic process of hydrogen purification and storage. As depicted in Figure 1.10. at temperatures higher than 150°C the CO poising effect is diminished considerably. As the consequence cell performance is less affected by CO concentration that of the in LT-PEM fuel cells (Figure 1.10b) [23].

| (a) | (b) |
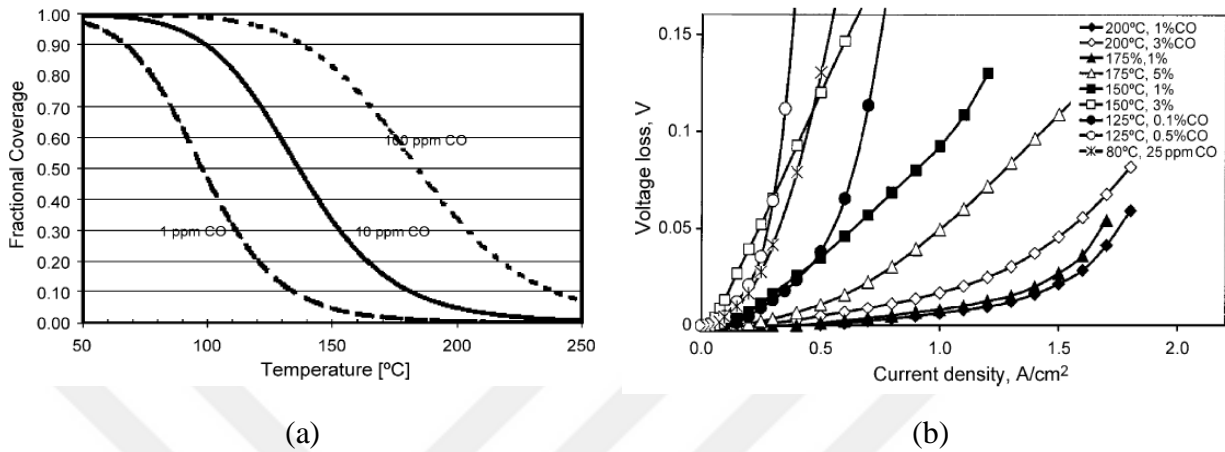
Figure 1.10. The effect of temperature on (a) the amount of CO adsorption onto Pt
particles, and (b) fuel cell performance for various CO concentrations [23]

3. Elimination of water management problems

Less or non-dependent proton conductivity of HT-PEM fuel cells on water results in elimination of water management problems such as blockage of the catalytically active surface area, back diffusion phenomenon and control of water content in at optimized condition to provide a sufficient proton conductivity as well as prevent flooding at the cathode electrode [21, 23, 25, 26].

4. Improved heat management

Heat generates as one the byproducts of the exothermic reaction which takes place in the fuel cell. In the case of LT-PEM fuel cells about 40-50% of the chemical energy of the reactants, converts to heat that can be lead to degradation of different components of system if not remove immediately from the system. Therefore, an efficient cooling system is considered as an essential component for LT-PEM fuel cells, however in terms of HT-PEM fuel cells there is no need to such equipment due to the higher difference of the temperature of the generated heat gradient with environment. Hence, HT-PEM fuel cells are more compact and simple. Furthermore, the high quality generated heat in these systems can be used to

cogeneration of energy process that enhance their efficiency notably compared with LT-PEM fuel cells [21-23, 25, 26].

1.5.2. Solid Oxide Fuel Cells

Solid oxide fuel cell (SOFC) refers to the category with a general operation temperature of 400 to 1000°C, which dependents on the material used as the electrolyte, and have an efficiency up to 70% and infinitesimal emission base on elevated operating temperatures. Their superior characteristics in terms of efficiency and life time make them well suited choice for stationary application. The core constituent of a solid oxide fuel cell is consisted of a solid ceramic electrolyte such as zirconia that is surrounded by two electrodes from both sides. In ITSOFCs (intermediate SOFCs) with operation temperature range from 600-800°C, using inexpensive metallic electrode materials lowers the cost of system, but it results in an undesired drop in cell performance [27]. Mixture of NiO with electrolyte material as anode electrode and Lanthanum included compounds as well as CeO2 based materials as cathode material are remarkably used in SOFCs that leads to cut off in price of final product [27, 28]. Using both proton conducting and Oxygen ion conducting material is possible as porous electrolyte material in this category. The type of conductivity defines the electrode (anode or cathode) in which water is generated. The most important issue that should be put under consideration, is well thermal expansion matching between different components high as well as using materials with sufficient toughness and chemical stability that can be withstand upon corrosion under harsh operation condition [27].

1.5.3. Molten Carbonate Fuel Cells

Molten carbonate fuel cells (MCFCs) date back to the research of Broers and Ketelaar in the 1960s. Generally, alkali metal carbonates such as Li/Na and Li/Na/K carbonates in a porous lithium aluminate matrix, Ni and NiO have been used as electrolyte, anode and cathode material respectively, in the MCFCs. Their operation temperature is from 600 to 700°C, which is approximately the melting point range for most of the alkali carbonates. The generated carbonate ions are the product of oxygen combining with carbon dioxide at the

cathode side migrate through the ionic conducting electrolyte, and these ions combine with H_2 at the anode side. Water, CO_2, electrons and heat are the products of the anode reaction. Electrons in a similar way to other types go towards the cathode through external circuit. The produced heat and CO_2 are used for the next cycles. MCFCs benefit from the internal reforming of methane by using generated high quality heat and high efficiency because of their considerable heat recovery, no need for expensive as metallic catalysts despite of the low temperature cell systems [29, 30]. Despite their high efficiency, the leakage of molten electrolyte through porous electrodes leads to the corrosion of the different components and diminishing electrolyte amount, creep of anode at that high temperatures and dissolution in electrolyte are the most challenging issue associated with them. Considering their potential high efficiency (60-90%), several approaches and techniques have been reported to overcome the existent shortages of this category. Such as coating bipolar plates with an alumina layer to protect them from corrosion, utilization of some alternative Ni-based composite materials as anode electrodes (e.g. $La2O_3/SmO_3$) and cathode electrodes (e.g. $LiCoO_2$), adding of some alkaline-earth carbonates to electrolyte [31-33].

1.5.4. Phosphoric Acid Fuel Cells

Phosphoric acid fuels are considered as one the most efficient and commercial developed fuel cells with 37% electrical efficiency, 87% total efficiency in the other words combination of heat and power (CHP) and more than 40000 h life time [34, 35]. PAFCs are categorized as the intermediate-temperature fuel cells the same as high-temperature PEM fuel cells due to their operating range which is between 150 and 200°C. Diluted phosphoric acid and platinum were used as the proton conducting medium and electrode respectively, in early PAFCs. Generally, SiC is used as the container for liquid acid electrolyte. Depositing catalytically active Pt particles on carbon base support material as electrode for these systems results in a noticeable impact on lessen the final cell cost and durability [34]. In recent decades many studies have been focused on new material and engineering designs to overcome the relevant durability shortage of these systems, such as Kauffman *et al*. have been reported Pt-decorated carbon nanotube as new generation of carbon-based materials,

cathodes with improved stability approximately 20 times compared to the traditional electrodes [36].

1.5.5. Alkaline Fuel Cells

In 1970 Kordesch had been built a car using an alkaline fuel cell (AFC) with potassium hydroxide membrane electrolyte [37]. The name of this category is turned in to the basic nature of the membrane material (metal hydroxide membrane) which is responsible for conducting the hydroxide ion from cathode to anode side. The ion transferring direction and water formation electrode of AFCs are the same as MCFC and SOFC systems, but opposite of a PEM system as shown in Figure 1.11 [10, 38].
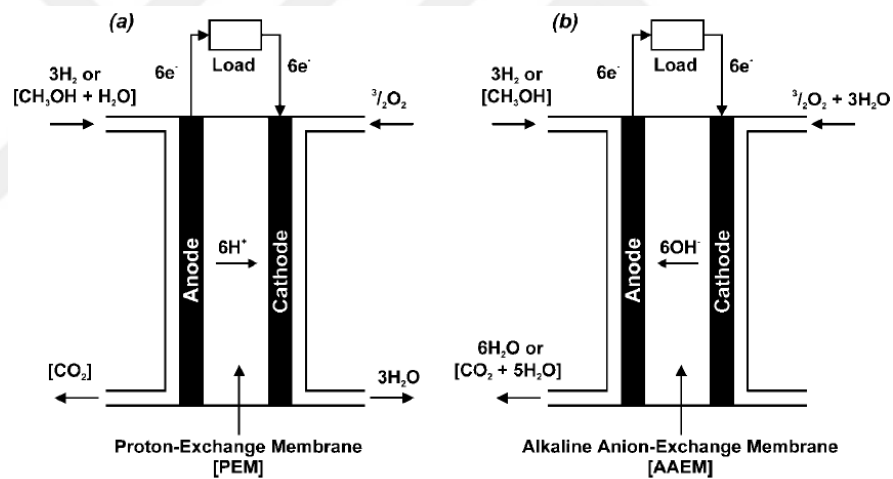
Figure 1.11. Representation of the reactions, direction of ion migration and fed fuels in the (a) PEM fuel cell and an (b) AFC fuel cell [38].

They can be fueled either with hydrogen or with methanol. In contrast to acidic membranes the kinetics of both reactions are high despite of their low operating temperature range (23-70°C) and an non-noble catalyst can be used in both electrodes such as nickel [38, 39]. The ability of methanol utilization benefits from hydrogen fuel due the difficulties of dealing with hydrogen storage and manipulating the related problems with pure hydrogen. Nevertheless, the most problematic issue associates with this type, which relates to its liquid

membrane material, is still challenging. Metal hydroxide (i.e. KOH) as a basic compound has extensive tendency to react with existence carbon dioxide in feed fuel or oxidant and form metal carbonate/bicarbonate species (i.e. K_2CO_3, $KHCO_3$). Blockage of GDL pores as a result of solid carbonate particles precipitation which move with liquid electrolyte, and consumption of the hydroxyl ions during this undesired process, are the two major destructive effects of metal hydroxide membranes [37]. Using an alternative solid polymer electrolyte similar to the PEMFCs, have been investigated through tremendous number of studies. Replacing the traditional metal-carbonate membranes in AFCs with a metal-cation-free, polymer based alkaline anion exchange membrane (AAEM) as the electrolyte in AFC systems have been showed significant advantages over conventional membranes [40]. In addition, AAEM membranes offers a well performance DMFC system in which methanol is directly injected to system as the fuel. In this regard Varcoe *et al.* have been reported the preparation of anion exchange membranes via grafting quaternary ammonium derived functional groups as basic centers responsible for conducting hydroxide anions from cathode to anode, on the ETFE and FEP backbone polymers as substrates, using radiation induced grafting method.

Figure 1.12Figure 1.12 represents the possible ionic conductivity mechanisms via these membranes [40].
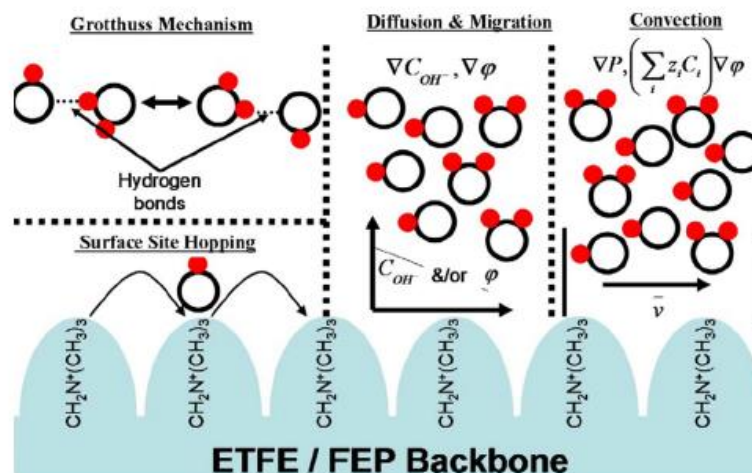
Figure 1.12. Different mechanisms of hydroxyl anion transportation in AAEM fuel cell [40].

This approach is considered as a successful and straightforward method relevantly used for production of membranes for PEMs as well (sulfonated ETFE and FEP membranes) [40-42]. Applying this method results in improvement of the durability and mechanical integrity of the resultant membranes as the most challenging issues associates with AFCs. Despite of the PEMFCs the direction of ion migration is from cathode to anode.

1.6. Membranes for PEM Fuel Cells

Perfluorinated, partially fluorinated, non- fluorinated, non- fluorinated with aromatic backbone, acid-base composite and non- fluorinated hydrocarbon membranes are the relevant membranes for PEM fuel application Figure 1.13 [43].
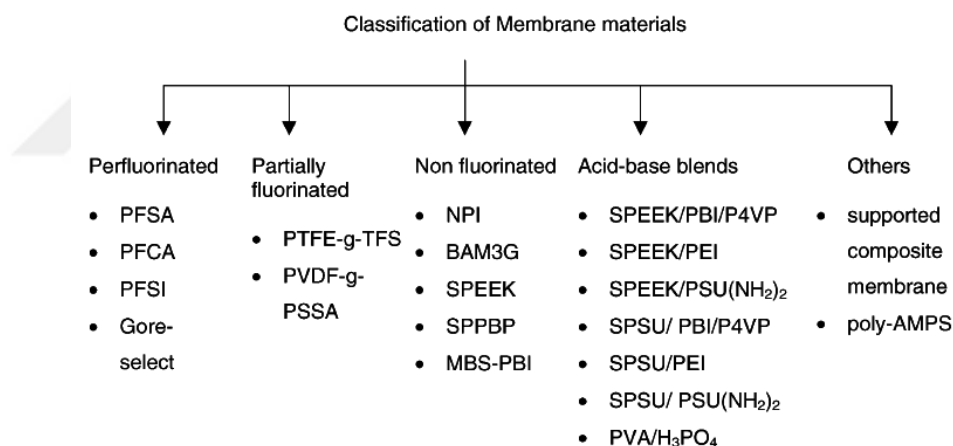
Figure 1.13. Classification of membranes materials [43]

Perfluorosulfonic acid (PFSA) membranes are the so-called branch of perfluorinated membranes which are made up of a polytetrafluoroethylene (PTFE) backbone and perfluoroalkyl side chains which are connected to sulfuric acid groups (Figure 1.14) [43, 44]. In a hydrated condition the interaction between acid region and water molecules brings about the ionic conduction throughout the membrane[45]. The invention of Nafion® as the dominant member of PFSA dates back to 1970 by Due Pont which showed an enhanced performance in terms of ionic conductivity (100 mS/cm) and lifetime (60000 h) compared to

previously developed membranes in a way that even today is used to as reference membrane for PEM fuel cells [43, 46]. Despite the superior properties of Nafion®, the reliability of its ionic conduction on fully humidified condition limits its application to temperatures under the boiling point of water. Moreover, high production cost of Nafion® is another non-solved critical issue that restricts its application in the commercial systems. In this fashion development of partially fluorinated and non-fluorinated membranes have been developed as inexpensive alternative options [47, 48]. Due to the aforementioned shortages of Perfluorosulfonic acid membranes, impregnation of Nafion® in order to preparation of Nafion®-based membranes with less water dependent ionic conductivity and improved mechanical properties have been investigated. Furthermore, in terms of the applied preparation method grafting of non-fluorinated or partially fluorinated monomers on the base polymer films such as FEP, which is followed by acid doping is considered as an alternative approach for obtaining more cost-effective membranes. Non-fluorinated styrene monomer is widely used by several groups for this purpose [45-47].
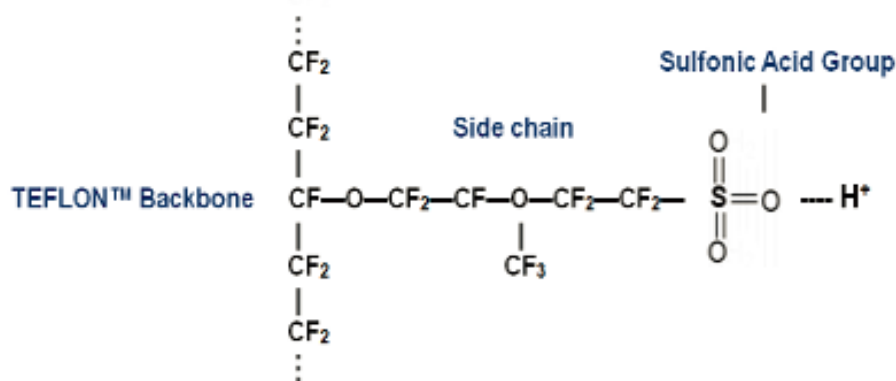
Figure 1.14. Chemical structure of Nafion® [44]

Predominantly, temperature, morphology of the membranes' components and water content determine the extent of its ionic conductivity [9]. Indeed, mainly three different approaches are applied to enhancement of the membranes required properties for specific applications as shown in Figure 1.15. [49]. Blending is referred to the physically mixing of the desired polymers whereas grafting is a chemical process that includes bonding of side

20

chain polymers to the backbone polymers covalently and curing method in which a coating layer applied to the substrate.
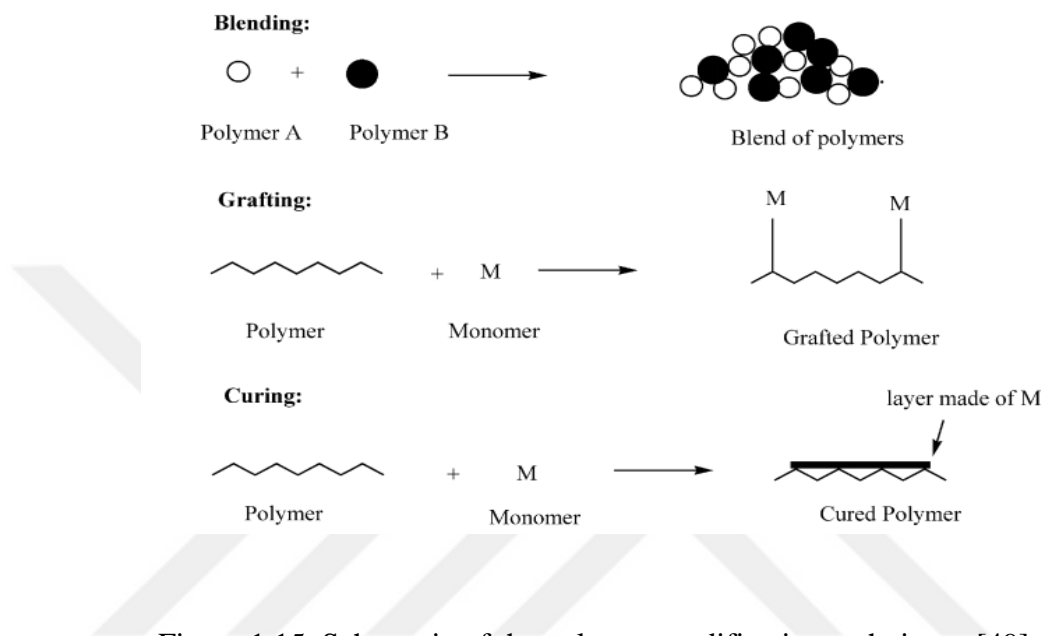
Figure 1.15. Schematic of the polymer modification techniques [49]

1.6.1. Mechanisms of Conductivity in the PEM Fuel Cells

Protonic defects or in other words protonic charge carriers are the responsible elements for proton conducting phenomena in a proton-conducting medium. Regardless of the type of conduction mechanism and protonic defects species, the existence of the hydrogen bonds in the structure of the membrane are required for occurring conduction process; Since continuously hydrogen band formation and breakage is the main reason of proton transfer through the membrane. Water, oxo-acid anions and heterocycles are the relevant species that are used frequently as charge carriers; however, the procedure is different to some extent for each type of material. For example, in the case of phosphoric acid, charge carriers are produced via self-dissociation of the acid. According to the literatures hopping of protons between two different N atoms or transferring protons via Grotthuss mechanism from NH^+ site to the phosphoric acid anions, hopping along $H_2PO_4^-$ anions also via water in hydrated condition are the possible mechanism for proton conduction in phosphoric acid systems [50-

53]. The strength of hydrogen bonds, morphology and structure of the membrane, mobility and concentration of the protonic defects, degree of hydration in water dependent systems and operation temperature are significant factors, which affect the magnitude of the resultant conductivity. Figure 1.16 shows the effect of difference in morphology for two water dependent proton conductive membranes. For an effective conduction of protons. The presence of channels with proper size, and sufficient amount of water for diffusion is essential, hence, for Nafion® and sulfonated aromatic polymer membranes, the level of hydration has a direct effect on their ionic conductivity. Hopping and diffusion are the most predominant mechanisms for proton transfer through a hydrated proton conducting medium [25, 53, 54].

Figure 1.16. Structure of Nafion® and sulfonated polyetherketone membranes [54]

1.6.2. Graft Co-polymerization Methods
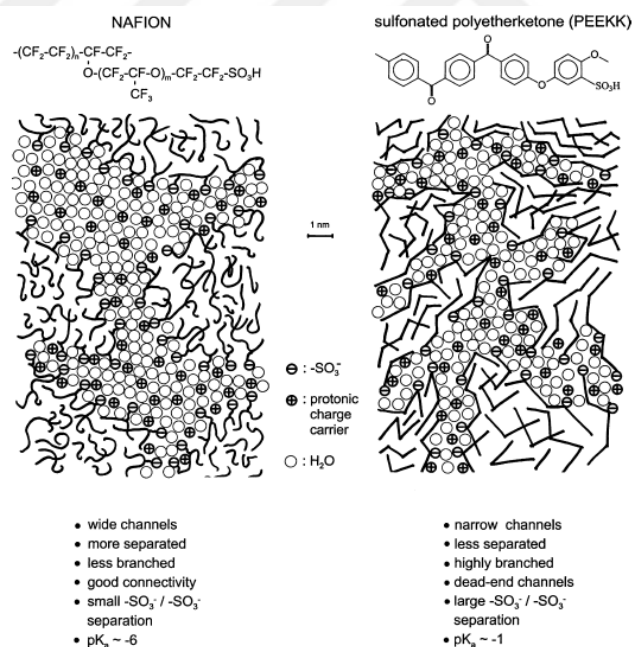
Graft co-polymerization is applied to modify of the existence polymers via introducing of functional groups. There are five well-known methods [49]:

1. Chemical Grafting: An initiator is used to produce free radicals or charged species (acid-base reactions).
2. Photochemical Grafting: Light is used to create active sites in this technique.
3. Radiation Grafting: Creation of free radicals brings about an interaction between the monomers and base polymer.
4. Plasma-induced Grafting (chemical vaper deposition): High-energy electrons from the plasma create the free radicals on substrate, which is ended up with a macromolecular radical.
5. Enzymatic Grafting: enzymes are responsible for initiation grafting reaction.

1.6.2.1. Radiation-induced Graft Copolymerization

Among different techniques of membrane preparation, radiation-induced graft polymerization (RIG) is considered as one of the most attractive topics of publication in membrane science field for last three decades. The ability of conserving intrinsic properties of used polymers in addition, numerous coupling options of monomers and base polymers without restrictions associate to their configuration and nature (resins, fibers and films) are the main notable advantages of using this method [8, 55-57]. Furthermore, high production speed and simplicity of the procedure compared to complicated traditional casting methods for membrane fabrication results in to end up with homogeneous, defect-free and cost-effective polymeric membranes. Considering the adjustable graft parameters in a simple way, is the other significant benefit of RIG process, which provides an ability to tune the membrane physicochemical characteristics. Consequently, RIG technique can be an effective step to commercialization of fuel cells according to its scalability and low-cost. In this regard, many studies has been focused on preparing membranes via RIG method as the state-of-the-art method of membrane fabrication applicable in different types of fuel cells [55-57]. There are three major approaches of RIG that differs in the applied atmosphere for reaction and also the time of irradiation as shown in Figure 1.17. [57].
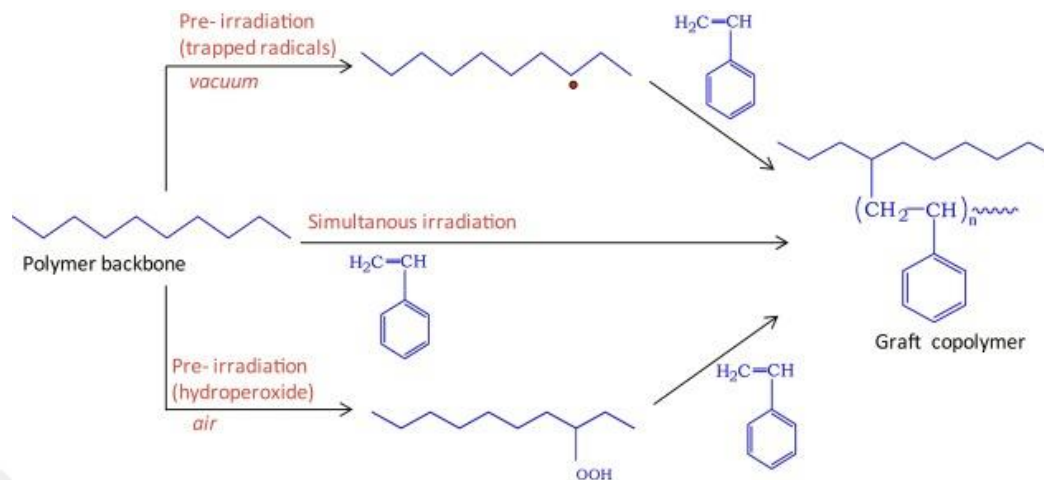
Figure 1.17. Radiation-induced grafting methods [57]

1.6.2.2. N-containing Heterocyclic Monomers

In pre-irradiation method, free radicals are generated by exposure of a selected base film to high energy electron beam or ɣ-rays. In the second step, grafting reaction is conducted by immersing the pre-irradiated backbone polymer film into the desired monomer solution. This step is done very immediately in an ambient atmosphere to not lose the generated active sites, from which the grafting is initiated. The monomer is grafted onto the activated regions as the side chains during the grafting reaction. Graft time, graft temperature, amount of the absorbed radiation dose, and monomer concentration are the key factors that have extensive influence on the graft yield of the product co-polymer [50, 51, 55, 58]. For each systems conducting series of experiments leads to obtain an optimized condition. The most relevant base polymers materials are PTFE, FEP, PVDF, ETFE, PE, PFA and PVF. In addition, Styrene, AMS, TFS and substituted trifluorostyrene are the common monomers that are widely used in this technique [56, 57]. In some systems, cross linker agent is also added to reaction solution to improve the mechanical properties the co-polymer films.

As mentioned in the previous sections for conduction of proton in a water-free medium, addition of proton donor and accepter species through functionalization or doping of the membrane is an essential process [48, 59]. Among variety of heterocycles, thermally and chemically stable N-vinyl imidazole monomers that contain two nitrogen atom (i.e. 1-

Vinylimidazole) are considered to be as one of the most promising categories for a variety of applications. Their specific features such as highly inclination to form of different types of complex species with organic substances and metal ions, as well as their hydrophobic nature give rise to notable attention of several research groups [58, 60, 61]. In the case of PEM fuel cell applications, they have been widely used in the chemical structure of the proton conducting membranes; Either for chemical modification of Nafion® membranes or preparing new composite membranes via RIG method for HT-PEM Fuel Cells application [55, 58, 60, 62-65]. Meanwhile, 4-Vinylpyridine as another N-containing compound have been attracted extensive attention for proton conducting membrane preparation in which the strong and polar chemical bond between nitrogen and hydrogen atoms has the key role in ionic conduction [50, 51, 66, 67]. Regardless of the other physicochemical characteristics of these species, in all cases the N atoms performs as a base (proton accepter) material, which can participate in reaction with dopant agent. As the consequence, the proton conduction across this category of membranes takes place whereby the aforementioned ionic conductivity mechanisms [48, 50, 59]. The entire procedure of the membrane fabrication steps via radiation induced grafting and subsequently doping with acid is shown in Figure 1.18 [51].
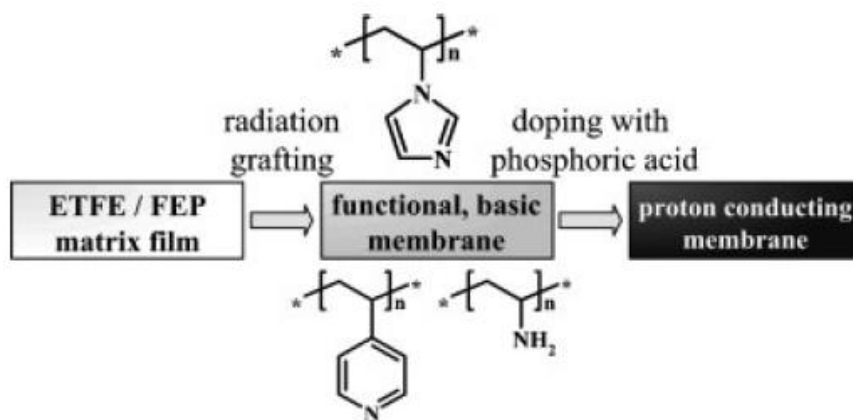

Figure 1.18. 3- stepped membrane preparation procedure via radiation-induced grafting technique [51]

Schmidt *et al*. [58] described the grafting of 1-vinylimidazole onto ETFE films as substrate. They were irradiated the ETFE films in vacuum by using an electron beam with three different applied doses and later exposed them to monomer for the grafting reaction. They investigated the effect of four different factors on the obtained graft yield as, the concentration of Fe^{2+} salt as an initiator, radiation dose, monomer concentration in the solution and reaction time to find the optimize condition for obtaining the maximum degree of grafting. They analyzed the characteristics of the grafted films via thermogravimetric analyses, mechanical test and FT-IR-PAS measurements. They achieved to the 120% graft level in optimized condition.

The same group latter reported [51] the fabrication of acid-base composite membranes for HT-PEM fuel cell application, using the pre-irradiation FEP and ETFE films (EB-150 kGy) as base polymer and grafted 4 distinct monomers which, are 4VP, 1-VIm, N-vinylformamide (NVF), vinylamine (VAm). They conducted fuel cell test at 120°C and 0% RH, in addition to analyze them for thermal and mechanical stability. They claimed that resultant membranes application is not limited to high-temperature PEM fuel cells but also can be utilized in other electrochemical devices such as batteries and sensors. Furthermore, they demonstrated high uniformity and 150 mW.cm^{-2} power densities for the membrane contains 1-VIm.

Nasef *et al*. [67] studied the effect of various graft parameters such as reaction time and temperature, absorbed dose and monomer concentration on the graft level of 4VP onto ETFE films that were synthesizing via RIG process. Later they converted the resultant grafted films using PA as dopant. Most promising membrane possessed 34 -49% GL showed 10 mS.cm^{-1} at 130°C and non-humidified environment. The thermal and mechanical analysis indicated the reliable stability of the product membranes up to 160°C and elongation of 161% for sample of 34% GL, respectively.

Lepit *et al*. described [63, 68] the preparing proton exchange membranes for HT-PEM fuel cells via simultaneous radiation induced grafting method. They chose 1-VIm monomer as side chain polymer, robust PVDF films as base polymer, and sulfuric acid for doping the grafted polymer. The graft level was investigated as a function of absorbed irradiation does through applying five various doses also as function of monomer

concentration. They obtained 4.47 mS.cm^{-1} conductivity at 333-373K for the membrane with superior acid doping level.

Nasef *et al*. [52] provided proton conducting membranes using RIG method to graft 1-VIm onto ETFE films (EB-100 kGy)and subsequently doped the film with phosphoric acid, with 54% graft yield. They claimed the formation of N-H and C-H bonds referred to the grafted imidazole rings through the FTIR characterization. They measured the ionic conductivity of the synthesized PA-doped membranes at the RH% and the temperature range of 20-100% and 20-120°C, respectively. The maximum ionic conductivity was 140 mS.cm^{-1} for 120°C at 20% RH. In addition, they showed an increasing trend of conductivity with enhancement of the temperature in their report.

Saidi *et al*. [61] conducted the synthesizing of phosphoric acid doped membranes based on RIG technique. They used the combination of 1-VIm and 1-V-2-P (1-vinyl-2-pyrrolidone) as heterocyclic vinyl rings contain monomers, and grafted them onto the pre-irradiated ETFE film (EB- 100 kGy) as base polymer. The resultant membranes showed maximum ionic conductivity of 53 mS/cm at 120°C at zero RH%. In addition, they reported the influence of the various graft reaction parameters on the graft yield such as reaction time at various monomer concentration and absorbed dose.

Gubler *et al*. [69] reported preparing proton conducting membranes using pre-irradiated ETFE films, styrene and DVB (divinylbenzene) as the substrate, side chain and crosslinker agent, respectively. They claimed that ETFE possess superior mechanical properties compare to other relevant polymers for the same purpose. A range of applied reaction time (0.67-7.5h), reaction temperature (40-90°C) and absorb does (0.75-3.5 kGy), ended up with 2.3 to 69% graft level. According to fuel performance of selected membranes, samples of 20-30% GL showed a comparable performance, which is obtained for Nafion®.

Sanli *et al*. [50, 66] investigated the conditions of the graft copolymerization reaction via RIG method for 4VP, 2-VP and NVP onto ETFE films. They followed their work with protonation of selective samples with phosphoric acid in their next paper. They found that ETFE-*g*-4VP membranes, which exhibited reliable mechanical property and 55 mS/cm

proton conductivity at 130°C in dry condition can be the promising option for elevated operation temperature applications.

1.7. Objective of this work

The global warming and pollution of the environment as the remarkable issues associated with the relevant power generation systems, which are based on fossil fuels. In this regard, the urgent need for an alternative system is the hottest topic of science society. Among various under developing power plants systems, fuel cells are thought to be as one the promising options. Despite the extensive efforts to improve the fuel cells until now, still several shortages to meet the targets in terms of the cost, and the sufficient characteristics are unsolved. HT-PEM fuel cells as the potential choice for several applications, suffer from the shortages of the existing commercial membranes such as Nafion® membranes because of their high cost and low performance at elevated temperatures. In this fashion, the PBI/PA membranes are considered as the most promising alternative membrane material for HT-PEM fuel cells up to now. However, PBI-based membranes show reliable performance for temperatures above 150°C. Therefore, searching for the new membrane material which can operates properly and fulfil the essential requirements in terms of the high proton conductivity, reliable durability, and chemical and mechanical stability at the temperature range of 80-150°C is missing. As the consequence, the main goal of the present study is producing of promising proton exchange membranes for potential application in HT-PEM fuel cells at the abovementioned temperature range. The facile radiation induced grafting method gives the opportunity to consuming time based on its high production rate and ending up with cost effective membranes via utilizing less expensive precursors. In previous works grafting of 1-VIm, 4VP individually or combination of these monomers with other monomers to prepare proton conducting membranes through RIG method have been reported [50-52, 61, 67, 68] , however, the combination of hydrophilic 1-VIm and 4VP is not reported before. Considering promising performance of above mentioned monomers due to their well-established inherent characteristics in addition to the numerous specific merits of ETFE films as a base polymer, these materials are chose as the precursors for this study. In addition, ferrous salt used as an additive in synthesizing of some of the samples, based on previous

studies in which they indicated the enhancement of graft yield in water/1-VIm systems by utilizing of abovementioned salt [58, 70]. Moreover, the reason for usage of phosphoric acid as dopant agent underlies in amphoteric nature of this acid, which can dissociate to several complexes, which leads to a notable contribution in proton conductivity as well as high interaction with basic grafted side chains

Chapter 2. Experimental

In the first set of the experiments, volumetric ratio of 1-VIm and 4VP monomers was altered to achieve to optimum ratio with reasonable graft level for subsequent set of experiments. In those experiments, the solvent and monomer concentration ratio was kept constant; however, the volumetric ratio of two monomers was changed. The second set was conducted with constant solvent to monomer volumetric ratio (40:60), as well as a fixed ratio of two monomers (50:50), but with altering the solvent composition. Finally, third sets of the experiments was performed by utilizing of iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$) as an additive in some samples as well as the volume ratio of the monomer to solvent was raised to (87.5:12.5). To compare the effect of iron salt on the membranes properties, samples of with and without of this additive was prepared.

2.1. Materials

ETFE films of 25µm thickness were purchased from Nowofol GmbH (Siegsdorf/Germany). 1-VIm (purity > 99%), 4VP (purity > 99%), 2-propanol, tetrahydrofuran, iron (II) sulfate heptahydrate (purity> 99%), phosphoric acid (purity > 85%) and hydrochloric acid (purity > 99%) were obtained from Sigma Aldrich and used without further purification.

2.2. Irradiation of ETFE-Films

ETFE films were cut into 8 cm*8 cm size. The prepared films were washed with ethanol very carefully and dried in a vacuum oven overnight. The films were kept in thin polyethylene bags before irradiation. The weight of each film was written on the container bags after weighing very precisely. ɣ- rays from ^{60}Co source with an irradiation dose of 100 kGy were used for irradiation process at room the temperature. The irradiated films were stored in a deep freezer at -60°C immediately.

2.3. Graft Copolymerization

The glass reactors were poured with reaction mixtures in the compositions given in Table 2.1 as three distinct sets. The prepared mixtures were purged with nitrogen gas for 15 min to provide an inert atmosphere. Irradiated films were immersed in the mixture immediately and reactors were sealed tightly. Nitrogen purging continued for 15 min after immersing the films in solution and then reaction time was started. The graft copolymerization reactions were conducted on an agitated thermostat at 60°C for 24 hours as shown in Figure 2.1.

Figure 2.1. Grafting reaction set up

Table 2.1. Composition of Mixtures

Experiment	Solvent	$V_{4VP}/V_{1\text{-}VIm}$	$V_{monomer}/V_{solution}$	$FeSO_4.7H_2O$
Set 1	IPA/THF (2 mL/4 mL)	0-1	50 %	
Set 2	H_2O (4.8 mL)	1	60 %	
	Ethanol (4.8mL)	1		
	H_2O/Ethanol(2.4/2.4 mL)	1		
Set 3	H_2O (1.5 mL)	0	87.5%	150 mg
		1		150 mg
		1		0 mg

The samples of set 1 and set 2 were washed in ethanol overnight to remove unreacted monomer, followed by drying the produced graft co-polymer films for 24 hours in the oven at 60°C. For the third set of experiments, after grafting reaction as the same for the previous sets, washing step was done in 1 M HCl overnight and followed by subsequent washing in deionized water. The drying process, temperature and time was the same as for previous sets. The dried grafted films were weighed once more in a careful way and their weight was written on their bags. The graft level (GL%) was calculated via following equation:

$$GL\ (\%) = [(m_G - m_O)/m_O] \times 100 \tag{2.1}$$

where m_O and m_G are the weight of film before grafting and after grafting respectively.

2.4. Membrane Preparation

The protonation and doping of grafted films to bring membrane functionality were carrried out via immersing them in phosphric acid (85%) for 20 hours at 60°C. The overall preparation steps are shown in

Figure 2.2. Set 1 and set 2 were washed with distilled water for 24 hours to rinse the excess acid and then were dried overnight at 60°C. However, for set 3, a tissue paper was used for cleaning the membranes surface. All the membranes were weighed once again after doping step to recognize the weight increase extent of the resultant membranes. The acid doping level (acid uptake) of the membranes was calculated by following equation:

$$AD\ (\%) = [(m_A - m_G)/m_G] \times 100 \qquad (2.2)$$

where m_G and m_A are the weight of film after grafting and after acid doping respectively.
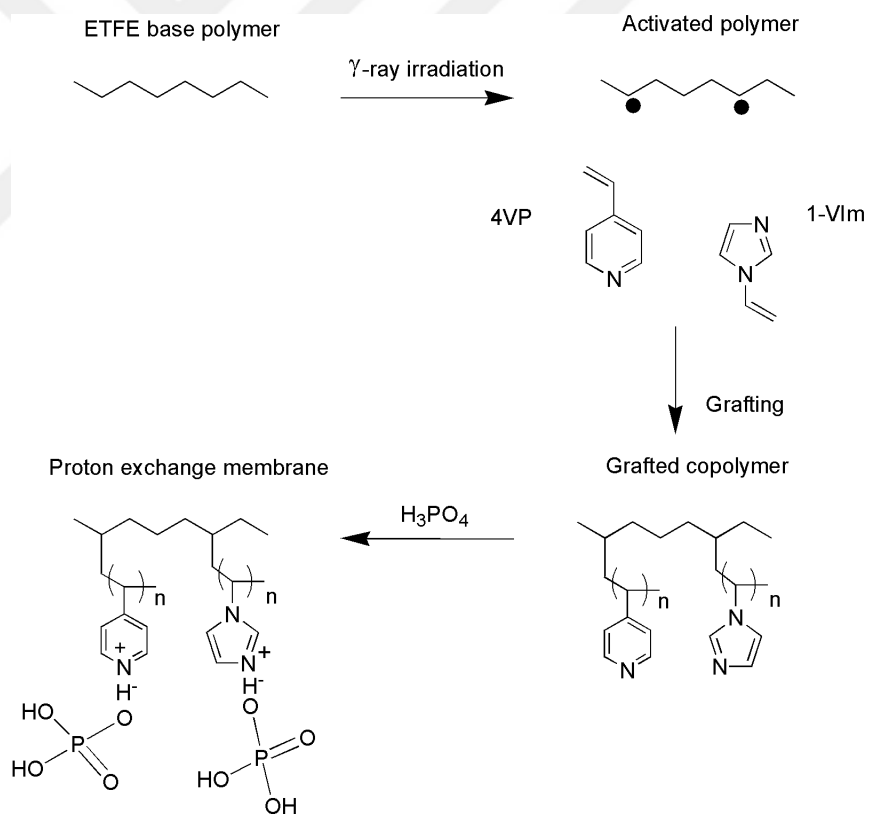

Figure 2.2. Membrane preparation steps

2.5. Characterization

For measuring the ionic conductivity at room temperature in fully humidified condition, samples of 2 cm × 2.5 cm from the membranes were cut. Then the samples were put in deionized water for 4 hours before measurement. Each sample were put in the conductivity cell and Beckktech/Gamry set-up was used to conduct 4-probe conductivity measurements by electrochemical impedance spectroscopy. The ionic conductivity was obtained as follows:

$$\sigma \ (S/cm) = L / (R \times W \times T) \tag{2.3}$$

where R is resistance (Ω), T is the thickness of membrane after acid doping step (cm), W is the width of the sample (2 cm), L is the distance between the probes (0.425 cm).

Ionic conductivity of membranes at varying humidity and temperature conditions were investigated as well. These measurements were conducted under controlled temperature in 80-110°C range and humidity in 20-100% range, by Bekktech four-point-probe conductivity set-up and Scribner 850e fuel cell test station (Figure 2.3).

For testing the mechanical properties of the resultant membranes, Universal Tensile Machine (Zwick/Roell Z100) at 60%RH at RT was used. The aspect ratio of samples were 1:10 and the elongation rate was set to 100 mm/min.

Thermogravimetric analysis (TGA) was conducted at the rate of 10°C/min up to 800°C by means of Shimadzu DTG-60 under N_2 atmosphere.

The fuel cell performance of the most promising membranes (with salt 36% GL, without salt 34% GL) were performed by Scribner 850e fuel cell system. Prior to this test, selected samples used to fabricate of membrane electrode assemblies (MEA) (Figure 2.4). For that purpose, as-synthesized membrane was placed between 5 cm^2 two commercial (0.4 mg Pt/cm^2 loading) electrodes and hot-pressed with 2 MPa for 5 min (after 10 min pre-heating at 135°C without applying pressure). The fuel cell tests were performed in various humidity conditions at 80, 100 and 110°C with 500 cc/min of H_2 and O_2.
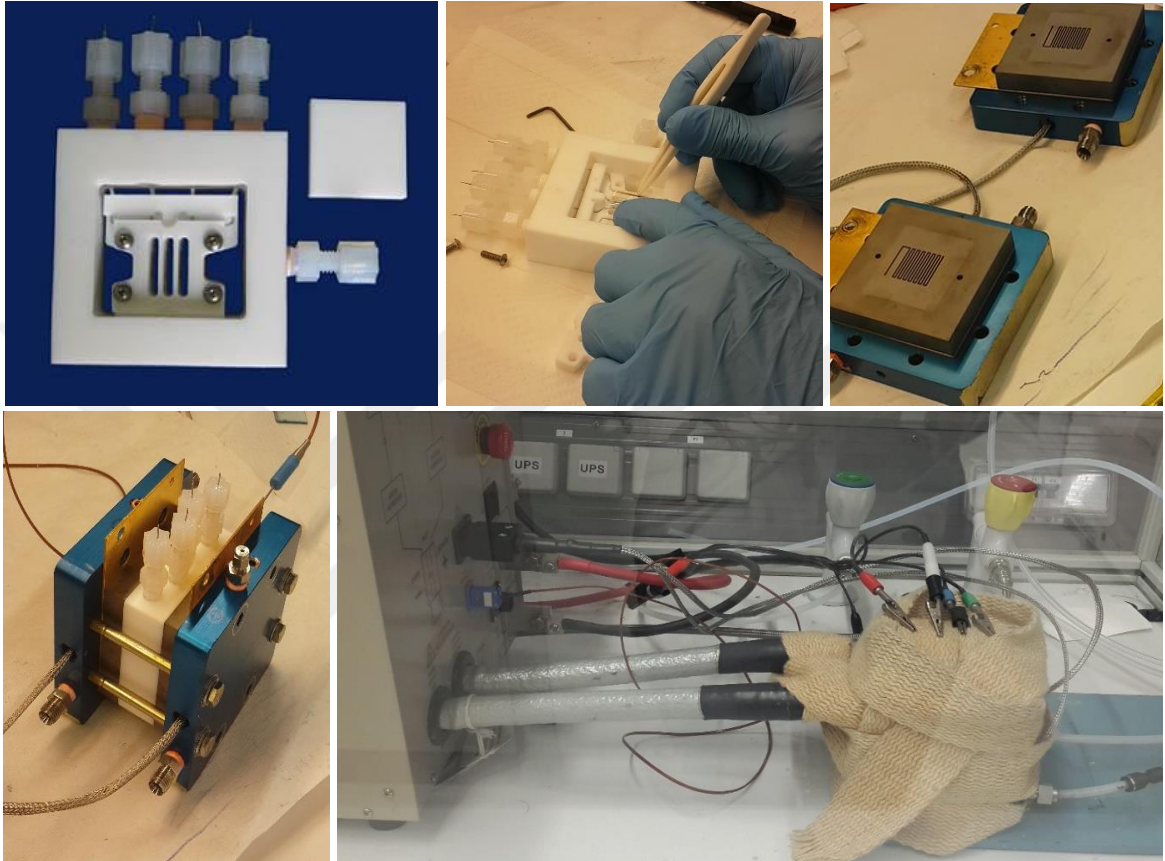
Figure 2.3. The components of conductivity cell
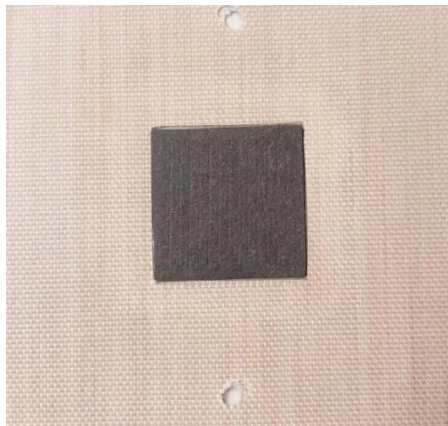
Figure 2.4. MEA for fuel cell test

Chapter 3.   Results and Discussion

3.1.   Effect of Monomer Volumetric Ratio on Graft Level

In the first set of experiments, the effect of varying volumetric ratio of the used monomers on graft level, acid doping level and ionic conductivity of the fabricated membranes at RT and at constant total monomer concentration with respect to solvent, was investigated. Considering the poor reactivity of 1-VIm compared to 4VP, by increasing the concentration of 4VP in the reaction mixture the graft level is increased as shown in Figure 3.1.

Figure 3.1. Effect of 1-VIm concentration on graft level

By diminishing the ratio of 1-VIm from 1 to zero the graft yield increased from 5.5 to 58% for the sample with 100% 4VP. The reaction composition mixtures and characteristics of synthesized membranes are given in Table 2.1 and Table 3.1, respectively. The graft level is considered as the most pivotal parameter that determines the following characteristics of the resultant membranes [67].

3.2. Effect of Monomer Volumetric Ratio on Acid Doping Level

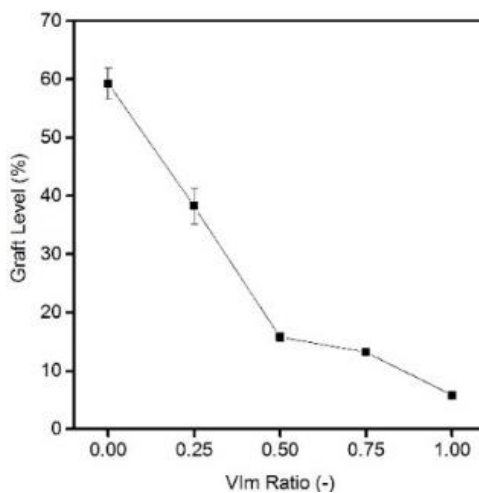The phosphoric acid groups are interacted with the present N atoms in the chemical structure of the grafted vinyl rings which are acts as the basic centers. Therefore, the acid doping level of the resultant co-polymers has a direct relation with graft level, since the more grafted branches leads to provide higher amount of basic centers to adhesion of acid groups, which is reflected in Figure 3.2.

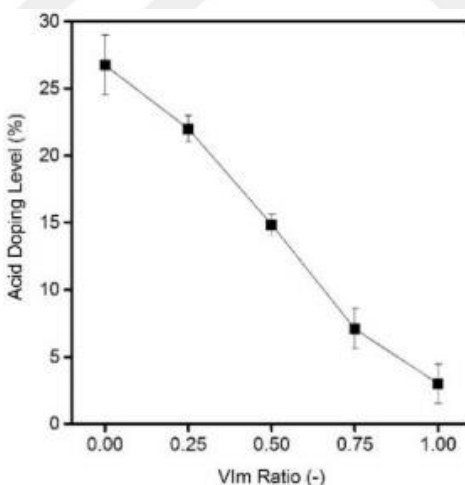Figure 3.2. Effect of 1-VIm concentration on acid doping level

The trend of acid doping level graph with respect to 1-VIm ratio, which is based on the experimental data calculated via equation (2.1) reveals the significant contribution of the amount of grafted side chains that are protonated by acid. In addition, grafting of more hydrophobic polymers on the base polymer brings about to further swelling of the

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hydrophobic ETFE polymer film that ends up with the higher number of protonated branches. According to the obtained data for sample of 0.5 VIm ratio the graft level is four times of the zero VIm ratio, however, the doping level is just doubled. This evidence can be referred to higher basicity of P1-VIm with $pK_b= 6.6$ than for the 4VP with $pK_b= 8.0$ due to one more N atom in its structure [51].

3.3. Effect of Monomer Volumetric Ratio on Ionic Conductivity

Among samples of set 1 and 2, maximum ionic conductivity at RT, 19.5 mS/cm, attributes to the membrane with 27% acid doping level. As shown in Figure 3.3 the proton conductivity is a function of graft level because the density of the grafted chains determines the density of the acid functional groups attached to the synthesized co-polymer via strong interaction between N atoms of grafted species that and H^+ of the dopant agent [67]. A comprehensive summery of physicochemical features of membranes are listed in Table 3.1.
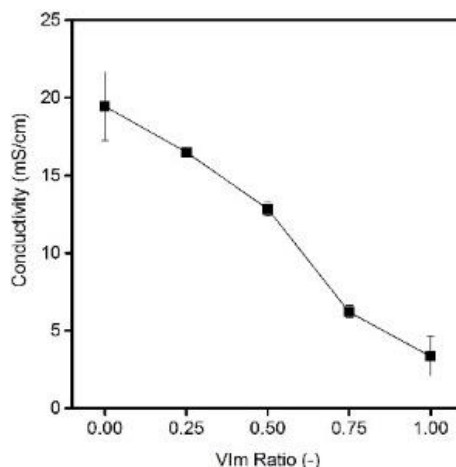
Figure 3.3. Effect of 1-VIm concentration on proton conductivity at RT

The graphs of Figure 3.4 exhibits the graft level, acid up-take and ionic conductivity data as a function of 1-VIm concentration in the same graphs for comparison in a simple way.
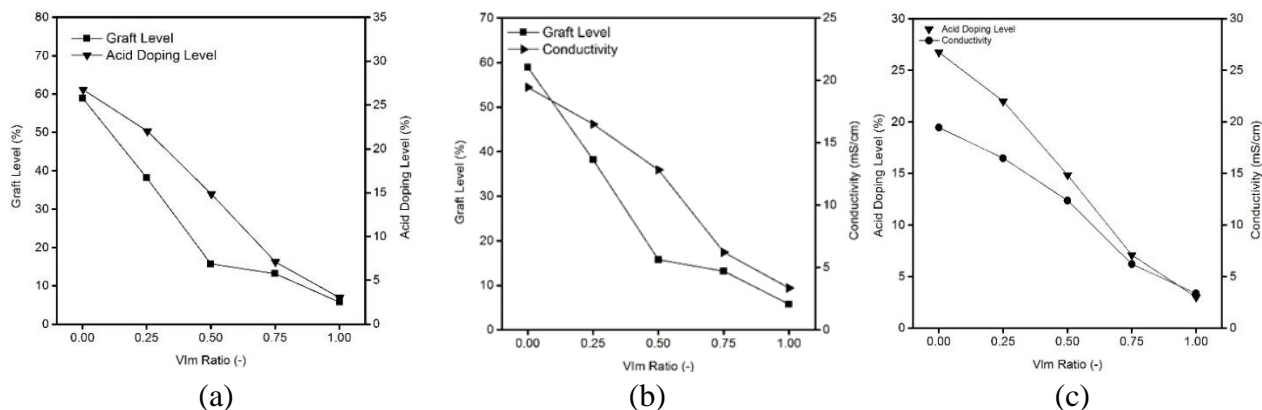
Figure 3.4. (a) Comparison of graft level with acid doping level, (b) Comparison of graft level with conductivity, (c) Comparison of acid doping level with conductivity of membranes, for variuos volumetric ratios of the monomers for set 1.

Table 3.1. Summary of membranes properties

Experiment	Variable parameter	Thickness (µm)	Graft level (%)	Acid doping level (%)	Conductivity (mS/cm) at RT
Set 1	**V1-VIm/V4VP**				
	0.0	41	59	27	19
	0.25	39	38	22	16
	0.5	33	16	15	12
	0.75	30	13	7	6
	1.0	26	6	3	3
Set 2	**Solvent**				
	H_2O	33	17	19	14
	Ethanol	36	25	26	11
	H_2O/Ethanol	32	17	13	10
Set 3	**FeSO$_4$.7H$_2$O**				
	Without salt	41	34	121	38
	With salt	40	36	145	50

Proton conductivity of the third set was measured at elevated temperatures (80, 100 and 110°C) and varying relative humidity (from 20-100%). Due to not using pressurized conditions during tests, the RH% of 100% in case of 100°C, and 80 and 100% in case of 110°C are not reported. The graphs ionic conductivity versus RH% at each applied temperature were plotted (Figure 3.5). A growing trend in terms of conductivity with increasing the temperature is shown for both samples. Moreover, the obtained data indicate that the presence of water has a positive effect on enhancement of the membrane conductivity. Appling higher temperatures provides more activation energy for charge carriers that results in enhancement of their mobility, in addition to existence of humidity facilitates the proton transfer due to improvement of their diffusion (Grotthuss mechanism) through the membrane [53]. However, the membrane with salt (36% GL) shows superior conductivities in all test conditions, which is an evident for its higher graft level and acid doping level.
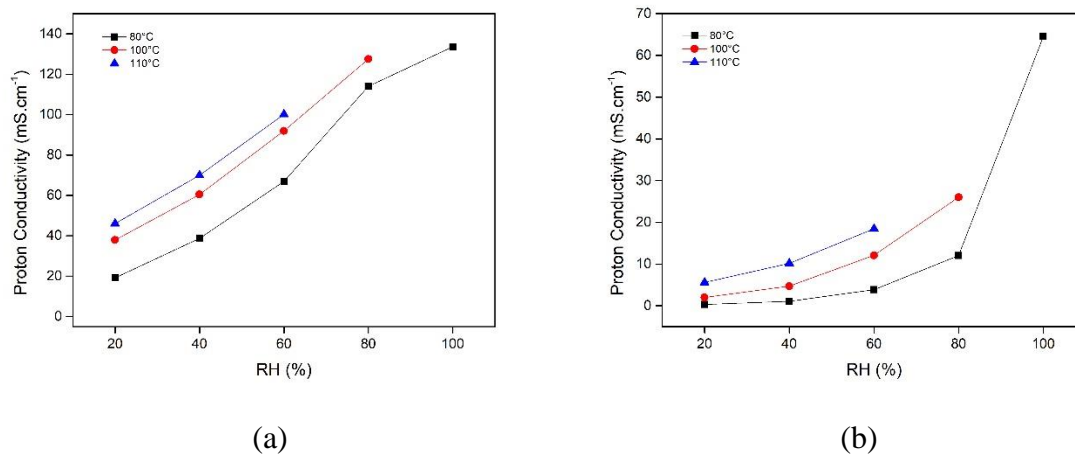

(a)   (b)

Figure 3.5. Proton conductivity of (a) 36% GL and (b) 34% GL, membranes (set 3)

3.4. Thermal Analysis

Thermal behavior of the membranes was studied via thermal analysis under N_2 atmosphere with the 10 °C.min^{-1} heating rate (Figure 3.6). A single step degradation pattern with a sharp weight loss starting at 450°C, corresponds to pristine ETFE film as reported elsewhere [52]. However, four-stepped curves relate to the acid-doped samples, which is a good agreement to existence of grafted poly vinyl rings and phosphoric acid groups onto the base polymer. The first two gradual mass losses at temperatures around 100 and 200°C indicates the evaporation of absorbed moisture from air via hydrophilic phosphoric acid groups and dehydration of acid groups, respectively. In the following step decomposition of P (1-VIm-*co*-4VP) were occurred between 260 to 300°C for the grafted membranes. In contrast to previous stages a remarkable weight loss from 420 to 480°C can be seen in final step reveals the degradation of the base matrix for all samples.
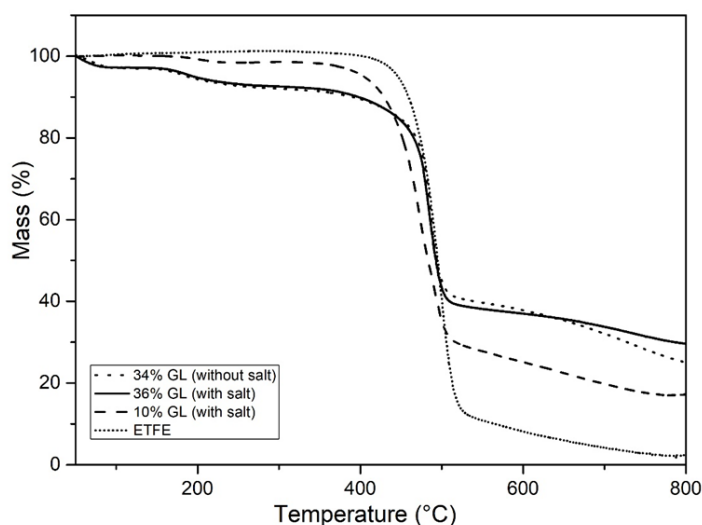

Figure 3.6. Thermal analysis of the phosphoric acid-doped samples of 10, 34, 36% GL from set 3 and pristine ETFE film

3.5. Mechanical Properties

The tensile tests were performed for the more promising acid doped membranes. That is to say, membranes with 10% graft level (with salt), 34% graft level (without salt) and 36%

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graft level (with salt) as shown in Figure 3.7. The samples were prepared with 1:10 aspect ratio and the elongation rate was set to the 100 mm/min. The graphs revealed that the doping of co-polymer films with phosphoric acid has inversely affected the mechanical behavior of the membranes. Since, by increasing the graft level further acid groups introduced to co-polymer structure, which affected mechanical stability as expected. Moreover, adding the ferrous salt caused to enhance the strength of the membranes, however, 36% GL membrane shows less elongation compared to 34% membrane.
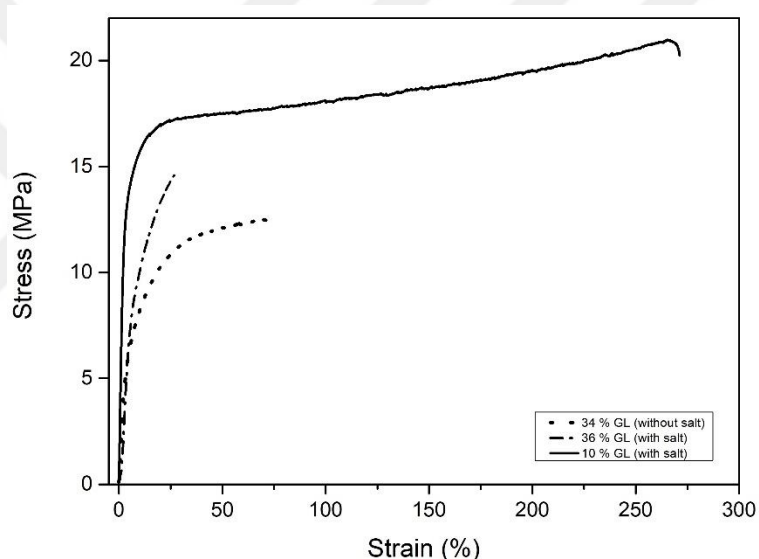
Figure 3.7. Schematic of the stress-strain curves of membranes

3.6. Fuel Cell Tests

Despite the several number of reports about membrane preparation via radiation-induced rafting membranes, there are limited number of studies in literature, which reported fuel cell performance of the resultant membranes. Therefore, it is worthwhile to investigate the performance of these cost-effective membranes in the harsh operation condition of the cell [50, 51, 71]. Therefore, fuel cell tests were carried out for two selected membranes as a function of relative humidity and temperature, using 500 cc/min of H_2 and O_2. Figure 3.8 indicates the polarization and power output curves of 36% GL (Figure 3.8a and b), and 34%

GL (Figure 3.8c and d) membranes. The polarization curves obtained at 80, 100 and 110°C cell temperature under 20, 60, 80 and 100% relative humidity (Figure 3.8). As expected from the previous characterization results, the membrane with 36%GL exhibited comparatively superior fuel cell performance. As exhibited in Table 3.2, maximum achieved power density of 237 mW.cm^{-2} is related to 36% GL with salt membrane at 110°C and 60% RH condition that can be considered as comparable performance with 150, 75 and 220 mW.cm^{-2} at 120°C for ETFE/P1-VIm/PA, ETFE/PVAm/PA and PA/PBI membranes respectively, which are reported in previously [51, 72]. Despite the difference in obtained values from the fuel cell test, polarization curves show a similar trend of increasing the maximum power density with increasing the temperature and relative humidity for both membranes. Aforementioned trend proves the pervious conductivity results for the same samples, which indicates the drastic reliability of the proton conduction to the mobility of charge carries as the function of temperature as well as to the ease of their diffusion in humidified condition [22, 50, 51]. The only unmatched order between the two graphs, is referred to the maximum value of power density and current density at 110°C/20% RH and 80°C/100% RH. The other point is the existence of the larger gaps between the graphs of without salt compare to with salt sample. It can be deduced that, the resultant membranes can be alternative membrane materials for HT-PEM fuel cells, as they could sustain the proton conducting behavior at high temperature and moderate RH condition.

Table 3.2. Maximum power densities at varying temperature and relative humidity

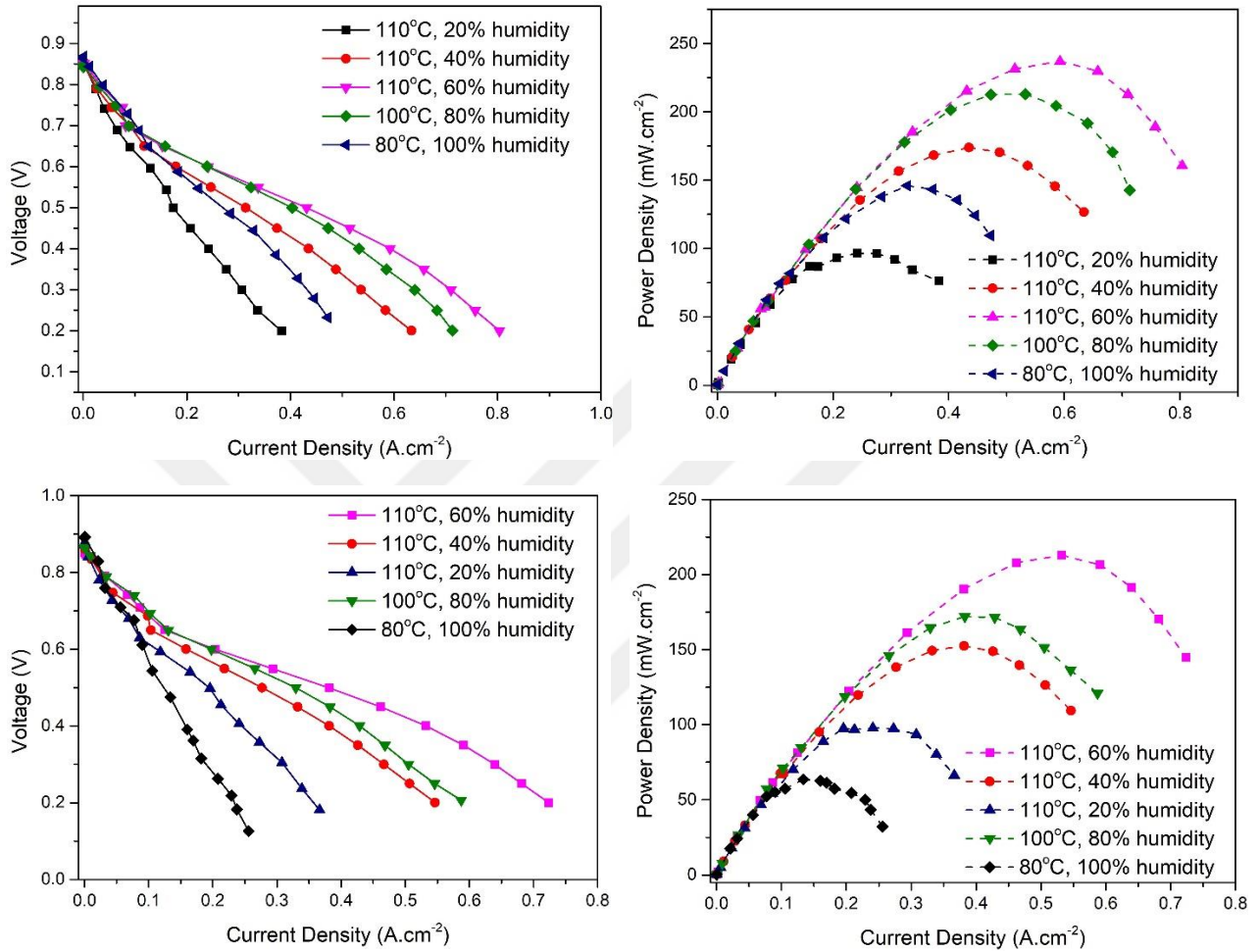| Temperature / RH%	110°C/20%	110°C/40%	110°C/60%	100°C/80%	80°C/100%
Max power density (mW.cm^{-2}) without salt 34% GL	97	153	213	172	64
Max power density (mW.cm^{-2}) with salt 36% GL	96	174	237	213	146

Figure 3.8. H$_2$/O$_2$ PEM fuel cell a) Polarization curves and b) Power output curves for the 36% GL (without salt), c) Polarization curves and d) Power output curves for the 34% GL (with salt) at different temperatures and relative humidity (%)

Chapter 4. Conclusion

In the present study, novel polymeric proton-conducting membranes with outstanding physicochemical characteristics were fabricated by radiation-induced grafting using the combination of 4VP and 1-VIm monomers for the first time. ETFE-g-P1-VIm/4VP co-polymer films were synthesized successfully using a facile and versatile radiation-induced grafting technique, and then converted to proton conducting membranes after doping with phosphoric acid. In this fashion, to identify the optimum composition of precursors, several samples with different component ratios were manufactured and investigated through various characterization techniques. Furthermore, a fuel cell test was carried out for each selected sample at different temperatures and relative humidities to clarify their efficient proton conductivity at temperatures more than boiling point of water, and lower levels of humidity. The ideal achieved properties were attributes to the samples of 87.5% volumetric ratio of monomer/solvent as well as the same amount of 4VP and 1-VIm. Mechanical test, TGA analysis, ex situ conductivity measurements at 80,100 and 110°C at various RH%, and fuel cell test reveal their superior properties at elevated temperature ranges and low humidities to those of commercially available membranes. As the consequence, they can be considered as potential membranes for high temperature fuel cell systems.

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