FABRICATION OF POLY (*m*-TOLYLOXY-*co*-4-PYRIDINOXY PHOSPHAZENE) BASED PROTON EXCHANGE MEMBRANES FOR FUEL CELL APPLICATIONS

by

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In memory of my father
Kassim Ali

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ABSTRACT

Nafion® is the most commonly used commercial proton-exchange membrane for polymer electrolyte membrane fuel cells (PEMFCs) due to its excellent thermo-mechanical properties. The main drawbacks of Nafion® membranes are their temperature dependent conductivity, degradation at temperatures greater than 80 °C and relative humidity less than 100% and also high cost, hence it is necessary to find the alternative membranes for PEMFC. Polyphosphazenes are a potential candidate owing to their ability to incorporate unlimited side-groups and their good thermal and chemical stability. In this work, three poly (*m*-tolyloxy-*co*-4-pyridinoxy phosphazene)s with varying heteroatom containing and not containing aryl side chains in varying ratios were studied.

Through sulfonation the sulfonic acid group which promotes proton conduction was incorporated. Different parameters such as effect of temperature, time and varying amounts of each side groups of the polymers on the sulfonation process were investigated and the results reported. After sulfonation membranes with thicknesses in the range of 80-120 μm were obtained through solution casting and later on characterized. Structural characterizations by use of NMR (^{1}H, ^{13}C and ^{31}P) and FTIR were carried out before and after sulfonation in order to check the post process changes. FTIR revealed extra peaks at 1300 cm^{-1} that belonged to the sulfonic acid groups. DSC and TGA were used to check the membranes' thermal properties while the mechanical stabilities was investigated using the DMA.

The resultant membranes were then evaluated for the basic PEMFC relevant properties such as IEC, water uptake and proton conductivity and the results compared to those of Nafion® 115. In this work, we reported IEC values of as high as 1.07 meq/g which was comparable to that of Nafion® 115 (0.91 meq/g) in the literature. Conductivity of the membranes varied depending on the sulfonation parameters and values obtained were comparable to the membranes in the literature and Nafion® 115 as well.

YAKIT PİLLERİ İÇİN POLİ (*m*-TOLİLOKSİ-*ko*-4-PRİDİNOKSİ FOSFOZEN) ESASLI PROTON DEĞİŞİM MEMBRANLARININ ÜRETİMİ

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Anahtar Kelimeler: Ariloksi Fosfozen, Heteroatom, Sülfonasyon, Membran, PEMFC

ÖZET

Nafion® polimer üstün ısıl ve mekanik özellikleri sebebiyle elektrolit membranlı yakıt pillerinde (PEMFC) yaygın kullanılan ticari bir proton değişim membranıdır.. Nafion® membranlarının temel problemleri ise iletkenliklerinin sıcaklığa bağlı olması, 80 °C'nin üzerinde ve 100% ün altındaki nemliliklerde bozunmaya uğramaları ve yüksek maliyetleridir. Bu sebeplerle PEMFC uygulamaları için alternatif membranların üretilmesi gerekmekdir. Polifosfazenler, sınırsız yan gruplarla bağlanabilmeleri ve ısıl ve kimyasal kararlılıkları sebebiyle önemli bir potansiyel oluşturmaktadırlar. Bu çalışmada değişen heteroatom grubu içeren ve içermeyen olmak üzere- değişen aril yan zincirlerden oluşan üç çeşit poli(*m*-toliloksi-*ko*-4-pridinoksi fosfazen)ler üzerinde yoğunlaşılmıştır.

Sülfonlama tepkimesiyle, proton iletimini sağlayan sülfonik asit grubu yapıya eklenmiştir. Sıcaklık, tepkime süresi ve polimerlerdeki değişen miktarlardaki yan grupların sülfonlama tepkimesi üzerindeki etkileri incelenmiş ve sonuçlar gösterilmiştir. Sülfonlama sonrasında çözeltiden dökme yöntemiyle 80-120 μm kalınlığında membranlar üretilmiş ve karakterizasyonları gerçekleştirilmiştir. Sülfonlama öncesi ve sonrasında, NMR (^{13}C, ^{31}P and ^{1}H) ve FTIR yöntemleri kullanılarak yapısal değişiklikler incelenmiştir. FTIR sonuçlarına göre 1300 cm^{-1} de sülfonik asit gruplarına ait bölgeler görülmüştür. DSC ve TGA yöntemleriyle ısıl özellikleri çalışılırken DMA yöntemiyle de mekanik özellikleri incelenmiştir.

Ardından, üretilen membranlar PEMFC'ye özgü temel özelikler olan; iyon değişim kapasitesi (IEC), su alımı ve proton iletkenliklerinin belirlenmesi için detaylı olarak karakterize edilmiş ve elde edilen sonuçlar, aynı koşullarda karakterizasyonları gerçekleştirilen Nafion® 115 membranlarına ait sonuçlarla kıyaslanmışlardır. Bu çalışmada üretilen membranların IEC değerleri 1.07 meq/g gibi oldukça yüksek ve literatürdeki Nafion® 115 (0.91 meq/g) membranlara ait değerlere oldukça yakındır. Üretilen membranların iletkenlikleri ise sülfonlama parametrelerine bağlı olarak değişmekle birlikte Nafion® 115 membranlarının iletkenlikleriyle kıyaslanabilir değerler elde edilmiştir.

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ABBREVIATIONS AND SYMBOLS

FEP : Fluorinated ethylene propylene

ETFE : Ethylene tetrafluoroethylene

PTFE : Polytetrafluoroethylene

PFA : Paraformaldehyde

PBI : Polybenzimidazole

PANI : Polyaniline

PVDF : Polyvinylidene fluoride

PFSA : Perfluorosulfonic Acid

γ- ray : Gamma ray

meq : Milli equivalent

1. INTRODUCTION AND LITERATURE REVIEW

1.1. Background and Motivation

Fossil fuels which, still account for about 80% [1] of today's global primary energy supply is among the most debated issues because of its impact on human beings. For centuries since the invention of the steam engines, fossil fuels have been extensively used and its usage has brought with it economic growth, development of industries and better living standards. However, one of the biggest concerns is that there is need to find an alternative source of energy which will supplement the already diminishing fuel reserves, as a result of continued consumption by the growing world population. Furthermore, critics have also raised alarms due to the devastating effects fossil fuels have had on the environment resulting from the rapid rise in harmful emissions of greenhouse gases during their use. These gases released mainly from industries and transportation sector which have consequently caused gradual climatic changes, depletion of ozone layer, global warming and health problems.[2]

The above mentioned drawbacks have motivated the search for alternative, sustainable and renewable sources of energy which must be technically feasible, affordable and environmentally acceptable.[3],[4] Examples of sustainable energy sources currently under investigation include solar, wind geothermal, hydrogen and so on. Hydrogen being the most abundant and most simple substance in the universe proves to be a potential candidate that can equally compete with fossil fuels [5]. In addition to this hydrogen has zero specific carbon emission and has the highest specific energy of all conventional fuels [6], [7]

Hydrogen can be easily utilized in the fuel cells which normally generate energy and have much less environmental harm due to the fact that there is no emission of greenhouse gases compared to combustion engines that use fossil fuel.[8],[9] However, the technology has lagged behind due to factors like durability of materials for the different components, high manufacturing and operating costs involved, fuel storage among others reasons.[9]. Fuel cell components design is of importance since it increases the efficiency during performance.

In the literature there is still a missing link for membranes (a component of fuel cells) working at high temperature (above 80 ˚C) due to dehydration which results in lowered conductivity and finally reduced performances. With this in mind this study is intended at making a contribution to the on-going research in membranes that are reliable and durable for the functioning of fuel cells by proposing three novel polyphosphazene structures.

1.2. Overview and History of Fuel Cells

Fuel cells are electrochemical devices that convert chemical energy directly to electricity through redox reactions by consuming a fuel and an oxidant.[10] When compared to the other traditional energy like internal combustion engines it has very high efficiencies since the energy conversion process bypasses the intermediate paths of first converting the chemical energy to heat energy then to mechanical energy before finally converting the energy to electricity.[11]

Research on fuel cells was started since 1839 by Sir W. Grooves when he used four cells each with hydrogen and oxygen as shown in Figure 1 below so as to produce electricity. He further demonstrated how the electricity produced could also be used to split the water formed to hydrogen and oxygen.[12] However it was only until 1950's that the alkaline fuel cells were first used commercially by NASA's space programs[13] to generate power for probes, satellites and space capsules. Since then, fuel cell use has increased and still more investigations are on-going in order to improve its performance and develop other economical materials in order to reduce its overall costs. Later on, using these basic principles many different and complex types of fuel cells have been manufactured to cater for applications which range from small to large scale.

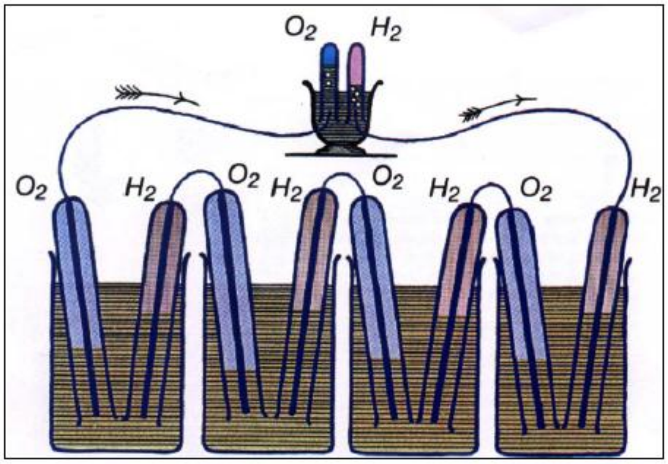
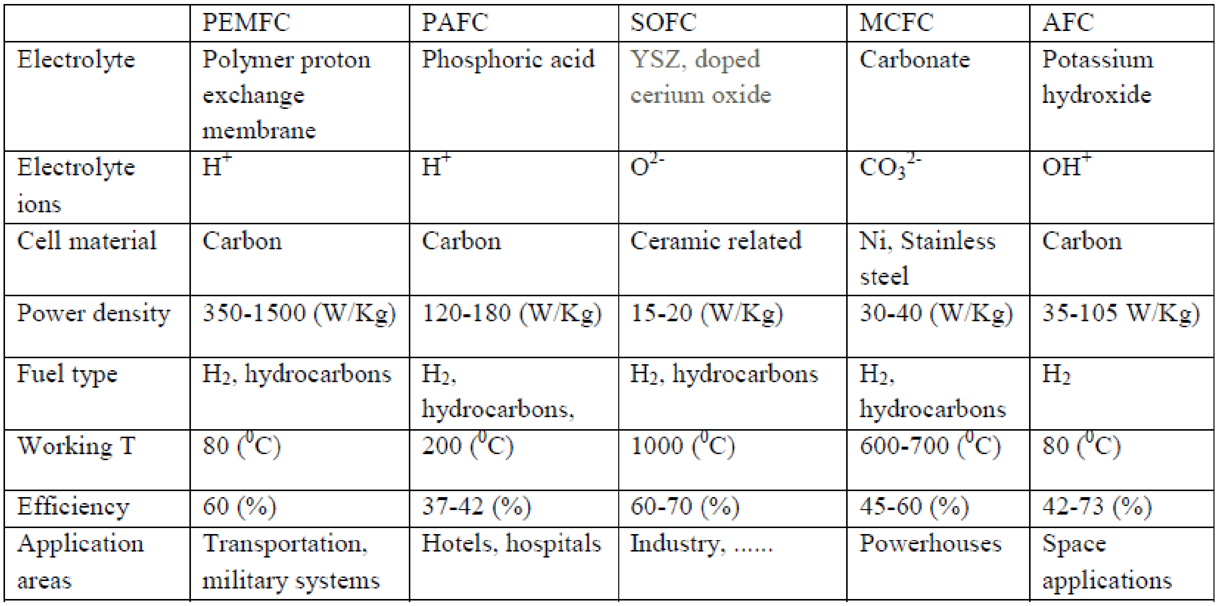


Figure 1: A schematic of the first fuel cell that was built by Sir W. Grooves to produce electricity[12]

1.3. Classification of Fuel Cells

Although there are several types of fuel cells they basically work from the same principle of redox reaction arising from supplying fuels (pure hydrogen, hydrogen carbon fuels or chemical hydrides) on the anode side, and oxidant (oxygen or air) on the cathode side. Fuel cells have been classified as depending on the temperature of their operation and also according to the type of electrolytes used, the latter is as observed from the Table 1 below. They are namely: alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC).[14] The table also summarizes their applications, the basic reactions occurring at their electrodes, and more characteristics. The polymer exchange membrane fuel cell (PEMFC) which operates at low temperatures is the main focus of this thesis and its electrolyte will be discussed in more detail in later chapters.

Table 1: Features of different types of fuel cells[10]



	PEMFC	PAFC	SOFC	MCFC	AFC
Electrolyte	Polymer proton exchange membrane	Phosphoric acid	YSZ, doped cerium oxide	Carbonate	Potassium hydroxide
Electrolyte ions	H^+	H^+	O^{2-}	CO_3^{2-}	OH^+
Cell material	Carbon	Carbon	Ceramic related	Ni, Stainless steel	Carbon
Power density	350-1500 (W/Kg)	120-180 (W/Kg)	15-20 (W/Kg)	30-40 (W/Kg)	35-105 W/Kg)
Fuel type	H_2, hydrocarbons	H_2, hydrocarbons,	H_2, hydrocarbons	H_2, hydrocarbons	H_2
Working T	80 (^{0}C)	200 (^{0}C)	1000 (^{0}C)	600-700 (^{0}C)	80 (^{0}C)
Efficiency	60 (%)	37-42 (%)	60-70 (%)	45-60 (%)	42-73 (%)
Application areas	Transportation, military systems	Hotels, hospitals	Industry, ……	Powerhouses	Space applications

1.4. Proton Exchange Membrane Fuel Cells

1.4.1. Overview and Main Components

PEMFC are categorized as low-temperature fuel cell for the reason that they usually operate in temperature ranges between 80-120 °C. This temperature range is advantageous for many applications such as use in stationary, portable systems and transportation which require quick start-up temperatures especially in the latter application.[9] Other reasons why this system is preferred is high power densities, high efficiencies, and above all clean by-product which is water. Despite these advantages PEMFC still has some shortcomings in issues related to heat and water management which usually limit the operating power[14] of a practical system. In addition to this, the relatively low operation temperatures poses a problem of carbon attack [15] on the catalyst which directly affects the performance of fuel cells.

The main components of a single cell PEMFC consists of the membrane electrode assembly (MEA), the catalyst layer, the backing layer /gas diffusion layer (GDL) and the current collectors as shown in Figure 2 below. The current collectors (bipolar plates) basically have two functions to provide flow for the gas though the channels engraved in it and also to collect current as the name suggests. The GDL is fabricated from carbon cloth or carbon paper and is usually porous in the thickness range of 100-300 μm. Its main purpose is to facilitate the diffusion of reactant and product gases at the electrodes and also transport electrons to and from the catalyst layer. At the times of high humidity it controls the hydration of the membrane since it is coated with Teflon for wet-proof. This Teflon layer also facilitates the removal of product water at the cathode electrode to prevent flooding.[9]

The catalyst layer located at the interface between the membrane and the GDL stimulates each of the half reaction at both electrodes and is also simultaneously involved in ion and electron conduction. The catalyst mostly in use is Platinum which is a very costly material therefore it is utilized in the form of particles spread out on carbon-based powder in order to increase the surface area available for the reactions. The main concern is to reduce the amount of platinum loading and also develop other platinum-based catalyst while at the same time achieve better fuel cell performance.[16] To improve the ionic transport to and from the electrolyte membrane a considerable amount of ionomer is added to the catalyst layer during the MEA fabrication.[17]

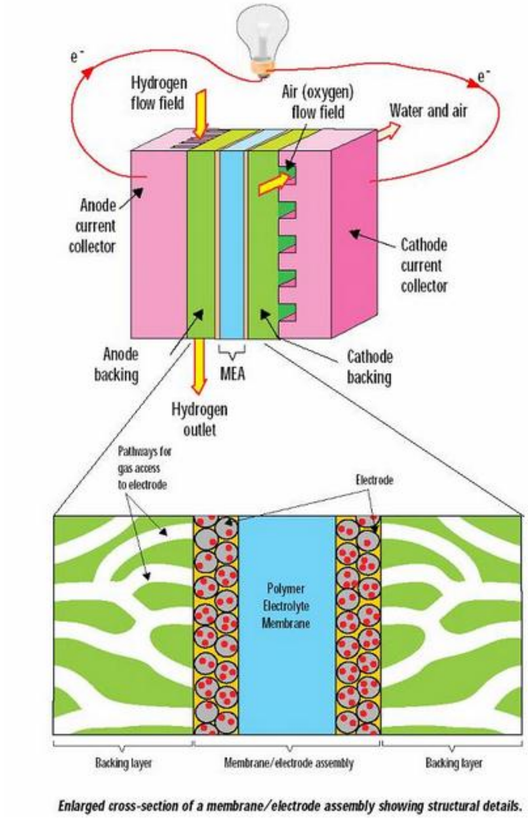


Figure 2: Components of a PEMFC. The zoomed view is of the MEA and the backing layers[12]

The anode and cathode provide the sites for the oxidation and reduction of the reactant gases respectively which later on recombine to form water. Finally, the membrane separates the reactants and the products from crossing over to the opposite side, facilitates the protons from the anode to the cathode and acts as a barrier for preventing electrons from crossing over.

The performance of fuel cells is characterized by the current-voltage graph as shown below in Figure 3 during the operation period. The three major regions in the figure point out to the causes of voltage losses with the first one coming from the slow reaction kinetics at the cathode. The mid-region is represented by losses occurring due to internal resistance and also membrane and electrode resistance to flow of ions. In the last region, losses are mainly due to the transport limitations in the gas diffusion layer.

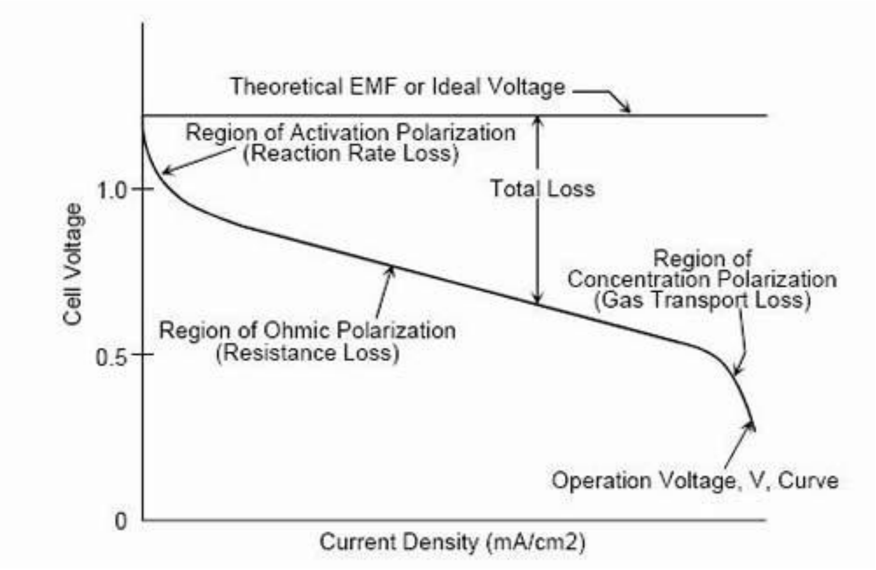


Figure 3: Graph showing the performance of a typical PEMFC[18]

Therefore, it is of great importance that emphasis be put in the design of all the fuel cell components so as to ensure both the durability and also better performance for the fuel cell.

1.4.2. Proton Exchange Membranes

The reliability and durability of the membrane are major concerns due to the fact that most of the PEMFC failures occurs as a result of its degradation.[9] Table 2 below outlines some of the characteristics required for PEMFC membranes however at no one time have all these properties been accommodated in one particular membrane [19] which necessitates a give and take in some of the characteristics.

Table 2 : Characteristics of a desired membrane for PEMFC[19]

Essential	**Function-related**
low permeability to fuel and oxidant	high proton conductivity (~0.1 $S \cdot cm^{-1}$)
good interfacial properties	capability of fabrication into MEA’s
good mechanical stability (dry and hydrated state)	water management (For those using water as the proton conducting species)
low electronic conductivity	
good thermal and chemical stability	
low cost	

Materials for membranes can be categorized into three groups: perfluorinated ionomers (or partially perfluorinated) and their blends, non-fluorinated hydrocarbons (including aliphatic or aromatic structures), and acid-base complexes [20] and example of the classified membranes can be seen in the Figure 4 below.

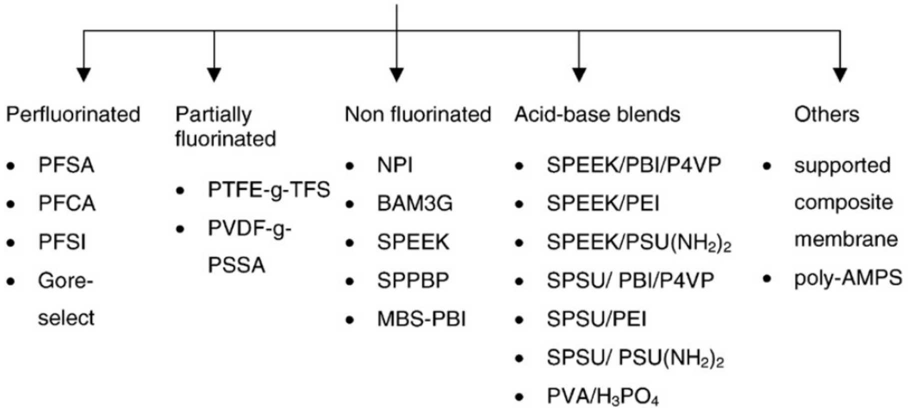


Figure 4: Broad classification of the types of membranes [20]

Perfluorinated ionomers and partially perfluorinated have their structure comprising of hydrocarbon and fluorocarbon bonds which are known to be very stable in terms of chemical and thermal properties. The non-fluorinated polymers usually comprise of carbon backbone and have also been extensively investigated in order to bridge the gap left by the first category of membranes.

For proper functioning the membranes must have specific requirements that can be combined so as to survive the harsh fuel cell environment. There is many on-going research in order to fully exploit the possibilities of coming up with the best performing membrane.

1.4.3. Nafion® Membranes

The major breakthrough in fuel cell technology was with the discovery of the now state-of-the-art membrane Nafion® by DuPont Company in the 1970s. Nafion® is a perfluorinated sulfonic acid membrane which has been extensively studied owing to its better specific conductivity and long lifetime as membranes for fuel cells.[20]. Many reviews have on many occasions highlighted its structural and physical properties, transport properties and application.[21], [22]

Its extraordinary structure combines the PTFE-like backbone, ion clusters consisting of sulfonic acid and a side chains that connects the two previous regions and is as shown in Figure 4 below. These structural properties ensure a high chemical inertness against both oxidative and reductive environments, durability of about 60,000 h.[23] and also high protonic conductivities of as high as 0.2 S/cm in well-humidified conditions[24]

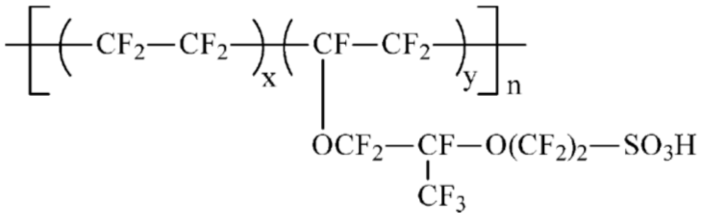


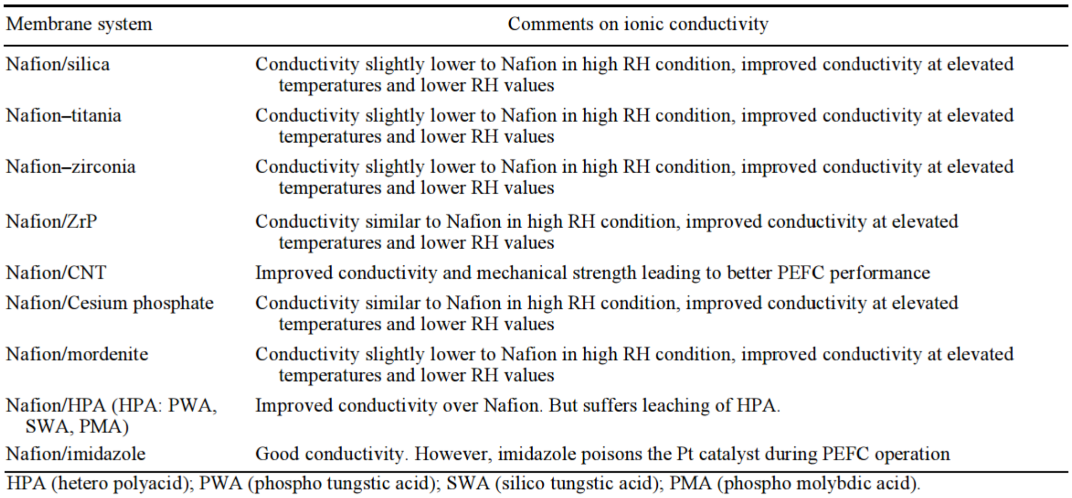
Figure 5: Chemical structure of Nafion®. [22]

Even with these outstanding characteristics of Nafion® it is hard to overlook the problem of degradation that these perfluorinated membranes incur which affect their long-term durability. There have been reported cases of membrane thinning and fluoride ion detection in the product water which indicate that the polymer undergoes chemical attack.[21] Additional worries include its high cost [51], structural instability at temperatures above 100 ˚C [52], lower conductivity at lower relative humidity, and safety problem during synthesis.[25],[26] These drawbacks have prompted for a need to find alternative membranes that are cheaper than PFSA, Rirukawa and Sanui in their review [27] have supported the fact that compromises need to be made for material lifetime and mechanical properties as long as cost factors are commercially realistic. Many approaches have been dealt with and some have been discussed in the following parts of this thesis.

1.4.4. Nafion® Modification and Alternative Membranes for PEMFC

To establish better properties for Nafion®, approaches like polymeric blend membranes and polymer/inorganic composite membranes are being investigated.[28] Of these two methods, use of polymer inorganic membranes has caught the greatest interest due to the fact that there are many inorganic additives that can be used at higher temperatures than the pure Nafion® itself. These inorganic particles promote higher proton conductivities, better mechanical support and even higher water retention abilities at high temperatures.[29] Nafion-based composite proton exchange membranes have been prepared using a wide range of fillers such as SiO_2, zirconium phosphate, phosphotungestic acid[30] molibdophosphoric acid, organically modified silicates, silane based fillers and zeolites. The Table 3 below summarizes effects of the fillers on the conductivity performance of the modified Nafion membranes.

Table 3: Effects of Nafion modification on the conductivity performance[29]



Membrane system	Comments on ionic conductivity
Nafion/silica	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion–titania	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion–zirconia	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/ZrP	Conductivity similar to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/CNT	Improved conductivity and mechanical strength leading to better PEFC performance
Nafion/Cesium phosphate	Conductivity similar to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/mordenite	Conductivity slightly lower to Nafion in high RH condition, improved conductivity at elevated temperatures and lower RH values
Nafion/HPA (HPA: PWA, SWA, PMA)	Improved conductivity over Nafion. But suffers leaching of HPA.
Nafion/imidazole	Good conductivity. However, imidazole poisons the Pt catalyst during PEFC operation

HPA (hetero polyacid); PWA (phospho tungstic acid); SWA (silico tungstic acid); PMA (phospho molybdic acid).

Polymer blending techniques cited in the literature include use of PBI[31], PANI[32], vinylidene fluoride-co-hexafluoropropylene polymer,[33] PVDF [34] and so on in order to improve the performances of Nafion® at higher temperatures. Examples of such polymer blends are shown in the Figure 6 below. With blending, the overall product characteristic is most of the time dependent on the volume fraction of the individual components, therefore careful tailoring of the process should be done so as to keep the desired characteristics of both the components.

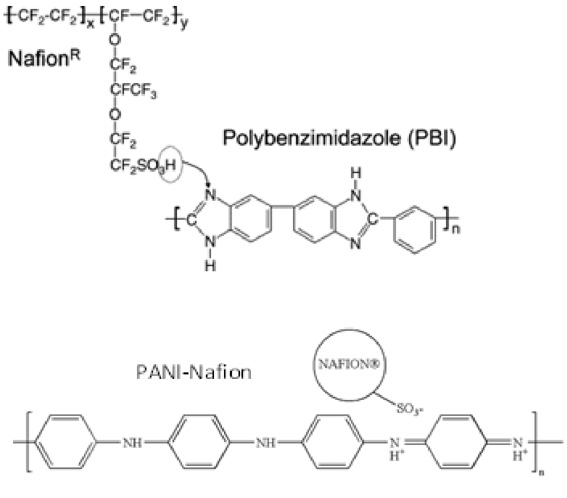


Figure 6: Some examples of Nafion blends studied [31],[32]

Another approach has been use of alternative membranes such as non-fluorinated hydrocarbons, and acid-base complexes,[20] however most of these new membranes are not naturally conductive and therefore require addition of acid moieties like sulfonic acid, phosphoric acid, phosphonic acid, and sulfonimide units so as to convert them to proton exchange membranes.

Hydrocarbons which can be either aliphatic or aromatic are another promising group since they can be easily available, are cheap and permits the introduction of polar sites as pendant groups.[35] These polar sites gives full control to the required water uptake since the type and amount attached can be carefully tailored. The backbones of aliphatic hydrocarbons are inclined to undergo attacks and to prevent this aromatic side chains are incorporated in order to protect the main chain. In this way stability at higher temperatures is enhanced and in other cases conduction of protons has been promoted when the bulky group is in the backbone.[23]

Acid-base complexes on the other hand involve integration of an acid group into alkaline polymers in order to boost the proton conductivity. They have been seen as a possible alternative since they do not suffer from dehydration and therefore can maintain conductivity at elevated temperatures.[23]

Inexpensive materials such as polyimides,[36] poly (ether ether ketones),[37] and polybenzimidazole [26] have been studied at large however none of them has emerged to surpass Nafion® so far. Some of them usually fail due to excessive swelling, poor oxidative stability, moderate proton conductivity, brittleness when dry and so on. Others like sulfonated poly (ether ketones) and polybenzimidazole have been noted to possess an electro-osmotic drag that is lower than that in Nafion® [25] however long-term stability still remains a concern for them. Other aromatic polymers like phosphazene [38] have been studied however there is not much reported in the literature about their application of fuel cells.

Another approach to fabricate membranes has been through radiation induced grafting of polymers with functionalized monomers. The grafting is usually initiated by electron-beam, γ-ray, and ultraviolet (UV) light irradiation or by plasma and this creates active sites from where the functionalized polymers can be incorporated after which sulfonation is carried out to introduce sulfonic acid groups. This technique has been observed to have several advantages one of which is the elimination of chemical initiators or catalyst use during the membrane fabrication and also the easy control of degree of grafting and sulfonation. [39]. In their review Gürsel et al. [40] have discussed the many factors that may affect this technique which include the choice of base polymer, nature of radiation, irradiation dose and dose rate and so on. Several base polymers have been extensively explored using this method examples of which include FEP, ETFE, PVDF, PTFE and PFA [41],[42],[43],[44],[45],[46],[47] and so on using simultaneous and pre-irradiation techniques. From the several base polymers studied it was observed in the literature that FEP-based radiation grafted membranes had comparable fuel cell characteristics to that of Nafion® 112 membranes [48], [49]. ETFE-based membranes also demonstrated lifetimes of the order of 1000 h before substantial degradation was noticed,[50],[51]. This radiation grafted technique is still being developed and so far has shown some promise from the latest literature reports.

2. POLYPHOSPHAZENE BASED MEMBRANES FOR FUEL CELL APPLICATIONS

2.1. Overview of Polyphosphazene

Polyphosphazene belong to inorganic polymer group and have a –P=N- polymer backbone which when compared to that of carbon based chains are less restricted due to their bonding angles. The bond angle of $(PCl_2N)_n$ at phosphorus (N-P-N) is 115°, and the angle at nitrogen (P-N-P) is 131° as depicted in Figure 7 below [52]. Bond lengths in the skeleton also affect the bond torsional mobility, and the longer the bond lengths, the smaller will be the torsional barrier energy. The P-N in $(PCl_2N)_n$ is 1.67 Å which is longer than that of the C-C bond length (1.54 Å) in linear alkanes. As a consequence, they have high segmental mobility and low glass transition temperatures [53]. They can also be combined with numerous side chains such as organic, organometallic, or even inorganic units, a property which has favored them for applications such as solid polymer electrolytes for batteries, membranes for gas and liquid separations, optically active polymers, and proton exchange membranes for fuel cells [54]. Their hydrophilic backbone has also been useful for applications that require water soluble properties such as for biomaterials and phosphazene hydrogels. In addition to these they have also been extensively used as flame retardants additives, performance polymers and so on.[55]

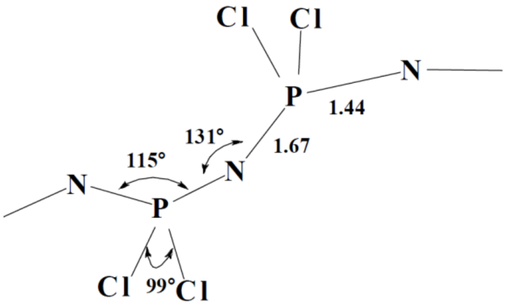


Figure 7: Illustration of the bond angles (˚) and bond lengths (Å) in $(PCl_2N)_n$ [52].

The discovery of polyphosphazene is owed to H.N.Stokes who in 1895 managed to synthesize hexachlorocyclotriphosphazene ($[NPCl_2]_3$) through thermal ring opening polymerization. However, since the product was hydrolytically unstable it could not be used for any technological applications. It was not until 1960's that Allcock and Kugel et al. successfully synthesized a linear, poly (dichlorophosphazene) by carefully controlling the time and temperature for the thermal ring opening polymerization of hexachlorocyclotriphosphazene.[56] Replacing the chlorine atoms (which caused the hydrolytic instability though its highly reactive polar phosphorus–chlorine bonds) with organic or organometallic nucleophiles further resulted in hydrolytically stable, soluble and high molecular weight polyphosphazene products as shown in Figure 8 below.

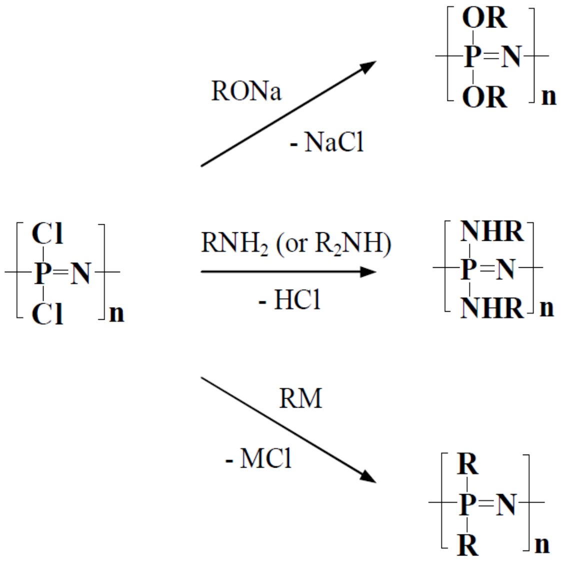


Figure 8: Scheme showing the synthesis of various types of polyphosphazenes. [55]

Ever since, in order to overcome the drawbacks inherent in ring-opening polymerization other methods such as living polymerizations and so on had to be discovered. The table below shows the summary of the other methods developed and their characteristics.

Table 4: The summary of polyphosphazene synthesis methods and their characteristics. [57]

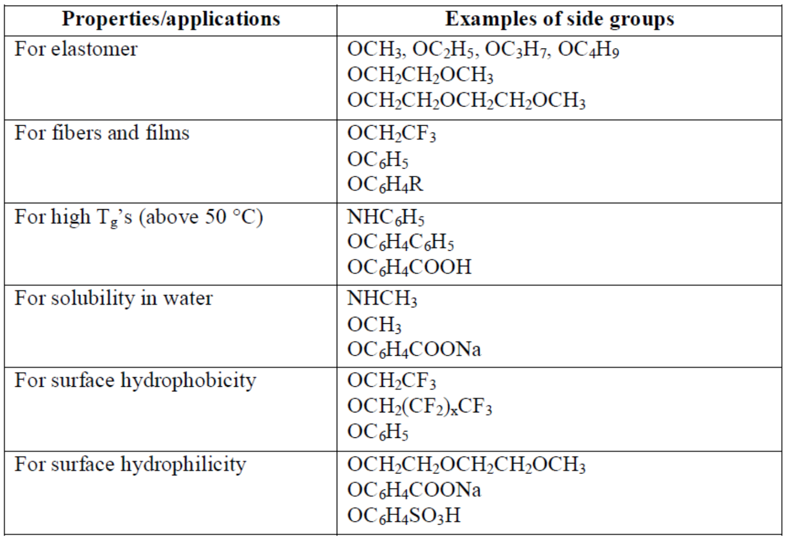
Synthesis method		Reactions	Characteristics*
Thermal ring opening	Allcock$^{1-3}$	$N_3P_3Cl_6 \xrightarrow{250\ ^\circ C}$ **(1)**	High MW, broad PDI
Condensation polymerization	De Jaeger$^{1-3}$	$Cl_3P{=}NP(O)Cl_2 \longrightarrow$ **(1)**	MW=10^3 D, PDI =1.5-3.0
Condensation polymerization	many researchers	$PCl_5 + NH_4Cl \longrightarrow$ **(1)**	Medium MW, very broad PDI
Living anionic polymerization	Matyjaszewski$^{1-3}$	$(RO)_3P{=}NSiMe_3 \longrightarrow$ **(1)**	Medium MW, PDI= 1.3-2.4
Living cationic polymerization	Manner, Allcock$^{1-3}$	$Cl_3P{=}NSiMe_3 \longrightarrow$ **(1)**	Controlled MW up to 10 D, narrow PDI close to 1

*MW: number average molar mass in g/mol; PDI: polydispersity index (ideal is 1); D: Dalton (unit for molecular weight)

2.2. Polyphosphazene Based Membranes for Fuel Cells

With the on-going search for other materials for membranes, polyphosphazene has attracted some attention for membranes of fuel cells. However the biggest challenge with polyphosphazene is that they have poor mechanical properties and also their backbone is quite hydrophilic due to the presence of the nitrogen atoms with their lone-pair electrons. As previously discussed different side chains may be integrated to change the overall properties the Table 5 below shows example of these side groups and their effects.

Table 5: Side groups of polyphosphazenes related to their properties and applications. [55]



Properties/applications	Examples of side groups
For elastomer	OCH_3, OC_2H_5, OC_3H_7, OC_4H_9 $OCH_2CH_2OCH_3$ $OCH_2CH_2OCH_2CH_2OCH_3$
For fibers and films	OCH_2CF_3 OC_6H_5 OC_6H_4R
For high T_g's (above 50 °C)	NHC_6H_5 $OC_6H_4C_6H_5$ OC_6H_4COOH
For solubility in water	$NHCH_3$ OCH_3 OC_6H_4COONa
For surface hydrophobicity	OCH_2CF_3 $OCH_2(CF_2)_xCF_3$ OC_6H_5
For surface hydrophilicity	$OCH_2CH_2OCH_2CH_2OCH_3$ OC_6H_4COONa $OC_6H_4SO_3H$

Hydrophobic side chains can therefore be added to act as a shield for the skeletal atoms from hydrolytic breakdown and also at the same time allow the surface structure of the product to be dominated by the hydrophobic characteristics. Examples of different side groups that have been shown in the table above to promote hydrophobic properties to phosphazene include fluoroalkoxy, aryloxy ororganosilicon side groups.[58]

The mechanical properties of polyphosphazenes to be used for fuel cell applications can be improved with appropriate side groups that are able to hinder the backbone flexibility.[56] Some studies have shown that aromatics and substituted aromatic side groups can hinder backbone rotations and provide a polymer material with a higher T_g [55] which is a wanted property. An example of this behavior has been documented for polyphosphazenes that bear aryloxy substituents.[56],[59] These aryloxy side groups restrict the re-orientational freedom of the polymer backbone due to their steric bulk and rigidity; they raise the glass transition temperature and improve the mechanical strength of a polymer.[59]

Throughout the literature there are very few reports of phosphazene membranes that have been tested in *in situ* fuel cell environment despite the fact that very good *ex situ* proton exchange membrane properties have been reported. A well referred to example is the sulfonamide polyphosphazene membrane that was fabricated and tested by Allcock and Lvov [60]. They reported an IEC value of 0.99 mmol/g, equilibrium water swelling of 42%, and a proton conductivity of 0.058 S/cm. The *in situ* performance was as shown below in Figure 9 and although the membrane had performances comparable to that of Nafion, there was no long-term stability analysis reported a step very important in evaluation of membranes for fuel cells.

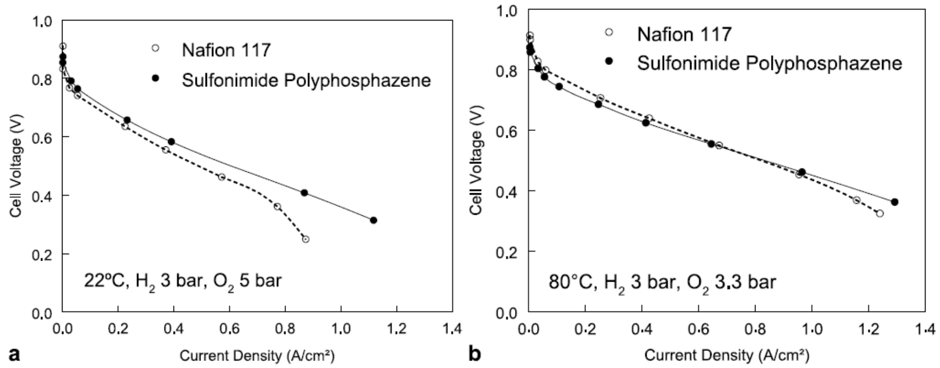


Figure 9: Hydrogen fuel-cell performance curves with a sulfonimide polyphosphazene proton exchange membrane at (a) 22 ˚C and (b) 80 ˚C[60]

2.3. Acid Functionalized Polyphosphazene Membranes

Proton exchange membranes should have protogenic functionality that facilitates proton conductivity. For aryloxy polyphosphazene this is achieved by addition of functional groups such as phosphonic acid [61], sulfonic acid [54],[56], and sulfonamide units [60] to the aryloxy side groups. It has been widely observed that these named functional groups impart different water retention, and proton conduction to the membranes. For instance, Lvov *et al*. in their study [61] have showed that phosphonic acid had lower water uptake values and conductivity compared to both sulfonimide based and sulfonic acid based polyphosphazene despite having a higher IEC value than both. The reason could be due to phosphonic acid being less hydrophobic than the others resulting in less water uptake and conductivity values.

Of these all, sulfonation is the most widely used and the sulfonating agents include sulfuric acid, oleum and chlorosulfonic acid. These agents are preferred because they usually react though electrophilic sulfonation which demonstrates effective sulfonation capability for aromatic compounds and its mechanism and its kinetics has been studied extensively.[62] Attempts to sulfonate aryloxy and arylamino polyphosphazene was carried out by Allcock *et al*. [56] and they managed to obtain both water soluble and insoluble sulfonated products by varying the degrees of sulfonation from 5-100% by optimizing the durations and temperature of each process.

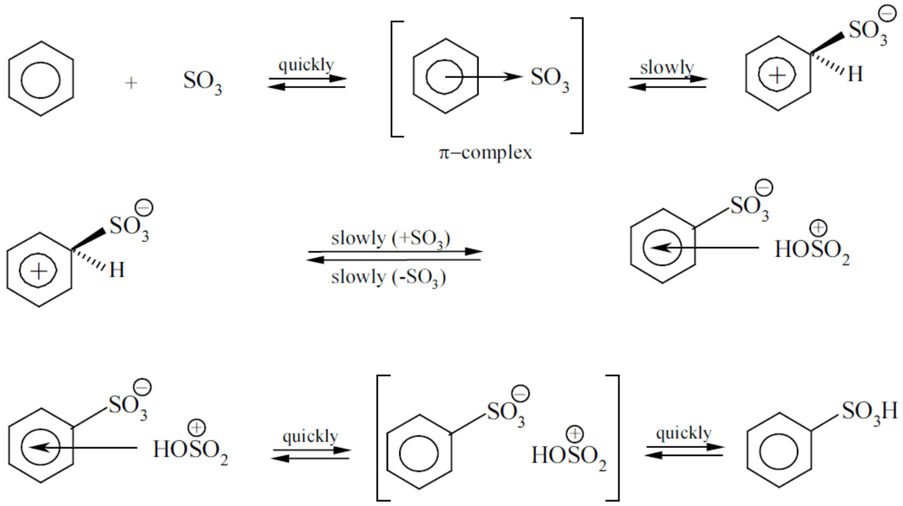


Figure 10:Steps of the electrophilic sulfonation of aromatic polymer using SO_3[63]

In sulfonation using sulfur trioxide, the SO_3 group which is present in the sulfonating agents reacts with the aromatic structure to produce crosslinked sulfonated products as can be illustrated in the Figure 10 above. However the backward reaction – desulfonation - can sometimes be favored in situations where there is presence of hot aqueous sulfuric acid. This necessitates the careful adjustments of the reaction parameters (duration, temperature, and so on) so as to strike a compromise between the starting material and product degradation.

Sulfonation of membranes has been achieved so far though postsulfonation and also though direct sulfonation whereby polymerization of already sulfonated products is carried out [27]. The former is advantageous because it is easier to carry out however degree of sulfonation is difficult to control. There have also been reports of the possibility of desulfonation and partial degradation especially when strong agents are used [62]. In direct sulfonation unwanted side reactions can be easily controlled and there is better control over final material properties however there are issues with the starting polymer which resulted in polymer degradation in the reported trials.[54], [2] For polyphosphazenes in the literature, both methods of sulfonation have been carried out. For the direct method where the acid functionality is assimilated at the polymer synthesis step Ganapathiappan et al. [25] though a two-step process managed to carry out sulfonation using disodium salts of 2-hydroxyethanesulfonic acid and 2-(2-methoxyethoxy)ethanol as illustrated below in Figure 11.

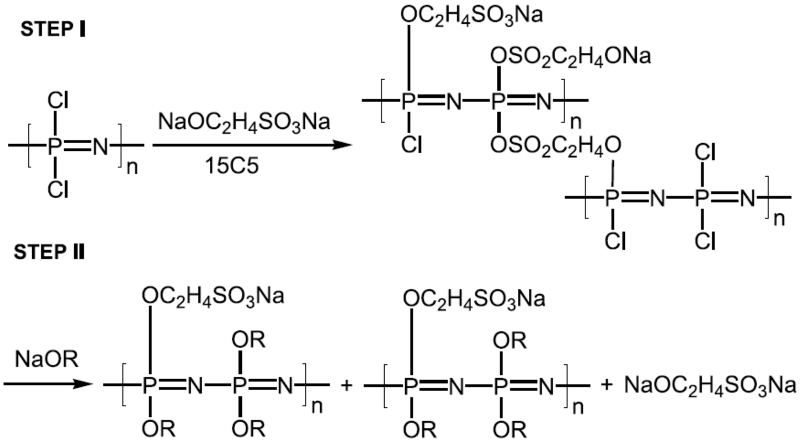


Figure 11: Two-step direct sulfonation of polyphosphazene[64]

Postsulfonation of poly[(aryloxy)phosphazenes] was first carried out by Pintauro and co-workers and they used dichloroethane as the polymer solvent and sulfur trioxide as the sulfonating agent[65],[66],[67] as depicted in the Figure 12 below. In addition to SO_3, other reagents such as sulfuric acid have also been used widely for post sulfonation processes. Part of this study will also investigate the use of sulfuric acid and other sulfonating agents for polyphosphazene membranes.

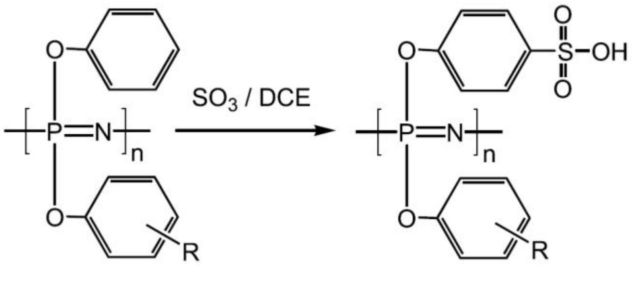


Figure 12: Postsulfonation of aryloxy polyphosphazenes[65]

The sulfonic acid groups in the sulfonated products usually dissociate in the presence of water and therefore play a major role in proton conduction during the functioning of the fuel cell. Proton conduction has been explained in the literature by the vehicular and Grotthuss mechanism.[68] In the vehicular mechanism protons diffuse in the form of H_3O^+ and H_5O^+ ions and so on present in the acidic aqueous medium. For the Grotthuss mechanism the protons hop from one hydrogen site to another by the breaking and reforming of hydrogen bonds. Kreuer has made a very good illustration as shown in Figure 13 below so as to describe the proton mechanism.

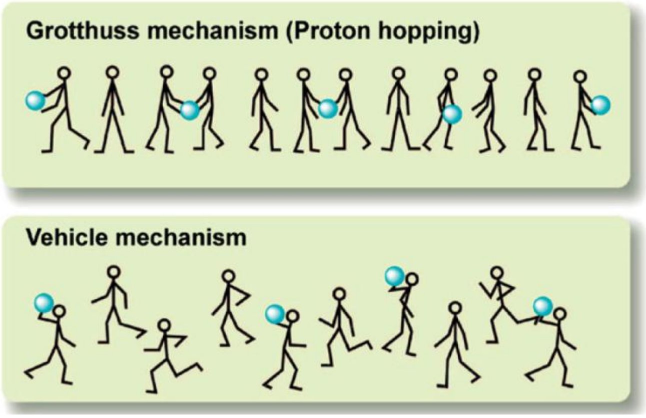


Figure 13: An illustration for proton conduction mechanism, the humans are representative for the water or base while the balls are protons [68]

In most cases within the PEMFC these two mechanisms are in competition. For this particular N-heteroatom containing polymer, the nitrogen site in the heteroatom can be protonated by the sulfonic acid group thus enabling the hopping of the proton from one nitrogen site to another or from an oxygen atom of a sulfonate anion group to another by the Grotthuss mechanism. The two mechanisms could be playing a role simultaneously, however studies to find out which mechanism dominates has not been looked into at this level.

3. EXPERIMENTAL SECTION

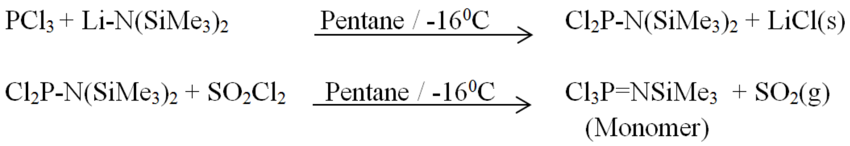
3.1. Materials

The polyphosphazene polymers used were synthesized at Ahi Evran University, N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich, 99%), N-N-dimethylacetamide (DMAc) (Sigma Aldrich, 99%), chlorosulfonic acid (Fluka, 98%), sulfuric acid (Fluka, 98%), sodium hydroxide (Lab Kim, 99%), sodium chloride (Sigma Aldrich, 99.5%) and DuPont Nafion® 115. All the chemicals were used without further purification.

3.2. Polymer Synthesis

The poly (*m*-tolyloxy-*co*-4-pyridinoxy phosphazene) polymers have been synthesized at Ahi Evran University by Burak Yiğen under the supervision of Dr.Yunus Karataş and for more details please refer to the thesis or paper "Synthesis of Poly (*m*-tolyloxy-co-4-pyridinoxy phosphazene) s for Fuel Cell Applications" (in preparation).

The polymer synthesis involves thee major steps which include the synthesis of the monomer, precursor polymer and the targeted polyphosphazene polymer. The monomer synthesis was carried out as shown in the Figure 14 below:



$$PCl_3 + Li\text{-}N(SiMe_3)_2 \xrightarrow{\text{Pentane / -16}^0\text{C}} Cl_2P\text{-}N(SiMe_3)_2 + LiCl(s)$$

$$Cl_2P\text{-}N(SiMe_3)_2 + SO_2Cl_2 \xrightarrow{\text{Pentane / -16}^0\text{C}} \underset{\text{(Monomer)}}{Cl_3P{=}NSiMe_3} + SO_2(g)$$

Figure 14: Synthesis of the trichloro-(trimethylsilyl) phosphoranimine (monomer)

The obtained monomer was then isolated by vacuum distillation and the purity checked by ^{31}P-NMR before the next synthesis stage. Following this, the synthesis of the precursor polymer (polydichloro phosphazene) was performed via living cationic polymerization as summarized in the Figure 15 below:

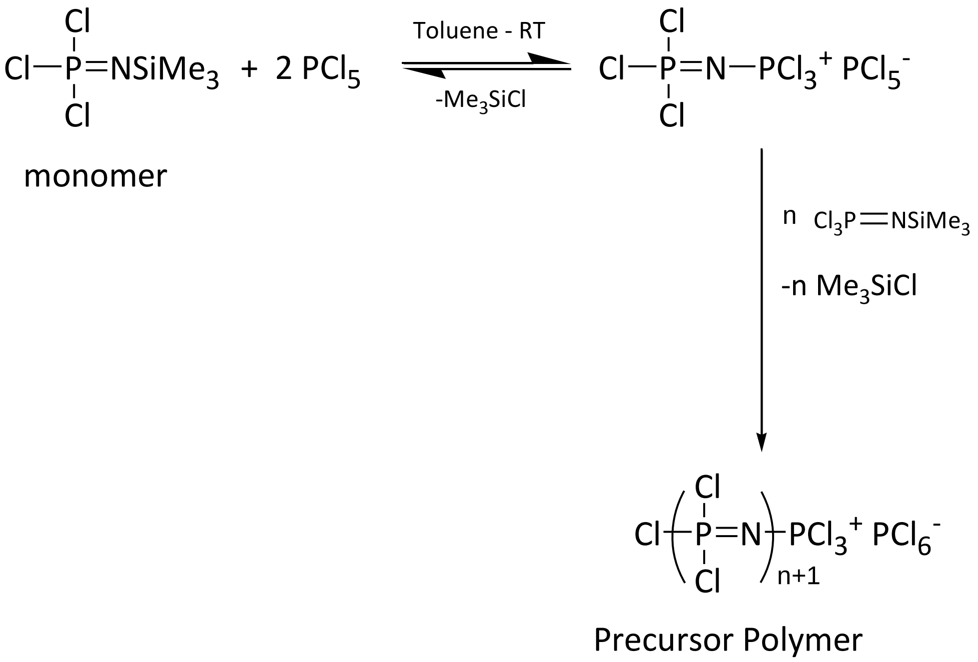
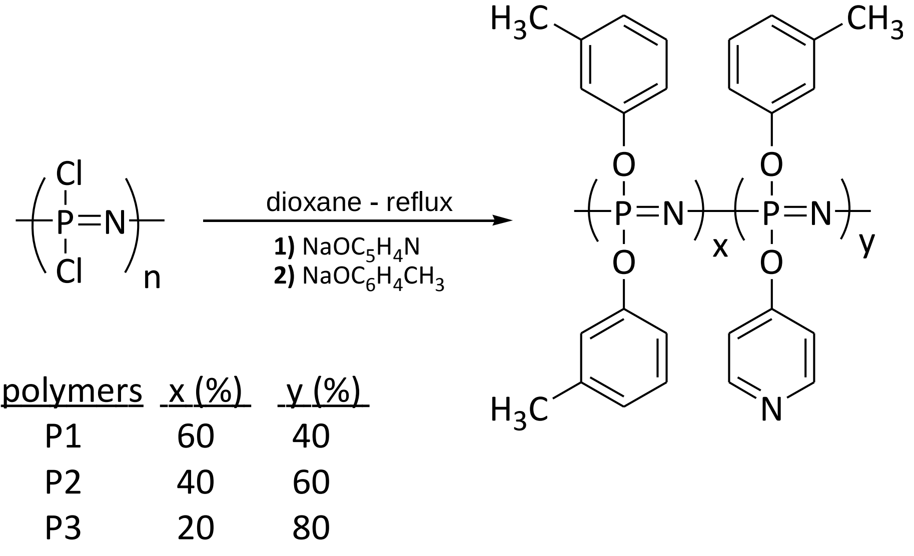


Figure 15: Showing the synthesis of the precursor polymer PDCP

Finally the PDCP was subjected to macromolecular substitution method with 4-pyridinoxy and 3-methyl phenoxy sodium salts to produce three polymers with varying side group ratios as shown in the Figure 16 below:



polymers	x (%)	y (%)
P1	60	40
P2	40	60
P3	20	80

Figure 16: Macromolecular substitution of the PDCP to produce the targeted polymers (P1, P2 and P3)

3.3. Fabrication of Membranes

3.3.1. Solution Casting

The membranes were fabricated through solution casting and several solvents such as DMAc, THF and NMP were tried. Membrane properties like thickness and porosity were tailored by controlling the weight percentage of polymer put in solution and the temperature at which the casting process was done. After trying the different solvents the solvent preferred for most fabrication of membrane was DMAc and a known weight percentage of the polymer was dissolved in the solvent and casted in Polytetrafluoroethylene (PTFE) molds at 70 ˚C for 24-48 h after which they were removed from the mold.

3.3.2. Sulfonation Experiments

Post sulfonation approach was carried out for our polymers and the two sulfonating agents below were investigated to investigate the effect of sulfonation on the Poly (*m*-tolyloxy-*co*-4-pyridinoxy phosphazene) based polymers.

3.3.2.1. Chlorosulfonic Acid Sulfonation

A known weight of the polymers was first dissolved in 50 mL of dichloromethane (DCM) and stirred for 24 h. at 50 ˚C to ensure all polymers is fully dissolved. Afterwards a given amount of chlorosulfonic acid in 10 mL of DCM was added drop-wise to the polymer solution in a dry nitrogen atmosphere as seen in the Figure 17 below. The inert atmosphere served to moderate the process which is otherwise quite exothermic due to the excessive reactivity of chlorosulfonic acid.

Figure 17: Set up for the sulfonation process.

For the sulfonation process parameters optimized were the concentration of chlorosulfonic acid and the durations for the process. The process was optimized for the concentrations of 0.04 mol, 0.02 mol, 0.01 mol and durations of 3 h, 1 h., 15 min. The resultant precipitate was stirred for 3 h in nitrogen atmosphere and followed by the addition of a NaOH solution to terminate the reaction. After evaporation of the solvent at 70 ˚C for 24 h, the polymer was then preconditioned by soaking sequentially in distilled water, 0.1 M NaOH, distilled water, 0.1 M HCl, and distilled water (each soaking for 48 h.). The resulting polymer product was then dried thoroughly and casted in DMAc to obtain the membrane.

3.3.2.2. Sulfuric Acid Sulfonation

3.3.2.2.1. Mild Sulfuric Acid Concentrations

In this second method we again attempted several concentrations of sulfuric acid in order to check their effect on the sulfonation process. First of all, mild sulfonation using low concentrations of 1.0 M, 2.0 M and so on was used while also adjusting the duration for the process in order to study their effects. The membranes were basically soaked into the freshly prepared solutions for durations of 18-72 h and the outcome analyzed through different characterization methods.

3.3.2.2.2. High Sulfuric Acid Concentrations

Effect of higher concentrations of sulfuric acid on the polymers was also investigated and concentrated sulfuric acid (98%) was used for this part of the study. A weighted amount of polymer (either in its original form or as casted) was dissolved in concentrated sulfuric acid. The sulfuric acid acted both as a solvent in which the dissolution of the polymer occurred in the initial stages of the reaction and also as a sulfonating agent. A range of different temperatures and durations were employed and the effect of these two parameters on the overall process was studied. The sulfonation for the three different polymers at hand was optimized for different temperatures and durations as shown in the Table 6 below.

The viscous polymer-acid solution was then cooled to room temperature by pouring onto ice in order to consume the heat of dilution. The solution formed a precipitate of the polymer and it was further isolated by centrifuging the solution. The polymers were then extensively washed under running water for several hours thoroughly till the pH was neutral to remove the excess acid. This was followed by soaking the sulfonated polymer in 0.1 M NaOH overnight to convert it to Na^+ form and to decompose any sulfones resulting from any crosslinking reactions with the polymer. Next the sulfonated products were casted using DMAc and the membranes were soaked in distilled water in order to remove the residual solvent and then soaked in 1.0 M H_2SO_4 to further convert them from their salt form (Na^+) to their acidic form (H^+). The membranes were then rinsed with distilled water to remove any excess acid solution and dried at room temperature and stored till further characterization.

Table 6: Showing the parameters used for the sulfonation process

	Temp. (°C)	Time at RT (min)	Time at High Temp. (min)	Total Time(min)
A	RT	30	0	30
B		45	0	45
C		60	0	60
D		90	0	90
E		120	0	120
F	65	15	0	15
G		30	0	30
H		45	0	45
J	65	30	30	60
K		60	60	120
L	90	60	60	120

3.4. Polymer and Membrane Characterization

3.4.1. Chemical Structure

A Bruker Equinox 55 FTIR spectrometer equipped with an ATR system was used to conduct the FTIR study in order to check the molecular structure of the sulfonated and unsulfonated membranes. The study was done by 64 scans at a digital resolution of $4cm^{-1}$ and over the range of 500-4000 cm^{-1}. OPUS™ software was used for the evaluation of resulting spectrums.

NMR studies were carried out using the Unity Inova 500 spectrophotometer (Varian) for

^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR. The solvents used to dissolve the polymer samples were $CdCl_3$ and DMSO-d_6. The spectra were analyzed by MestReNova software.

3.4.2. Thermal Properties

Thermogravimetric analysis (TGA) was performed on Netzsch STA 449 C Jupiter simultaneous thermal analyzer where samples were heated in ceramic crucibles from room temperature to 700 ˚C at a rate of 10 ˚C/min under nitrogen purge.

Differential scanning analysis (DSC) of the samples was performed using a Netzsch Phoenix DSC 204 differential scanning calorimeter with aluminium sample pans. In a nitrogen gas atmosphere the samples were subjected to a cooling stage at a rate of 10˚C /min from 25 ˚C to -100 ˚C followed by a first heating from -100 ˚C to 150 ˚C and a second cooling again to -100 ˚C. A second and final heating was done from -100 ˚C to 300 ˚C. In between the dynamic steps, isothermal steps of 5 min. were included so that the system attains stability after each cycle.

3.4.3. Mechanical Properties

The mechanical property of the membranes was analyzed using the Netzsch DMA 242C dynamic mechanical analyzer. The samples were cut into 6.5 mm by 21 mm dimensions and the test was performed in tensile mode and the temperature profile varied from -60 ˚C to 100 ˚C at a 3 ˚C /min heating rate with a frequency of 1 Hz.

3.4.4. Water Uptake and Ion Exchange Capacity (IEC)

Before this fuel cell related properties were carried out, the reference membrane which is Nafion® 115 usually available in its inactivated form was first processed. The Nafion$^{®}$ 115 was activated according to the standard procedure by boiling for 1 h in 3% solution of H_2O_2 followed by 1 h in boiling 1.0 M sulfuric acid. The membranes were then rinsed in boiling distilled water for 1 h and this process was repeated twice in order to remove H_2SO_4.

The fabricated membrane samples and the activated Nafion$^{®}$ 115 were then soaked in deionized water for 24 h. and then their weight was taken as W_1. The samples were then dried at 70 ˚C for at least 8 h or until constant weight is achieved and then their weight recorded as W_2. Water uptake was then calculated from the Equation 1 below:

$$\Delta W(wt\%) = \left(\frac{W1-W2}{W2}\right) * 100 \text{……………………Equation 1}$$

IEC measurements on the other hand was carried out by soaking a known weight of Nafion® 115 and also that of the acidic form of the sulfonated membrane in 100 mL of a 0.5 M KCl solution for 24 h and then 3-4, 20 mL aliquots were titrated with 0.05 M KOH using automatic titration equipment. The IEC of the sample was calculated according to the following Equation 2:

$$IEC = 0.05 \cdot \frac{V_{KOH}}{m_{dry}} \cdot 1000 \text{ (meq/g)………………………..Equation 2}$$

$$m_{dry} = m_{salt} - 38.1 * 0.05 * V_{KOH} \text{ (g)}$$

Where:

0.05 (M) : concentration of KOH solution
V_{KOH} (mL) : volume of KOH solution consumed in titration
m_{dry} (g) : corrected weight of the membranes
m_{salt} (g) : dry weight of membranes in their salt form
38.1(g/mol) : correction of the mass obtained by subtracting the molar mass of hydrogen (1 g/mol) from the molar mass of potassium (39.1 g/mol)

After calculation of the IEC values the degree of sulfonation was obtained from the Equation 3 below:

$$\text{Degree of Sulfonation } (\mathbf{DS}) = \frac{\mathbf{IEC * M_{ppzn}}}{\left[\mathbf{1 - (IEC * M_{SO_3H})}\right]} \text{………………………….. Equation 3}$$

Where:

IEC : Ion Exchange Capacity
M_{ppzn} : Mass of the monomer-unit
M_{SO_3H} : Mass of Sulfonic acid group

3.4.5. Proton Conductivity

To check the proton conducting capability of the membranes produced, measurements were done from Gamry PCI4/750 Potentiostat/Galvanostat together with the BT-1005 BekkTech Scanning DC Software. The four-point-probe cell with two platinum foil outer current-carrying electrodes and two platinum wire inner potential-sensing electrodes was mounted on a Teflon plate the schematic view of the cell is shown in Figure 18 below. The single cell Teflon set up can be seen in the Appendix. Membranes were soaked in water prior to measurement for 3 h and cut into 20 mm by 20 mm dimensions and set up in the BekkTech conductivity cell which was then placed in a faraday cage to shield the cell during measurement as shown in the Figure 17 below. The membrane thicknesses were determined and recorded in the software interface and the system was left to stabilize until consistent data started to be recorded.

Figure 18: Setup used for conductivity measurements. The aluminium box acted as a faraday shield during the experiments

4. RESULTS AND DISCUSSION

4.1. Fabrication of Membranes

4.1.1. Solution Casting

Both the sulfonated and pristine membranes were successfully prepared by solution casting in DMAc solvent. According to the literature polyphosphazene polymers have been casted by a wide range of solvents such as DMF, THF, NMP, and so on. Reports have shown that the type of solvent used plays a major role and generally affects the membrane properties like mechanical strength and proton conductivity. In a study by Kaliguine *et al.* [69] they claimed that the conductivity of sPEEK membranes decreased when DMF was used in comparison with other solvents. In their ^{1}H-NMR analysis they reported that DMAc gave no evidence of hydrogen-bonded data in contrary to when DMF was used which bonds with $–SO_3H$ groups. Based on these findings the solution casting of all membranes in this study was done using DMAc. In the below Figure 19 the photos of the casted membranes are shown. After trying different conditions for temperature and duration for casting the membranes, it was observed that 70 ˚C and durations between 24- 48 h gave homogeneous and desired membranes.

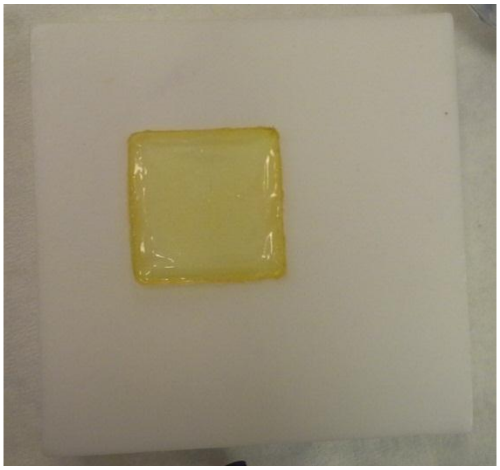


Figure 19: Solution casted membrane

4.1.2. Sulfonation Experiments

The sulfonation process involves the integration of the sulfonic acid groups into the aryloxy polyphosphazene. The sulfonic acid group integrated in the membrane is responsible for the proton conduction and since the aim is to increase the conductivity of membranes it may be assumed that an increased amount of this group would result in maximum conductivity. However, this comes with a price since highly hydrophilic membranes which then become hydrogels [70] are formed with increasing levels of sulfonic acid groups leading to deterioration of the mechanical stability and other membrane properties like water uptake and conductivity. Therefore, a balance has to be found between the optimum amount of these side groups that will have both maximum conductivity and good water uptake and mechanical properties.

The choice of sulfonation agent also played a very important role since these reagents like chlorosulfonic acid produce very highly sulfonated products yet at the same time cause cleavage to the polymer. With mild reagents polymer degradation was avoidable however the drawback was that the resulting membranes had somewhat low degrees of sulfonation and low proton conductivity.

In precious works [71] there have been reports where polyphosphazenes were sulfonated by use of chlorosulfonic acid to produce membranes with promising fuel cell characteristics however, attempts to use it for the sulfonation of the poly (*m*-tolyloxy-*co*-4-pyridinoxy phosphazene) polymers in this work failed. The sulfonated products were robust in nature due to the crosslinking that resulted in the incorporation of the sulfonyl chloride group to the aromatic structure [72] as shown in the Figure 20 below. The products underwent dissolution during the preconditioning stage and therefore this method was discarded.

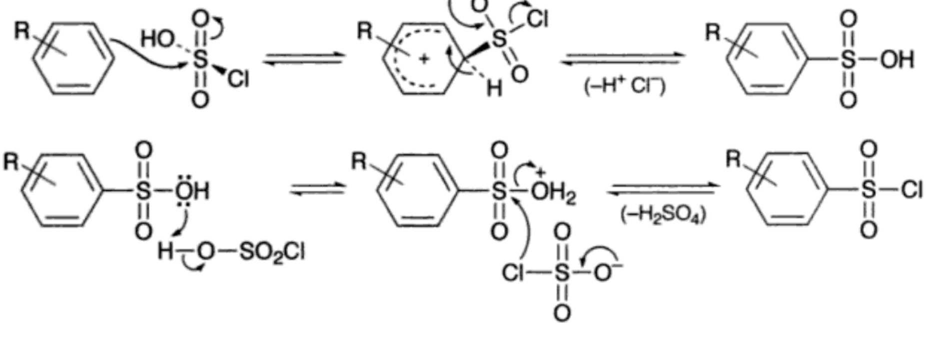


Figure 20: The mechanism for the sulfonation using chlorosulfonic acid [72]

During the chlorosulfonation all the parameters shown in the Table 7 below were optimized but did not work and no final products were obtained.

Table 7: Showing the conditions optimized for the process, x represents not successful.

	0.04 mol	0.02 mol	0.01 mol
180 min	x	x	x
60 min	x	x	x
15 min	x	x	x

This reagent was too harsh for the polymers and probably caused cleavage on the backbone which resulted in drastic loss of molecular weight of the polymer. The attack may also have occurred at the initial stages after the dissociation of chlorosulfonic acid into intermediates thereby forming a complex between SO_3 and the backbone nitrogen atoms as illustrated in the Figure 21 below [73] before the sulfonation of the aromatic side groups of polyphosphazenes. The nitrogen atom in the pyridine side chain could also have succumbed to attack and by doing so contribute to the hydrolysis of the products also. This behavior is in agreement with some reports in the literature which have suggested that polymer degradation and crosslinking are the major problems associated with sulfonation using strong agents like chlorosulfonic acid and 100% H_2SO_4.[74]

During the sulfonation process, sulfone formation which is usually favored at low temperatures may have occurred and contributed to the crosslinking of the polymers. The tendency of its formation has been reported to increase in the order of 97.4% H_2SO_4 <100% H_2SO_4<<HSO_3Cl [74] for the different reagents. We therefore concluded that chlorosulfonic acid was unsuitable for all the three polymers of this study and sulfuric acid was employed in the subsequent reactions.

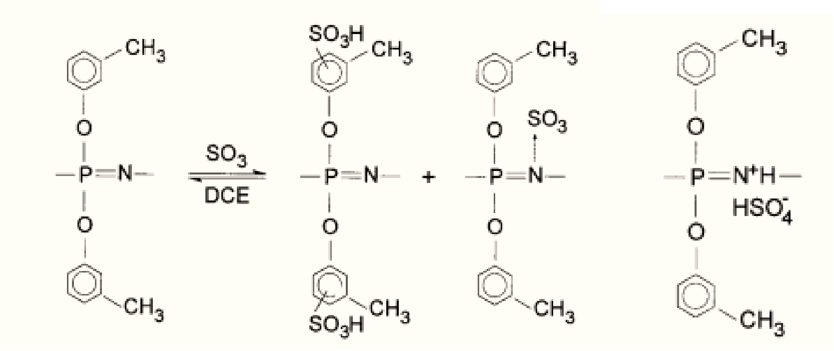


Figure 21: Steps involved in the sulfonation of aryloxy phosphazenes

In the second method which involved use of mild concentration of sulfuric acid the membranes were soaked in low concentrations of sulfuric acid as described in the previous chapter. The resultant membranes did not show signs of dissolution in the sulfonation media and after rinsing it was observed that the membranes hardened and became brittle. FTIR studies carried out gave very weak signals and so this method, although being milder than chlorosulfonic acid was discarded for fabrication of the targeted membranes for fuel cell studies.

As explained in the above sections the tendency for crosslinking side reactions was decreased when sulfuric acid that was not 100% was used when compared to the other reagents. From observations during the sulfonation of PEEK, several groups did report that by using 95-98% sulfuric acid which contains little percent of water, the crosslinking presumably resulting from the sulfone groups decreased because the H_2O decomposes the aryl pyrosulfate intermediate that is responsible for sulfone formation.[74]

This reagent was used for all three polymers however, only one of them (P1) showed promising results and several parameters were optimized for it. The other two polymers (P2 and P3) underwent hydrolysis during the pre-conditioning steps and even with slight modifications in the method used for sulfonation[75] there was no improvement in the results. By looking at Gleria's model as shown in Figure 19 above and from the fact that there is an increasing amount of pyridinoxy in the polymers from P1>P2>P3 we can speculate that in addition to the backbone nitrogen lone pair the nitrogen at this side group is also attacked. Its electronegative nature attracts hydrogen from surroundings this in turn resulted in increased hydrophilicity of the membranes produced which then led to their hydrolysis during the preconditioning stages.

4.2. Chemical Structure

4.2.1. FTIR Results

The pristine polymers which contained increasing ratios of pyridinoxy side group in the order of P4>P1>P2>P3 were investigated for their chemical structure. Here P4 contains 100% of the tolyloxy group with zero amount of the pyridinoxy side group. The structural properties of both the pristine polymers and the sulfonated membranes were investigated using the FTIR. The polymers had varied amounts of pyridine containing side groups and the difference was observable as shown in the Figure 22 below. At 3000-3200 cm^{-1} stretching bands for C-H belonging to the benzene aromatic structure can be seen overlapping with those from the CH_3 at around 2800-3000 cm^{-1}. Aromatic C=C stretch were also seen at around 1600 cm^{-1} and 1500 cm^{-1}. Signals associated to C=N stretching bonds were seen at 1420 cm^{-1} in addition to the weak band at 3300-3500 cm^{-1}.

At 3000-3200 cm^{-1} stretching bands can be seen C-H belonging to the benzene aromatic structure overlapping with those from the CH_3 at around 2800-3000 cm^{-1}. A look at Figure 22 shows that at around 850 cm^{-1} we have the methyl group decreasing in the P4>P1>P2>P3 as depicted by the formulas for the polymers. Aryl-N can be assigned to the signal at 1200-1250 cm^{-1} which increases with the pyridinoxy group while other stretching of pyridine peaks are seen at 1600 cm^{-1}, 1420 cm^{-1}. Understanding the structure of the pristine polymers provided a baseline for the changes that occurred during the sulfonation process.

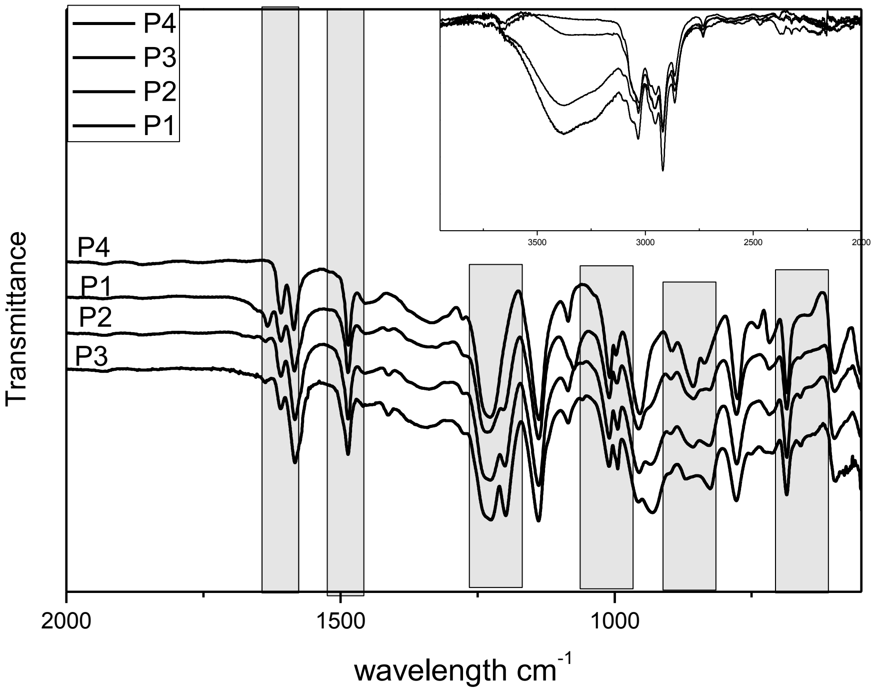


Figure 22 : FTIR results for the pristine polymers

Sulfonated polymer membranes showed extra peaks that were associated with the modification that occurred during this optimization. The FTIR study for the different optimized parameters has been discussed below and some of the figures are as displayed in the Appendix 2 and 3. The effect of temperature, time and temperature application modes have been investigated in this study

From the Figure 23 below new peaks at ~ 1300 cm^{-1} represented the O=S=O asymmetric stretching which is an indication that sulfonic group was integrated. However, since these sulfonation processes were carried out for longer durations and higher temperatures extra doublet peaks were observed at around 2350 cm^{-1} which was associated with the P-O-H indicating some attack to the phosphazene backbone. This behavior is most severe for the condition L (which is described Table 5 in experimental chapter) due to the length and higher temperature. A look also reveals a decrease in the peak signal at 1240 cm^{-1} which is attributed to C-N and is seen in the spectra for all the conditions.

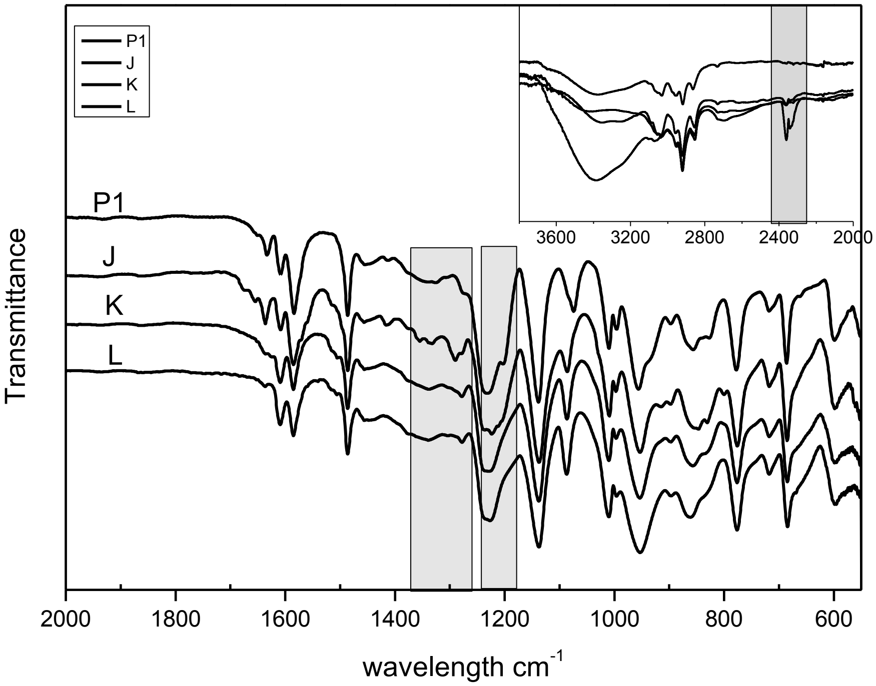


Figure 23: The effect of step-wise sulfonation by inducing both room temp., and higher temperature Sulfonation at 65 ˚C for J: 30+30 min, K: 60+60 min. Sulfonation at 90 ˚C for L: 60+60 min

The broad band observed at 3250-3700 cm^{-1} was attributed to O-H stretching bands due to the interaction of the sulfonic acid with molecular water. However, major differences in the relative intensities may have been due to many reasons one of which being the effect of humidity during the measurements and also samples from different batches of starting material. Another viable reason could also be due to the variations in sample thicknesses, low polymer concentrations and also low IR-absorption coefficients[70]

The effect of different durations for medium temperatures 65 $^{\circ}$C was investigated and again sulfonic acids with varying intensities were observed at 1300 cm^{-1} as seen in the Appendix. It seems that the intensities of these peaks are increasing, a trend which is expected because the polymer's interaction with the sulfonation reagents increases and this result in more incorporation of the sulfonic group. [76]. However, again as much as this may be a desired outcome so as to increase the conductivity of the membranes the fact that there is extended interaction with the reagent results in P-O-H associated peaks.

More FTIR spectra for comparison of the different parameters such as room temperature sulfonation processes at different durations as seen in the figures in the Appendix; O=S=O groups were integrated and O-H broad bands was also visible.

4.2.2. NMR Results

In addition to FTIR the structural properties of the polymers was also investigated by the NMR. In agreement with the FTIR it was seen that sulfonic groups were incorporated into the structure for different sulfonation parameters. Indications of polymer degradation were also seen from some of the spectra from the disappearance of the aromatic groups completely from the ^{1}H-NMR spectra. The Spectra below show the outcome of the processes in more detail.

There are two different types of hydrogen in the Structure those from methyl group and those from benzene ring. The methyl group hydrogen have been assigned peaks at 1.82 ppm and those that come from the benzene ring to the 6.37-6.75 ppm broad peak. The splitting at this broad peak is also due to the influence of the magnetic field coming form the pyridine side group. The extra peak at 8 is also attributed from the hydrogen in the pyridine peak and as can be seen its intensity increases in the order P1>P2>P3 as the pyridinoxy side group increases. The Figure 24 below gives the ^{1}H-NMR for the pristine polymers.

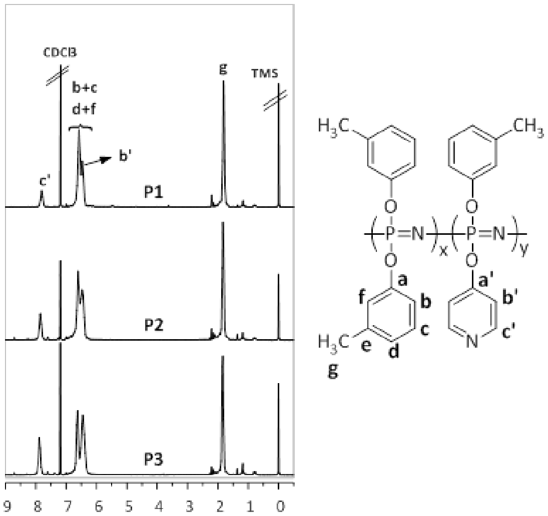


Figure 24: the ^{1}H-NMR spectra of pristine polymers

The ^{1}H-NMR was also used in order to check the success of the sulfonation process and to analyze the post process structure. The spectra for the process carried out at 65 ˚C was investigated and shown as follows in Figure 25:

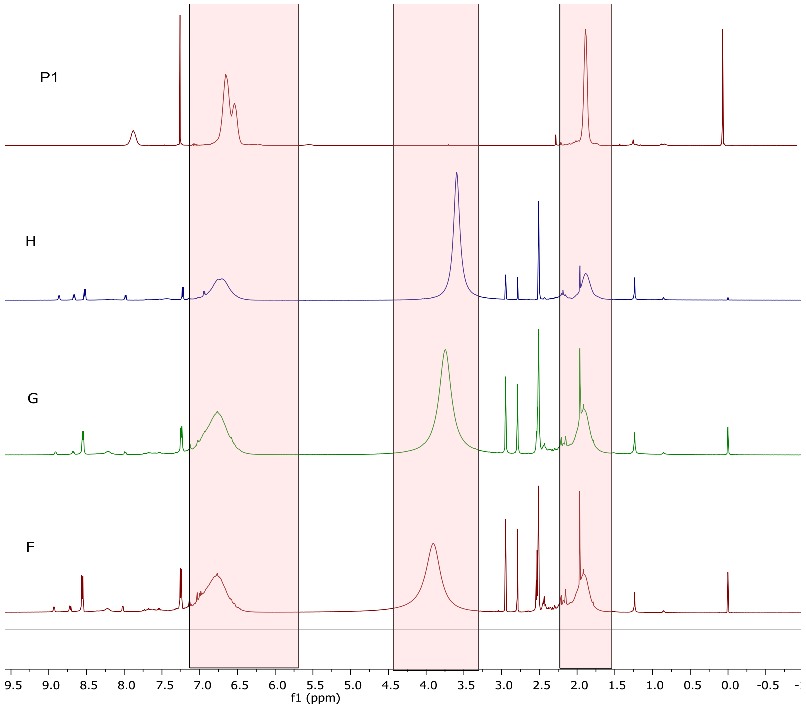


Figure 25: ^{1}H-NMR for membranes sulfonated at 65 ˚C. F: 15 min, G: 30 min, H: 45 min

When compared to the pristine polymer it can be seen that a new peak due to the incorporation of SO_3H occurs at 3.59 with a downfield shift as the degree of sulfonation decreases. Its intensity was seen to increase with the increase in sulfonation time an indication that the number of substitutions increase and its position was also seen to shift. The intensity of the protons on the benzene ring is also seen to decrease as the degree of sulfonation is increasing while the one associated with pyridine ring at 8 is seen to disappear. An explanation to the peaks that are responsible for pyridine shifting upfield could because of the co-ordination to nitrogen atom resulting in decrease in the electron density of the ring.

Sulfonation at room temperature spectra is as shown below in Figure 26 and it can be observed that the chemical shift assigned to SO_3H is at around 2.5 ppm.

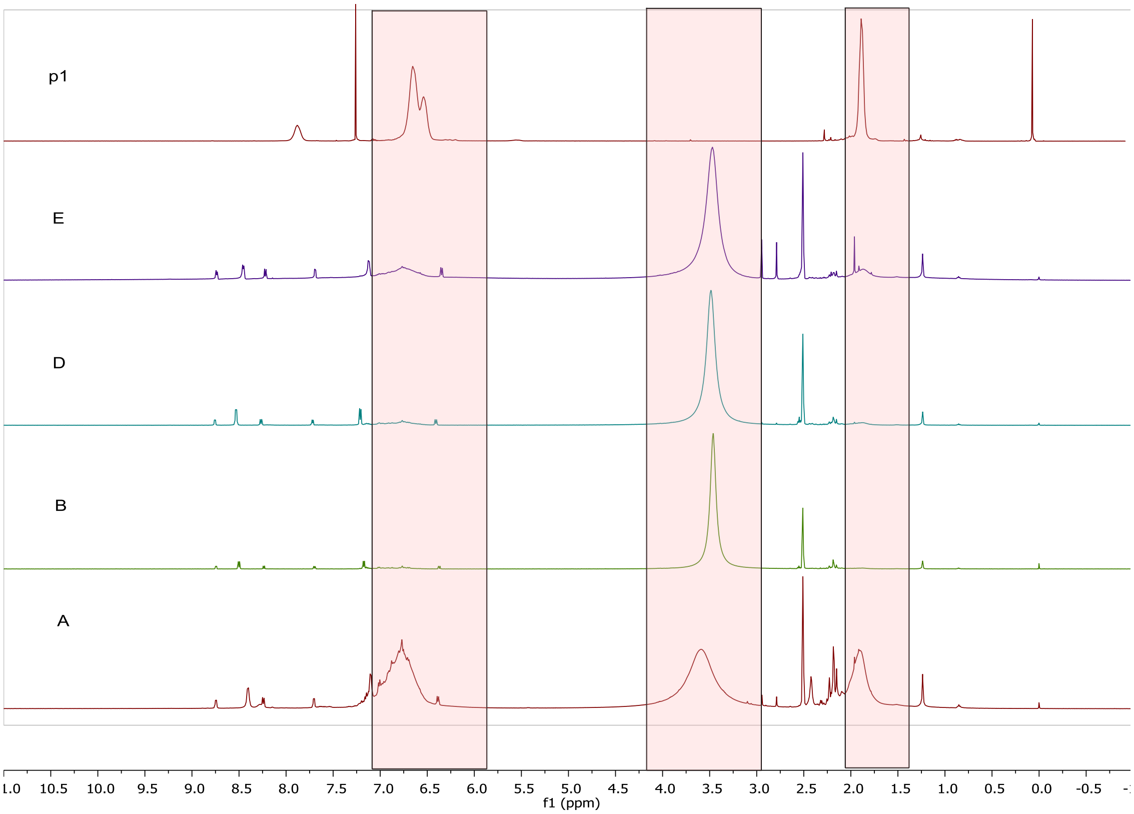


Figure 26: ^{1}H-NMR for membranes sulfonated at room temperature. A: 30 min, B: 45 min, D: 90 min, E: 120 min.

Steric hindrance due to the presence of the bulky methyl group on the benzene ring was also evident from the spectra. Again here we see the signal associated with pyridine ring at 8 ppm to disappear.

To check whether there was degradation in the sulfonated membranes in addition to the ^{1}H-NMR, ^{31}P-NMR was also used. The latter gives much clearer understanding since only the phosphorous element is considered. ^{31}P-NMR of membranes sulfonated using the step-wise method were carried out and the results are shown in the Figure 27 below:

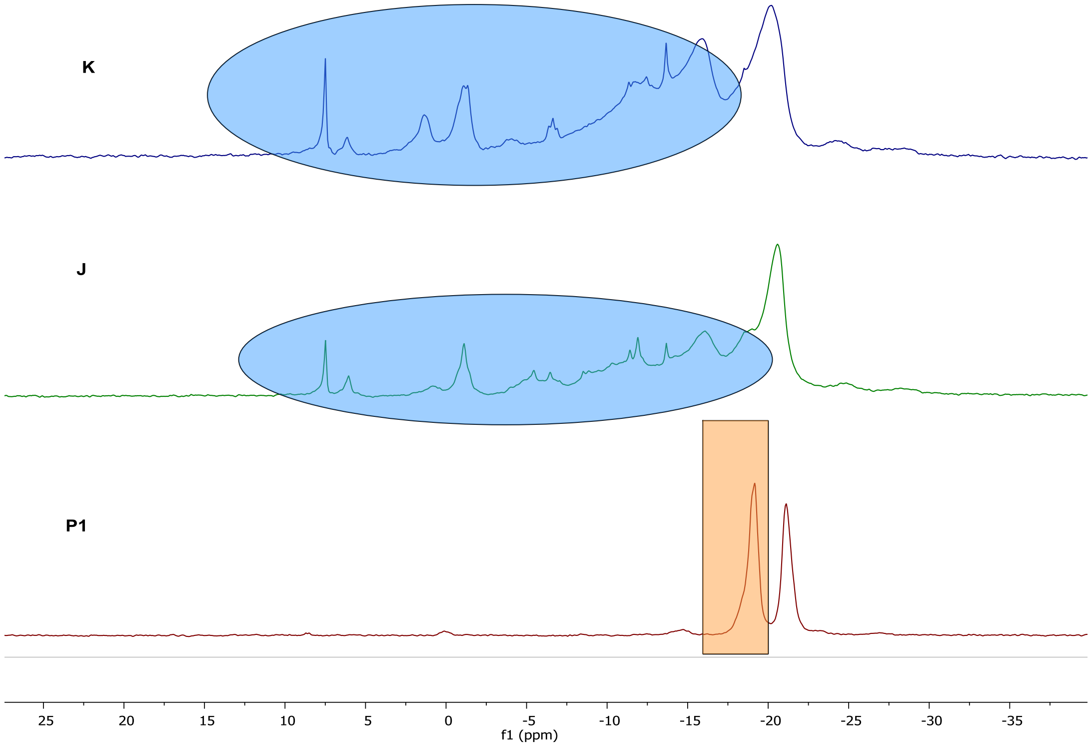


Figure 27: ^{31}P-NMR showing the backbone degradations for harsh sulfonation conditions. Sulfonation at 65 ˚C for J: 30+30 min, K: 60+60 min.

As observed that there was some degradation of the backbone for some of the harsh sulfonation conditions as seen from the decrease in the intensity assigned to the tolyloxy side group as was predicted from the Gleria model previously discussed. New peaks could also be seen to form upfield to around 10 ppm and these could be associated to the P-O-H-related products resulting from attack of the backbone by hydrolysis. The broadening of the initial peaks is an indication of the overall backbone degradation that is occurring in the membranes.

4.3. Thermal Properties

Heat which is usually a by-product of the fuel cell reaction may result in degradation of fuel cell components and this therefore necessitates that these components be able to withstand this heat without a decrease in their performance. Membranes are prone to thermal degradation due to the detachment of the sulfonic group or decomposition of its polymer backbone and also due to thermo-hydrolytic chain scissions. The membrane must have very good thermal stability in order to maintain its performance at high temperatures. The conductivity and other properties like water uptake usually depend highly on the thermal properties of the membrane as has been shown in the literature [25], [77]. In this section the thermal properties were investigated for both the pristine polymer and their sulfonated counterparts.

4.3.1. DSC Results

The reported DSC data were those of the final heating since the first heating was performed in order to erase the thermal history of the samples which would otherwise mislead during the analysis stage. Analysis was done for both the pristine and sulfonated polymers. It was observed from the Figure 28 below that as the heteroatom containing group increased from P1 to P2 to P3, the glass transition of the polymers increased from -16.31 °C to -11.29 °C to -8.51 °C respectively.

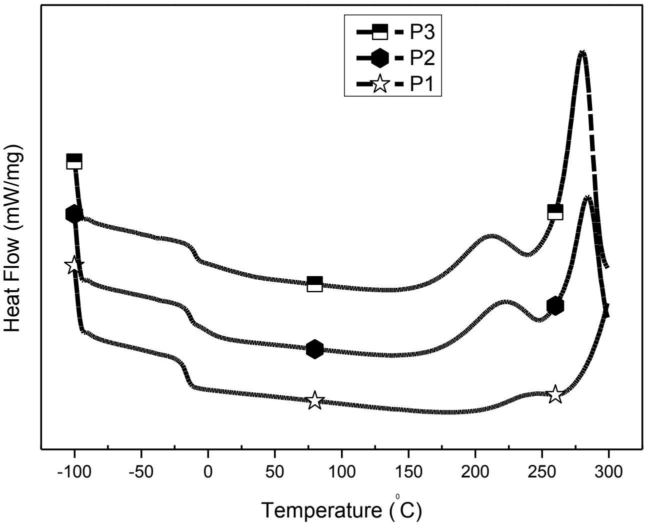


Figure 28: Illustration of the T_g of the pristine membranes

The effect of time and also different temperature application methods have been investigated in this study. As can be seen in the Figure 29 below the T_g of the polymer increased after the sulfonation process and the new T_g values are as summarized in the Table 8. The increase in the T_g values is as a result the restriction in the polymer chains of the product induced by the intermolecular interactions by hydrogen bonding which hinder rotations of polymers.

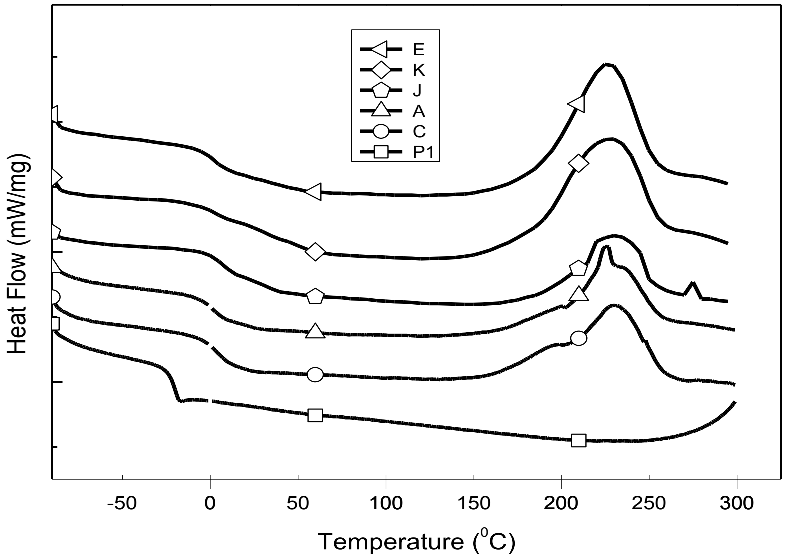


Figure 29: The DSC of Sulfonated membranes where P1: pristine polymer, A: 30 min_RT, C: 60 min_RT, E: 120 min_RT, J: 30+30 @ 65 ˚C, K: 60+60 @ 65 ˚C

The T_g of the sulfonated polymers was seen to increase with the duration as well as the time for the process as depicted in the Table 8 below. For elongated durations the polymer had a longer interaction with the reagent resulting in more incorporation of the sulfonic acid group which is responsible for causing an increase in the structural rigidity of the polymer. This is an anticipated characteristic because it is a clear indication of the improved mechanical property of the membranes a desired outcome.

Table 8: Values of the T_g values for the sulfonated polymers in comparison with the pristine polymer

Polymer	Glass Transition Temperature (˚C)
P1	-16.3
A	3.3
C	4.6
E	10.0
J	11.5
K	13.6

Also as was observed with the combined effect of longer time and higher temperatures it was observed that the increase in T_g was enormous compared to when only one of this parameter was adjusted. This effect observed at higher temperatures sulfonation is due to the effect of the increased reaction kinetics that temperature plays by decreasing the activation energy hence favoring the sulfonation process and resulting in increased T_g.

4.3.2. TGA Results

The Pristine polymers were seen to have very good thermal stability and experienced two-step decomposition. The backbone was seen to start decomposing at temperatures about 400 °C while a second stage was observed at around 100 °C and the second weight loss was credited to the decomposition of the pyridinoxy side group as shown in the Figure 30 below.

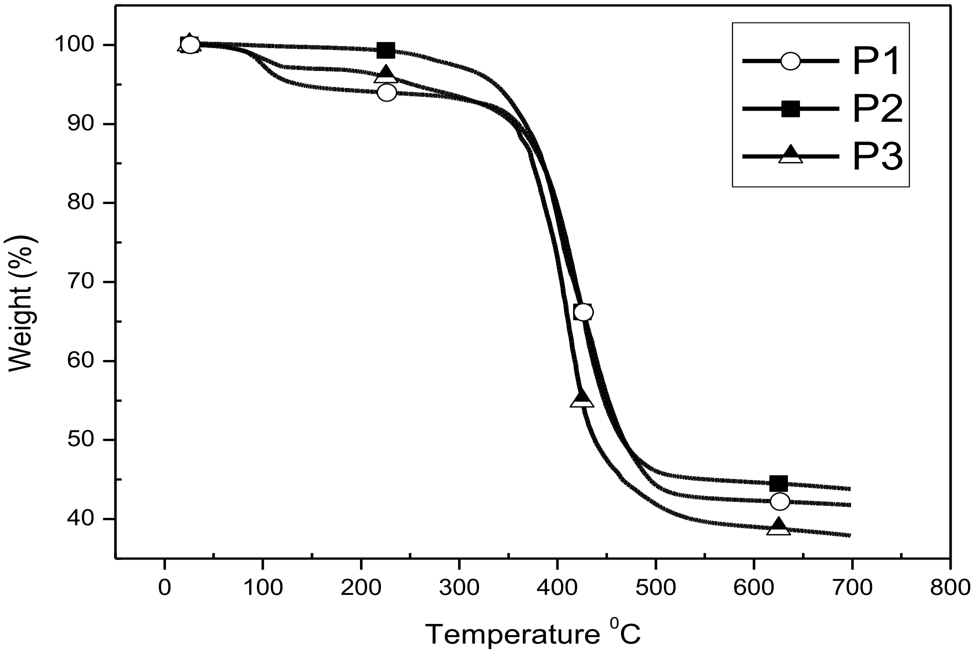


Figure 30: Illustration of the mass loss of pristine polymers

The exact values of the decompositions were tabulated as seen below:

Table 9 : Mass Losses of the pristine polymers

Polymer	1st Decomposition (%)	2nd Decomposition (%)	Residual Mass (%)
P1	4.58	44.34	41.77
P2	1.14	40.84	39.93
P3	1.88	21.35	34.12

The thermal stability changes occurring for sulfonated membranes was investigated and the following Figure 29 shows the behavior of the membranes sulfonated at 65 °C. With the integration of sulfonic acid group we expect an extra weight loss due to the its dissociation at temperatures starting from around 240 °C [78],[77]. The mass loss seems to increase as the sulfonation time increases from 15 min to 30 min as seen in the Figure 31 below; this is expected because sulfonation increases with increase in time. In this study it was difficult to distinguish between the mass loss associated with the evolution of water and that of the sulfonic acid groups possibly due to low degrees of sulfonation. The % mass losses have therefore been shown in the Table 9 below. It was observed that the residual masses values were close to those of the pristine polymer which is a good indication that sulfonation does not deteriorate the membrane properties.

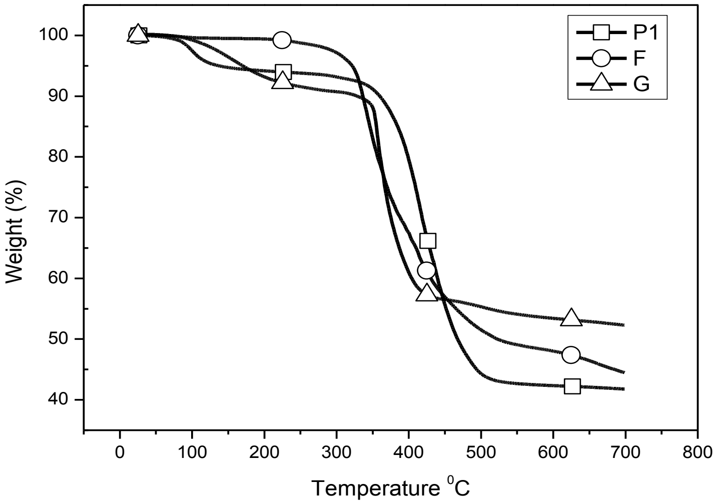


Figure 31: Sulfonation at 65 ˚C for different durations P1: pristine polymer, F: 15 min, G: 30 min

The results for room temperature sulfonation have also been shown in the Figure 30 below. If compared to the high temperature sulfonation we generally see a much less first stage mass loss which is according to our expectation. Similarly due to small mass losses the values have been reported in the Table 10 below.

Table 10: Mass loss for sulfonated membranes.

Sulfonated membrane	1st Mass Loss (%) (Sulfonic acid detachment)	2ndMass Loss (%) (Backbone degradation)	Residual Mass (%)
A	0.29	35.39	40.30
B	7.80	36.35	37.77
E	0.22	35.39	40.30
F	4.85	31.49	44.45
G	6.09	29.99	52.29

Also in this case the residual masses were close to those of the pristine polymer which is a good indication that sulfonation does not deteriorate the membrane properties. The polymer backbone degradation temperatures did not change much from the sulfonation process as observed in the Figure 32 above and this is a good property because membranes need to have good thermal stability. We can therefore conclude that the sulfonated membranes also had good thermal properties as their pristine ones.

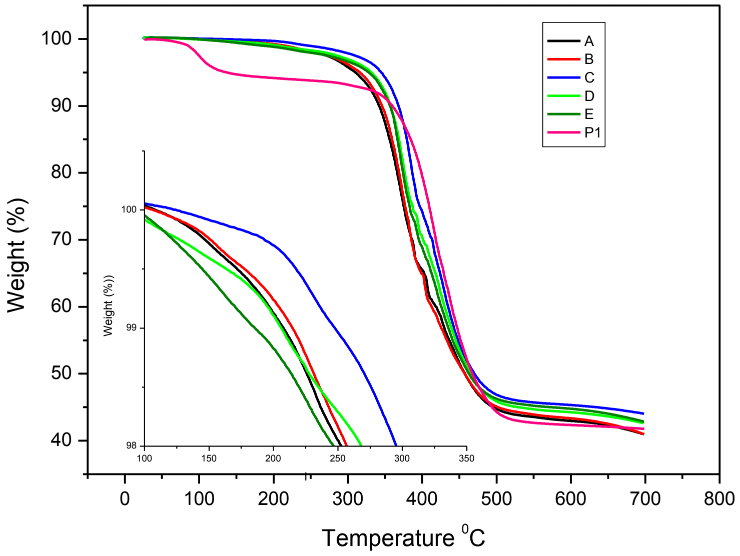


Figure 32: TGA analysis of membranes sulfonated at room temperature. P1: pristine polymer, A: 30 min, B: 45 min, C: 60 min, D: 90 min, E: 120 min

4.4. Mechanical Properties

The DMA which uses forced vibrations to study the viscoelastic response of a sample was used and from the resulting graphs the storage and loss modulus (E’ and E”) and damping coefficient (tan δ) of a material as a function of temperature and frequency were determined. The loss modulus E” represents the energy dissipated as heat for a material, while the storage modulus E’ represents the stored energy. The ratio E”/E’ represents the tan δ which is the ratio of energy lost per cycle to the maximum energy stored and therefore recovered per cycle. [79]

In the Figure 33 below it was observed that the storage modulus is decreasing and the drop in the modulus indicates that the polymer undergoes a transition from the glassy stage to the rubbery stage which is normally referred to as the α-transition or simply T_g. The temperature of the T_g can be exacted from the first peak of the tan δ curve from the Figure 33 below. It was observed that the membranes had decreasing E’ values as the duration of sulfonation increases and this is expected because the stiffness of the membranes decreases as process time decreases from E to B. Sulfonation process done at 65 ˚C for 15 min yielded very close values to the membrane prepared at 60 min at room temperature.

From the tan δ graph two peaks were seen, and while the first one indicated the T_g of the membranes the other peak could have been due to phase separation which occurred by spinodal decomposition during the solvent evaporation at the solution casting stage. The effect of this is seen to increase as the sulfonation conditions become harsher and this can be disadvantageous because it results in un-reproducible degree of sulfonation due to possible phase separation of polymer chains from the reaction mixture [80] [80][80] Therefore a compromise has to be stricken between the parameters optimized so as to obtain both mechanically stable and highly performing membranes.

The T_g values obtained from the DSC and DMA for example for membrane E (120 min_RT) was observed to be 7.2 ˚C and 9.9 ˚C respectively. This is according to expectation since this transition occurs over a wide range and is usually affected by the method of determination. For DMA measurements many parameters such as frequency affect the value of T_g.

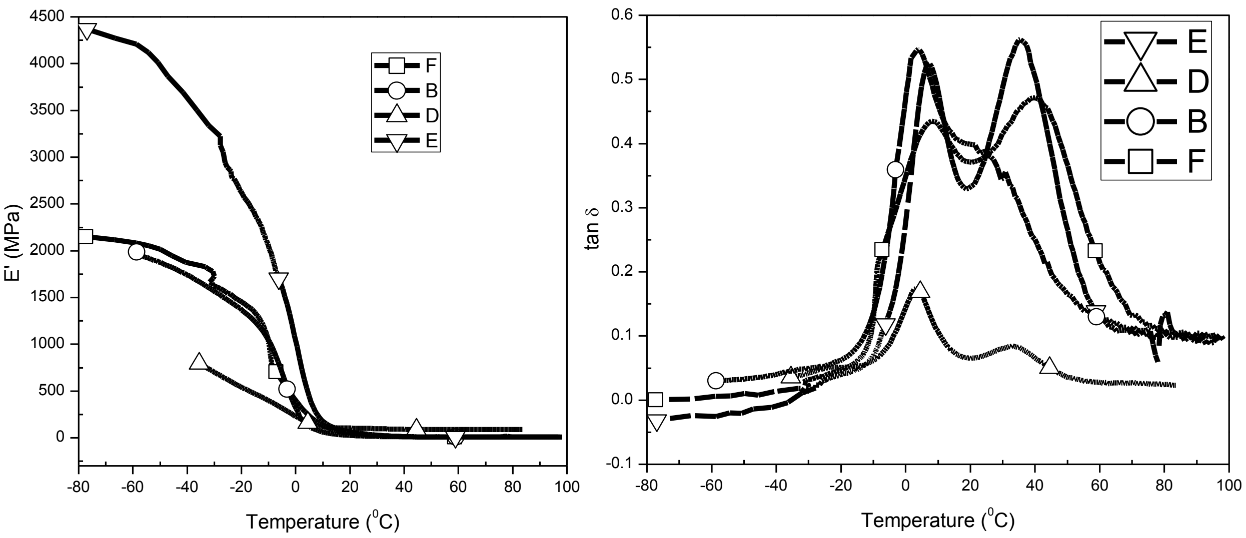


Figure 33: The dynamic mechanical analysis some membranes. Left graph shows the variation of storage modulus while the right graph shows the variation of tan δ with temperature. B: 45 min_RT, D: 90 min_RT, E: 120 min_RT, F: 15 min_65 ˚C.

4.5. Water uptake and IEC

Water content is important in a fuel cell environment as it aids the acidic groups to dissociate and therefore enables proton conductivity. As degree of sulfonation increases the hydrophilicity of the membranes is expected to increase and this may result in highly swollen membranes. For this reason, an optimum degree should be achieved so that the membranes contain just enough water uptake capacity to facilitate conductivity yet at the same time to maintain the mechanical stability during functioning. It is expected due to the nitrogen containing hetero-atomic structure that water uptake capacity will be high and for this reason we may expect excessive swelling of some membranes. Depending on the sulfonation procedures the membranes showed a wide range of water uptake values. Water uptake was seen to increase for both cases of temperatures, however for 65 ˚C sulfonation process the effect of both the temperature and time resulted in a rapid increase than that observed at room temperature. Figure 34 below showed that for longer times such as 45 min and higher temperature of 65 ˚C very high water uptakes were observed resulting in highly swollen membranes which were not suitable for this application. Room temperature sulfonation conditions also showed the same trend as shown in Figure 35 below.

IEC is also dependent on the sulfonation conditions because it directly conveys information about how much of the sulfonic groups have been introduced into the structure. The IEC values were obtained though back titration and the values compared to Nafion® which is the reference sample.

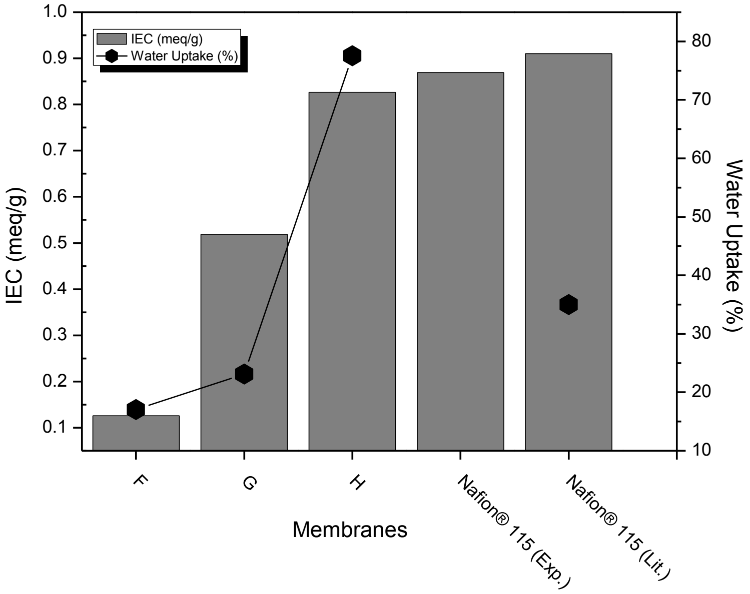


Figure 34: The water uptake and IEC for membranes sulfonated at 65 ˚C. F: 15 min, G: 30 min, H: 45 min.

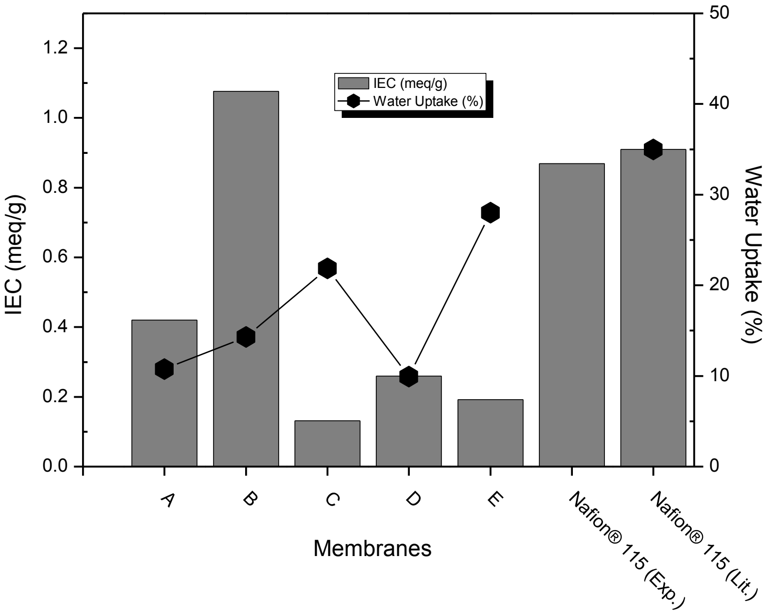


Figure 35: The water uptake and IEC for membranes sulfonated at room temperature. A: 30 min, B: 45 min, D: 90 min, E: 120 min.

According to the literature, the reported IEC value of Nafion® is 0.91 mmol/g; in our results as tabulated below in Table 11 we were able to obtain values close to that of the literature and the values obtained from the rest of the membranes were also tabulated. From the IEC values the degree of sulfonation which shows the number of sulfonic acid integrated into the membrane was calculated from the equations shown previously. It was observed that as the duration for the different temperature increased there was an increasing trend in the degree of sulfonation which is an expected result. More time means more interaction of sample with the reagents however after a certain threshold there was a drop in these values due to deteriorating of membrane property.

Table 11: IEC and water uptake values for the membranes for membranes sulfonated at room temperature for different durations (A: 30 min, B: 45 min, C: 60 min, D: 90 min, E: 120 min) and at 65 ˚C (F: 15 min, G: 30 min, H: 45 min)

Membranes	IEC (meq/g)	DS (eq/kg)	Water Uptake (%)
A	0.42	0.11	10.8
B	1.08	0.30	14.3
C	0.13	0.03	21.9
D	0.26	0.07	9.9
E	0.19	0.05	28.0
F	0.13	0.03	17.0
G	0.52	0.14	23.1
H	0.83	0.23	77.6
Nafion® 115 (Exp.)	0.87	-	
Nafion® 115 (Lit.)	0.91	-	

As reported in the literature polymer swelling behavior is directly related to IEC of the membranes [71] an increasing trend of the IEC and water uptake was observed however some conditions did not agree well with this expectation. A reason to this could be that during these measurements it is assumed that the measured portion of the sample is a representative of the whole sample yet it can be due to non-uniform distribution of the sulfonic acid groups on the membrane that caused such variations between these data.

4.6. Proton Conductivity

The proton conductivity is the ability of the membrane to conduct protons and is the most important characterization for fuel cell. The *ex situ* conductivity gives a rough idea of the performance of the membrane. It is desirable for fuel cell membranes to have as high conductivity as possible but this usually comes with the deteriorating of other membrane properties like water uptake and mechanical properties therefore a balance needs to be achieved between all these properties. The Figure 36 shows the conductivity for some of the fabricated membranes and was compared to the reference sample which was Nafion®.

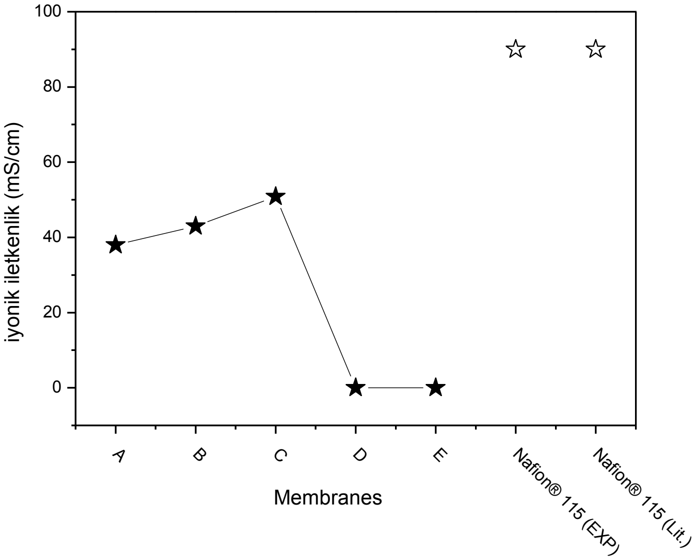


Figure 36: The conductivity of room temperature sulfonated membranes in comparison to Nafion® 115. A: 30 min, B: 45 min, D: 90 min, E: 120 min.

The variation of conductivity with time was seen to increase however longer sulfonation durations resulted in a drop in the conductivity. As the duration increased the number of sulfonic acid group which are responsible for the proton conduction increase hence the upward trend. For longer durations, factors like polymer degradation and increased water uptake values which result in loss of mechanical stability begin to set in and despite the high levels of sulfonic acid sites available, conductivity deteriorates. The obtained conductivity values for shorter time durations were compared to those of Nafion® 115.

There was an increase in conductivity as the duration for the process increased however for much longer times the conductivity suddenly dropped as can be seen in the Figure 36 above. The reason for this could be the fact that the conductivity measurements were taken for long durations to attain stability from the very high fluctuations at the beginning, which resulted in the membranes losing their dimension stability as can be observed from Figure

37 below. This could be the main contributing factor the sudden drop of the conductivity in the figure given above as the durations for sulfonation increased.

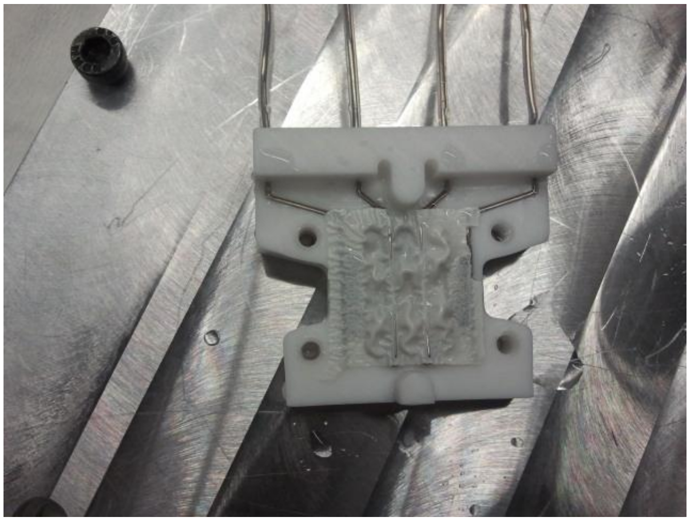


Figure 37: Resulting membrane after conductivity measurement of membranes with high water uptake.

5. CONCLUSION & FUTURE WORK

The main objective of this study was to investigate the capability of the proposed novel polyphosphazenes to act as fuel cell membranes. The synthesized polymers were functionalized though sulfonation using different reagents and some were ruled out due to their unsuitability. Two of the polymers (P2 and P3) did not pass the sulfonation test and therefore the rest of the study was focused on the polymer with the lowest pyridine containing side group. It can be concluded from here that the increase in this pyridine amount in the phosphazene resulted in hydrolytically unstable membranes in these highly acidic conditions which underwent dissolution during the fabrication steps. P1 showed promising results because free standing sulfonated membranes were attained after the functionalization process. The sulfonated membranes were then characterized by means of FTIR and NMR in order to check the incorporation of the sulfonic groups. Thermal analysis was also carried out and they revealed that the obtained membranes did not lose their thermal stability after sulfonation when compared to the pristine polymers and this was a desired characteristic. The mechanical properties of the tested membranes showed that phase separation occurred which is an unwanted thing due to the deterioration it causes to functionality of membranes.

The objectives and findings arrived at in this work have been summarized as below:

- Effect of heteroatom-containing side chain – increased levels of heteroatom side group resulted in hydrolytically unstable membranes.
- Effect of temperature and time durations were seen to be important since they directly controlled the hydrophillicity of the products formed.
- From the NMR anf FTIR we were able to deduce that polymer degradation occured for longer durations and higher temperature processes
- Effect of reagent-This was observed after trying both chlorosulfonic acid and sulfuric acid and the former was seento be harsh for the polymers in this study since it resulted in polymer degradation and chain cleavage due to unwanted side reactions.
- DSC measurements showed increased T_g values, thus we can conclude that membranes had improved mechanical properties which is a desired property

- An increasing trend was observed in the IEC, water uptake and conductivity measurements, an expected outcome due to the increase in the sulfonic acid group incorporated in the membrane. Further increase resulted in deteriorating properties due to membrane degradation and loss of mechanical stability.
- Membranes fabricated in this work had comparable fuel cell characteristics to those of other membranes in the literature and also to Nafion®
- As a final conclusion P1 was seen to yield promising results and sulfonation process carried out at low and average temperatures for short durations resulted in good overall results.

Future Works

After the *ex situ* characterizations the next step was to carry out *in situ* characterizations in order to check the performance of the membranes in an actual fuel cell environment. However due to starting material and hardware constraints such measurements could not be carried out at the Sabanci University and will be carried forward as part of the future work. The fuel cell equipment available as seen in the Appendix 1 as A.4 requires a membrane an active area of 25 cm^2 and since less material was available there will be need to design a much smaller measurement set up appropriate for our type of membrane.

The polyphosphazenes with higher heteroatom containing pyridinoxy- side chain on the main chain apparently didn’t work as PEMs. The heteroatom effect thus could not be systematically investigated due to this drawback. Therefore, a new polyphosphazene architecture again containing heteroatom that will resist to these aggressive sulfonation conditions could be designed and investigated for this purpose.

Another preposition regarding improvement of the polymers (P1 and P2) that did not give good results could be crosslinking or blending so as to form composite membranes which could improve their processability.

APPENDIX

ADDITIONAL FTIR DATA FOR SULFONATED MEMBRANES

Figure A.1 and A.2 show the FTIR graphs for additional parameters that were tried. All showed the presence of sulfonic acid groups at 1300 cm^{-1} as was shown in the other conditions discussed previously.

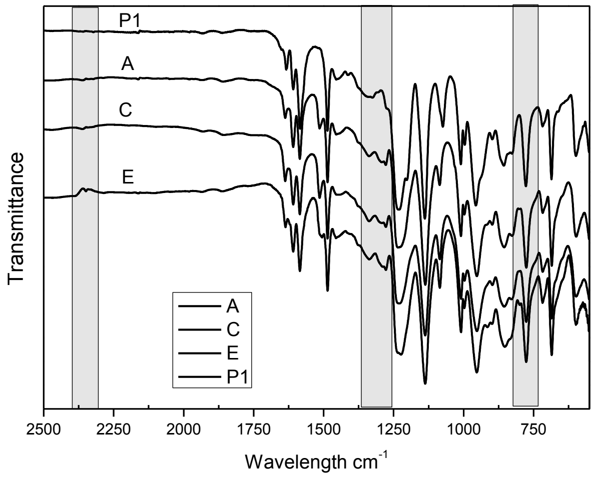


Figure A. 1: Room temperature sulfonation for different durations A: 30 min, C: 60 min, E: 120 min.

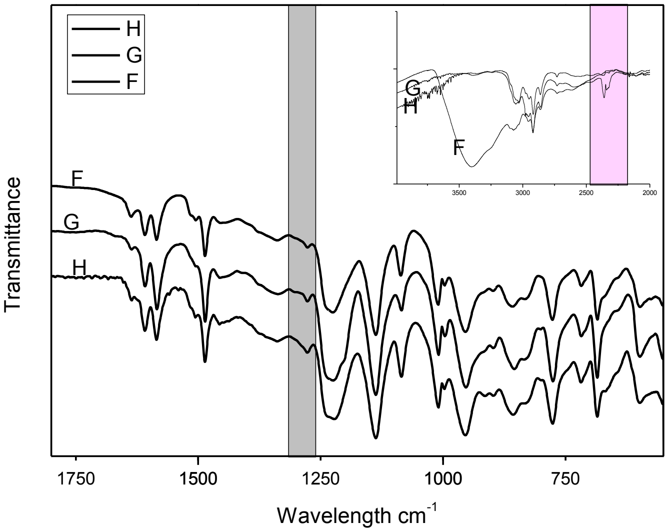


Figure A. 2: Sulfonation for different durations at 65 ˚C. F: 15 min, G: 30 min, H: 45 min

FOUR PROBE CONDUCTIVITY MEASUREMENT COMPONENTS

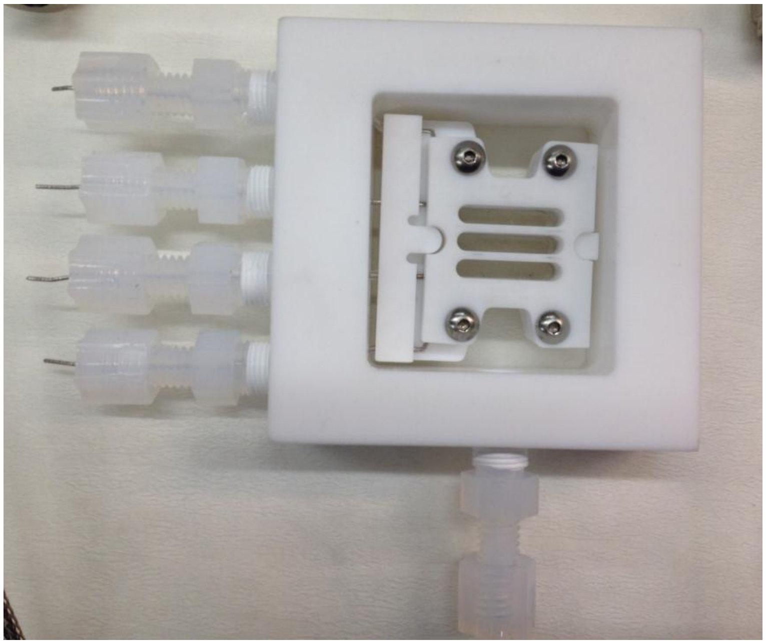
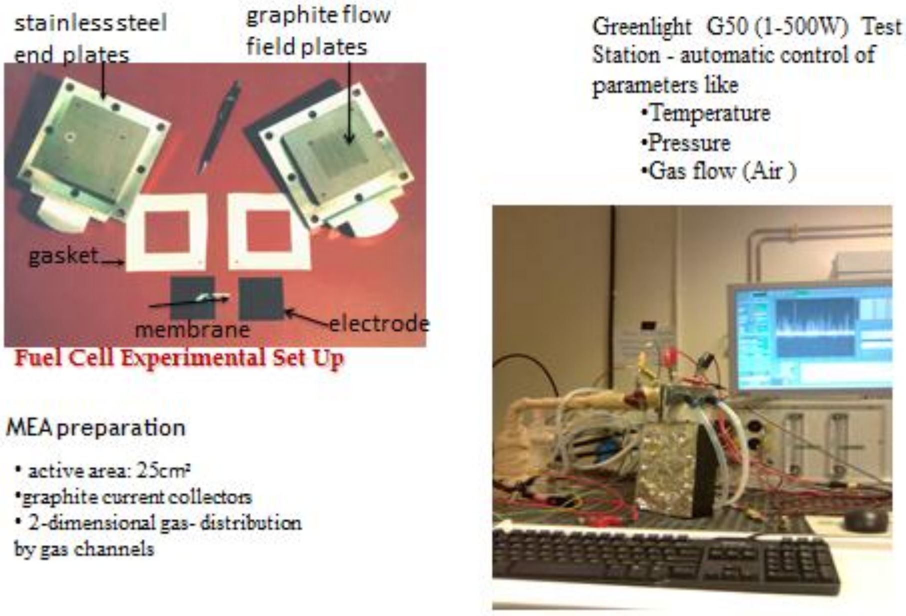


Figure A. 3: The single BekkTech® cell for four point probe conductivity



Fuel Cell Experimental Set Up

MEA preparation

- active area: 25cm²
- graphite current collectors
- 2-dimensional gas- distribution by gas channels

Greenlight G50 (1-500W) Test Station - automatic control of parameters like

- Temperature
- Pressure
- Gas flow (Air)

Figure A. 4: The Fuel cell set up available at Sabanci University

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