DEVELOPMENT OF sPEEK / TiSiO_4 and sPEEK / SULFONATED TiSiO_4 NANOCOMPOSITE MEMBRANES FOR APPLICATION IN DIRECT METHANOL FUEL CELLS

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Tanya Fadzai CHIKUMBA

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MASTERS THESIS
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This thesis titled **"Development of sPEEK/ TiSiO_4 and sPEEK/ sulfonated TiSiO_4 nanocomposite membranes for applications in Direct Methanol Fuel Cells"** has been prepared and submitted by **Tanya Fadzai CHIKUMBA** in partial fulfillment of the requirements in "Anadolu University Directive on Graduate Education and Examination" for the Degree of Master of Science (M.Sc.) in Energy Resources and Management in Advanced Technologies Department has been examined and approved on 26/08/2019**.**

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ÖZET

DOĞRU METANOL YAKIT HÜCRELERİNDE UYGULAMALAR İÇİN SPEEK/ $TiSiO_4$ ve SPEEK/ SÜLFONLANMIŞ- $TiSiO_4$ NANOKOMPOSİT MEMBRANLARIN GELİŞTİRİLMESİ

Tanya Fadzai CHIKUMBA

İleri Teknolojileri Anabilim Dalı

Anadolu Üniversitesi, Fen Bilimleri Enstitüsü, Ağustos 2019

Danışman: Prof. Dr. Süleyman KAYTAKOĞLU

Şu an itibariyle, birçok araştırmacı dikkatlerini daha düşük maliyetli PEEK'e, bir alternatif olarak ortaya çıkan bir polimer olarak odakladılar. Bu çalışma, yüksek su alımı, proton iletkenliği ve iyi DMFC performanslarına sahip sPEEK / $TiSiO_4$ ve sPEEK/ sülfonlanmış $TiSiO_4$ nanokompozit membranları geliştirmeyi ve üretmeyi amaçlanmaktadır. Baz polimer olarak PEEK, poli (eter eter keton) seçildi ve %53 dereceli bir sülfonasyon ile sPEEK polimeri oluşturmak için 35°C'de 18 saat süreyle sülfonasyon sonrası tekniği ile aktive edilmektedir. Bir FTIR ve XRD analizleri, PEEK'in sülfonatını ve yeni polimerin armofor doğasını doğruladı. Ayrıca FTIR'den saf ve modifiye edilmiş $TiSiO_4$ dolgu maddelerinde titanya ve silis oksitlerin bazı etkileşimlerini de ortaya çıkardı. %53 DS değerine sahip saf sPEEK, tüm sıcaklık aralığında en düşük proton iletkenlik değerlerini göstermiştir. x2 ve y3 membranları su alımında ve 80ºC'deki iletkenlikte önemli artışlar göstermiştir. 80°C'de, y3, 49.14mW/ $cm^{2'}$ lik bir zirve güç yoğunluğuna ulaşırken, x2 membranı, 29.21mW/ $cm^{2'}$ ye ulaştı. Bu sonuçlar, DMFC' nin modifiye edilmiş membranlarla performansında bir gelişme olduğunu ortaya koymaktadır.

Anahtar Sözcükler: Doğru metanol yakıt hücresi, Nanokompozit membranlar, İnorganik oksit, Sülfonasyon derecesi, Proton iletkenliği

ABSTRACT

DEVELOPMENT OF sPEEK / TiSiO_4 and sPEEK / SULFONATED TiSiO_4 NANOCOMPOSITE MEMBRANES FOR APPLICATIONS IN DIRECT METHANOL FUEL CELLS

Tanya Fadzai CHIKUMBA

Department of Advanced Technologies

Anadolu University, Graduate School of Sciences, August 2019

Supervisor: Prof. Dr. Süleyman KAYTAKOĞLU

As of now, many researchers have focused their attention on the less expensive PEEK, a polymer that is emerging as a promising alternative with low cost. This current work aims at developing and fabricating sPEEK/ TiSiO_4 and sPEEK/ sulfonated-TiSiO_4 nanocomposite membranes with high water uptake, proton conductivity and good DMFC performances at a much lower cost as compared to the Nafion membranes. PEEK, poly (ether ether ketone) was chosen as the base polymer and it was activated by the post sulfonation technique for 18h at 35ºC to form sPEEK polymer with a 53% degree of sulfonation. An FTIR and XRD analyses confirmed the sulfonation of PEEK and the armophous nature of the new polymer. Furthermore the FTIR also revealed some interaction of the titania and silica oxides in the pure and modified TiSiO_4 fillers. The pure sPEEK with a 53% DS exhibited the lowest proton conductivity values over the entire temperature range. The x2 and y3 membranes showed significant increases in water uptake and conductivity at 80 ºC. At 80 ºC, the y3 attained a peak power density of 49.14mW/cm^2 whereas the x2 membrane attained 29.21mW/cm^2. These results reveal an enhancement in the performance of the DMFC with the modified membranes.

Keywords: DMFCs, Nanocomposite membranes, Inorganic oxide, Degree of sulfonation, Proton conductivity

…/…/2019

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and this study has been scanned for plagiarism with "scientific plagiarism detection program" used by Anadolu University, and that "it does not have any plagiarism" whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all ethical and legal consequences that are involved.

Tanya Fadzai CHIKUMBA

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TABLE OF CONTENTS

TABLE OF TABLES

Page

TABLE OF FIGURES

NOMENCLATURE

AFC:	Alkaline Fuel Cell
ATR:	Attenuated Total Reflection
BL:	Backing Layer
CL:	Catalyst Layer
DCFC:	Direct Carbon Fuel Cell
DLFC:	Direct Liquid Fuel Cell
DMFC:	Direct Methanol Fuel Cell
DS:	Degree of Sulfonation
DMF:	Dimethyl Formamide
DMSO:	Dimethyl Sulfoxide
DTG:	Derivative Thermogravimetry
EIS:	Electrochemical Impedance Spectroscopy
EELS:	Electron Energy- Loss Spectroscopy
FTIR:	Fourier Transform Infrared
GDL:	Gas Diffusion Layer
H NMR:	Proton Nuclear Magnetic Resonance
IEC:	Ion Exchange Capacity
IPA:	Isopropyl Alcohol
MCFC:	Molten Carbonate Fuel Cell
MEA:	Membrane Electrode Assembly
MeOH:	Methanol
MFC:	Microbial Fuel Cell
MPL:	Macroporous Layer
NMP:	N- Methyl- 2- Pyrrolidone
NPs:	Nanoparticles
PAFC:	Phosphoric Acid Fuel Cell

PEM:	Proton Exchange Membrane
PEMFC:	Proton Exchange Membrane Fuel Cell or (Polymer Electrolyte Membrane) Fuel Cell
PTFE:	Polytetrafluoroethylene
s- $TiSiO_4$:	Sulfonated Titanium Silicate
TEM:	Transmission Electron Microscope
σ :	Proton Conductivity
α :	Slope of Methanol permeation
P :	Methanol Permeability

1. INTRODUCTION

There is a constant increase in the demand for energy and its resources due to the rapid growth of population and urbanisation. The currently available energy sources are insufficient to meet the ever growing needs. Most of our energy needs are fulfilled by the conventional energy resources such as coal, petroleum and natural gas. However these resources are depleting with time as predicted by a report by (BP, 2016), the number of years of global coal, oil, and natural gas left given as the reserves to product (R/P) ratio left relating to known reserves and annual production levels in 2015 were 114, 52.8 and 50.7 years respectively. There are many downsides related to the use of fossil fuels such as land degradation, global warming, water pollution and acid rain formation. According to a report (Agency, 2017) based on global pollutants from 2010, the 25% share of global greenhouse gas emissions was as a result of electricity generation and heat production. Combusting of fossil fuels is the biggest source of the worldwide greenhouse emissions. Thus finding cleaner alternatives to replace fossil fuel powered systems would ensure sustainable energy security for the future generations.

The PEM solid electrolyte used in the DMFC is often viewed as the heart of the fuel cell defining the additional component's properties (Zaidi, 2003). Fuel cells work best at elevated temperatures to produce high energy values. There however is a limitation to the choice of polymer materials with ability to withstand these high operational conditions and this has led researchers over the past few years to focus their work on PEEK, a polymer working at intermediate temperatures (Mossayebi, Parnian and Rowshanzamir, 2018). PEEK is a hydrocarbon polymer material that is functionalised by electrophilic substitution through reacting it with sulfonating agents such as concentrated sulfuric acid to produce sPEEK, sulfonated poly (ether ether ketone). PEEK polymer possesses good mechanical strength, high chemical stability and low cost. It is meant to be a noble replacement for Nafion® only after some adequate modification. Pure sPEEK's mechanical and electrochemical properties depend on the degree of sulfonation attained after functionalisation. A highly sulfonated sample has an unfavourable effect of a weakened polymer backbone whilst a lowly sulfonated one exhibits very poor proton conductivity. Despite its ability to withstand high temperatures, this polymer shows inferior ionic conduction ability at elevated temperature conditions due to water loss. Titania and silica are hygroscopic inorganic oxides which when incorporated within the sPEEK's polymer matrix help improve it's

water uptake characteristics. Including small amounts of such oxide materials would enhance the proton transportation properties since they improve the water retention ability of a membrane at high temperature. At high temperatures, the vehicular mechanism which uses water as a vehicle is dorminant in transporting protons in a fuel cell so the oxides would be highly beneficial.

1.1. Fuel Cells

One of the most promising energy sources regarded nowadays are the fuel cells due to their clean operational nature, high energy efficiency values and versatility. Electrocatalytic processes occuring in a fuel cell cause a direct transformation of chemical energy of the fuel to electricity (Ikram et al., 2017). When current flows, theres a potential deviation from the equilibrium position which relates to the cell's electrical work. Fuel cells were first discovered independently in 1839 by Sir William Robert Grove and Christian Friedrich Schöbein. Sir William Grove built the first fuel cell termed the 'Gaseous voltaic battery'.

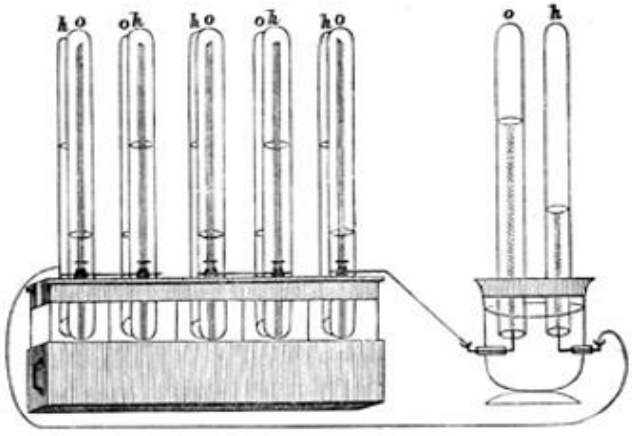

Figure 0.1. *Gaseous Voltaic battery (Institution, 2004)*

No information was recorded on fuel cells for close to a century then in 1937 Francis T. Bacon began his work on this field which led to the development of a 5kW power cell in the 1950's known as the 'Bacon fuel cell' (Carrette, Friedrich and Stimming, 2000). The first known practical application of fuel cells was in the US space program. In the 1960's, the first PEMFC unit was developed as a result of collaboration of NASA with industrial partners. This led to the development of the

Grubb-Niedrach fuel cell which was used in the Gemini space program (Zaidi and Matsuura, 2008). The Apollo space missions then followed in which the fuel cell provided electrical power and drinking water for the astronauts. Before the 1990's fuel cells only found their use in space programs then after that they were used for small stationary applications. Ballard, a Canadian company in 1989 built the first PEMFC powered submarine. In 1993, it further developed fuel cell powered buses and Perry energy systems produced the first passenger car running on fuel cell power. Up until today, the portable fuel cells have seen rapid growth rates. Fuel cells are currently powering portable devices like laptops and mobile telephones and they continue to be an active research field with many studies focusing on harnessing the fuel to run the system from cleaner renewable energy sources like solar and biomass.

1.1.1. Fuel cell classification

Fuel cells are classified according to the electrolyte they use with the exception of a DMFC in which methanol is directly electrochemically oxidised in the fuel cell (Carrette, Friedrich and Stimming, 2000). They can also be classified based on their operating temperature (Ikram et al., 2017). The electrolyte is a determining factor to the kind of the chemical reactions that will take place within the cell, the catalyst type to be used, the operating temperature range of the cell and the fuel needs.

Based on the electrolyte the most commonly used fuel cells are classified as;

1. Polymer electrolyte or proton exchange membrane fuel cells (PEMFC)
2. Alkaline fuel cells (AFC)
3. Phosphoric acid fuel cells (PAFC)
4. Molten carbonate fuel cells (MCFC)
5. Solid oxide fuel cells (SOFC)
6. Direct carbon fuel cells (DCFC)

1.2. PEMFCs

In PEMFCs, the power-generating system consists of an electrochemical reaction with fuel feeds such as hydrogen, methanol or ethanol and an oxidant. The PEMFC is classified according to the fuel applied to run the system. They can be categorised as the direct hydrogen- fueled (H_2 – PEMFC) or direct liquid fuel cell (DLFC). The direct liquid fuel cell can be powered by ethylene glycol, ethanol, methanol or formic acid.

They are low temperature fuel cells, operating at a temperature range of 85 −105°C (Carrette, Friedrich and Stimming, 2000). They can deliver a power density of 350 mW/m^2. Their first use was in space powering space ships as well as a source for the astronaut's clean drinking water. The Gemini program employed a 1 kW fuel cell stack as an auxiliary power source. The PEMFC is susceptible to CO contamination thereby reducing the cell performance and also damaging the cell's catalytic materials. PEMFCs are fed with hydrogen and an oxidant (ambient air) and these gases must be humidified before being fed into the system. The humidification needs of a membrane dictates the upper limit of temperature in which it can operate. The DLFCs have various favourable characteristics over the H_2 – PEMFC of high theoretical energy density, simple energy storage and transportation as well as no need of a fuel reformer or humidifiers (Samimi and Rahimpour, 2018). Compared to the other fuel cell types, the PEMFC cells possess very high power density values with quick start- stop operational abilities.

1.3. Direct Methanol Fuel Cells

This is a low temperature fuel cell type that is based on PEM technology operating at a temperature range from 30– 80°C (Ikram et al., 2017). They were developed to try to tackle issues related to fuel reforming and storage associated with hydrogen (Goor, Menkin and Peled, 2019). It's invention and development was in the 1990s by United States researchers together with NASA and Jet Propulsion laboratory. They can be classified as active, semi- passive or passive according to the manner of supply of the fuel and oxidant. In active systems, methanol solutions and oxidant are fed by means of pumps, sensors, heaters and humidity components. By using such devices, the fuel and oxidant feed supply rates can be accurately controlled. On the other hand passive systems utilise no additional equipment, using only natural flow to circulate the fuel. Methanol is a desirable fuel cell feed as it can be easily obtained from renewable biomass resources, it has a high specific energy density, is a liquid at operating temperatures and the already existing infrastructure for petrol may be easily transformed for its transportation. Similar to the PEMFC, it also uses a polymer membrane as electrolyte which needs optimisation for methanol blocking.

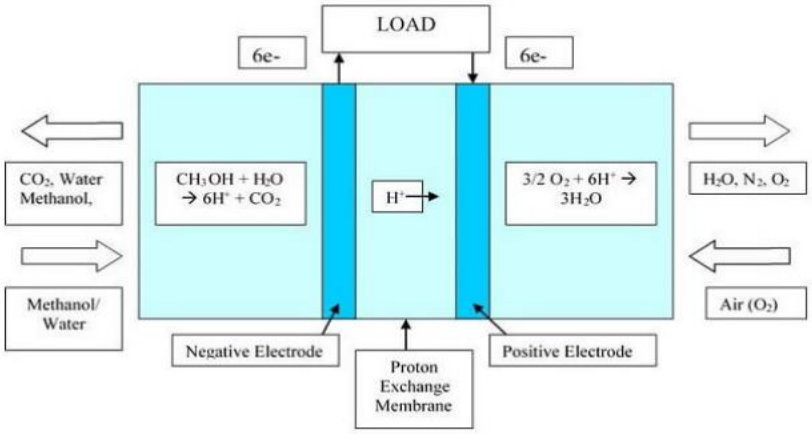

Figure 0.2. *DMFC Schematic (https://www.fuelcellstore.com/blog-section/direct-methanol-fuel-cell-improvements)*

The reactions taking place at the respective electrodes; (Samimi and Rahimpour, 2018)

Anode reaction:

$$CH_3OH + H_2O \rightarrow CO_{2(g)} + 6H^+ + 6e^- \qquad (1.1)$$

Cathode reaction:

$$\frac{3}{2}O_{2(g)} + 6e^- + 6H^+ \rightarrow 3H_2O \qquad (1.2)$$

Overall reaction:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_{2(g)} + 2H_2O \qquad (1.3)$$

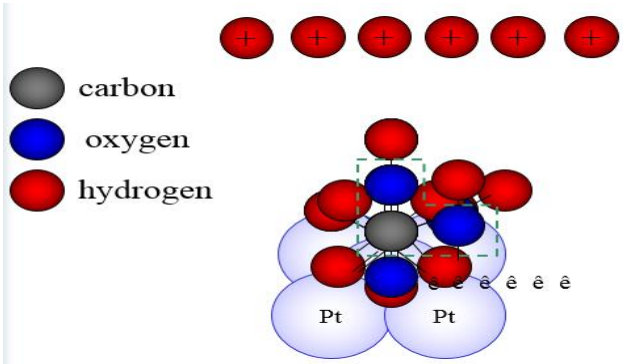

Figure 0.3. *Mechanism of methanol oxidation*

1.4. Comparison of Different Fuel Cell Types

Below is a summary of the characteristics of the various fuel cell types mentioned above.

Table 0.1. *Summary of Fuel Cells (Energy, 2016)*

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)	Perfluoro sulfonic acid	50-100°C 122-212° typically 80°C	< 1kW–100kW	60% transpor-tation 35% stationary	• Backup power • Portable power • Distributed generation • Transporation • Specialty vehicles	• Solid electrolyte re-duces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 194-212°F	10–100 kW	60%	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components	• Sensitive to CO_2 in fuel and air • Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 302-392°F	400 kW 100 kW module	40%	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start up time • Low current and power
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/ or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW-3 MW 300 kW module	45-50%	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature cor-rosion and breakdown of cell components • Long start up time • Low power density
Solid Oxide (SOFC)	Yttria stabi-lized zirconia	700-1000°C 1202-1832°F	1 kW–2 MW	60%	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle	• High temperature cor-rosion and breakdown of cell components • High temperature opera-tion requires long start up time and limits

1.5. Problem Statement

sPEEK, exhibits Nafion® like behaviour of intensely hydrophobic backbone and intensely hydrophylic functional groups nanoseparating when exposed to humidified conditions. The sPEEK polymer's properties depend on it's degree of functionalisation, under sulfonating the polymer results in inferior proton conductivities inappropriate for fuel cell applications whilst over sulfonated samples possess poor mechanical strength. However the pure sPEEK has low water uptake and cant exhibit good performance to transport protons effectively.

1.6. Aim

This study serves to investigate the performance of sPEEK/ TiSiO_4 and sPEEK/ s-TiSiO_4 nanocomposite membranes in DMFC as an alternative PEM.

1.7. Objectives

1. To sulfonate PEEK to between 52- 55 % D.S
2. To prepare pure sPEEK, sPEEK/ TiSiO_4 and sPEEK/ s- TiSiO_4 nanocomposite membranes

3. To examine the characteristics of pure sPEEK, sPEEK/ TiSiO_4 and sPEEK/ s-TiSiO_4 nanocomposite membranes related to their performance in DMFCs

4. To test the pure sPEEK and its nanocomposite membranes in a single direct methanol fuel cell

1.8. Justification

Fuel cell systems are a favourable alternative to fossil fuels due to their quiet operation and zero atmospheric pollution. The DMFCs run on methanol liquid fuel produced from fermentation of organic plant residue thus it is seen as a renewable energy resource. As compared to conventional power plants running on coal or petroleum and internal combustion engines, the fuel cell systems can yield a higher efficiency (Dohle et al., 2002). The generation of electrical energy from fuel cell systems only involves a single- step process in which the chemical energy in the fuel is directly converted to electricity. On the other hand, the conventional power generators have quite a number of steps with some energy loss at each conversion stage. Based on the electrolyte and system size, the fuel cell systems can attain 40-60% efficiency whilst the coal plants can reach overall system efficiency values lower than 30% (Sedighizadeh and Rezazadeh, 2007). .

sPEEK qualifies as a favourable PEM because of its low cost coupled with its good mechanical strength and high thermal stabilities (Ikram et al., 2017). This PEM's fabrication step permits direct electrophilic substitution which is easily followed by the solvent casting method for membrane preparation. In the DMFCs, thicker Nafion® membranes are essential to counteract the high methanol permeability. The Nafion® membranes applicable in DMFCs cost between \$600 -1200 m^{-2} based on the preferred thickness to be used whereas the sPEEK has an average cost of \$375m^{-2} (Neburchilov et al., 2007). Unlike Nafion®, the sPEEK PEM is less susceptible to methanol permeation because its microstructure is greatly branched and it has a lower electro-osmotic drag hindering methanol transfer. The methanol permeability leads to some consumption of the cathode reactants lowering a fuel cell's performance. Methanol transport through the membrane causes fuel losses and subsequent lowering of the cathode's effective area which leads to a negative impact on the oxygen reduction reaction (Zaidi and Matsuura, 2008). The sPEEK based membranes possess a high operational temperature range due

to their good thermal stability. At a high operational temperature, the electrodes exhibit an increased CO tolerance, enhanced methanol oxidation and an improvement in the conductivity of protons (Neburchilov, 2007).

Adding nanocomposite particles to sPEEK may lead to membranes with good proton conductivity comparable to that of the Nafion® membranes. Inorganic oxides such as TiO_2 and $(SiO_2)n$ are hygroscopic in nature and in ionomers they are used with the expectation of increasing water retention in the hot and dry fuel cell operating conditions. Membranes with TiO_2 nanoparticles with an average size diameter of approximately 25nm have been found to have enhanced water retention properties better than the pure sPEEK. Due to titanium dioxide's photocatalytic properties, it has improved membrane fouling performance and hydrophilic characteristics. At a temperature of 100°C and 30% humidity PEMs incorporated with nanocomposite particles have shown a higher cell electrochemical performance. For most metal oxide–based inorganic fillers there was an improvement in the mechanical strength, effective methanol cross over blockage and an enhancement in the proton conductivity. The selectivity values of the pure sPEEK and it's nanocomposite based inorganic membranes have been found to be higher as compared to that of the Nafion® membrane in some studies done previously.

2. LITERATURE REVİEW

2.1. Polymer Electrolyte Membranes

The PEM is often seen as the centre of the fuel cell defining the properties for other cell components. It works as a selective electrolyte allowing only protons to permeate from the anode to the cathode side. Hydrogen ions (H^+) move through the PEM to the cathode producing an electric current and water as a by-product (Jang and Han, 2012). The PEM´s principle function is to behave as a selective barrier which blocks the flow of the electrons and fuel from crossing over to the cathode part.

Ogungbemi et al (2019) summarised some essential properties of the fuel cell types to exhibit desirable cell performance are;

i. High ionic conductivity
ii. Good chemical stability
iii. Strong mechanical qualitities
iv. Ease of obtaining and producing the membrane at a relatively low cost.

2.1.1. PEM components and development

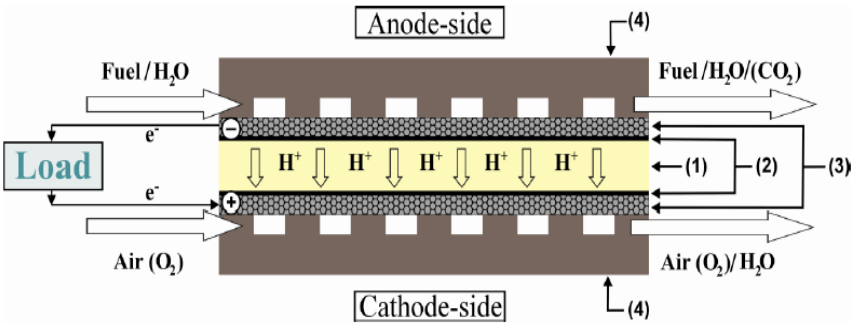

Figure 0.4. *Schematic representation of a PEM (Roelofs, 2010)*

1) Proton electrolyte membrane 2) electrodes 3) gas diffusion layers 4) current collectors

At the anode, the methanol gets oxidised by catalysts to carbon dioxide, hydrogen ions and electrons. The selective PEM (1) only allows the flow of the protons to the cathode and blocks electrons from moving across it. The electrons pass through the external circuit to the cathode. At the cathode, catalytic reduction takes place with oxygen as the oxidant. The hydrogen ions unite with the electrons which moved through

the cell's external circuit and with oxygen from the air producing water as a by-product.

The MEA is the principal component of a fuel cell comprising of the PEM sandwiched between the anode and cathode electrode layers (2). The electrodes of a DMFC are made up of an electrical conductive material with a Pt/ Ru/C catalyst on the anode and Pt/C cathode catalyst. They need to be porous for gas diffusion to take place ensuring a constant supply of reactant gases to the active zones. The three- phase boundary lies between the fuel supply, the catalyst particle and the ionic conductor. It is at this phase where the supplied fuel has to interact with the catalyst layer's species splitting the methanol fuel into protons which move across the ionic conductor and the waste carbon dioxide gas exits the cell. The GDLs (3) lie outside the catalyst layers and they serve the purpose of assisting the reactant's transport into the catalyst layer. The MEA and GDLs are finally held together between the endplates or current collectors (4) with a specific flow field to establish an unvarying fuel and air supply across the membrane's two sides.

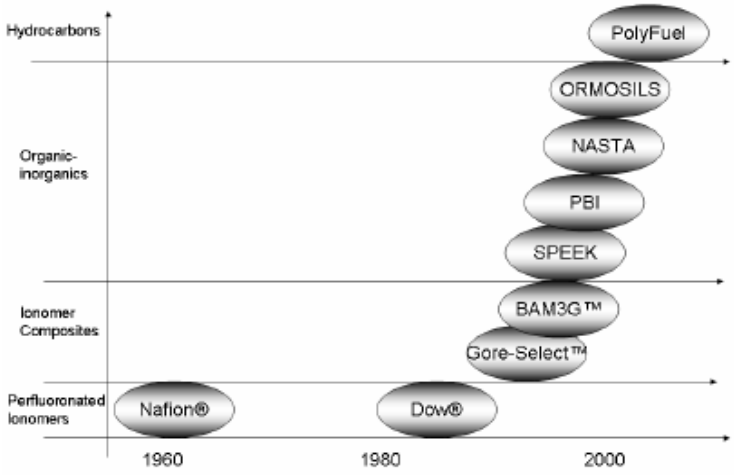

Figure 0.5. *Development of PEMs over the years (Erdener, 2007)*

The invention of fuel cells dates back to 1838 but their real implementation as a means for electricity generation was in 1955 by a General Electric scientist named WT Grubb. These fuel cells utilised membranes with inferior proton conductivity values which in turn had a poor power output yield and the C-H bond's lack of stability led to poor strength (Page, 2012). Before Nafion® was introduced, poly (styrene sulfonic acid) based membranes were used but in unhumidified conditions they were very brittle

then as a substitute cross-linked polystyrene- divinyl benzene sulfonic acid membranes were utilised instead (Zaidi and Matsuura, 2008). Similar to the previously mentioned membrane type, the new replacement had drawbacks of instability and easy deterioration. The development of perfluorinated membranes is often termed as a 'quantum leap' since the fuel cells showed enhanced performance and strength (Costamagna and Srinivasan, 2001). Nafion® was originally made for chloroalkali cells, later in 1962 as a membrane separator then in 1966, it was employed as a PEM in a H_2/O_2 fuel cell (Page, 2012). Today Nafıon®, a poly (perfluorosulfonic acid) with sulfonic acid group terminating a perfluoroethylene backbone is the most extensively used PEM ever since its development.

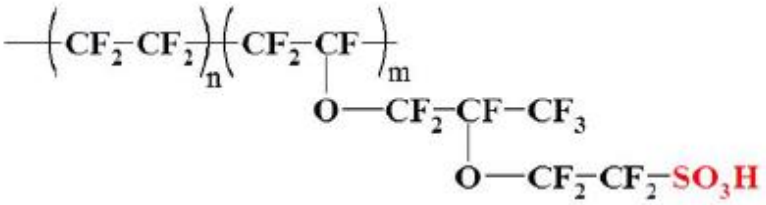

Figure 0.6. *Chemical structure of Nafion (Page, 2012)*

2.2. Nafion®

Nafion® is the brand name of the DuPont electrolyte that is built on a teflon support and is sulfonated. It is a costly PEM with drawbacks of poor proton conduction ability at high temperature and low humidity which has led scientists to continue their research to try and find its possible replacements. Dow and Asahi Chemical companies progressed by developing shorter side chain perfluorosulfonic acid membranes similar to Nafion® membranes in structure and morphology but with varying lower equivalent weights. Over the years, the non- fluorinated membranes have been developed to counter the fluorinated membrane's high cost as well as high methanol permeability when they are applied in DMFCs. These substitute membranes require functionalisation to introduce sulfonic acid groups to the polymer matrix.

2.3. SPEEK Polymer

PEEK, poly (ether ether ketone) is a hydrocarbon that lies in a class of copolymers known as poly(arylene ether ketone). This class of copolymers possess outstanding toughness, chemical resistance, and thermal stability allowing it to find use

as a metal replacement in construction industries (Patel et al., 2010). For PEMs they are quite appealing due to their high oxidative and hydrolytic stability. The Poly(arylene ether ketone)s are classified according to the differences in the positioning of the ether and ketone groups as well as their molar quantity per monomer (Roelofs, 2010). Many researchers have focused their work on these polymer materials because like Nafion®, they nanoseparate when exposed to humidified conditions.

2.3.1. Sulfonation of PEEK

PEEK is a thermostable semi crystalline polymer with an aromatic, non fluorinated backbone with the 1,4- disubstituted phenyl groups separated by ether (-O-) and carbonyl (-CO) linkages (Zaidi and Matsuura, 2008). The sulfonation reaction functionalises the PEEK polymer and the extent of sulfonation is a function of the reaction time, sulfonation temperature and acid concentration. In PEEK's sulfonation the electrophilic substitution is the mostly applied method taking place on the phenyl ring with the greatest electron density resulting in a structure as in the figure 2.4 below;

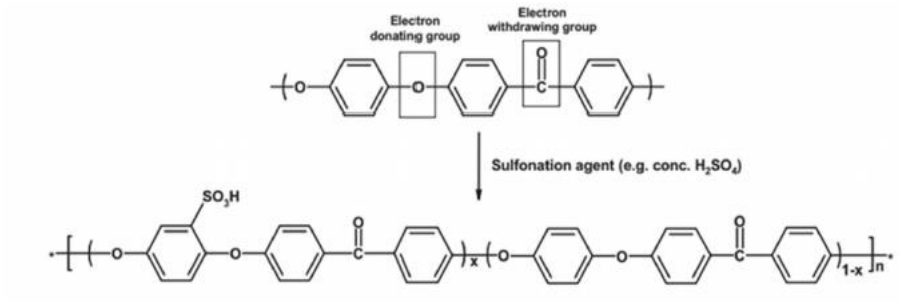

Figure 0.7. *Sulfonation of PEEK*

Sulfonation is an essential modification technique that brings sulfonic acid (-SO_3H) groups to a material. Concentrated sulfuric acid and chlorosulfonic acid are some common sulfonating agents usually used. PEEK´s chemical character is altered by sulfonation, which increases its solubility in polar solvents thereby giving the new sPEEK polymer some new characteristics like proton conduction ability, ion exchange capacity and hydrophilicity. The attainable degree of sulfonation depends on the quantity of the aromatic rings linked by oxygen atoms as O-phenyl-O units and preferential sulfonation takes place on these units. On the other hand, the O-phenyl-CO groups have an electron withdrawing nature due to the carbonyl group hence they are left unsulfonated. The sulfonic group possess 3 oxygen atoms joining with the sulfur

generating a strong inductive effect resulting in a pulling effect of the electron density from the ring.

The sulfonation reactions can either take place on a monomer prior to polymerisation (pre-sulfonation) or on the polymer (post-sulfonation) (Pica, 2015). The post- sulfonation can be further split into heterogeneous and homogeneous sulfonation in which a solvent like methyl sulfonic acid is initially used to dissolve the polymer and afterwards sulfuric acid is finally added for the reaction completion (Do and Kim, 2008). The post- sulfonation reactions are less preferred because the degree of sulfonation cannot be accurately controlled, lacking site specificity for the sulfonic groups and the polymer backbone can be degraded (Zaidi and Matsuura, 2008). sPEEK lies in a category of non- fluorinated PEMs that were developed as a means to totally replace the costly fluorinated ones.

2.3.2. Determination of the degree of sulfonation

The degree of sulfonation measures the quantity of sulfonic acid groups per repeat unit of sPEEK (Zaidi, 2003). A higher DS is a denotation of the sulfonation of many repeat units of the polymer.

The degree of sulfonation can be determined by three different methods namely;

1) Titration (ion exchange capacity);
2) H NMR spectra and;
3) Elemental analysis to determine the amount of sulfur present in the sPEEK.

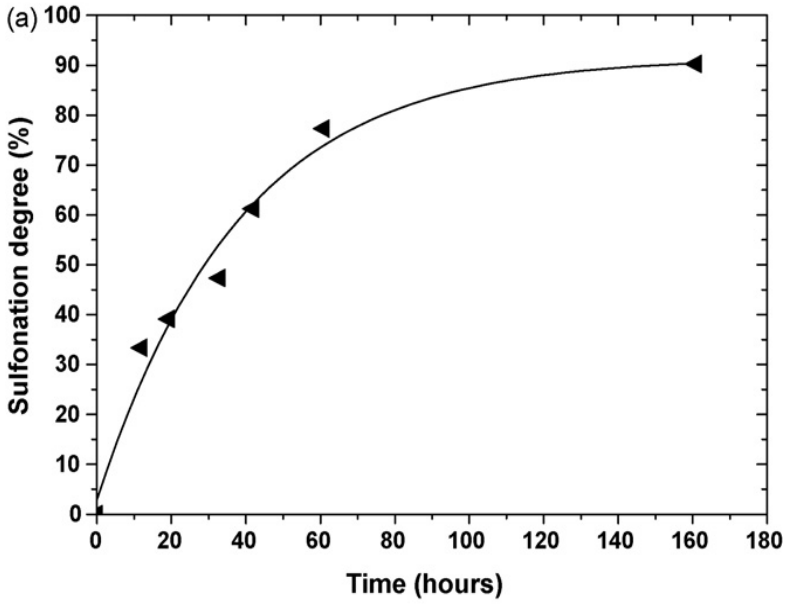

Figure 0.8. *Heterogeneous sulfonation kinetics of PEEK at room temperature (Do and Kim, 2008)*

2.4. Characterisation of SPEEK

2.4.1. FTIR spectroscopy

By using an infrared light to scan specimens, it identifies the organic, polymeric and sometimes inorganic constituents in a material. To confirm the chemical make-up of sPEEK, the functional groups present in the polymer matrix are determined by the FT-IR spectroscopy technique. In one study related to sPEEK, the FTIR data confirmed that PEEK is only sulfonated at a single position on the phenylene ring between the ether groups (Rikukawa and Sanui, 2000). On the PEEK spectra at 1489 cm^{-1} the peak is due to the vibration of the C-C band but in sPEEK the bond is broken into 1492 and 1474cm^{-1} as a result of the replacement which took place after the sulfonation reaction (Park and Kim, 2016). The symmetric and asymmetric stretching vibration of the sulfonic acid $(-SO_3H)$ group was observed in sPEEK at 1024 and 1080 cm^{-1} (Park and Kim, 2016). The resultant peaks are a clear reflection of the successful incorporation of sulfonic acid groups into the PEEK polymer's matrix through the heterogeneous sulfonation reaction.

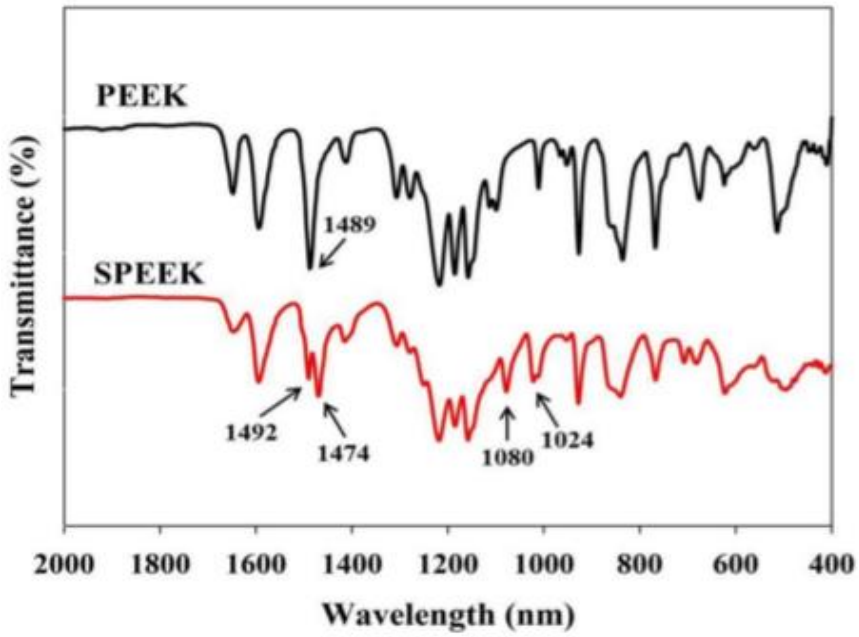

Figure 0.9. *FTIR spectra of PEEK and Speek (Park and Kim, 2016)*

2.4.2. The effect of sPEEK's sulfonation extent on crystallinity and solubility

The $-SO_3H$ groups present in a membrane matrix alter the membrane's chemical and mechanical properties and over sulfonation causes easy deterioration of the polymer's backbone chain. As mentioned beforehand, sulfonation alters a polymer's chemical behavior reducing its crystallinity directly affecting the material's solubility. The X-ray diffraction pattern for a low sulfonated PEEK sample reflects weaker, less intense crystalline peaks. This shows that even low sulfonated samples have some influence on altering the crystallinity. As sulfonic acid groups are added to a structure, the chain conformation and packing is modified leading to crystallinity loss and polymer solubility. On the other hand, the medium and highly sulfonated PEEK has diffractograms with only a broad amorphous scattering background (Zaidi, 2003).

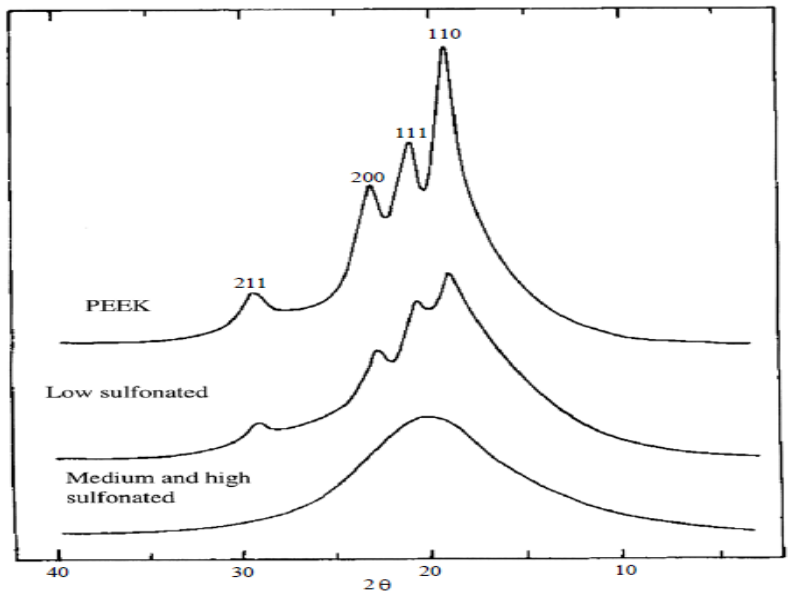

Figure 0.10. *Wide angle X-ray diffractogram of PEEK and sPEEK (Zaidi, 2003)*

Depending on the DS, the solubility behaviour of sPEEK samples varies in different solvents. Below is a summary of the solubility of sPEEK polymer samples in various solvents with varying DS. To be applicable in fuel cells, a DS between 50%- 60% would be the most favourable.

Table 0.2. *Solubility of sPEEK polymer at different DS with various solvents (Iulianelli & Basile, 2012).*

sPEEK Polymer Solubility	
DS	**Type of solvent**
<30%	DMF
	DMSO
	NMP
>50%	DMAc
>60%	MeOH/ Water Solution
>70%	MeOH
100%	Hot Water

2.4.3. Ion exchange capacity

The ion-exchange capacity (IEC) of sPEEK polymers is a measure of the number of counter ions exchangeable in the polymer material (Zaidi, 2003). The DS as well as the sulfonation reaction time are determinant factors of sPEEK's IEC and from (Iulianelli and Basile, 2012), IEC values greater than 2.0 meq/g are attainable with a DS greater than 90% whereas DS values beneath 70% can realise IEC values in the range of

1.3- 1.9 meq/g. To work effectively as a fuel cell membrane permitting good proton transfer, sPEEK's IEC must lie between 1.4- 1.7 meq/g.

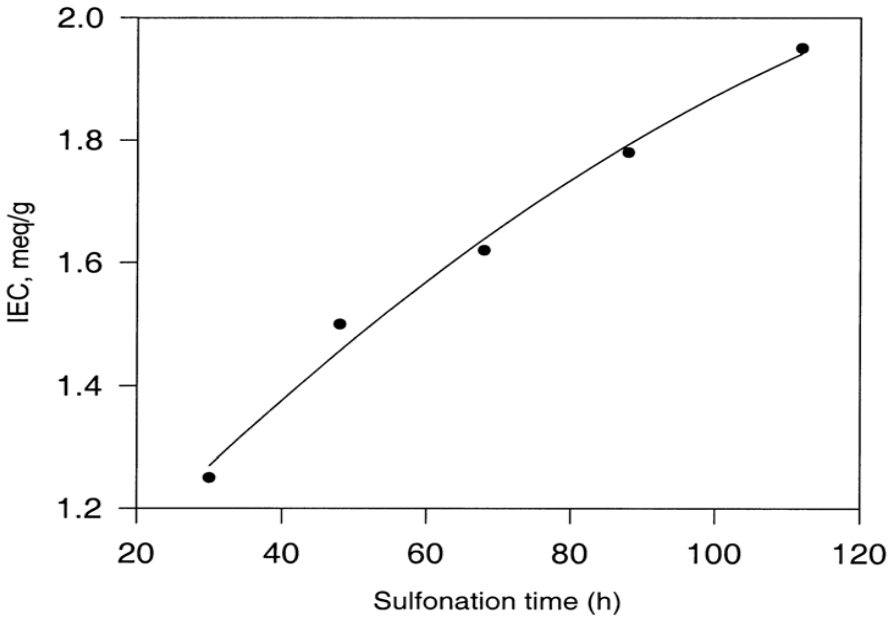

Figure 0.11. *Sulfonation time effect on IEC of PEEK (Zaidi, 2003)*

Table 0.3. *IEC, DS, sulfonation time, water uptake and proton conductivity of sPEEK membranes and Nafion115 (Yang, 2008)*

Sulfonation time (h)	IEC (mequiv/g)	DS (%)	Water Uptake (%)		σ at 80°C and 100%RH (S/cm)
			25°C	80°C	
15	0,98	31	-	-	-
25	1,23	39	-	-	-
35	1,36	44	1,4	8,6	0,0011
40	1,42	46	2,4	22,8	0,0018
45	1,62	54	5,1	140	0,0032
50	1,74	58	5,3	509,5	0,007
65	1,92	65	19,9	Dissolved	-
85	1,95	67	17,4	Dissolved	-
115	2,06	71	18,3	Dissolved	-
135	2,09	72	25,1	Dissolved	-
Nafion 115	0.91	-	18	26,7	0,014

2.4.4. Thermal stability of PEEK and sPEEK polymers

The thermal stability test is conducted with the thermogravimetric analysis technique. This technique monitors the mass of a sample as a function of temperature or time when it is exposed to a controlled temperature program in a specified enviroment. In this analysis, upon heating, the substance under test either increases or loses its weight and throughout the course of the experiment the changes in the sample's mass are monitored and recorded.

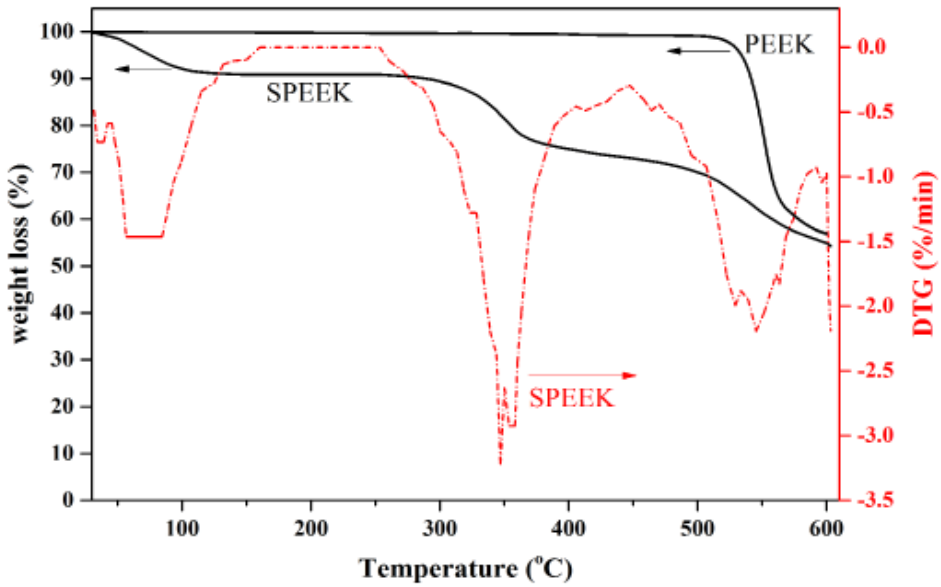

Figure 0.12. *TGA curves and DTG curves of pure PEEK and sPEEK (40% DS) membranes (Parnian, Gashoul and Rowshanzamir, 2017)*

PEEK is a highly thermostable polymer having a $T_g \sim 150℃$. İts thermal degradation begins at about 500℃, as shown in Figure 2.9. In another source, Victrex PEEK's degradation has been reported to begin at 550℃ (Xing et al., 2004). This is not the case however after sulfonation as the sPEEK now presents a non- identical curve with three significant weight loss regions. The weight losses in the three segments illustrated above were also confirmed by the DTG curve of sPEEK (40% DS). The first weight loss region is related to the evaporation of water as well as the loss of solvent which would not have been fully evaporated. The two steps that follow are associated with thermal degradation shown on the DTG curve as wide peaks. In the second stage at 250- 440°C, acid catalytic breaking off of -SO_3H groups takes place. The third weight loss phase from 450°C to 540°C is for the polymeric backbone's thermal decomposition.

For the sPEEK samples with DS values of 64%, 79% and 99%, there were 2 well defined degradation steps as in Figure 2.10. At 250- 280°C, the weight decrease was found to be as a result of sulfonic groups loss whilst the final one occuring at 400- 580°C was associated with the deterioration of the main backbone chain (Xing et al., 2004).

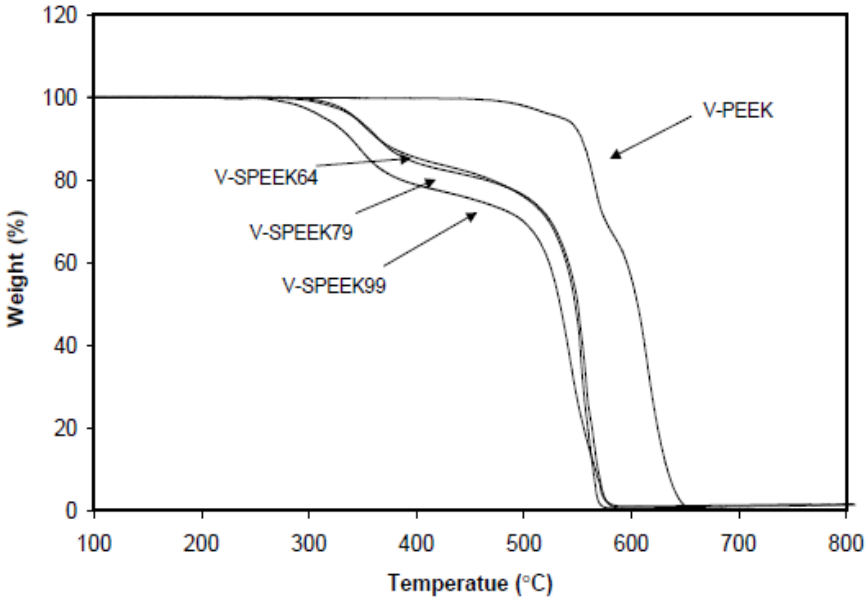

Figure 0.13. *TGA curves of PEEK AND Speek (Xing et al., 2004)*

2.4.5. Water uptake and proton conductivity

Sulfonation aims at adding some hydrophylic sulfonic acid groups to a polymer structure. When sulfonic acid groups are added to the aromatic PEEK polymer it's hydrophilicity is improved leading to an ease of proton transfer. The PEM's conductivities are greatly enhanced in water as protons are thought to move together with hydrogen- bonded ionic passages and cationic mixtures hence for protons to transport in a given medium they rely on the connectivity of the hydrated domains (Yang, 2008). The amount of acid groups that are present in an ionomeric membrane and their ability to separate in water determines the proton conductivity values. The Nafion® microstructure has wide water channels that ensure good connectivity amongst species and it is less branched allowing good interaction amongst species. Contrarily to this, the sPEEKK water channels are narrow with some dead end channels leading to some unsatisfactory connectivity with passing species.

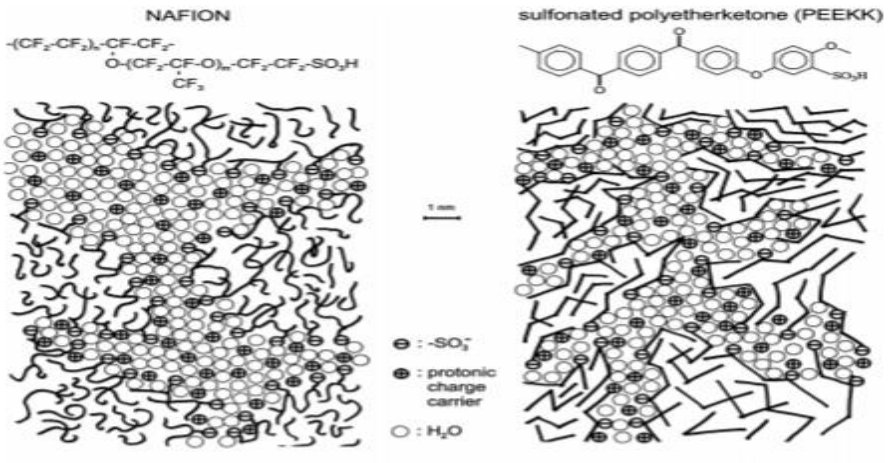

Figure 0.14. *Microstructures of Nafion and sPEEKK ketone showing interaction of -SO3 and protons with water (Kreuer, 2001)*

The water uptake stands as an essential parameter which propels acid functionality thereby accelerating transfer of protons within a fuel cell membrane. For the highly sulfonated level sPEEK membrane samples, some clustering may occur attributable to a greater amount of sulfonic acid groups that are present and this may increase the water uptake (Zaidi, 2003). The highly sulfonated membrane samples possess excessive water uptake values resulting in their swelling and the mechanical properties fail easily. In the plot below of water uptake and the number of sulfonic acid groups, the water uptake gradually increased linearly to around 30wt% at 65% DS and after 70% DS onwards this rise is sharp. At 80% DS, the water uptake reached 120wt% because of the increased density of hydrophylic sulfonic acid groups in the membrane samples. Sulfonation leads to a rise in the amount of protonic sites and creates formation of water mediated pathways (Zaidi, 2003).

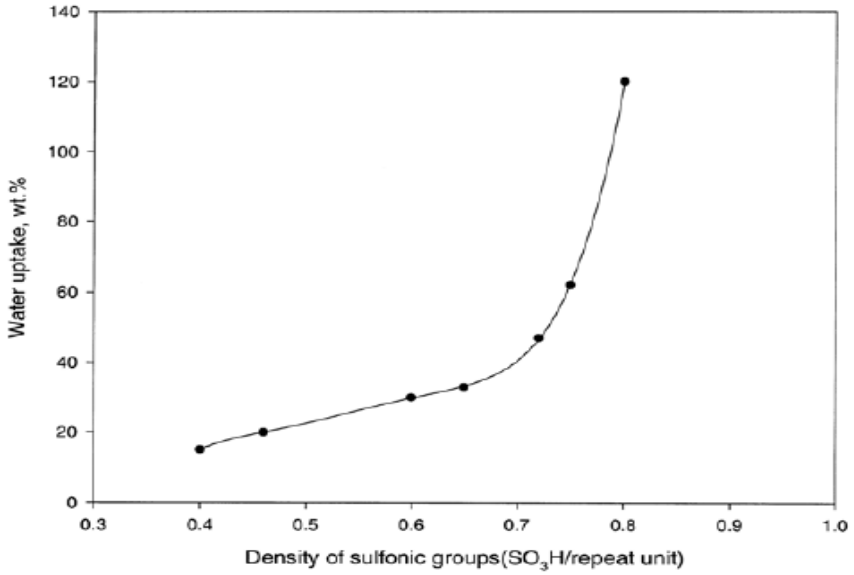

Figure 0.15. *Water uptake of sPEEK membranes (Zaidi, 2003)*

The sPEEK membrane's proton conductivity is dependant on the DS, polymer brand, membrane pretreatment technique, hydration state, casting solvent and temperature (Bauer et al., 2000) (Kaliagune et al., 2003). The PEM's proton conductivity is measured by simulating the proton conductivity as an electrical circuit by using the Electrochemical Impedance Spectroscopy (EIS). Either the 2- probe or 4-probe techniques are used to measure the impedance across a membrane's surface area in partially or completely hydrated conditions. The impedance measures a system's capability to prevent an electrical current from passing through it.

The PEEK polymer can be found under 2 different commercial names; Victrex and Gatone, the two being distinguished from each other by their methods of polymerisation. From a study by (Kaliagune et al., 2003), Victrex and Gatone PEEK polymer membrane samples with varying DS and casting solvents were examined. It can be deduced from this study that the membranes cast with DMAc had notably high proton conductivities in comparison with the DMF cast ones. In all the membranes, before carrying the proton conductivity tests, any solvent remaining trapped within the samples was driven off under vacuum at 125°C. Due to the possibility of a chemical reaction occuring between the sulfonated polymer and solvent, the V88F and V88A samples were only dried at atmospheric conditions for 2 days. Their proton conductivities are shown in the Figure 2.13.;

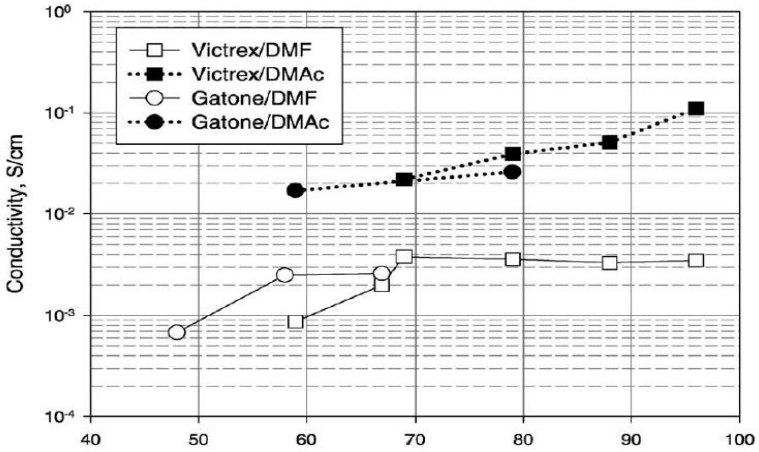

Figure 0.16. *Victrex and gatone PEEK proton conductivities cast with DMAc and DMF (Kaliaguine, 2003)*

Performance of the membranes was compared with those vacuum treated at 125°C, it was noted that the DMF cast membranes showed significantly poor conductivity when compared to the DMAc cast ones and the decrease became significant with an increase in vacuum treatment.

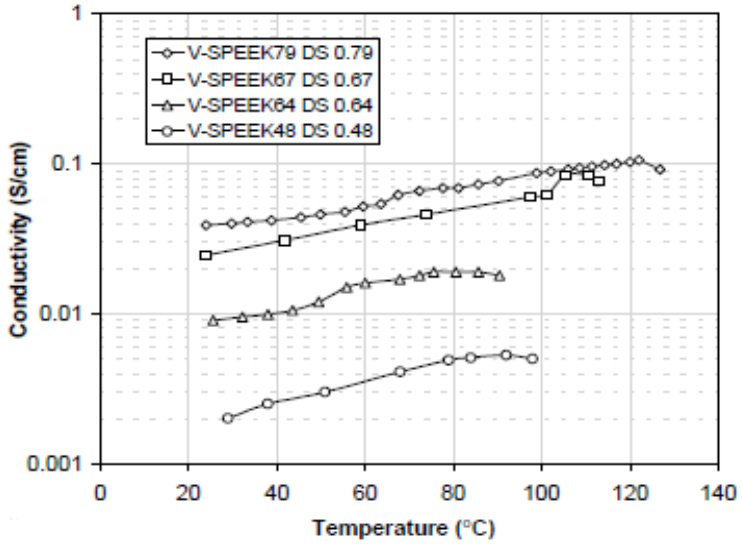

Figure 0.17. *Proton conductivities of sPEEK cast from DMAc at various temperatures (Xing et al., 2004)*

The proton conductivity of sPEEK is highly dependent on the sample's DS as shown in Figure 2.14. At a 48% DS and 80- 100°C, a proton conductivity of 0.004S/cm is observed whilst for a 64% DS sample the conductivity increases by a magnitude of 10. At 79% DS, the proton conductivity reached a value similar to Nafion's of 0.1S/cm.

2.4.5.1. Transport mechanisms of protons in water

The hydrophobic backbone of the PEMs provides a repulsive surface that allows easy movement of water within the membrane matrix. Water is permitted to move in a membrane by means of electroosmotic drag and concentration gradient owing to diffusion (Ogungbemi et al., 2019). Protons move in a membrane medium by using either/ both the vehicular and the Grotthus mechanisms (Erdener, 2007).

In the first mechanism, protons transmit through a medium by using a vehicle like H_2O/H_3O to propel them thus the conductivity largely depends on the diffusion velocity of the vehicle (Erdener, 2007). In this medium, protons are propelled by diffusion taking place as water carrying protons flow from the membrane`s surface across the cell due to concentration gradient (Ogungbemi et al., 2019). The second mentioned mechanism conducts protons from one vehicle to another by utilising hydrogen bonds (proton hopping) (Erdener, 2007). The vehicular transport mechanism prevails over the Grotthuss mechanism at high temperature due to breaking of the hydrogen bonds at these conditions.

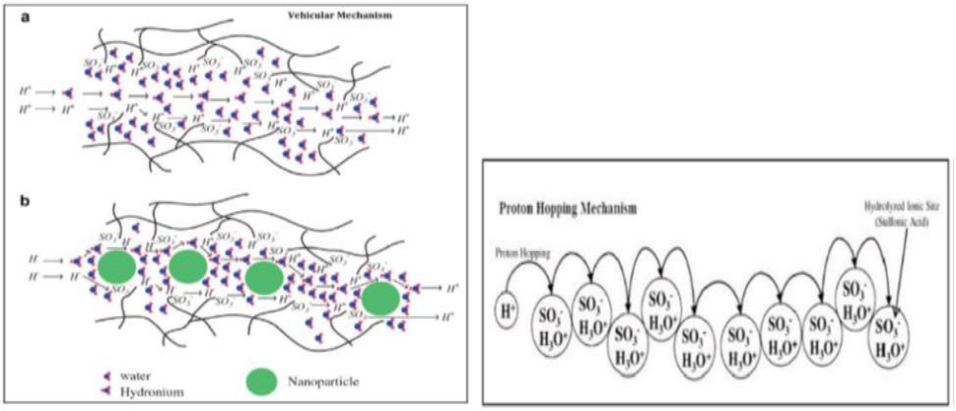

Figure 0.18. *Schematic of vehicular and proton hopping mechanisms (Ogumbemi et al., 2019)*

2.4.6. Methanol permeability in sPEEK and Nafion

The methanol crossover test measures the amount of fuel feed permeating across a polymeric membrane without being utilised to generate any electricity. The permeability is dependent on the cell´s operating temperature, pressure, concentration of the methanol feed as well as the membrane's structure and morphology (Ahmed and Dincer, 2011). To determine this, a methanol permeability test system is conducted.

When applied in DMFCs, Nafion membranes exhibit high methanol cross over values leading to interference with the oxygen reduction reaction kinetics (Iulianelli and Basile, 2012). According to (Ahmed and Dincer, 2011) by utilising the cathode platinum catalyst, the methanol is chemically oxidised at the cathode leading to unfavourable effects of depolarisation of the electrode and a mixed potential that results in an open circuit voltage under 0.8V.

The methanol permeability is calculated as below as reported by (Awang, Jaafar and Ismail 2018);

$$P = \alpha * \frac{V_B}{A} * \frac{L}{C_A} \quad (2.1)$$

Here; P methanol permeability ($cm^2 s^{-1}$), α slope of methanol permeation of sample (M/s), V_B volume of water in compartment B (cm^3), L membrane thickness (cm), A membrane cross-section area (cm^2) and C_A concentration of methanol in compartment A at time t (M) = 1 M.

The slope is found by;

$$\alpha = {C_B(t)}/{t - t_0} \quad (2.3)$$

Here; $C_B(t)$ methanol concentration in compartment B at time, t (M) and t_0 time lag related to the diffusivity (s).

2.4.6.1. Methanol permeability in sPEEK nanocomposite membranes

As mentioned beforehand, sPEEK polymer solubility in organic solvents like methanol increases with an increasing degree of sulfonation. Above a 60% DS the polymer swells significantly and starts to be soluble in aqueous methanol/water solutions whilst above 70% it dissolves in methanol solution.

The methanol permeability of sPEEK/sulfonated titania submicrospheres composite membranes was analysed by (Xu et al., 2011) and the results revealed that the pure sPEEK yielded a permeability value of $5.72 * 10^{-7} cm^2/s$. On the other hand, the composite ones had a significant reduction in the methanol permeating with increasing filler ratio (as shown in Figure 2.17.). With the filler content increasing from 5 to 20 wt%, the sPEEK/ TiO_2 membrane's permeability reduced by 10.0% to 33.7% whilst that of the sPEEK/ TiO_2-SO_3H decreased by 17.7% to 36.2%. The fillers caused a reduction in the methanol permeability across the membranes due to inhibition of the polymer chain mobility as a result of strong interaction between the fillers and sPEEK

membranes. The inorganic fillers also have an impermeable nature to the methanol feed leading to the methanol pathway's tortuosity.

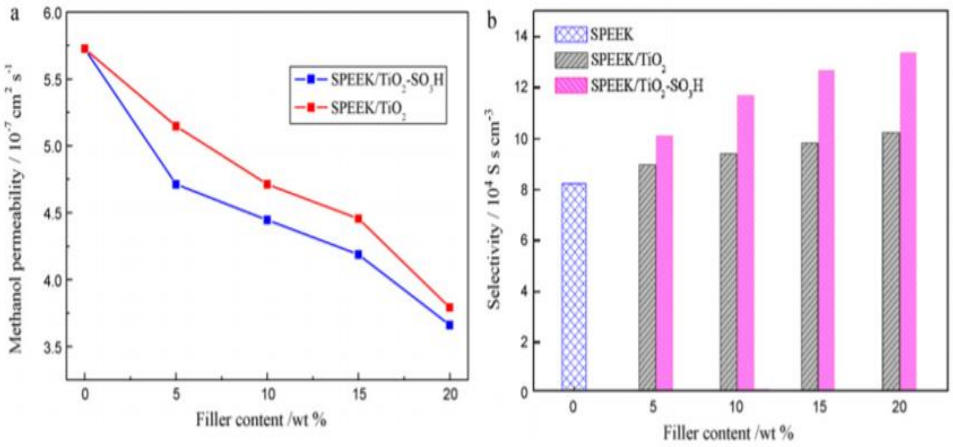

Figure 0.19. *pure sPEEK and sPEEK hybrid membrane's methanol permeability and selectivity (Xu, 2011)*

From the Figure 2.16, the sPEEK/ TiO_2- SO_3H hybrid membranes with a 20wt % filler ratio had the highest selectivity in comparison with the others.

In one study, a 2M (aq) methanol solution was fed to a DMFC single cell system, the cell was equilibrated then brought to a steady state (Peera et al., 2013). The pristine sPEEK with a 54% DS had a methanol permeability value of $2.5*10^{-7}cm^2s^{-1}$ whilst for similar experiments recast Nafion had a value of $6.5*10^{-7}cm^2s^{-1}$. The variation between the methanol amount supplied and that collected at the anode exit port within a specific time range was taken at open circuit and voltage (OCV) with a temperature of 60ºC kept constant. By using a gas chromatography detector, the sample's methanol concentration was analysed and computed.

Li, L et al analysed the methanol permeability of sPEEK samples with different DS (Li, Zhang and Wang, 2003). The sample solutions were analysed with a differential refractometer and the slope of a straight line plot of methanol concentration vs permeation time calculates the methanol permeability(P). The experiments were controlled from room temperature to 80 ºC. The Nafion 115 membrane had a crossover value of $1.32 * 10^{-6}cm^2/s$ whereas for the sPEEK membranes the permeability values increased with an increasing DS. They were far lower than that of Nafion attaining $9.07 * 10^{-8}cm^2/s$ at 80ºC. The 39% and 47% DS samples yielded permeability values of $1.321 * 10^{-7}cm^2/s$ and $1.453 * 10^{-7}cm^2/s$ respectively.

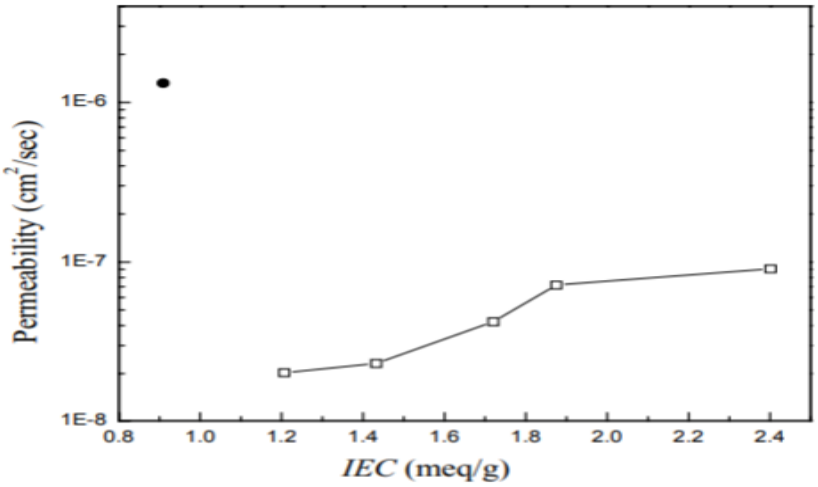

Figure 0.20. *Room temperature methanol permeability values of Nafion 115 and sPEEK membranes (Li, Zhang and Wang, 2003)*

In the Figure 2.19. all the membranes had lower permeability values as compared to the Nafion 117 membrane. A methanol permeability test was conducted with a home-made glass diffusion cell at 22 ºC. Similar to the above mentioned tests 2 compartments with two solutions were assembled and in between them different membranes were fitted for analysis. Unlike the other tests which used distilled water as a reference solution, ethanol (0.5vol%) in DI water was employed whilst in the other compartment a 10vol% methanol solution was utilised. As illustrated on the right hand side graph of Figure 2.20. the 59% DS sample had the highest selectivity in comparison with the highly sulfonated sPEEK samples and Nafion.

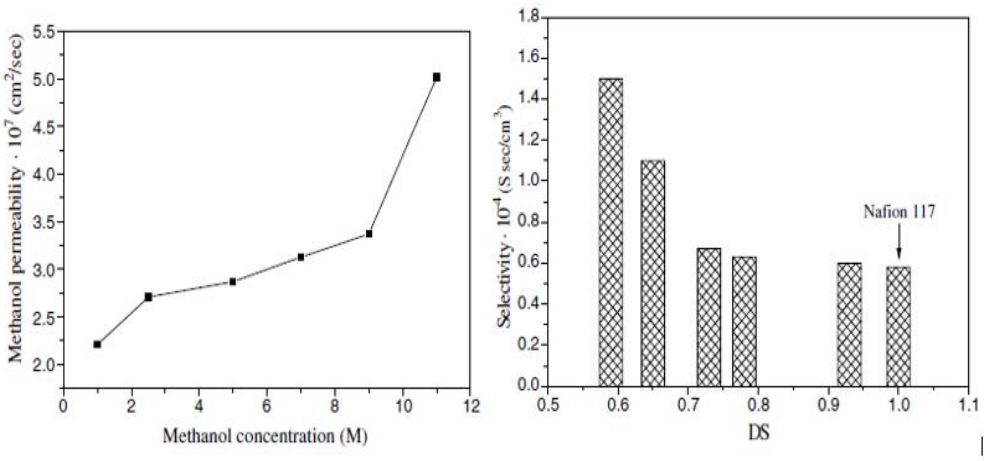

Figure 0.21. *Methanol permeability of sPEEK (59% DS) as a function of methanol concentration and selectivity vs DS (Xue and Yin, 2006)*

2.5. Poly (ether ether ketone) Based Composite Membranes

Composites added to sPEEK membranes can be classified according to the effect they bring as in the following;

2.5.1. Hygroscopic composites

Hygroscopic materials attract water with ease by absorption or adsorption. These types of composites are made through the introduction of a hygroscopic material (eg silica) to a polymer structure. The hygroscopic oxides are passive fillers which do not have much effect on the intrinsic proton conductivity but they prove beneficial when a PEM is subjected to very hot and dry operational conditions exhibiting high water uptake properties (Venkatesan and Dharmalingam, 2015). At low relative humidity, these materials greatly enhance the swelling of membranes whilst preventing fuel crossover in DMFC. It has been reported that at an optimal level, the inorganic particles would enhance both a membrane's proton conductivity and its mechanical stability through inorganic-organic interfacial interactions and it is estimated that up to 10 wt % of oxide additives may be deposited to an ionomer without protonic conductivity deterioration (Venkatesan and Dharmalingam, 2015). In inorganic composite membranes, the polymer and inorganic components can both be able to transmit ions or they can also work as mechanical supporters (Carbone et al, 2008).

2.5.2. Conductive composites

When a second proton conducting species (eg ZrP) is added into a polymer structure, this results in a reduction in the methanol and water permeability. These conductive species are thought to contribute to loss of conduction as a result of lower water uptake of a membrane.

2.5.3. Water substituted composites

In these composites, alternative proton transporter materials (eg heteropolyacids, acid doped polybenzimiadazole) are introduced to a polymer matrix (Venkatesan and Dharmalingam, 2015). The purpose of this is to bring in a highly conductive acid into the structure in order to limit the proton conductivity's dependence on only hydration and electro-osmotic effect. Over time however, the substituted composites are prone to leak from the membrane.

The newly modified membranes must exhibit outstanding chemical resistance, high thermo oxidative stability, outstanding mechanical properties, ability to operate at high temperature, high proton conductivity at lower water contents and reduced methanol crossover (Hakim et al., 2012).

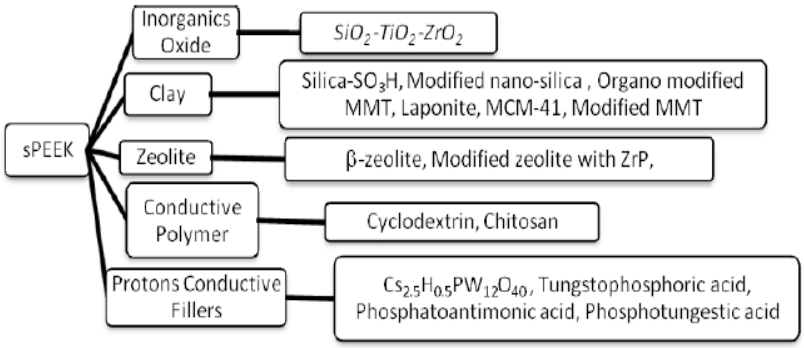

Figure 0.22. *Summary of sPEEK's modification materials (Peighambardoust, Rowshanzamir and Amjadi, 2010)*

2.6. Effect of Inorganic Oxides on the Proton Conductivities of sPEEK and Nafion Membranes

2.6.1. sPEEK inorganic composite membranes

2.6.1.1. Titania/ sPEEK composite membranes

For adding hydrophilicity to a polymer membrane, nanosized titanium dioxide particles (less than 100nm) have been found as a good candidate. Many researchers have used TiO_2 as an inorganic filler for sPEEK membrane modification particularly aimed at enhancing the transport phenomena in a membrane's matrix (Ikram et al., 2017). Titanium dioxide is a semiconductor material possessing photocatalytic properties which under the fuel cell operating conditions it provides satisfactory membrane hydration. In general this filler leads to more interlinked proton pathways, maximum power density increment and enhanced electrochemical characteristics (Sarirchia and Rowshanzamira, 2017). Many researchers who have conducted research on this subject have claimed that the inclusion of TiO_2 nanoparticles in sPEEK would reduce both the membrane swelling in water and methanol cross over values.

According to (Kalappa and Lee, 2007), work on sPEEK/ TiO_2 nanocomposite membranes revealed a decrease in water swelling, methanol crossover and proton

conductivity. In this study sPEEK with a 57% degree of sulfonation incorporated with TiO_2 nanoparticles it was discovered that the particles led to a reduction in proton conductivity and water swelling. If the amount of oxide particles increased, a significant decrease in methanol permeation was noticed. Di Vona, (2011) carried out a study which used surface- functionalised TiO_2. One part had hydrophilic tri-(hydroxymethyl)-propane whilst the other had hydrophobic molecules of silicone oil. In this work, it was reported that the hydrophilic titanium particles showed a non-uniform microstructure which had TiO_2 particles clustering together. The membranes had good strength, low ductility, increased water uptake and proton conductivities. On the other hand, the composites comprising of the hydrophobic titanium particles had a uniform microstructure, lower water uptake and proton conductivities.

Dou et al employed a sol-gel technique using a differing amount of TiO_2 nanosized particles to get sPEEK/ TiO_2 mixed membranes which exhibited elevated water uptake and retention as well as low methanol permeability (Dou Z, 2008). In a related study conducted by (Ji, Tay and Li, 2017), sPEEK/ TiO_2 composite membranes were made for use in vanadium redox flow batteries. In this work, TiO_2 (3%, 5% and 7%) was loaded in sPEEK samples which had varying degrees of sulfonation. It was found that the 5% TiO_2 loaded samples had fairly good qualities such as high ion selectivity and good proton conductivity. In another study, TiO_2 (rutile) and sPEEK composite membranes were prepared using a sol-gel method (Venkatesan and Dharmalingam, 2015). The membranes had enhanced proton conductivity values, electrochemical features, ion exchange capacity and water absorption values. For a loading of 7.5% TiO_2, the membranes gave large power and current densities of 98.1mW/m^2 and 300mA/m^2 respectively much greater than Nafion 117 PEMs.

2.6.1.2. Silica/ sPEEK composite membranes

Silica based nanoparticles are preferred as additives for membranes because of their low price, negligible electrical conductivity and good water holding characteristics as compared to the other inorganic materials (Sarirchia and Rowshanzamira, 2017). They also possess an ease of synthesis, functionalization and accurate control of particle size and distribution which meets most requirements for PEM fuel cells. In the DMFC, SiO_2 based inorganic membranes have been found to have improved proton conductivity, swelling resistance, good mechanical stability, lower methanol

permeation, at high temperature and low humidity conditions the membranes have good cell performance (Ikram et al., 2017) (Sarirchia and Rowshanzamira, 2017).

Some drawbacks of this filler particle are a reduction in the ductility of the resultant material, difficulty in dispersing the silica nanoparticles in a polymer matrix as they have a low affinity to interact with the non polar polymer materials. Some researchers have claimed that this filler´s hydrophilic particles form some hydrogen bonds leading to particle agglomeration which causes an uneven distribution of the nanoparticles. Such active inorganic additives like amines, thiols, isocyanates and vinyl groups are often introduced to the silica particles to stop their agglomeration. In a study done by (Nunes et al., 2002) it was concluded that with this filler a reduction in water permeability did not result in a notable decrease in conductivity.

sPEEK/ SiO_x – S composite membranes exhibited good dimensional stability, high proton conductivity and low methanol cross over (Qijun, 2009). sPEEK/ SiO_2/ ZrP composite membranes had methanol cross over values lower than that of pure SPEEK and Nafion 117 PEMs (Zhang et al., 2008). sPEEK/silica with sol-gel polyethoxysiloxane (PEOS) showed higher proton conductivity values greater than the pure sPEEK. sPEEK and sulfonated silica (SiO_2-SO_3H) nanocomposite membranes were made for microbial fuel cell applications (Sivasankaran, 2015). Composite membranes which had a loading content up to 7.5wt % of sulfonated SiO_2 showed a homogeneous distribution of the inorganic filler with no cracks whilst a loading greater than 7.5wt % led to the filler agglomerating within the membrane. Under the same conditions, sPEEK and sPEEK-SiO_2 membranes had peak power density values of 680mWm^{-2} and 802mWm^{-2} respectively. The composite membranes delivered power density 3 times greater than Nafion 115 (320mWm^{-2}) in a similar MFC setup (Sivasankaran and Sangeetha, 2015).

2.7. Nafion® Inorganic Composite Membranes

Nafion® belongs to perfluorinated polymers and it is used extensively in DMFCs because it posseses outstanding proton conductivity values, very good mechanical properties and strong chemical resistance. However when applied in this fuel cell type it is costly, permits high fuel levels to permeate to the cathode side, loses its proton conductivity at high temperature and degrades quickly thereby limiting the lifetime of the device. This PEM has low water uptake ability at high temperatures (Ikram et al.,

2017). There have been many studies by various researchers aimed at enhancing the mechanical properties and reducing fuel crossover by incorporating some inorganic oxides in the polymer matrice.

2.7.1. Titania/ Nafion composite membranes

A number of studies have been done based on Nafion/ titanium dioxide composite membranes because of the inorganic compound's hygroscopic nature. At high temperatures Nafion® loses its water retention properties thus the proton conductivity value diminishes. TiO_2/Nafion® 115 composite membranes studied by Liccocia et al at 0.54V and 110ºC yielded power density values reaching 0.514 mWcm^{-2} against 0.354 mWcm^{-2} for pure nafion 115 (Licoccia and Traversa, 2006). Nafion composite membranes with a 2.5wt% loading of TiO_2 were made to apply in DMFCs. In these composite membranes, at 30ºC there was a decrease in the protonic conductivity from 0.135 to 0.130S/cm whilst at 55 and 85ºC it showed slight increases to 0.190 and 0.280 S/cm respectively (Ercelik et al, 2017). In this study the maximum power density of Nafion/ TiO_2 MEA increased significantly from 412.08W/m^2 to 641.16W/m^2 from 60 to 80ºC. Nafion TiO_2 nanocomposite membranes were produced for comparison of the in situ sol gel and the solvent casting method. In comparison to the casting method, the sol-gel technique produced membranes with an even dispersion of Ti nanoparticles. The Nafion doped membranes had higher water uptake values as compared to the pure membranes and at high temperature of 110ºC, it showed greater fuel cell performance (Ikram et al., 2017).

2.7.2. Silica/ Nafion composite membranes

Nafion membranes were doped with SiO_2 nanoparticles (1.55wt%, 4.51wt% and 7.3%) and it was discovered that there was a decrease in conductivity with an increasing SiO_2 amount. The water content in these membranes increased significantly with the increasing ratio of SiO_2 particles due to the nature of the hygroscopic filler and this resulted in the displacement of proton concentration (Tai et al., 2018). In another study by (Yin et al, 2018) Nafion- SiO_2 hybrid membranes had elevated water uptake values but there was no notable variation in the IEC between the pure and composite Nafion membranes. At low humidity conditions, the inorganic oxides possess improved water retention and at high humidity more proton transport pathways are formed leading to

elevated proton conductivities above 6wt% humidity (Yin et al, 2018). Nafion/SiO_2 hybrid membranes doped with heteropolyacids produced for DMAc fuel cells had an extended operational span which yielded maximum power densities of 400mWcm^2 and 250mWcm^2 at 145°C respectively with oxygen and air feeds (Staiti et al., 2001).

2.8. Titanium Silicon Oxide

It is an inorganic oxide that can be synthesized by mixing together nanosized silicon dioxide and titanium dioxide particles. The particles in the nanosize range are essential as dopants in PEMs as they enhance the surface area per unit volume with increased molecules/ atoms on their surface. Mixing two or more phases leads to the formation of nanocomposite materials with a blend of properties which would not be otherwise present in the individual oxides. Depending on the level of humidity of the preparation medium, different intermolecular forces exist between the oxide particles when they are mixed together like the van der Waals and electrostatic attraction at low humidity conditions. The $TiSiO_4$ hybrid inorganic oxide was prepared by suspending SiO_2 and TiO_2 oxides in ethanol solution, then the mixture was ultrasonicated and dried (Wei, Dave and Pfeffer, 2002).

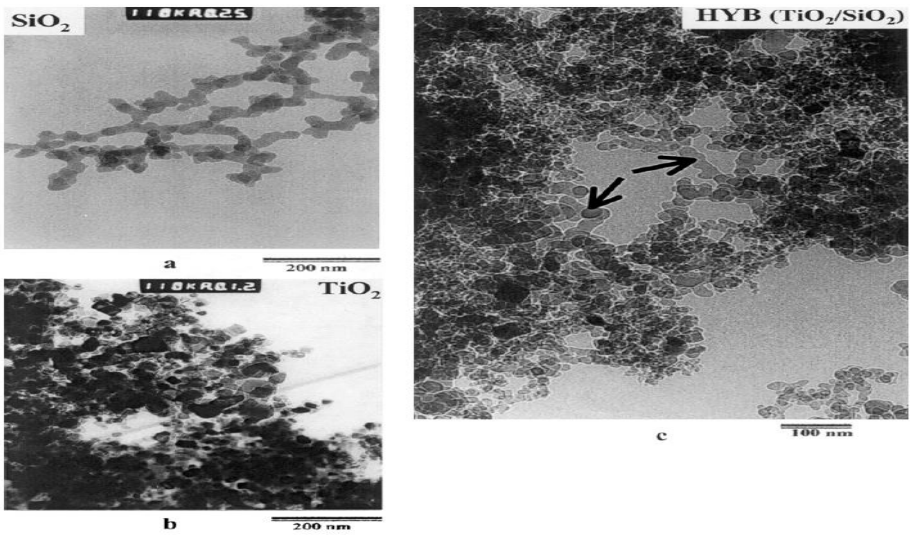

Figure 0.23. *TEM micrographs of a) SiO_2 b) TiO_2 and c)SiO_2/TiO_2 mixture (Wei, Dave and Pfeffer, 2002)*

The SiO_2, TiO_2 and the fabricated nanocomposite oxide powder were characterised with a high resolution TEM to evaluate the features of the surface morphology of the powders. From the images taken, the SiO_2 particles appear as chain

like clusters while the TiO_2 look like crystalline particles. On Figure 2.21. (c), arrows on the middle of the images taken reveals that the SiO_2 particles were not well incorporated in the oxide matrix. Nanoparticles tend to cluster to chains acting like polymers with strong bonds inbetween them which are not easily breakable thus the poor interaction shown. The TEM analysis fails to distinguish the separate particles in a mixture and an EELS (Electron energy- loss spectroscopy) analysis was further undertaken to try and distinguish the individual particles.

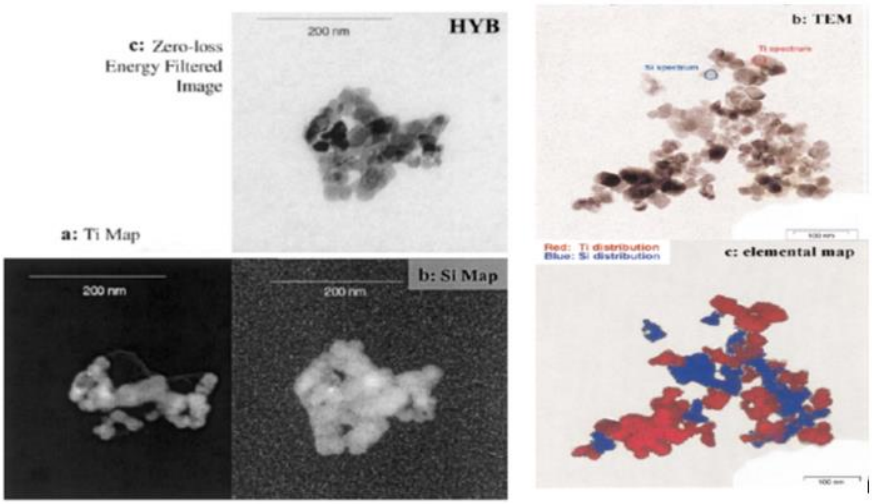

Figure 0.24. *Left side: EELS micrographs of c) $TiSiO_4$ a) Ti map b) Si map right side TEM (Wei, Dave and Pfeffer, 2002)*

2.8.1. Characterisation of fabricated $TiSiO_4$ oxide

2.8.1.1. FTİR transmittance spectrum of $TiSiO_4$ nps

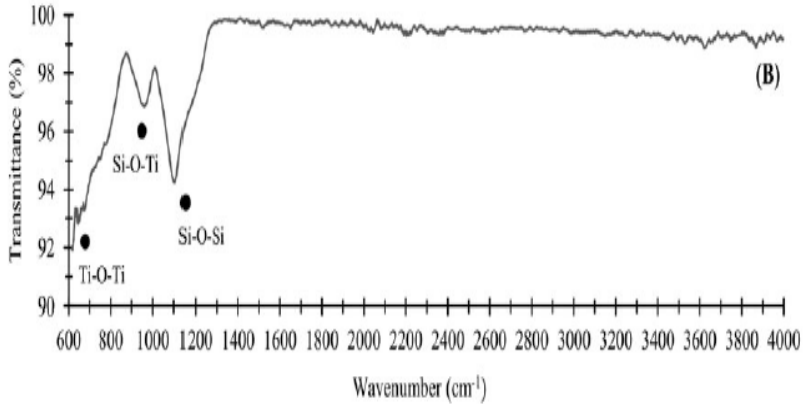

Figure 0.25. *FTIR spectrum of $TiSiO_4$ NPs (Taheri et al., 2019)*

The FTİR spectrum above shows the bands associated with the constituent elements in the $TiSiO_4$ matrice. The stretching of Ti-O-Ti in TiO_2 matrices is shown at 652cm^{-1} band whilst the band of 1097cm^{-1} is due to stretching of Si-O-Si in SiO_2 matrices. The 952cm^{-1} band is as a result of stretching of Si-O-Ti or the presence of Si-O defect sites formed when Ti^{4+} incorporated into the SiO_4^{-4} structures. There was no detection of bands related with the O-H bonds (1650 or 3350cm^{-1}) showing the absence of moisture in the filler (Zhang et al., 2018). The analysis reveals that there was embedding of TiO_2 into the SiO_2 matrices to form $TiSiO_4$ composite NPs.

2.8.1.2. XRD patterns of $TiSiO_4$ nps

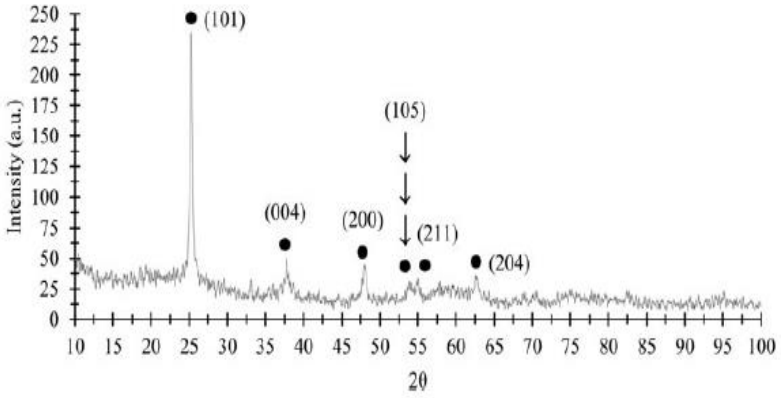

Figure 0.26. *XRD patterns of $TiSiO_4$ NPs (all peaks are related to anatase phase crystal plane in parenthesis) (Taheri et al., 2019)*

The 2θ peaks at various angles and their respective intensities are 25.3º (101), 37.75 º (004), 47.95 º (200), 53.95 º (105), 55.03 º (211) and 62.75 º (204) as shown on the XRD curve in Figure 2.23. (Taheri et al., 2019). The peaks shown by the XRD pattern belong to the anatase TiO_2 phase whilst the SiO_2 diffraction peaks are absent due to its amorphous nature.

2.9. Membrane Electrode Assembly (MEA)

The MEA is an important component of a fuel cell system comprising of the assembly of membrane, anode and cathode electrodes. To develop a good MEA, the performance, stability and life must be carefully considered. The carbon blacks, membranes, electrode ink preparation, hot pressing as well as the electrode's structure are some critical elements affecting the MEA's performance (Kurek and Elias 2007).

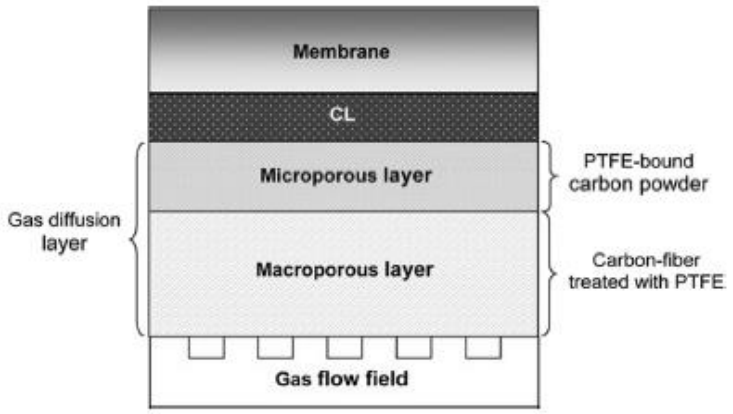

Figure 0.27. *PEMFC electrode basic structure (Majlan, 2018)*

The basic structure of an electrode comprises of a backing layer (BL), gas diffusion layer (GDL) and a catalyst layer (CL) but other scholars only regard the GDL and CL layers. The GDLs have a carbon powder macroporous layer (MPL), hydrophobic /hydrophilic agents and a carbon paper/carbon cloth backing layer (Majlan et al., 2018). The GDL serves to manage water, distribute gas, collect current and provide mechanical support (Kurek and Elias 2007). The MPL supporting the catalyst must have essential characteristics of satisfactory electrical conductivity, high surface area, water repulsion ability, corrosion resistance and good stability. A variety of coating methods can be employed to prepare the CL like spraying, thin layer deposition, electrodeposition, painting and brushing (Majlan et al., 2018). On the market the GDLs can be found with a carbon cloth/paper chemically treated with PTFE enabling hydrophobicity which allows the smooth flow of water vapour to continuously humidify the membrane during the fuel cell operation and also ensure exiting of the water by product from the cell.

2.9.1. Membrane electrode assembly of sPEEK based membranes

An MEA for sPEEK PEM was prepared by a spraying technique (Şengül et al., 2009). In this study, a H_2-O_2 PEMFC operating for 2 hrs at 1 atm and 70°C was used. The catalyst ink was prepared by blending together in an ultrasonic bath for 2h a 20wt% Pt on Vulcan X C-72 catalyst, 5wt % Nafion solution, distilled water and 2- propanol. Pretreatment of membrane was done by boiling in 0.5M H_2SO_4 solution and distilled water at 80°C. A paper frame secured the anode and cathode sides whilst coating the catalyst layer on the GDL. During the loading the GDLs were weighed at irregular intervals to control the catalyst loading and on the anode and cathode sides, up till a

0.4mgPt/cm^2 catalyst loading was attained then the GDLs were left to dry to remove the ink's solvent traces for 1hr and 80°C. Hot pressing of the membrane was done at 130°C.

Lee et al used sPEEK and Nafion ionomers to produce MEAs for DMFC and compared the performances of the two (Lee, Li and Manthiram, 2008). In preparing the sPEEK ionomer, sPEEK was first dissolved in N,N-dimethylformamide (DMF) and the required SPEEK/DMF solution was placed into a water/ isopropyl alcohol (IPA) mixture then afterwards the mixture was sonicated for 30-50mins. The catalyst ink was then added to the resultant mixture which was further ultrasonicated for 1-2h. The anode/cathode catalyst layers were formed by brushing the catalyst ink onto a GDL.

For the electrodes with the Nafion ionomer, water/IPA mixture dispersed the catalyst powder, then nafion solution was added and mixture was ultrasonicated for 1h. The painting method was employed to coat the ink on the GDL. As the anode catalyst, a 40 wt% 1:1 Pt-Ru alloy was loaded on VULCAN XC-72 carbon black with one of either sPEEK or Nafion ionomer. The cathode catalyst comprised of a 20wt% Pt coated on carbon black with either the sPEEK or Nafion ionomer. The total loadings of the anode Pt-Ru and cathode Pt content were 1.0mgcm^{-2}. To prepare the MEA, the anode and cathode electrodes were hot pressed onto either Nafion or sPEEK membrane at 140°C, 80psi for 2.5min and 100°C, 40psi for 3min respectively. To drive off the solvent left behind in the MEA as well as to bring the sPEEK to acid state a 1M H_2SO_4 conditioning solution was used and subsequently rinsing with water.

2.9.2. Summary of fuel cell operating conditions, current and power densities

Table 0.4. *Summary of fuel cell operating conditions, current and power densities*

Membrane	MeOH conc	Anode flow rate	Cathode Pressure, temp	Voltage	Current densities	Power densities
Sulfonated montmorillonite/ sPEEK (SMMT/sPEEK)	1.5M MeOH (aq)	5ml/min	2Bar, 60°C	0.2V	Speek- 76mAcm^{-2} (12h- acid treatment) 1 wt% (24h)- 103.96mAcm^{-2} 3wt% (36h)- 94mAcm^{-2}	max power densities speek- 15mWcm^{-2} 1 wt% (24h)- 21mWcm^{-2} 5 wt% (48h)- 18mWcm^{-2}
sPEEK/ functionalised bentonite clay	2M MeOH (aq)	2ml/min	Ambient pressure 300m/min (O_2), 70°C	0.9V		sPEEK- 60mWcm^{-2} sPEEK/HSO_3-Ben- 135mWcm^{-2}
sPEEK/ TiO_2 (57% DS)	2M MeOH (aq)	0.082l/min	Dried O_2, 2L/min, 70°C			speek/ 10wt% TiO_2- 6.5mWcm^{-2} sPEEK/ 7.5wt% TiO_2- 12.5mWcm-^{2} sPEEK/ 5wt% TiO_2- 16.5 mWcm^{-2}
sPEEK/ sulfonated graphene oxide filler	1M MeOH	1ml/cm	200ml/min (without back pressure)			sPEEK- 25mWcm^{-2} sPEEK/ Ssi- Go (5wt%)- 72mWcm^{-2}
sPEEK/ hydrated tin oxide ($SnO_2.nH_2O$)	2M MeOH	1ml/min, 100°C	0.2MPa (total cell pressure) 100°C		speek/SnO_2 - 350mAcm^{-2} (0.34V) 300mAcm^{-2}	80mWcm^{-2}
sPEEK/ clay nanocomposite membranes	1M MeOH	20psi back pressure (70°C)	Gradual pressure increase to 20psi, 70°C	0.5V	with 1M MeOH, 0.5V sPEEK-62/MMT1.0wt% - 35mAcm^{-2} with 5M MeOH, 0.5V sPEEK- 62/MMT-10wt% - 76mAcm^{-2}	with 1M MeOH sPEEK-62/MMT1.0wt% - 18mWcm^{-2} (0.5V, 1M MeOH (0.5V, 5M MeOH- 38mWcm^{-2}

sPEEK/s $SrZrO_3$@TiO_2 3wt%	2M MeOH	5ml/min, 80°C	200ml/min, 80°C	0.8V	639mAcm^{-2}	max- 140mWcm^{-2}
sPEEK/ZrO_2	1.5M MeOH	4ml/min, 2.5bar	Humidified air 600sccmmin-1 3bar, 100% relative humidity	35mV	5wt%- 109.2mAcm^{-2}	16.4mWcm^{-2} (sPEEK/ZrO_2)
		cell temp (40-110°C)			7.5wt%- 32.1mAcm^{-2}	8mWcm^{-2}
speek (homogeneous) 65%DS	2M MeOH	5 cm^3/min	100cm^3/min		65mA/cm^2	15mW/cm^2 (100°C) (homo sPEEK 65% DS)
					55mA/cm^2	13.5mW/cm^2 (80°C)
(heterogeneous)					45mA/cm^2	10.5mWcm^2
					12mA/cm^2	1.5mWcm^2 (50°C)
					35mA/cm^2	4mw/cm^2
3M MeOH	3M MeOH	1cc/min (60°C)	100cc/min	0.35V	50mA/cm^2	
				0.56V	27.5mA/cm^2	39.4mW/cm^2
	2M MeOH	2ml/min	150sccm		90 mA/cm^2	16mW/cm^2
		1 abs bar (70°C)	1 abs bar (70°C)		65mA/cm^2	11mW/cm^2
					62mA/cm^2	10mW/cm^2
		2abs bar (90°C)	2 abs bar (90°C)		200mA/cm^2	38mW/cm^2 (sPEEK/TiO_2-RSO_3H)
					150mA/cm^2	36mW/cm^2 (speek/TiO_2)
					150mA/cm^2	30mW/cm^2 (sPEEK)
	2M MeOH	3cc/min	200cc/min			26.95mW/cm^2 (27°C) (sPEEK/cloisite 15A clay/TAP)
						34.6mW/cm^2 (40°C
				0.53v	225mA/cm^2	54.93mW/cm^2 (60°C)

3. EXPERIMENTAL

The experimental section presents the methods and procedures employed to prepare, characterise the polymer, inorganic oxide filler and membranes materials. It is split into 3 sections namely material analysis, membrane characterisation and fuel cell tests.

3.1. Material Analysis

3.1.1. $TiSiO_4$ and $s-TiSiO_4$ inorganic powder synthesis

The titanium silicon oxide filler was synthesized according to the procedure previously done by (Devrim et al., 2013) (Wei, Dave and Pfeffer, 2002). 3.6g of TiO_2 (anatase< 25nm) (Sigma Aldrich) and 1.4g SiO_2 powders (fumed silica~7nm) (Aldrich) were suspended in a 60ml ethanol solution (Merck) then mixed on a magnetic stirrer for 15min and the suspension was further mixed in an ultrasonicator for 1h. The powder was allowed to dry overnight at 100°C and the residual powder was calcined at 550°C for 5h. Some amount of the prepared $TiSiO_4$ was sulfonated as reported by (Wang et al., 2008) (Ayyaru and Dharmalingam, 2015). In this method, 1g of $TiSiO_4$ powder was suspended in 15ml of 0.5M H_2SO_4 acid then ultrasonicated for an hour. The resultant mixture was dried at 100°C for 24h. The resultant powders were characterised by the FTIR and XRD analyses techniques.

3.2. Characterisation of Inorganic Oxide Powders

3.2.1. FTIR analysis

Prior to the preparation of the samples, the KBr and oxides were dried by placing them under vacuum at 100°C then mixed together and pellets were pressed. KBr pellets of TiO_2, SiO_2, $TiSiO_4$ and $s-TiSiO_4$ oxides were prepared by measuring 0.099g KBr and 0.001g of sample weights. A Thermoscientific Nicolet is10 FTIR spectrometer conducted the analysis over a range of 400- 4000cm^{-1} wave number.

3.2.2. XRD analysis

This was measured by a Rigaku Miniflex 600W XRD device using CuK radiation recorded in the 2θ range from 10º to 80º at a scan rate of 4º/min. It was done for all the

inorganic oxide samples TiO_2, SiO_2, $TiSiO_4$ and $s - TiSiO_4$. Some characteristic peaks were observed at 2θ ~25° for the $TiSiO_4$ as stated in literature by (Taheri et al., 2019).

3.3. Polymer Sulfonation

3.3.1. Sulfonation of PEEK polymer

Sulfonation ratio of victrex PEEK polymer to acid was taken as reported by (Jung et al., 2006). Before sulfonation the PEEK was placed overnight in a vacuum oven at 100°C and 200mb pressure to remove any moisture trapped within the polymer. 5g PEEK (victrex, PEEK 450 PF) was added gradually to 125ml concentrated H_2SO_4(95-97%) in a conical flask to get a 1/25 (weight/volume) mixture under vigorous stirring at 35°C. An hour was set to completely dissolve the polymer in the acid. Sulfonation reactions were initially done at 15, 18 and 24h to ascertain the optimum sulfonation conditions. After the prescribed reaction time elapsed, the resultant viscous solution is recovered by precipitating in ice cold water and washed repeatedly until a pH of 6 is attained.

Figure 0.28. *sPEEK precipitation in ice cold water and the washed samples*

The washed sPEEK samples were then dried at 60°C in an oven and left to dry off for 24h. The samples were further dried in a vacuum oven (80°C/ 200mb) for 12h.

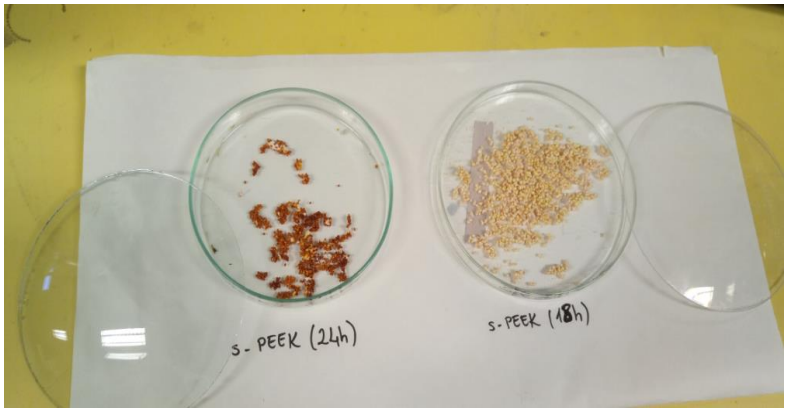

Figure 0.29. *Dried sPEEK: 24h and 18h samples*

3.4. Characterisation of sPEEK

3.4.1. Titration

The degree of sulfonation of sPEEK was determined by the titration and elemental analysis methods. This measures the quantity of sulfonic acid groups per repeat unit of sPEEK. The ion exchange capacity to quantify the number of counter ions exchangeable in solution was also determined by the titration method. In this procedure adopted from (Umsarika et al., 2018) 3, 0.1g sPEEK samples were measured and placed in identical conical flasks. Samples were placed in a 1M $NaCl$ solution, sealed and left on a magnetic stirrer for 24h to allow ion exchange to occur. After 24h, the samples were titrated with 0.05M $NaOH$ solution using phenophthalein indicator to determine the end point. Average weight and differences in initial and final titration volumes were noted as in table below.

Table 0.5. Titration Results

Sample weight	Initial volume	Final volume	Difference
A	0.4	3.5	3.1
B	3.5	6.7	3.3
C	6.7	9.9	3.2

Figure 0.30. *Titration of sPEEK*

From the titration, the IEC and DS were calculated as stated by (Selvakumar, Rajendran and Prabhu, 2019);

$$IEC(meq/g) = \frac{V_{NaOH}(ml) * C_{NaOH}(M)}{W_{dry}(mg)} \quad (3.1)$$

Here; IEC ion exchange capacity (meq/g), V_{NaOH} volume of NaOH, C_{NaOH} molar concentration of sodium hydroxide solution and W_{dry} mass of dry sample (mg).

To quantify the percentage of sulfonated repeating units of PEEK the following equation was used (Selvakumar, Rajendran and Prabhu, 2019);

$$DS\ (\%) = \frac{M_{PEEK} * IEC * 100}{(1000 - (M_{SPEEK} - M_{PEEK}) * IEC} \quad (3.2)$$

Here; M_{SPEEK} 288 and M_{PEEK} 368, these values are replaced in the equation above leading to;

$$DS(\%) = \frac{288 * IEC * 100}{1000 - 80 * IEC} \quad (3.3)$$

3.4.2. Elemental analysis

The elemental analysis measured the quantitative amount of carbon, hydrogen, nitrogen and sulphur in the sPEEK samples. By using a Thermoscientific Flashsmart CHNS/O analyser the degree of sulfonation for sPEEK was indirectly calculated to confirm the titration results for the optimum sulfonation time of 18h. In this analysis, 2, sPEEK samples measuring; 2.265 and 2.276mg were analysed for 36 min.

3.5. Membrane Casting

3.5.1. Pure sPEEK membrane casting

Before casting the membranes the dried sPEEK polymer sample was pulverised to enhance it's dissolution in the solvent.

Figure 0.31. *Pulverised sPEEK (53% DS)*

A 5wt % sPEEK/ DMAc solvent solution was prepared, the solution was placed under complete agitation on a magnetic stirrer at 45°C for 1h to allow complete dissolution of the polymer particles (Gashoul, Parnian and Rowshanzamir, 2017). Whilst casting the membranes, a sieve was used to remove any undissolved polymer particles trapped within the casting solution. The samples were then placed in an oven set at 60°C for 12 h and further dried under vacuum (100°C / 100mb) for 6h to completely remove any solvent left behind.

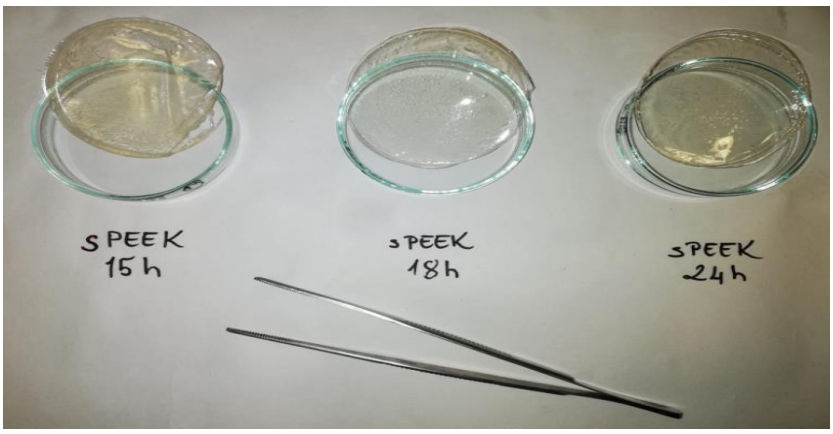

Figure 0.32. *Pure sPEEK membranes for 15, 18 and 24h reaction times*

3.5.2. Nanocomposite membrane casting

Nanocomposite membranes with varying ratios of sPEEK/ filler were measured and prepared. The ratios ranged from 1, 1.5 to 2.5 wt% as below;

Table 0.6. *Membrane casting ratios*

Membrane	$TiSiO_4$/s-$TiSiO_4$-sPEEK Ratio	DS (%)
X_1/Y_1	1/99	53
X_2/ Y_2	1.5/98.5	53
X_3/ Y_3	2.5/97.5	53

NB: $X\ /Y$ stands for sPEEK/ $TiSiO_4$ and sPEEK/s- $TiSiO_4$ (sulfonated titanium silicon oxide)

The sPEEK and $TiSiO_4$ nanocomposite inorganic oxides were measured and mixed to form 5wt% solutions with DMAc. Similar to the procedure applied for preparing pure sPEEK membranes, the mixtures were left in a water bath at 45°C for 1h and further ultrasonicated for 1h to disperse and dissolve the polymer and oxide particles respectively.

3.5.3. Pretreatment of membranes

The pretreatment step is done to achieve complete protonation of the membrane and to remove any residual solvent left behind in the drying processs. For pretreatment the membranes were immersed in a 0.5M H_2SO_4 solution at 80°C for an hour as stated by (Gashoul, Parnian and Rowshanzamir, 2017). After the protonation step, the membranes were soaked in DI water for 24 h before the proton conductivity tests.

3.6. Membrane Characterisation

After the fabrication and pretreatment processes, the characterisation of the membranes was done with different techniques as follows;

3.6.1. Proton conductivity

To measure the proton conductivity, the Electrochemical Impedance spectroscopy was used using the 2 probe method with a Solartron SI 1260 Impedance/ Gain- Phase Analyser over a frequency range of $10^2 - 10^5$Hz at an AC amplitude voltage of 10mV. To determine the in- plane proton conductivity, membrane strips of $2 * 2.5cm$ were sandwiched into a teflon conductivity cell with Pt electrodes and secured in place with screws as in Figure 3.7. The measurements were done at temperatures ranging from $30 - 80°C$ under inert and humidified conditions. The test system gave impedance values at the respective temperatures. The proton conductivity (δ) was calculated by;

$$\delta = \frac{2}{R.w.t} \qquad (3.4)$$

Here; R resistance (Ω) derived from low intersect of high frequency semicircle on a complex impedance plane re (z) axis, w width of the wet membrane sample , t thickness of the wet membrane sample and δ proton conductivity.

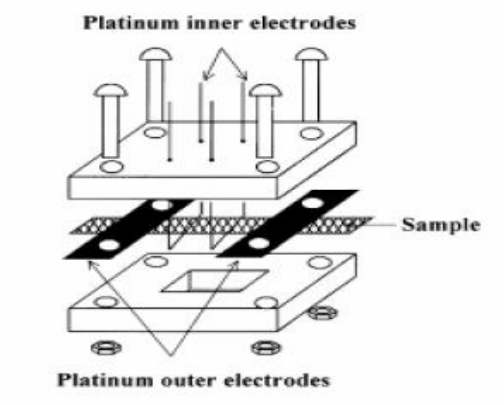

Figure 0.33. *Conductivity cell (Rikukawa, 2000)*

Figure 0.34. *Proton conductivity test system*

3.6.2. FTIR analysis

The FTIR analysis was done to evaluate the functional groups in the polymer samples by using a Thermoscientific Nicolet is10 FTIR spectrometer. The membrane films were analysed with an ATR device. For each membrane sample, three different points were analysed and the stability of the spectrum noted. The introduction of sulfonic acid groups to the pure PEEK polymer was confirmed by splitting of the C-C bond (cm^{-1}) into and cm^{-1} according to (Park, 2016).

Figure 0.35. *FTIR device*

3.6.3. XRD analysis

This analysis was done for the pure sPEEK, sPEEK/ $TiSiO_4$ and sPEEK/$s-TiSiO_4$ membranes to ascertain their crystallinity. It was conducted using a Rigaku Miniflex 600W XRD device using CuK radiation recorded in the 2θ range from 10º to 80º at a scan rate of 4º/min.

3.6.4. Thermogravimetric analysis

A Simultaneous Thermal Analyser (STA) 6000, PerkinElmer analyser conducted the TGA analysis. Samples measuring between 10- 15mg were heated in ceramic pans from 30 to 800°C at a heating rate of 10°C/min with continuous nitrogen gas at a flow rate of 50ml/min (Marrero et al., 2017).

3.6.5. Water uptake

The sPEEK membrane samples measuring $2 * 2.5cm$ were first dried in an oven at 100°C for 24h to remove any moisture trapped within them. After the prescribed time, the membrane's dry weights were recorded. Following this step, the membranes

were immersed in DI water for 24h at room temperature. A blot paper was used to remove the surface moisture then the membrane weight was taken. The method was adopted from (Jun, Choi and Kim, 2012). The water uptake of the membrane was measured by;

$$Water\ Uptake(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} * 100\% \quad (3.5)$$

Here; W_{wet} weight of wet membrane sample and W_{dry} weight of dry membrane.

3.6.6. Methanol permeability

A diffusion cell was used to ascertain the methanol permeability of the membranes. The diffusion cell comprised of 2 glass compartments, one comprising of water whilst the other had a 2M methanol solution. The membrane was fitted between the glass compartments, held in place and sealed by perforated O-shaped rings. In this system the variation in the concentration between the cells served as the driving force of the fluids. Mechanical agitation was provided in each cell by using magnetic stirrers. Inlet and outlet pipes connected the cells to water baths enabling continuous circulation of water keeping the entire system at the preferred temperature.

Prior to testing the membranes, they were immersed in DI water at 60°C to allow swelling, then they were pretreated in a 2M methanol solution to condition them. Varying methanol concentrations ranging from 0.03 to 4M were prepared and used to prepare a calibration curve. A 2M methanol solution was used in the experiments whilst the temperature was kept at 60°C and the analysis was done for durations of 1h, 2h, 3h and 4h. An ATAGO DD7 differential refractometer determined the refractive index of the measured samples. The thickness of the membrane samples were taken from 10 different positions and an average value was noted.

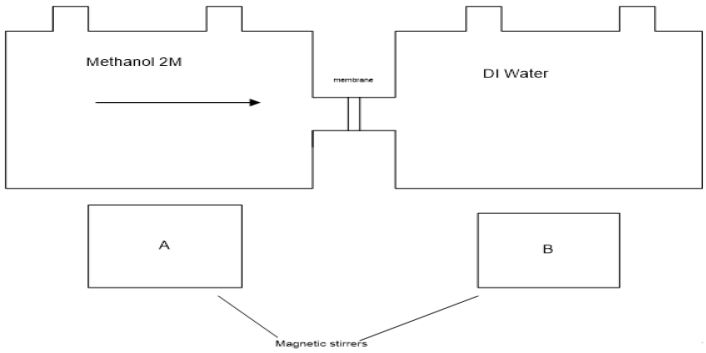

Figure 0.36. *Schematic of methanol/DI water diffusion cell*

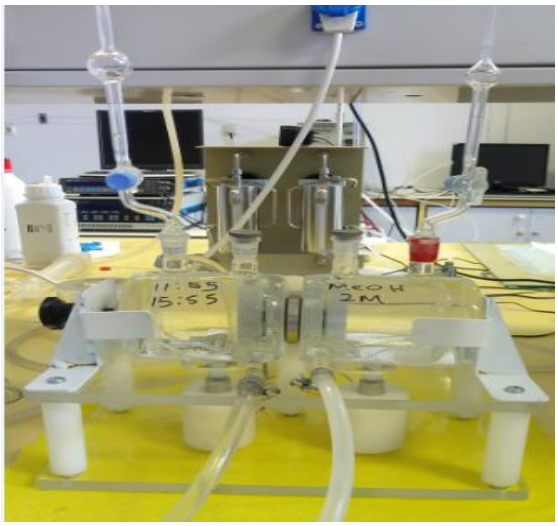

Figure 0.37. *Methanol permeability test system*

The methanol permeability is calculated according to;

$$P = \alpha * \frac{V_B}{A} * \frac{L}{C_A} \tag{3.6}$$

$$\alpha = {C_B(t)}/{t - t_0} \tag{3.7}$$

The permeability and slope coefficients are determined from the plots of methanol concentration against time.

3.6.7. Fuel cell tests

Proton conductivities of all the cast membranes were measured with the Electrochemical Impedance Spectroscopy and fuel cell tests were further conducted with similar equipment. A fuel cell test system shown in Figure 3.11(left side) below

was used to achieve this. The same system tested the prepared MEAs. The electrodes were fabricated by spraying the catalyst ink on a Elat LT1400W carbon cloth already fabricated with the GDL using a Sonotek ExactaCoat spraying device shown in Figure 3.1.1.(rightside).

The anode comprised of a 40% Pt, 20% Ruthenium powder and the cathode had a mixture of 60% Pt/C catalyst both on carbon black supports supplied by Alfa Aesar GmbH and Co. For the anode electrode the catalyst ink was prepared by mixing the 60% Pt-Ru /C catalyst with a 15% Nafion ionomer solution, Dİ water and IPA for 15 min on a Bandelin UW 2200 electronic homogeniser then the mixture was further ultrasonicated for 2h. The cathode catalyst ink consisted of a mixture of nominally 60% Pt/C catalyst, 15% Nafion ionomer solution, Dİ water and IPA.

The electrodes were weighed inbetween the coating step to attain a total loading of 4mgcm^{-2} of 70% Pt-Ru /C– 30% Nafion for the anode and 70% Pt/C- 30% Nafion for the cathode respectively with a 1:7 w/w (percent mass) water/IPA ratio. To fabricate the MEA, the hot pressing method was used by sandwiching it in kapton (130°C, 5min). Prior to the hot pressing, the membrane samples were pretreated at 80ºC in a 0.5M H_2SO_4 solution an 1h, then it was washed and immersed in DI water for 24h. The MEA had an active surface area of 5cm^2 (Figure 3.12.). A DMFC test unit analysed the performance of the cell at 60, 70 and 80 ºC with the pure and modified PEM samples. A peristaltic pump fed the methanol to the anode at a flow rate of 5ml/min whilst oxygen was supplied to the cathode at 100cc/min.

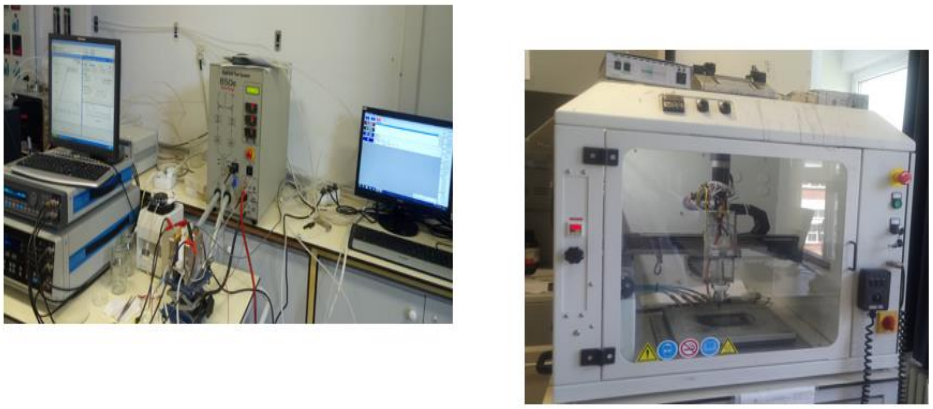

Figure 0.38. *Fuel cell test system and the Sonotek ExactaCoat spray device*

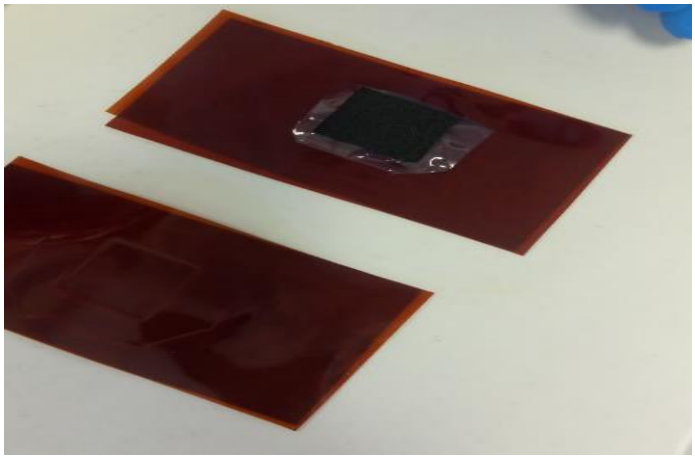

Figure 0.39. *Fabricated MEA with an sPEEK membrane, Pt/Ru anode and Pt cathode*

4. RESULTS & DISCUSSION

4.1. Titanium Silicate Synthesis

The synthesized titanium silicate nanocomposite powders were characterised by the FTIR analysis to confirm successful interaction of the titania and silica inorganic oxides and an XRD analysis was also conducted to examine the characteristic peaks of the $TiSiO_4$ crystals.

4.1.1. FTIR analysis of the oxides

In the FTIR analysis, the bands related with the separate constituent elements; titania and silica and the new resultant oxides; $TiSiO_4$ and $s-TiSiO_4$ powders were detected. For the TiO_2, its IR spectrum shown in Figure 4.1. had strong bands observed at 721 cm^{-1} and 497 cm^{-1} attributable to the distinctive vibrational manner of the TiO_2. The spectra also revealed some notable stretching of bands at 3420 cm^{-1} and 1634 cm^{-1} assigned to hydroxyl (-OH) groups from the adsorped water molecules on the oxide surface and from molecular water respectively (Zhao et al., 2007). There is an unexpected strong band evident at 2345 cm^{-1} as a result of the carbon dioxide gas phase (O=C=O) bond vibration from the environment.

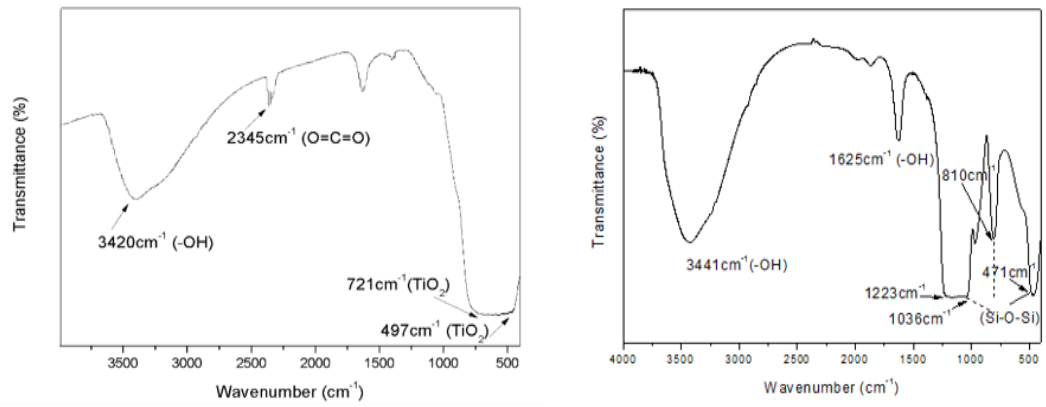

Figure 0.40. *FTIR spectrum of anatase TiO_2 and fumed SiO_2 oxides*

The same figure also shows the FTIR spectrum of the fumed silica. The strong bands observed at 471cm^{-1}, 810 cm^{-1}, 1036cm^{-1} and 1223cm^{-1} are as a result of the vibration of the Si-O-Si bond in the silica. The other bands seen at 3441 cm^{-1} and 1625cm^{-1} occurred due to the atmospheric moisture adsorped on the surface of the

oxides and some water molecules which were most likely trapped during pellet preparation step.

The $TiSiO_4$ sample was analysed first followed by the modified $s-TiSiO_4$ powder sample (Figure 4.2.). On the $TiSiO_4$ oxide spectra, the Ti- O- Ti bond stretching in the TiO_2 matrice is seen at 665cm^{-1} band whereas the SiO_2 stretching is detected at 1104 cm^{-1} band. The interaction of the oxide powders is noted at 966 cm^{-1} band where there is stretching of the Ti-O-Si bond in the $TiSiO_4$ matrice whilst in the $s-TiSiO_4$ the stretching was seen at 977 cm^{-1} band. In the $s-TiSiO_4$, the intensity of this peak was stronger revealing better interaction of the inorganic oxides influenced by the sulfonation reaction. The sulfonation reaction enhanced some bridges for the interconnection of the oxides through the Ti-O-Si bond.

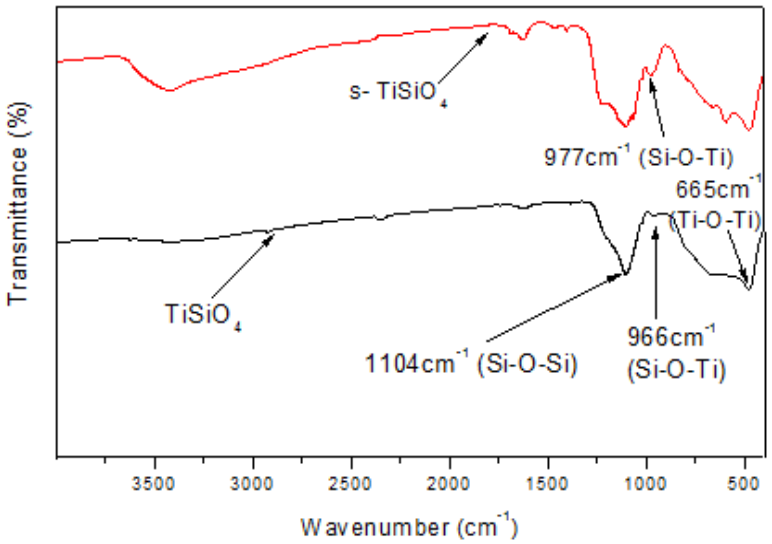

Figure 0.41. *FTIR spectrum of TiSiO₄ and s- TiSiO₄ oxide particles*

4.1.2. XRD analysis of the oxides

The XRD analysis was conducted on the separate TiO_2 inorganic oxide powders then on the hybrid oxides synthesized by the dry mixing method which used the titania and silica powders mixed with ethanol as solvent solution. Some characteristic peaks similar to those previously reported in the previous studies in literature were noted. The TiO_2 XRD spectra observed is plotted in Figure 4.4. The 2θ peaks at 25.3° and 48° confirm the anatase structure of this oxide (Theivasanthi and Alagar, 2013).

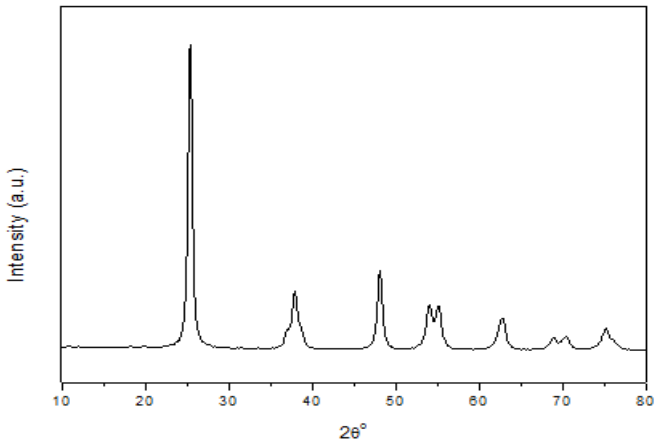

Figure 0.42. *XRD pattern of anatase TiO_2*

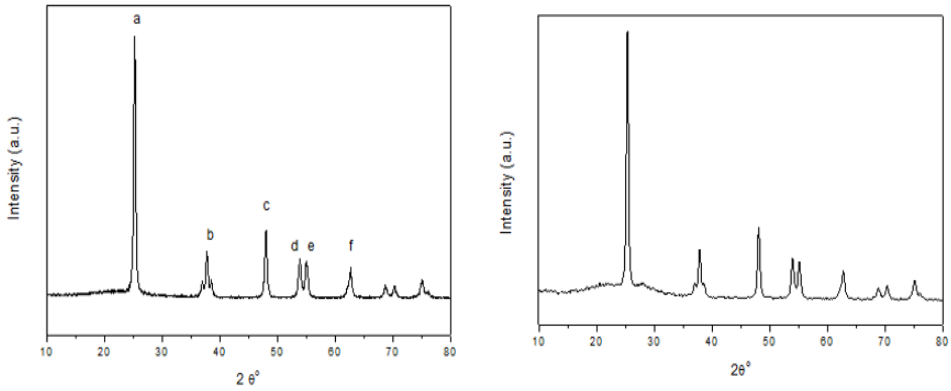

Figure 0.43. *XRD pattern of synthesized $TiSiO_4$ and s- $TiSiO_4$*

Figure 4.4. shows the XRD patterns of the synthesized $TiSiO_4$ and s- $TiSiO_4$. The patterns reveals some typical 2θ peaks at 25.3º (a), 38º (b), 48º (c), 54º (d), 55º (e) and 62.8º (f) confirming the results given in the literature (Taheri et al., 2019). Whilst the observed peaks belong to the anatase TiO_2 phase, diffraction peaks of SiO_2 are absent due to its armophous nature. The s- $TiSiO_4$ filler also showed a similar spectrum to that of the TiO_2 with the anatase peaks showing at 25.3° and 48°.

4.2. Polymer Sulfonation

The sulfonated PEEK polymer was characterised by the FTIR analysis to confirm the success of the sulfonation reaction since it shows vibrations of various functional groups such as sulfonic acid.

4.2.1. Titration

The prepared sPEEK was titrated with a 0.05M NaOH solution after staying for 24h immersed in a 1M NaCl solution as stated earlier in the experimental section. The results obtained for the 3 sulfonated samples for 15h, 18h and 24h reaction times are shown underneath;

Table 0.7. *Titration Results*

Time (h)	Temperature (ºC)	IEC (meq/g)	DS (%)
15	35	1.224	39
18	35	1.605	53
24	35	2.056	68

4.2.2. Elemental analysis

The results of the elemental quantity given as a percentage weight for the 18h sample as obtained from the elemental analyser are shown as follows.

Table 0.8. *Elemental Analysis results of the 18h sPEEK*

	Weight (mg)	C	H	N	S	O
Sample 1	2.265	62.578	4.052	0.764	4.38	28.226
Sample 2	2.276	61.763	4.29	0.688	4.475	28.784

The following formula computes the DS;

$$DS = \frac{S_E * 100}{S_T} \qquad (4.1)$$

For ultimate sulfonation, S_T is the theoretical value of $(-SO_3)$ group per repeat unit of PEEK (8.70%) and S_E is the experimental value taken from the table. A DS of 50.9% is obtained for the 18h sample.

4.3. FTIR Analysis

4.3.1. FTIR analysis of PEEK and sPEEK powders

In this segment, the FTIR analysis results for the pure PEEK and the sPEEK powders are presented to verify the sulfonation reactions that were conducted at

different reaction times. In the PEEK spectra in Figure 4.7., the strong peak at 1483cm^{-1} band is due to the C-H bond vibration which was broken into 2 bands of 1490cm^{-1} and 1469cm^{-1} during sulfonation. The sulfonation reaction led to the replacement of the C-H bond with the C- SO_3H introduced by the sulfonation reaction (Park, 2016). The symmetric and asymmetric stretching of the sulfonic acid group was identified at 1077 and 1007cm^{-1} bands. Thus these results prove that the sulfonation reactions were successful. After this analysis the membrane casting followed and the characterisation of the pure and nanocomposite membranes.

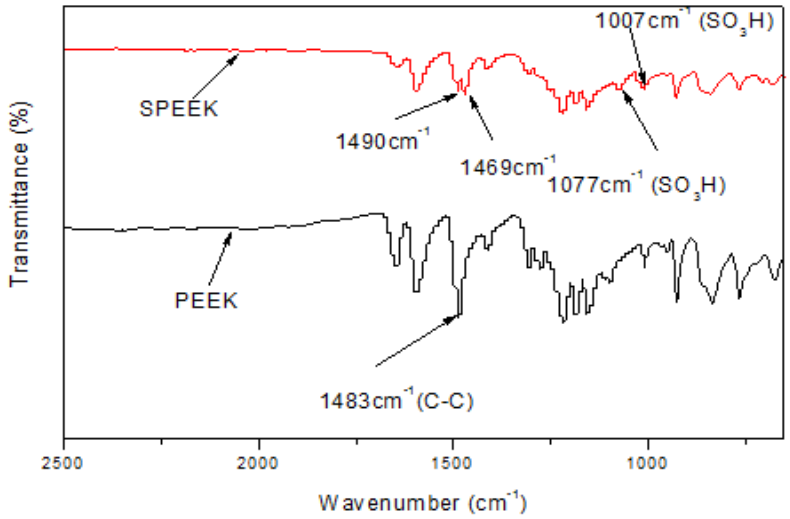

Figure 0.44. *FTIR analysis of PEEK and sPEEK powders*

4.3.2. FTIR analysis of sPEEK and sPEEK/$TiSiO_4$ membranes

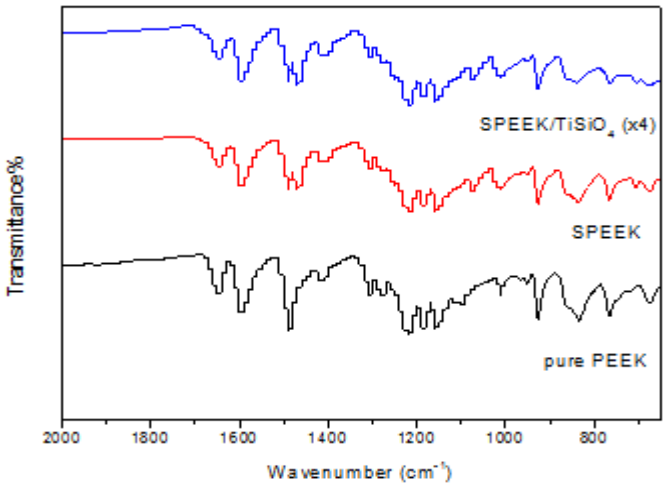

Figure 0.45. *FTIR spectra of pure sPEEK and sPEEK/ $TiSiO_4$ nanocomposite powders*

Figure 4.6. Illustrates the FTIR spectra of pure PEEK, sPEEK and the sPEEK/$TiSiO_4$ membranes having a 2.5wt% of filler. At 1483cm^{-1}, the pure PEEK's spectra shows an intense peak of the vibration of C-H bond which is split into bands of 1490 and 1469cm^{-1}. Like the sPEEK powder, the spectra of the sPEEK//$TiSiO_4$ membrane also shows the split band and its subsequent replacement of the C bond with the sulfonic acid group.

4.4. XRD Analysis of Pure SPEEK and Modified Membranes

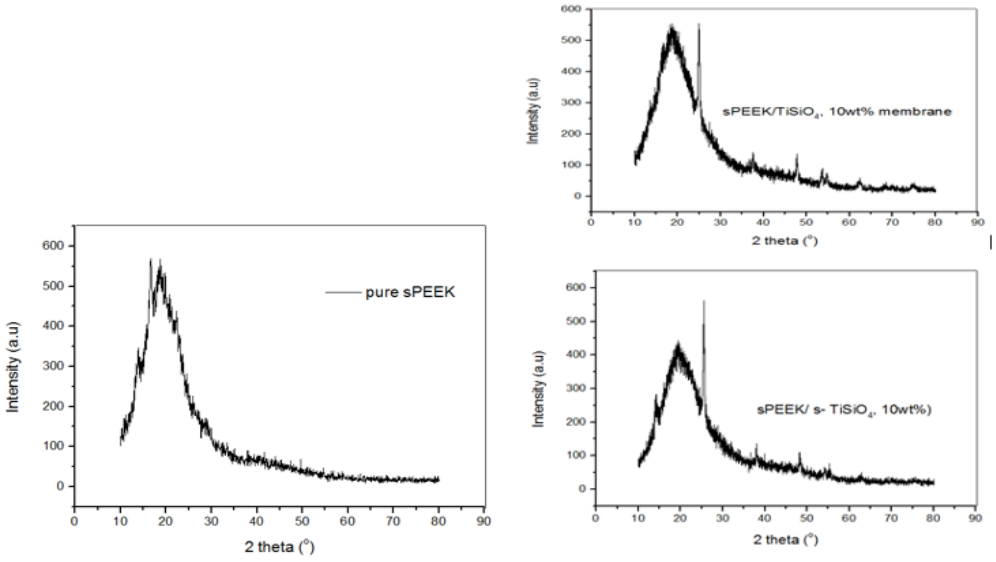

Figure 0.46. *XRD diffractogram of pure sPEEK and nanocomposite membranes (with 10% filler)*

In the titanium silicate diffraction spectrum, the characteristic TiO_2 anatase peak is shown at a 2θ angle of 48° confirming the anatase phase. The diffractogram of the 53% sulfonated sPEEK sample and its modified membranes (with a 10wt%) had patterns with a broad peak characteristic of the medium sulfonated PEEK. The diffraction pattern is in agreement with the results given in literature by (Zaidi, 2003) of the medium sulfonated PEEK sample having a diffraction pattern with only a single wide armophous diffused peak. At a 2θ angle of 18.75º for the pure sPEEK, a broad peak is observed which reveals the full amorphous property of the membranes with low crystallinity. Sulfonating the filler had the effect of making the membrane samples more amorphous giving a broader diffractogram as compared to the pure sPEEK. The armophous nature leads to polymer chains which can effortlessly move influencing quicker proton exchange ability hence the PEM can conduct more ions (Marrero et al.,

2017). The nanocomposite membranes with a 10wt% of filler showed some broad anatase peaks with little intensity.

4.5. Proton Conductivity and Water Uptake of As Cast Membranes

4.5.1. Proton conductivity of sPEEK and sPEEK/ $TiSiO_4$ composite membranes

The as cast membrane's thicknesses of the samples ranged from 55 to 117μm. As expected all the membranes exhibited high proton conductivity values at high temperatures due to an exponential rise of the catalytic activities in comparison with the lower temperature conditions. The intermolecular forces tend to diminish with an increase in temperature causing more kinetic energy to be transfered to the protons and an enhanced water uptake further propels the mobility of protons in the system (Parnian, 2016). Silica and titania are hygroscopic fillers which help by enhancing a membrane's water carrying capacity. It has been reported that membranes with high hydrophilic filler contents lead to very high water uptake and can result in the displacement of ions causing low proton conductivity.

The pure sPEEK membrane with an identical degree of sulfonation as the modified membranes had the lowest proton conductivity values over the entire temperature range as illustrated on Figure 4.11. The water uptake of the composite membranes showed an increasing trend with an increment in the filler amount confirming the hygroscopic nature of the oxide particles. As shown in Figure 4.10., the water uptake of the pristine sPEEK is the lowest having a value of 31.35% as compared with all the modified membranes. Of the $TiSiO_4$ modified membrane samples analysed, the x2 membrane with a 1.0wt% filler loading had the largest water uptake value of 50.58% and hence high proton conductivities of 5.12 and 9.38mS/cm at 30 and 80ºC respectively.

The integrated hydrophilic $TiSiO_4$ filler particles led to a significant enhancement in the water retention capabilities of the membrane samples similar to previously done studies for sPEEK modified with either titania or silica inorganic oxides (Dou et al., 2008), (Sarirchia and Rowshanzamira, 2017) (Venkatesan and Dharmalingam, 2015). However with an increasing filler ratio, the x3 membrane possessing a 2.5wt % filler content showed the least conductivity values of 2.37 and 4.63mS/cm at 30 and 80ºC.

The proton conductivity showed a decreasing trend with an increase in the filler content due to uneven distribution causing some filler agglomeration which hinders the proton transportation pathways. In previous studies for sPEEK with sulfonated/unsulfonated filler particles, SEM images of the sPEEK/SiO_2 revealed an unsmooth, non uniform distribution pattern of the filler whilst that of sPEEK/ SiO_2- SO_3H had good clarity with no separation of the different phases in the matrix (Sivasankaran and Sangeetha, 2015). In the membrane matrix, if the unsulfonated filler content exceeds 1.5wt% the intermolecular forces seem to dominate thereby hindering the effective transportation of the protons. In fairly large quantities, the agglomerated inorganic oxide particles act as as barriers blocking the passageway for protons.

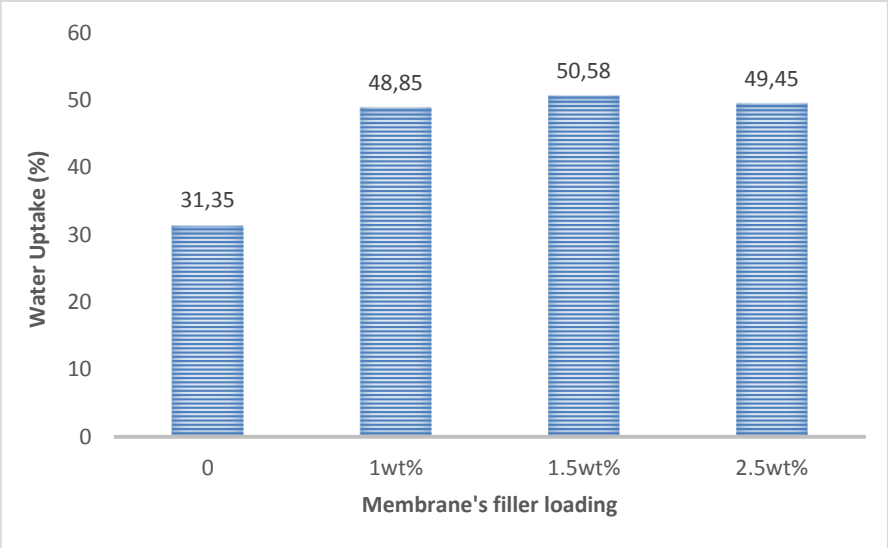

Figure 0.47. *Water uptake of pure sPEEK and sPEEK/ $TiSiO_4$ composite membranes*

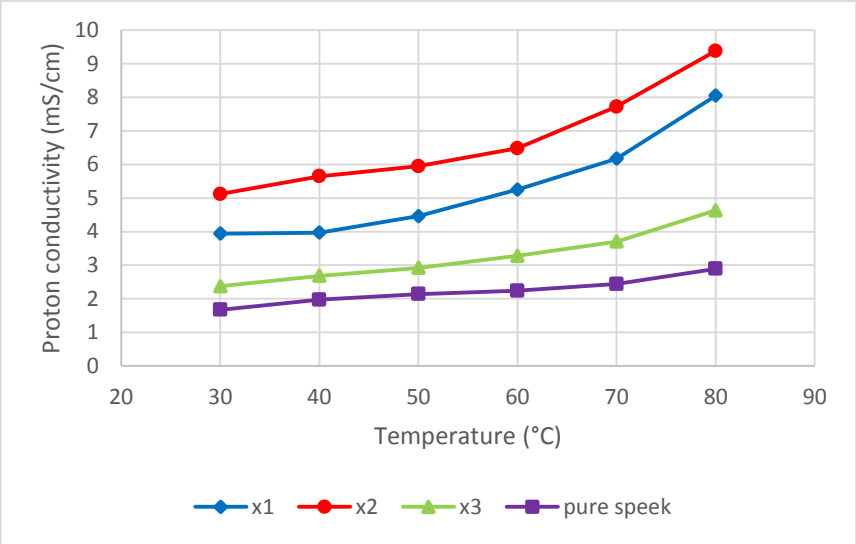

Figure 0.48. *Proton conductivities of pure sPEEK and sPEEK/ $TiSiO_4$ composite membranes*

4.5.2. Proton conductivity of sPEEK and sPEEK/ s -$TiSiO_4$ composite membranes

The sulfonated filler's existence led to some extra pathways for the movement of protons due to the absorption of some molecular water on the surface of the filler particles (Sivasankaran and Sangeetha, 2015). All the membranes with the sulfonated filler showed enhanced proton conductivities and water uptake beyond that of the pristine sPEEK. In contrast to the trend shown by the unsulfonated filler membranes, the y3 membrane with a 2.5wt% filler loading exhibited the highest proton conductivity values over the entire temperature range. This membrane had a water uptake of 51.4% higher than all the membranes. Sulfonating the filler had an effect on reducing agglomeration leading to an even dispersion of the inorganic oxide particles. With low filler content of 1.0wt%, the membrane showed low proton conductivity values. The y3 membrane's proton conductivity increased by nearly 4 times beyond that of the pure speek polymer sample from 30 ºC to 80ºC. Sulfonating the filler reduces the degradation of proton conductivity of membrane samples with a high filler loading.

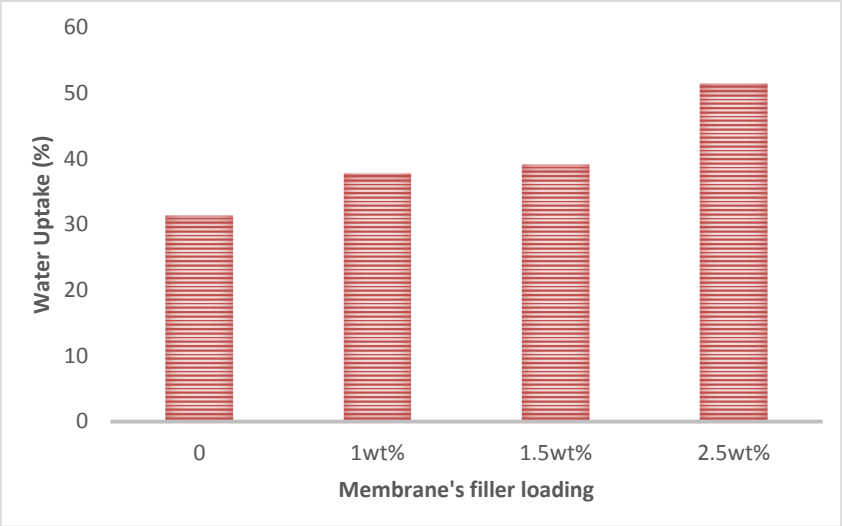

Figure 0.49. *Water uptake of sPEEK/ s- $TiSiO_4$ composite membranes*

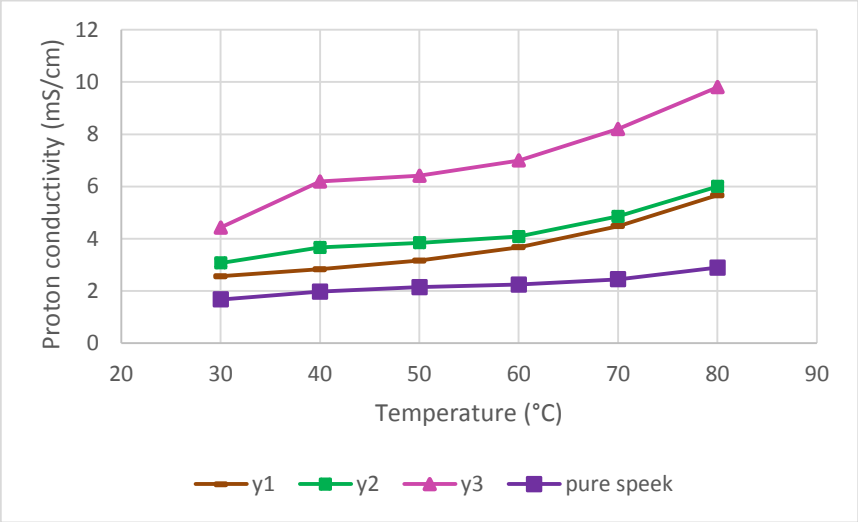

Figure 0.50. *Proton conductivities of pure sPEEK and sPEEK/ s- $TiSiO_4$ composite membranes*

4.5.3. Comparison of proton conductivities and water uptake of pristine sPEEK, sPEEK/ $TiSiO_4$ and sPEEK/ s -$TiSiO_4$ composite membranes

The x-series membranes comprised of the unmodified $TiSiO_4$ filler whilst the y-series ones consisted of the sulfonated ($s - TiSiO_4$) filler. Both the x and y membranes had a similar filler loading content of 1%, 1.5% and 2.5% from the first to the third respectively. The x2 and y3 membranes had elevated conductivity values of 9.38 mS/cm and 9.80mS/cm at 80 ºC respectively. Sulfonating the polymer had a good effect on the performance of the membrane samples with a high filler loading. The sPEEK/ $TiSiO_4$ composite membranes generally had higher water uptake values greater than the sPEEK/ s- $TiSiO_4$ membranes. Of all the membranes, the pure unmodified sPEEK

membrane showed the least proton conductivity values over the entire temperature range. Since protons make use of water as a transportation medium, the pure unmodified sample had a low water uptake of 31.35% as compared to all the modified membranes. For the low filler loading samples of 1.0 and 1.5wt%, the conductivity values were higher than for the sulfonated ones. However with a 2.5wt% the y3 sample showed better performance than the x3 due to reduced agglomeration. With filler sulfonation, there was a reduced hindrance to the smooth flow of protons. The sulfonated filler particles in the polymer support proton transportation at low and elevated temperatures by using the vehicular and Grotthuss mechanisms. It can be concluded that the sulfonated oxide particles are mostly effective in membrane samples with a high filler loading.

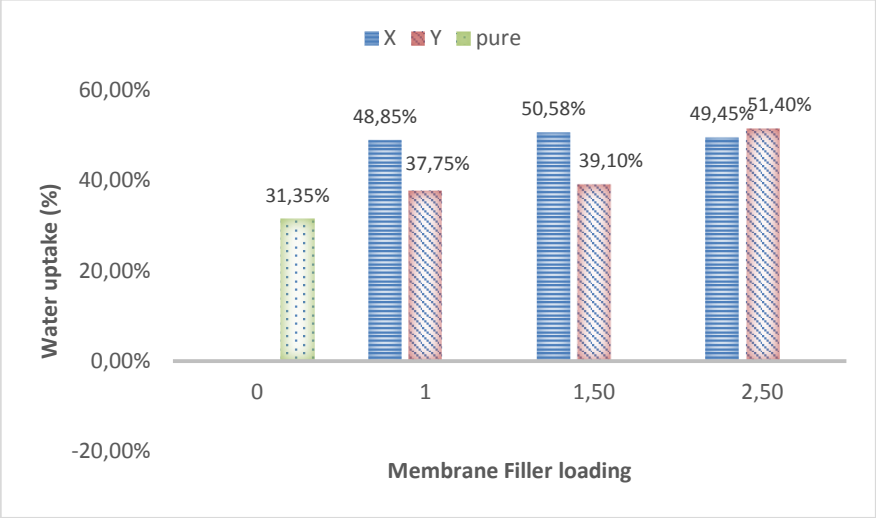

Figure 0.51. *Water uptake comparison of sPEEK / TiSiO4 and sPEEK/ s- $TiSiO_4$ composite membranes*

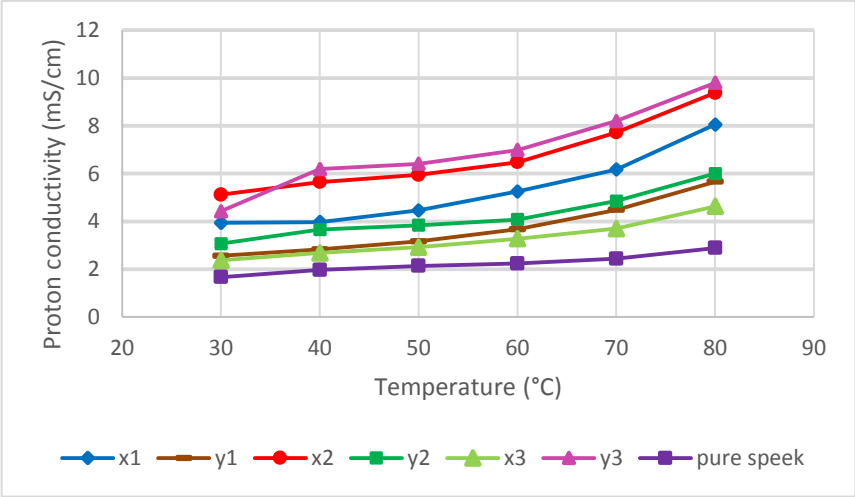

Figure 0.52. *Proton conductivity comparison of pure sPEEK and sPEEK/ $TiSiO_4$/ s-$TiSiO_4$ composite membranes*

4.7. Thermogravimetric Analysis

4.7.1. Thermogravimetric analysis of PEEK and sPEEK

The TGA was conducted on samples measuring 10-15mg over a temperature range of 30 to 800ºC at a heating rate of 10ºC/min under nitrogen atmosphere with a flow rate of 50ml/min. For the PEEK polymer, only a single major weight loss region was observed showing its high thermal stability. It's thermal degradation begins at 550ºC in agreement with the results of PEEK samples reported previously in the literature which decomposed at temperatures between 500 and 550ºC (Xing et al., 2004) (Parnian, Gashoul and Rowshanzamir, 2017). (Parnian, 2016). Sulfonation however affects the thermal degradation behaviour of the PEEK polymer and there are 3 main weight loss regions for the new sulfonated polymer. For the sPEEK polymer, the initial weight loss region began at a temperature below 100ºC due to the water loss and at around 233ºC the residual DMAc solvent loss not completely removed by vacuum drying also led to reduction in the sample weight. The percentage loss of the sample weight was confirmed by the DTG curve. The other 2 degradation stages are illustrated on the DTG curve in Figure 4.20. At around 323ºC, desulfonation occurs in which the SO_3H groups catalytically break off from polymer chain leading to the sample's weight loss. The final weight loss region occurs at 542ºC when pyrolysis thermally decomposes the polymeric backbone chain.

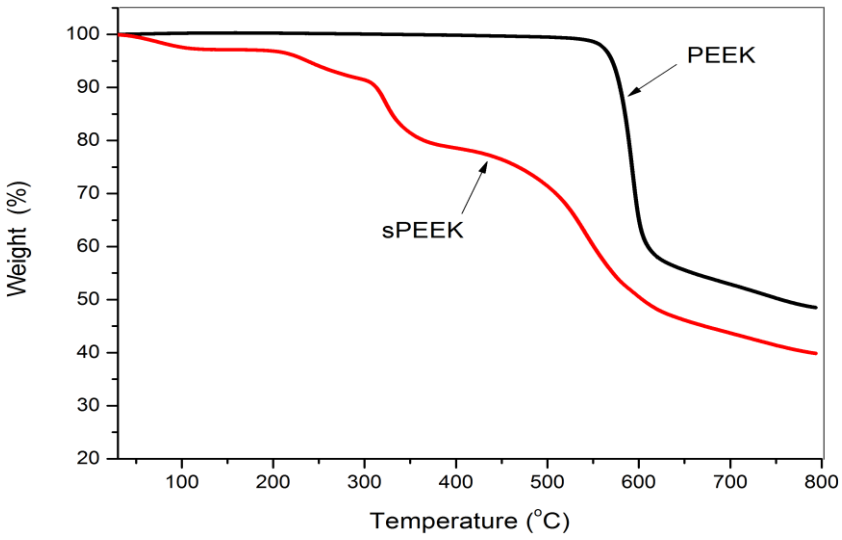

Figure 0.53. *TGA curve of PEEK and sPEEK*

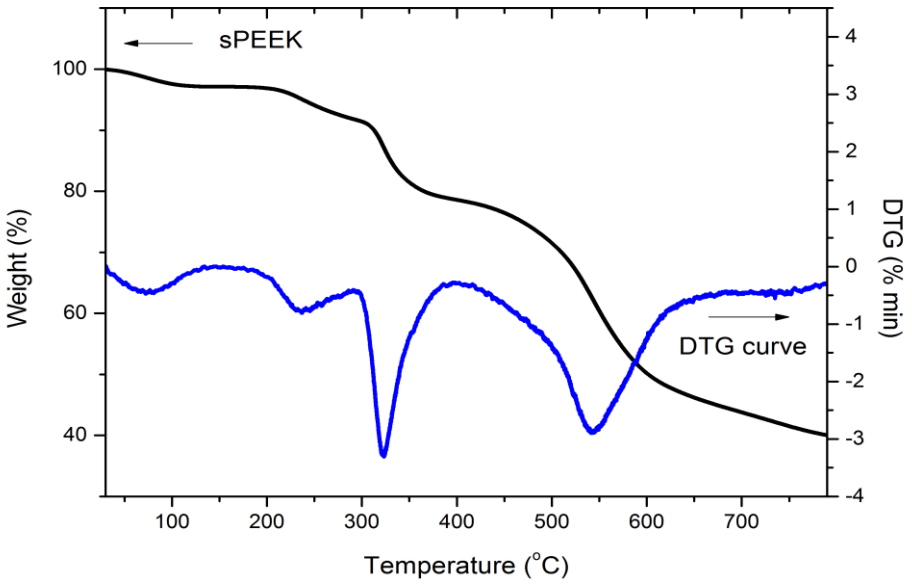

Figure 0.54. *TGA curve of sPEEK and its derivative*

4.7.2. Thermogravimetric analysis of sPEEK and sPEEK/ $TiSiO_4$ membranes

A plot of the TGA curve for sPEEK and its composite membranes is shown below. At around 100ºC, the first drop in weight of the membranes was observed due to moisture loss and at 209ºC the remaining DMAc solvent loss was evident. The thermal degradation pattern of the composite membranes was almost similar to that of the pure sPEEK. The curves for composite membranes showed a shift in the second

decomposition temperature to a lower temperature region. The second significant weight loss for the splitting of sulfonic acid groups of the sPEEK composite membranes happened at 320ºC. At 542ºC, similar to the pure polymer sample, the hydrophobic backbone completely decomposes until a final constant temperature is attained.

The sPEEK's hydrophobic backbone has a weak interaction with the inorganic particles leading to the slight shift in thermal degradation behaviour. An increase in the $TiSiO_4$ filler content results in easier degradation of the polymer sample. Poor interaction of the sulfonic group with the polar groups of the $TiSiO_4$ oxide is another cause of this shift. Similar to the literature, all the composites exhibited high water uptake hence showed low thermal stability but those which had a higher filler loading had better thermal stability (Ji, Tay and Li, 2017).

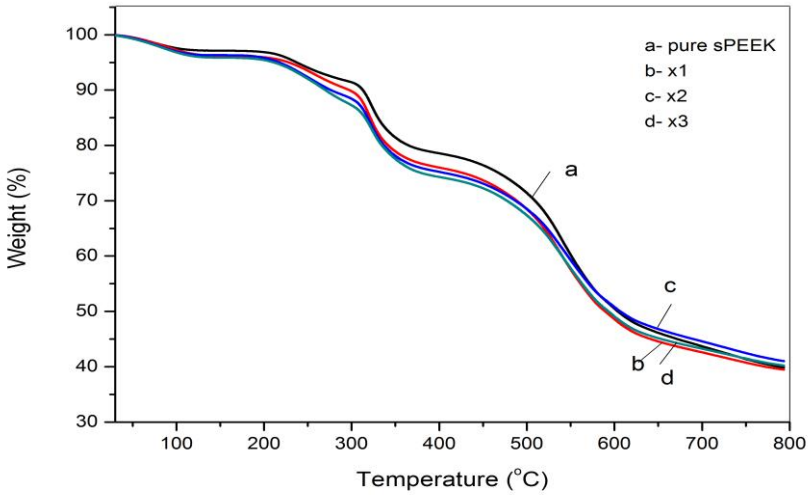

Figure 0.55. *TGA curve of sPEEK and sPEEK/ $TiSiO_4$ membranes*

4.7.3. Thermogravimetric analysis of sPEEK and sPEEK/ s- $TiSiO_4$ membranes

The thermal decomposition of the sPEEK/ s- $TiSiO_4$ nanocomposite membranes is shown in Figure 4.22. For the y1 membrane there was a shift in the degradation pattern as compared to the pure sPEEK decomposing at slightly higher temperature of 544ºC. The second weight loss for the catalytic splitting of the sulfonic groups occurred at 350ºC revealing greater stability of this membrane. This membrane had a lower water uptake than the x1 membrane so it's thermal stability improved with a delay in its degradation. Sulfonating the polymer may also have led to improved interaction between the filler and polymer matrix increasing its decomposition temperature. Nano

TiO_2 particles do not have any active hydroxyl groups on their surface but the SiO_2 nanoparticles possess some surface hydroxyl groups. These polar groups may have altered the polymer structure. Accordingly as the filler ratio increased, the membranes tend to be less thermally stable.

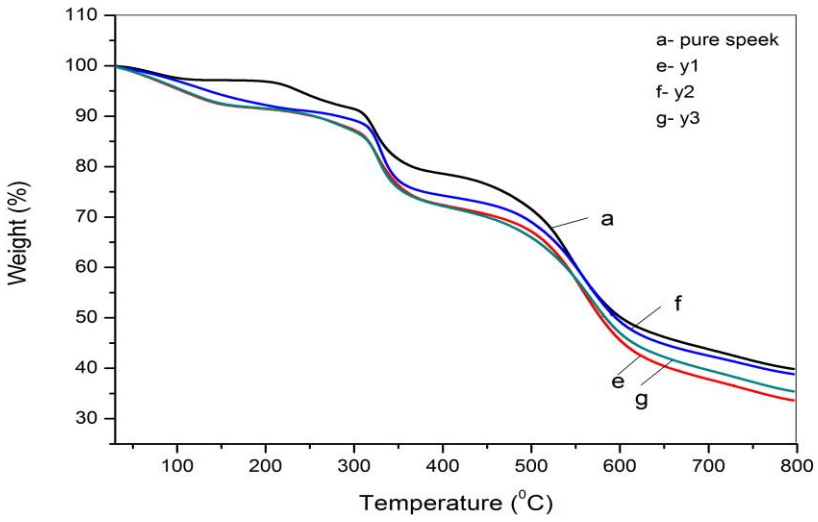

Figure 0.56. *TGA curve of sPEEK and sPEEK/ s- $TiSiO_4$ membranes*

4.7.4. Comparison of thermal stabilities of sPEEK/ $TiSiO_4$ and sPEEK/ s- $TiSiO_4$ membranes

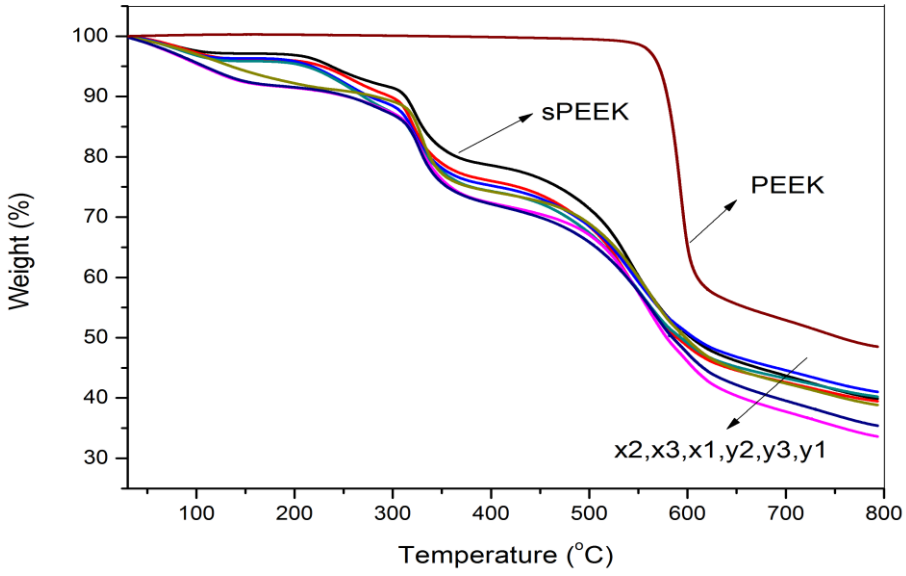

Figure 0.57. *Thermal Stability of all membranes*

The sPEEK/ $TiSiO_4$ membranes showed better thermal stability than the sPEEK/ s-$TiSiO_4$ membranes. The second weight loss region for all the composite membranes has a higher percentage weight loss because at this temperature, the added inorganic oxide particles also decompose. In the last degradation stage, the x2 membrane sample exhibited better stability hence the filler particles slow down the hydrophobic chain decomposition.

4.8. Methanol Permeability

The methanol permeability was analysed by using a home made test system as stated in section 3. Initially a calibration curve was prepared for the determination of the concentration of methanol that permeates to the other glass cell containing deionised water. Experiments were conducted for durations of 1h, 2h, 3h and 4h. The samples collected were measured by using a differential refractometer to determine their refractive indices. The experiments were done on the pure sPEEK, sPEEK/ $TiSiO_4$ and the sPEEK/ s-$TiSiO_4$ membranes to evaluate their methanol permeabilities.

4.8.1. Permeability of pure sPEEK, sPEEK/ $TiSiO_4$ and Nafion 117

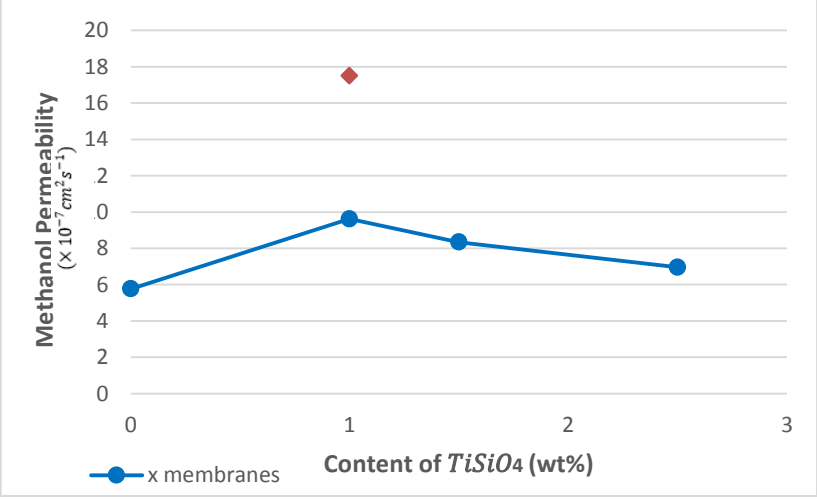

Figure 0.58. *Methanol permeability of pure sPEEK, sPEEK/ $TiSiO_4$ and Nafion 117*

The graphic, Figure 4.2., above shows the methanol permeability values of the pure sPEEK, sPEEK/ $TiSiO_4$ and the Nafion 117 membranes. The tested membranes had average thicknesses in the range of 0.076- 0.208mm taken from 10 different

positions of their surfaces. As illustrated, the Nafion 117 membrane exhibited a cross over value of $1.75 \times 10^{-6} cm^2 s^{-1}$ much higher than that of the sPEEK based membranes. Nafion has a microstructure with wide channels which have a negative impact on its methanol permeability (Kreuer, 2001). These wide channels serve as pathways for methanol to freely move within the membrane matrix and permeate across to the other side. The pure sPEEK had the lowest permeability value of $5.77 \times 10^{-7} cm^2 s^{-1}$ in comparison with the other sPEEK/ $TiSiO_4$ composite samples.

The water uptake of the pure sPEEK was the lowest of all the membrane samples permitting fairly less methanol to infiltrate through. This agrees with what was stated by (Kalappa and Lee, 2007) that a low water uptake minimises the methanol permeate. Since the filler is hygroscopic in nature, it enhances the water uptake thereby creating more pathways for methanol to cross over with ease across the PEM. All the modified membranes exhibited higher water uptake than the pure sPEEK, creating some extra routes within the membrane matrix leading to more methanol permeating through these channels. The methanol moves by being dragged by hydronium (H_3O^+) ions as a result of it's interaction with hydroxyl (-OH) groups. A decreasing trend is observed for the sPEEK/ $TiSiO_4$ nanocomposite membranes with an increase in the filler loading. The x3 membrane with a 2.5wt% of $TiSiO_4$ filler had a lower permeability value better than the other modified ones. This was influenced by the presence of a higher $TiSiO_4$ oxide content whose particles act as a barrier blocking the flow of methanol within the membrane matrix.

4.8.2. Methanol Permeability of pure sPEEK, sPEEK/ s -$TiSiO_4$ and Nafion 117

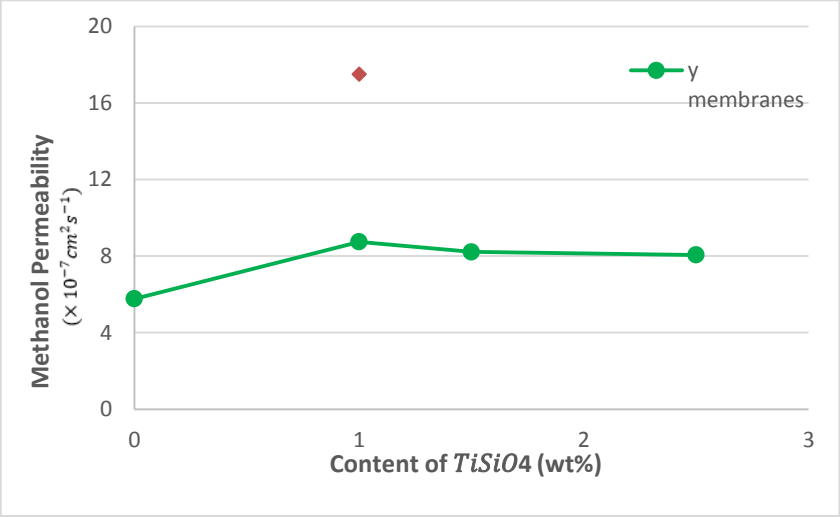

Figure 0.59. *Methanol permeability of pure sPEEK, sPEEK/s-$TiSiO_4$ and Nafion 117*

The methanol permeability of the sPEEK/ s-$TiSiO_4$ composite membranes are shown above. Similar to the above discussion on the methanol permeability of sPEEK/ TiSiO4, the pure sPEEK membrane also had a lower methanol permeability value as compared to the sPEEK/ s- $TiSiO_4$ nanocomposite membranes. Sulfonation of the filler changed the membrane's structure thereby increasing the methanol flow across the PEM. The sPEEK/ s -$TiSiO_4$ nanocomposite membranes also exhibited enhanced water uptake capacity as compared to the pure sPEEK sample due to the hydrophylicity of the filler. As compared with the $TiSiO_4$ pure filler membranes, the 1.0wt% sulfonated filler one had a fairly lower permeability value. The x3 membrane with a 2.5wt% filler content had a methanol cross over value of $6.96 * 10^{-7}\text{cm}^2s^{-1}$ whilst the y3 with a similar filler amount had a value of $8.06 * 10^{-7}cm^2s^{-1}$ due to extra hydrophylicity added to the membrane through the sulfonated oxide.

4.8.3. Selectivity of membranes

A plot of the electrochemical selectivity of the x membranes with varying filler ratios is shown on Figure 4.25. The selectivity revealed an increasing trend with a rise of the filler content from 1.0 to 2.5wt%. The pure sPEEK membrane had the lowest selectivity value of 3882S sec/cm^3 whilst the x2 sample with a 1.5wt% filler loading had the largest selectivity value of 7770S sec/cm^3. This membrane sample had good proton conductivity values higher than the pure sPEEK's by a magnitude of about 4 at 80°C. Despite its methanol permeability being higher than the pure sPEEK's, the proton

conduction was enhanced enough to improve the selectivity. On the other hand, the x1 and x3 membranes had low selectivity values of 5457 and 4713Ss/cm^3 respectively due to the former's high methanol permeability and the later's inferior proton conductivity at 60°C. With a low filler loading, the methanol crossover of the x1 membrane increased because of enhanced water uptake whilst the x4 membrane sample had some agglomeration of the filler particles taking place leading to proton conductivity degradation.

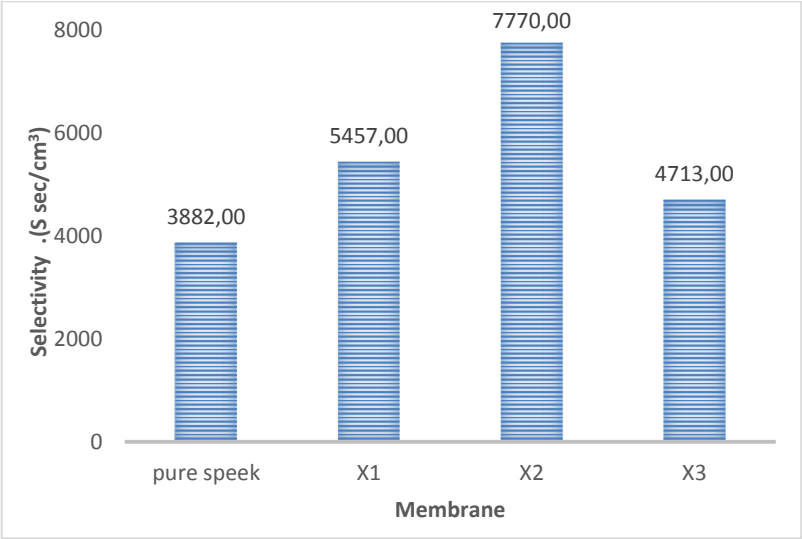

Figure 0.60. *Selectivity of pure sPEEK and sPEEK/ $TiSiO_4$*

The y3 membrane (sPEEK/s-$TiSiO_4$) with a 0.5wt% of filler showed the best selectivity value of 8672S s/cm^3 due to its high proton conduction ability of 6.99mScm $^{-1}$ at 60°C. All the membranes revealed an increasing trend in the selectivity from the pure to the y3 with a 2.5wt% of s-$TiSiO_4$. It had a selectivity value much better than the pure sPEEK membrane. On the other hand, the y2 sample showed a low selectivity value in comparison with all the sulfonated filler samples.

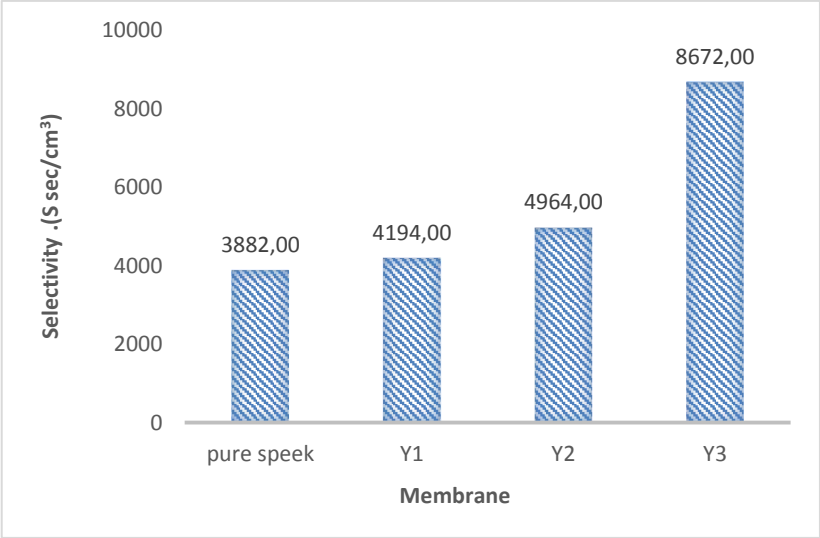

Figure 0.61. *Selectivity of pure sPEEK and sPEEK/ s- $TiSiO_4$*

Comparing the unsulfonated and sulfonated filler membrane samples, the y3 sample with a 2.5wt % filler showed the highest selectivity value of 8672S s/cm^3 whilst the pure membrane sPEEK had the lowest value of 3882Ss/cm^3. Of all the modified membranes, the y1 membrane with a 1.0wt% filler had the lowest selectivity because of its low proton conductivity value of 3.67mS/cm at 60°C. In small amounts, the sulfonated filler particles have a minimal effect on improving proton transportation and acting as an effective barrier to excess methanol flow. As the filler loading increases, the conductivity and methanol blocking is enhanced. Some fuel cell tests were further done to evaluate the real performance of all the membranes samples.

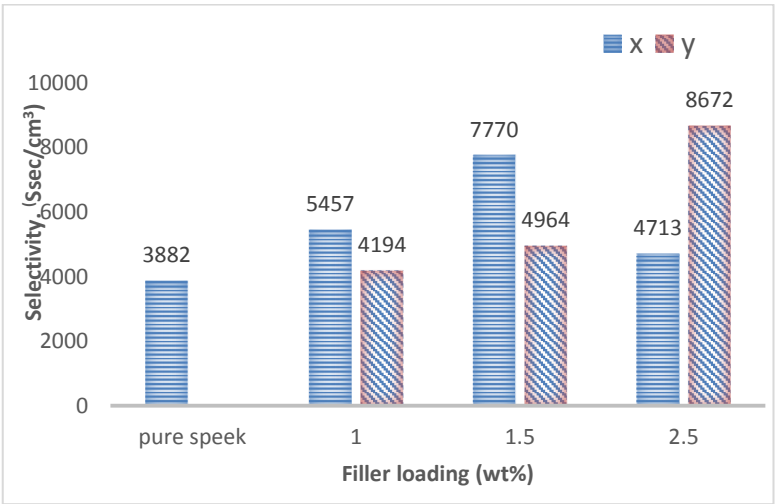

Figure 0.62. *Selectivity of pure sPEEK , sPEEK/ $TiSiO_4$ and sPEEK/s- $TiSiO_4$*

Table 0.9. *Proton conductivities, water uptake, methanol permeability and relative selectivity of sPEEK and its composite membranes*

Membrane	$TiSiO_4$ content weight (%)	Proton Conductivity ($mScm^{-1}$)			Water Uptake (%)	Methanol Permeability ($*10^7 cm^2/s$)	Selectivity ($*10^3 Ssec/cm^3$)
		60°C	70°C	80°C	30°C	60°C	
sPEEK	0.0	2,24	2,44	2,89	31,35	5,77	3.88
sPEEK, x1	1.0	5,25	6,17	8,05	48,85	9,62	5.46
sPEEK, x2	1,5	6,48	7,72	9,38	50,58	8,34	7.77
sPEEK, x3	2,5	3,28	3,70	4,63	49,45	6,96	4.71
sPEEK, y1	1.0	3,67	4,48	5,66	37,75	8,75	4.19
sPEEK, y2	1,5	4,08	4,85	6,00	39,1	8,22	4.96
sPEEK, y3	2,5	6,99	8,2	9,8	51,4	8,06	8.67

4.9. Fuel Cell Performance Tests

The DMFC performance was measured by a Scribner Fuel Cell Test station. Plots of polarisation curves (voltage vs current density) and power density vs current density relationships were generated at 60, 70 and 80°C. A description of the fuel cell performance is given by the power plot. Open- circuit voltages (OCV) for the fuel cell with varying membrane samples when they are at equilibrium with no reactions taking place or any current flowing are recorded. The methanol and oxygen where fed at constant feed rates of 5ml/min and 100cc/min respectively to the anode and cathode respectively. The polarisation curves showed a sharp decrease in the activation polarisation zone. On the electrode's surface slow oxidation reactions lead to significant activation losses. Some fraction of the voltage was lost in propelling chemical reactions that transfer electrons. In the ohmic polarisation zone, the samples revealed a gradual decrease in the voltage due to some resistance in the electron transportation which also result in voltage reduction. At the electrode surfaces loss of the concentration of the feed fuel takes place due to its continuous consumption causes the final voltage losses.

4.9.1. Pure sPEEK and sPEEK/$TiSiO_4$ membrane performance at 60, 70 and 80°C

4.9.1.1. Performance of x1, x2 and x3 membrane at 60°C

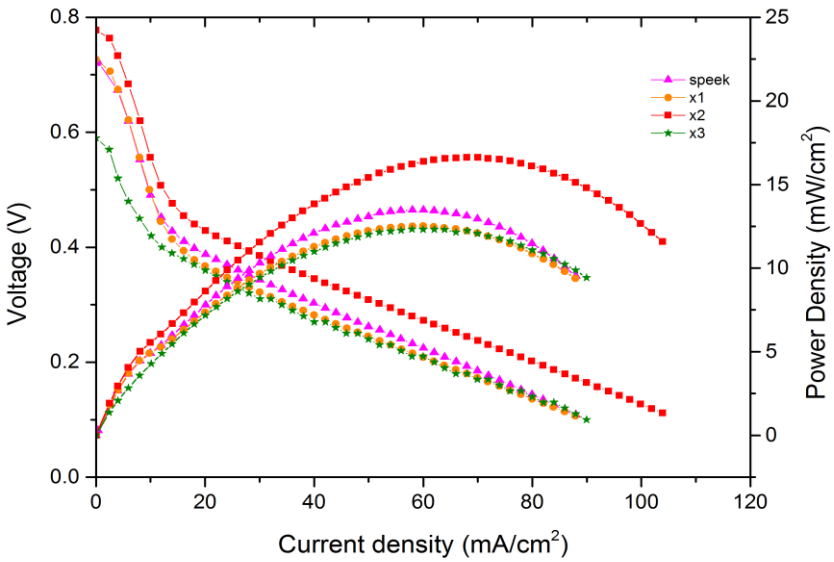

Figure 0.63. *Polarisation and Power Density curves of pur sPEEK, x1, x2 and x3 membranes at 60℃*

At 60°C, the x2 membrane with a 2.5wt% filler loading showed the best performance with a maximum power density of 16.62mWcm^{-2} and an OCV of 0.78V. The x3 membrane with a 2.5wt% filler had the least OCV and current density values as shown. At lower temperatures, there are high intermolecular forces hence less kinetic energy is transferred to the electrons to move effectively to the outside circuit. The pure sPEEK had a better performance of 13.5mWcm^{-2} fairly higher than the x1 membrane with a 1.5wt% filler content having a maximum power density of 12.52mWcm^{-2}.

4.9.1.2. Performance of x1, x2 and x3 membrane at 70°C

All the membranes exhibited improved performance at 70°C because of increased reaction kinetics. The x2 sample with a 1.0wt% had the best performance with a power density value of 20.95mWcm^{-2} having increased from 16.62mWcm^{-2} at 60°C. This membrane attained a maximum current density of 137.87mAcm^{-2}. The x3 membrane had the smallest power density value of only 12.33mWcm^{-2} with a current density of only 89.96mAcm^{-2}. This is due to low proton transportation capabilities of the membrane coupled with slow reaction kinetics at the anode surface.

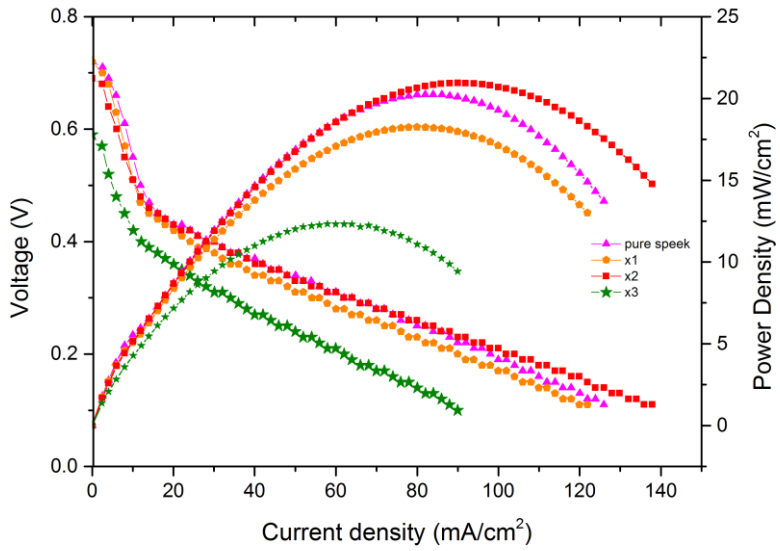

Figure 0.64. *Polarisation and Power Density curves of pure sPEEK, x1, x2 and x3 membranes at 70℃*

4.9.1.3. Performance of x1, x2 and x3 membrane at 80°C

As the temperature increased to the final operational value of 80°C, all the membranes exhibited good performances with a similar pattern as observed at 60 and 70°C. The x2 sample shows good performance with high current and power densities whilst the x3 had inferior performance. At these conditions, the x2 membrane had a higher power density of 29.21mWcm^{-2} with an OCV of 0.68V. The x3 membrane suffered from agglomeration of its $TiSiO_4$ filler particles therefore it had inferior fuel cell performance in the DMFC having a power density of 19.16mWcm^{-2} with an OCV of 0.59V. Despite it possessing a low methanol cross over value of 6.96cm^{2}s^{-1}, it had inferior proton conduction capabilities in the entire temperature range of 30 to 80°C. The pure sPEEK and x1 samples had good conduction behaviour in the real DMFC with power densities of 27.71 and 28.94mWcm^{-2} respectively.

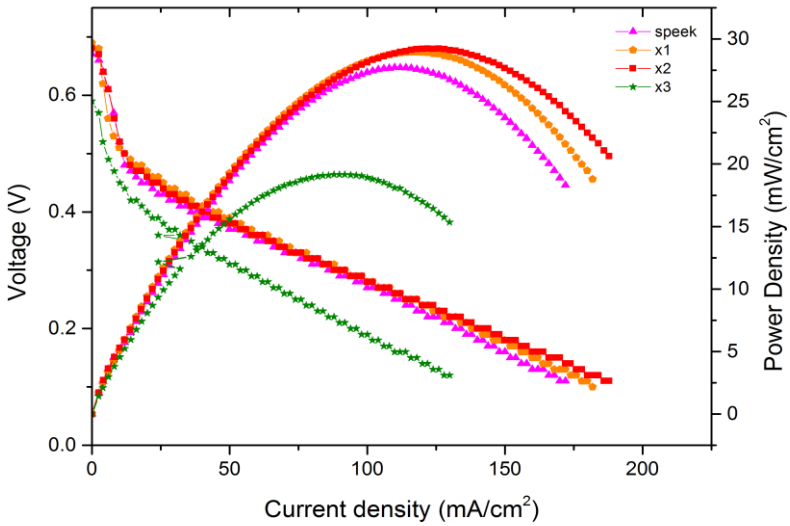

Figure 0.65. *Polarisation and Power Density curves of pure speek, x1, x2 and x3 membranes at 80℃*

4.9.2. Pure sPEEK and sPEEK/s- $TiSiO_4$ membrane performance at 60, 70 and 80°C

4.9.2.1. Performance of y1, y2 and y3 membrane at 60°C

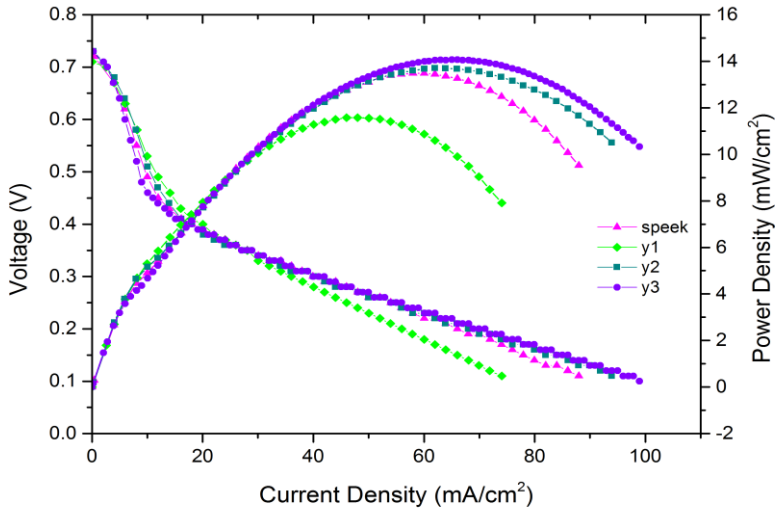

Figure 0.66. *Polarisation and Power Density curves of pure sPEEK, y1, y2 and y3 membranes at 60℃*

The sulfonated filler membrane samples showed different performance patterns in the real DMFC system in contrast to the unsulfonated filler ones. At 60°C, the y3 membrane with the 2.5wt% of s- $TiSiO_4$ oxide had the best performance having a power density of 14.07mWcm^{-2}. The y2 membrane had similar performance to the y3 one both

having OCVs of 0.73V since both had low methanol permeabilities at this temperature. As compared to the inferior performance of the x3 sample with a filler loading of 2.5wt%, the y3 showed enhanced working ability in the real DMFC. Sulfonation led to better dispersion, good interaction of filler with the membrane matrix as well as increased channels for protons to propel through. For these samples, the y1 showed the lowest power density value of 11.58mWcm^{-2} with a current density of 63.21mA/cm^{-2}. A low filler content had minimal effects on the performance of the sulfonated samples. At 60°C, the membranes would not have gained stability to work effectively in the fuel cell.

4.9.2.2. Performance of y1, y2 and y3 membrane at 70°C

At the higher temperature all the membranes showed enhanced performance better than at 60°C. The y3 sample had a power and current density values of 41.44 and 250.44 mA/cm^{-2} respectively. Despite the pure sPEEK membrane having a low methanol permeability of 5.77*10^{-}7cm2s^{-1}, it had poor proton conductivity values. The performance of the y3 membrane sample doubled from that of the pure sample which had a power density of 20.24mW/cm^2 and current density of 125.96mA/cm^{-2}.

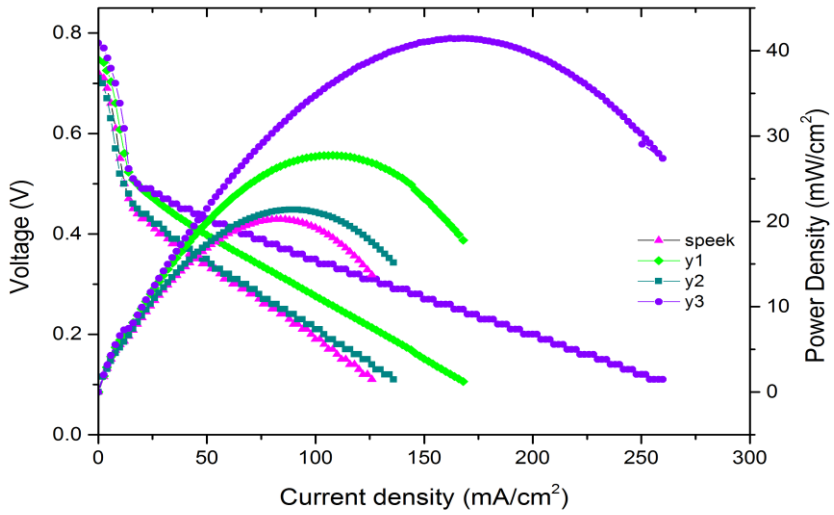

Figure 0.67. *Polarisation and Power Density curves of pure sPEEK, y1, y2 and y3 membranes at 70℃*

4.9.2.3. Performance of y1, y2 and y3 membrane at 80°C

The best DMFC performance for the sulfonated filler membranes was the y3 sample which had a maximum power density of 49.14mWcm^{-2}, 3.5 times higher than the membrane's performance at 60°C. Its current density reached 307.88mA/cm^{-2} far

greater than that of the other samples analysed. This is attributable to the better stability and good dispersion of the filler particles in the membrane matrix. The y1 showed inferior performance with a current density of 27.71mWcm^{-2} similar to that of the pure unmodified membrane. It had a current density of only 167.91mA/cm^{-2} whilst the pure one had 171.98mA/cm^{-2}.

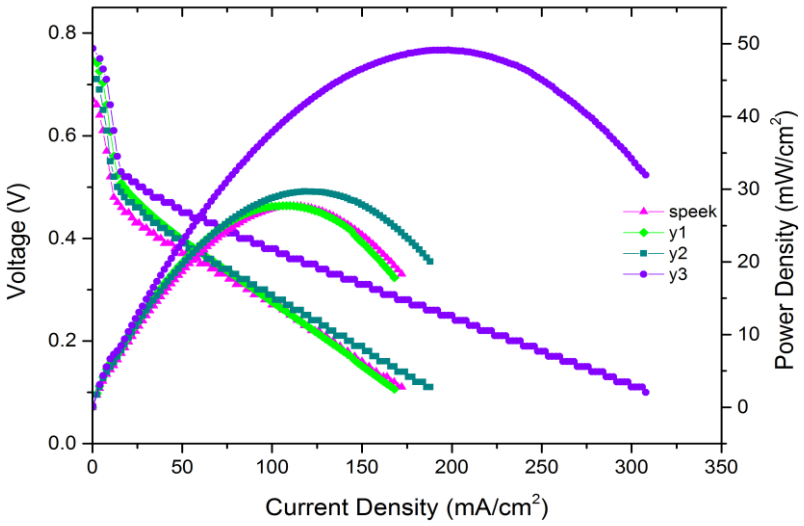

Figure 0.68. *Polarisation and Power Density curves of pure sPEEK, y1, y2 and y3 membranes at 80℃*

4.9.3. Comparison of the performance of x2 and y3 membranes at 60, 70 and 80°C

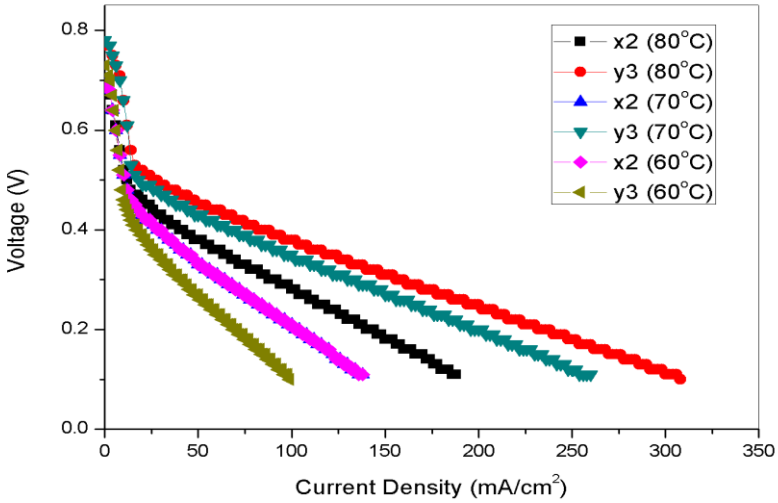

Figure 0.69. *Polarisation curves of x2 and y3 membranes at 60, 70 and 80℃*

A comparison of the performance of membranes with the best selectivity values, x2 (7770Ss/cm^3) and y3 (8672Ss/cm^3) is made. At 80°C, the y3 sample had a maximum current density of 303.88mA/cm^{-2} whereas the x2 had only a value of only 187.88 mA/cm^{-2}. The x2 membrane sample showed inferior performance at 80°C having a power density of 20.95mW/cm^{-2} as compared to that of the y3 which attained a value of 41.44mW/cm^{-2} at 70°C. Before gaining stability at 60°C, the sulfonated y3 membrane had the lowest current and power densities of 80.86mA/cm^{-2} and 14.07mW/cm^{-2} respectively. The effect of sulfonation is mostly evident at high operational temperature. The sulfonated membrane samples have a high impact on the overall DMFC performance.

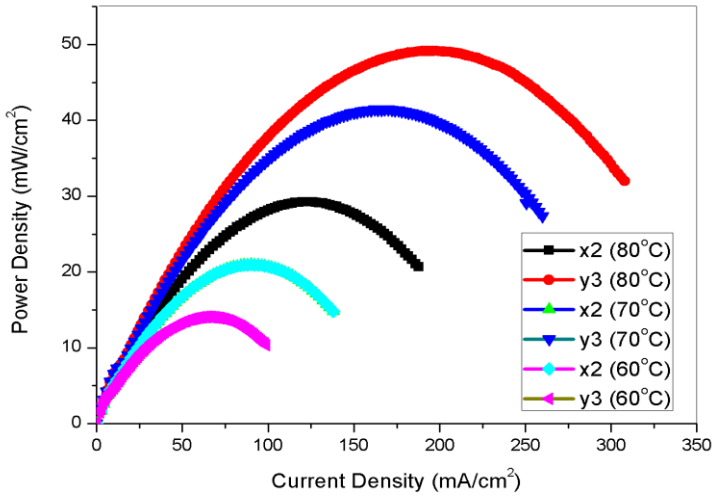

Figure 0.70. *Power density vs Current Density curves of x2 and x3 membranes at 60, 70 and 80℃*

4.9.4. Summary of performance of pure sPEEK and composite membranes at 60, 70 and 80°C

Table 0.10 *Summary of the performance of pure sPEEK and its composite membranes*

	60°C		70°C		80°C	
	Current Density (mA/cm^2)	**Power Density (mW/cm^2)**	**Current Density (mA/cm^2)**	**Power Density(mW/cm^2)**	**Current Density(mA/cm^2)**	**Power Density(mW/cm^2)**
speek	87.97	13.48	125.96	20.24	171.98	27.71
x1	87.94	12.52	121.92	18.24	181.87	28.94
x2	103.92	16.62	137.87	20.95	187.88	29.21
x3	101.89	8.71	89.6	12.33	129.87	19.61
y1	63.21	11.58	94	15.3	167.91	27.71
y2	93.94	13.7	135.88	21.38	187.91	29.69
y3	80.86	14.07	250.44	41.44	307.88	49.14

Fuel feed rate 5ml/min, 2M CH_3OH and 100ml/min humidified O_2.

(NB: OCVs of pure speek, x1, x2 and x3 at 80°C ~ 0.67, 0.69, 0.68 and 0.59V) (OCVs of y1, y2 and y3 at 80°C~ 0.75, 0.71 and 0.77V)

4.10.Conclusions and Recommendations

4.10.1. Conclusions

The present work aimed at producing alternative PEMs possessing good thermal stability, high water uptake, low methanol permeability, elevated proton conductivity and fuel cell performances. sPEEK/ $TiSiO_4$ oxide based membranes are developed, characterised and their performance is investigated in the real DMFC system. The fabricated sPEEK polymer's sulfonation method is reproducible with the time of sulfonation and temperature as the controlling parameters. By using the post sulfonation technique, an optimum DS of 53% was selected owing to its low swelling capabilities in hot DI water and methanol solutions exhibiting favourable stabilities. It had an IEC of 1.605meq/g. The fabricated polymer samples were analysed to note the vibration of available functional groups by the FTIR technique. This analysis revealed better interaction of the Ti and Si in the sulfonated oxide than in the unsulfonated one because of some additional bridges formed between the two oxides. This same analysis also confirmed the sulfonation reaction by the successful replacement of the H atom by the sulfonic acid group. The XRD also revealed a broad diffractogram characteristic of a medium sulfonated sample similar to what has been previously reported in other studies.

The proton conductivity was measured over a temperature range of 30- 80ºC under humidified nitrogen gas flow. The addition of the pure and modified $TiSiO_4$ inorganic filler particles was to enhance the water uptake of the membrane samples since protons require hydrated domains to accelerate their transfer in the system. As observed in the results, all the modified membranes had an improvement in the transport phenomena of the protons. The pure sPEEK had a low water uptake of 31.35% with inferior conductivities of 1.67 and 2.89mS/cm at 30 and 80 ºC respectively. All the modified nanocomposite membrane samples demonstrated good performance with high water uptake and proton conductivities in comparison to the pure membrane. Both the x2 and y3 membranes exhibited the highest proton conductivities at 80 ºC of 9.38 and 9.80 mS/cm. The sulfonated y3 membrane sample however had the best fuel cell performance at 80 ºC having a maximum power density of 49.14mW/cm^2 whilst the x2 sample achieved a maximum value of 29.21mW/cm^2 at the same temperature conditions. The fuel cell performance of the other sulfonated membranes also showed good performance though lower than the y3. The x3 sample with a 2.5wt% of filler had the least fuel cell performance having a power density of only 19.61mW/cm^2 at 80 ºC. It

can be concluded that filler sulfonation has considerable effect on the membrane's performance at high temperature and high filler loading.

In terms of thermal stability, the pure PEEK polymer had only a single major weight loss region which was altered by sulfonation leading to 3 main weight loss segments for the pure sPEEK and its modified membranes. The sulfonated nanocomposite membranes had the lowest thermal stability with a greater weight loss as a result of the added sulfonic acid groups. In the last degradation stage, the x2 membrane showed enhanced stability due to the pure filler particles slowing the hydrophobic chain's decomposition. The sPEEK membrane has good endurance completely decomposing at around 542ºC showing that it can be applied in high temperature fuel cell systems. Despite the modified membrane's methanol permeabilities being fairly higher in relation to the pure sample, the membranes still managed to attain lower methanol permeability amount as compared to the Nafion 117. Furthermore the modified membranes demonstrated high electrochemical selectivity values at 60 ºC. The samples which had the outstanding proton conductivities, x2 and y3 had high selectivity values of 8672 and 7770Ss/cm^3 whilst the pure sPEEK attained a mere 3882Ss/cm^3 at 60 ºC. This reveals the effectiveness of the employed modification techniques on the polymers.

In the real DMFC system the membranes showed varying behaviour at 60, 70 and 80ºC with a 5ml/min flow rate at the anode side whilst the cathode had a 100ml/min flow of humidied oxygen. At low temperature conditions, the membranes had low performance having low current and power densities. As the temperature was increased beyond 60ºC there was a significant improvement in the operation of the membranes. However there were high activation losses caused by some slowness of the reactions at the surface of the electrodes to release electrons. This may be caused by the use of a Nafion ionomer during electrode fabrication which leads to some small incompatibility with the sPEEK electrolyte. At 80ºC, the unsulfonated filler samples had low open circuit voltages of 0.69, 0.68 and 0.59V whereas the sulfonated filler ones had higher values of 0.75, 0.71 and 0.77V due to reduced methanol crossover of the later membranes.

These sulfonated filler membranes can be considered as a possible substitute to the costly and widely used PEMs due to their favourable characteristics and potential of yielding high power densities in the real fuel cell operation.

4.10.2. Recommendations

For future studies some recommendations have been brought forward as follows:

- ✓ It is proposed to use this electrolyte to operate in the hydrogen PEM fuel cell. Previous work has been done with the commercial Nafion and titanium silicate as a filler material but none is available comprising of an alternative polymer like sPEEK. In this fuel cell, a higher DS can be adopted because the feed fuel has no dilute methanol solution. However a good limit must be set for the DS to prevent its dissolution in hot water.
- ✓ In this work, a Nafion ionomer was used for the electrode preparation as an additive to the catalyst ink. Since the proton transportation pathways vary between the sPEEK and Nafion polymers a different ionomer from the membrane would hinder reaction kinetics. An sPEEK based ionomer might be considered in the future to reduce the sluggish reactions taking place on the electrode's surface to release electrons. The dramatic decrease observed in the polarisation curve's activation region can hence be minimised. An sPEEK ionomer quickly adheres and adapts to the membrane structure enhancing the transportation of ions.
- ✓ Since these filler types have high water retention capabilities, they can be used to operate at elevated temperatures. Beyond 80 ºC of operation, the Nafion PEM loses its performance. The oxide filler particles in this study possess an advantage of preventing proton conductivity degradation at higher temperature.
- ✓ An electrode with a catalyst loading lower than 4mg/cm^2 can be tried. In case an almost similar/ higher power densities are attained similar to the originally conducted tests, then this loading can be adopted to lower the system costs. Since a greater fraction of the cost of the fuel cell goes towards the anode and cathode platinum catalysts, this would be greatly beneficial.
- ✓ With a maximum amount of s- $TiSiO_4$ filler in the membrane structure, cross linking may be proposed with different techniques to reduce the methanol cross over in the fuel cell. A reduced methanol permeability would improve performance by reducing unfavourable reactions at the cathode and reduce fuel losses.

- ✓ The methanol feed should be preheated to the cell's operating temperature before it is fed to the anode side as it is drawn from its vessel at room temperature. This is likely to cause a time lag between its heating and the start of the electrode surface reactions. This will speed up the anode electrode reactions reducing the sharp drop in the activation polarisation. More back pressure can be added to further enhance the overall output of the cell
- ✓ The methanol concentration to feed the fuel cell can be changed to observe the different operation behaviour of this filler type together with varying the humidity values and comparing the performance with Nafion.

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APPENDIX

1. Elemental Analysis Data

Sample 1 (18h sulfonation)

Method Name : Default method
Method File : C:\Eager for FLASH\data\MRT\CHNS25102018TMR.mth
Chromatogram : PEEK5
Operator ID : Company Name :
Analysed : 10/25/2018 18:03 Printed : 10/25/2018 18:15
Sample ID : PEEK5 (# 20)
Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : 2.265

Calib. method : using 'K Factors'

Element Na		Ret.Time	Area	BC	Area ratio	K factor
1	0	30	116487	FU		0
Nitrogen	0.7643	46	42339	FU	164.9756	2445550
Carbon	62.5783	65	6984828	RS	1	4927920
Hydrogen	4.0519	189	1359076	RS	5.139396	14808800
Sulphur	4.3789	454	91718	RS	76.15547	924745.3
Totals	71.7734		8594446			

Sample 2 (18h sulfonation)

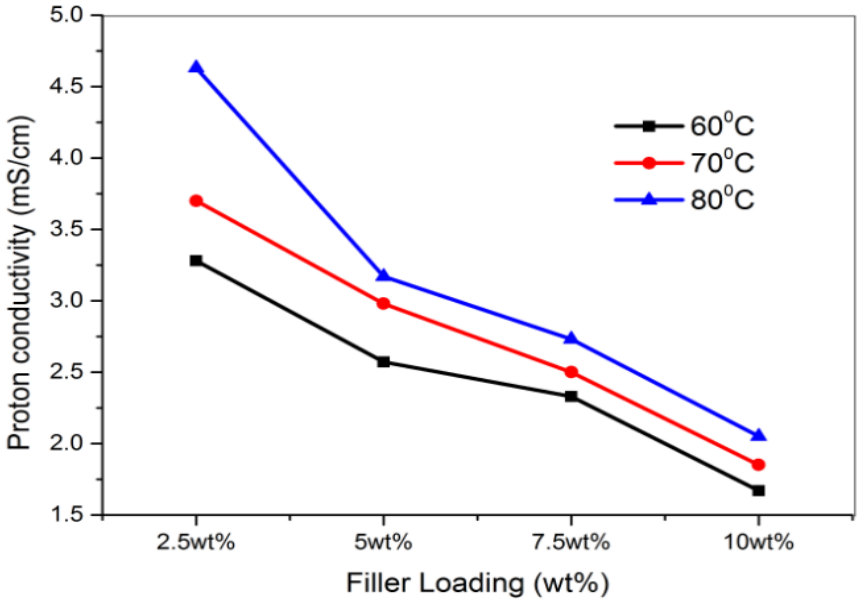
Method Name : Default method
Method File : C:\Eager for FLASH\data\MRT\CHNS25102018TMR.mth
Chromatogram : PEEK11
Operator ID : Company Name :
Analysed : 10/26/2018 13:00 Printed : 10/26/2018 13:12
Sample ID : PEEK11 (# 17)
Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : 2.276

Calib. method : using 'K Factors'

Element Na		Ret.Time	Area	BC	Area ratio	K factor
1	0	30	107521	FU		0
Nitrogen	0.688	46	38296	FU	180.8885	2445550
Carbon	61.7625	65	6927247	FU	1	4927920
Hydrogen	4.2901	190	1445969	RS	4.790731	14808800
Sulphur	4.4745	460	94175	RS	73.55717	924745.3
Totals	71.2151		8613207			

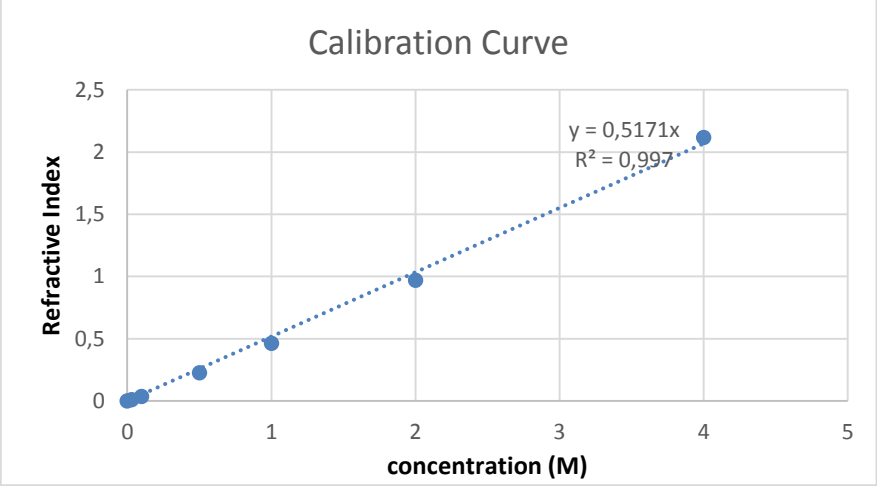
2. Proton Conductivity

Enhancing the proton conductivity was of utmost importance in this study hence initially nanocomposites with 2.5, 5, 7.5 and 10wt% of filler loadings were fabricated and tested. There was a decreasing trend with an increase in the filler amount thus a loading of 2.5wt% was chosen as the limit oxide content.



Proton conductivities of varying filler loadings at 60, 70 and 80°C

3. Methanol Permeability

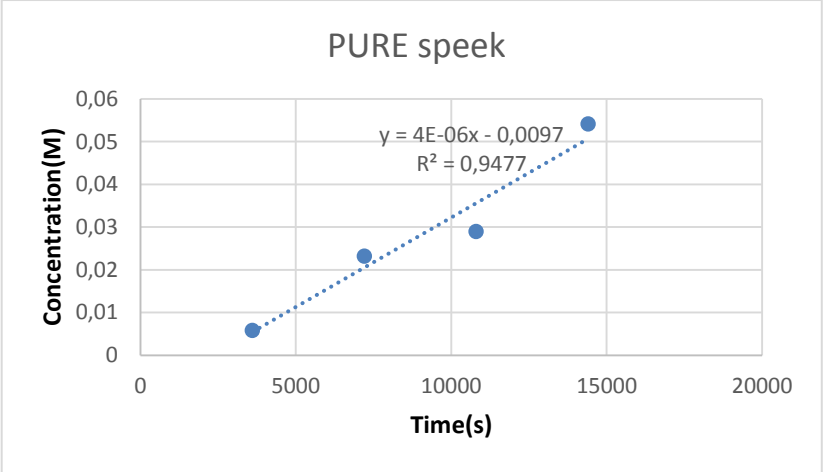


Refractive Indices , Concentration relationship

Concentration of Methanol that permeated to DI water cell

Time	3600	7200	10800	14400
pure speek	0.003	0.012	0.015	0.028
x1	0.005	0.018	0.024	0.035
x2	0.011	0.021	0.029	0.034
x3	0.007	0.015	0.023	0.030
y1	0.008	0.012	0.018	0.026
y2	0.009	0.013	0.021	0.030
y3	0.007	0.009	0.017	0.027

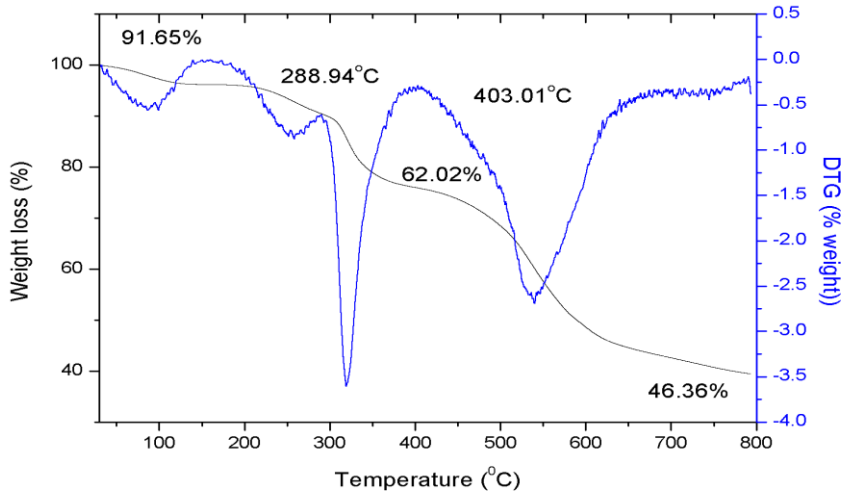
Pure SPEEK Concentration/Time relationship



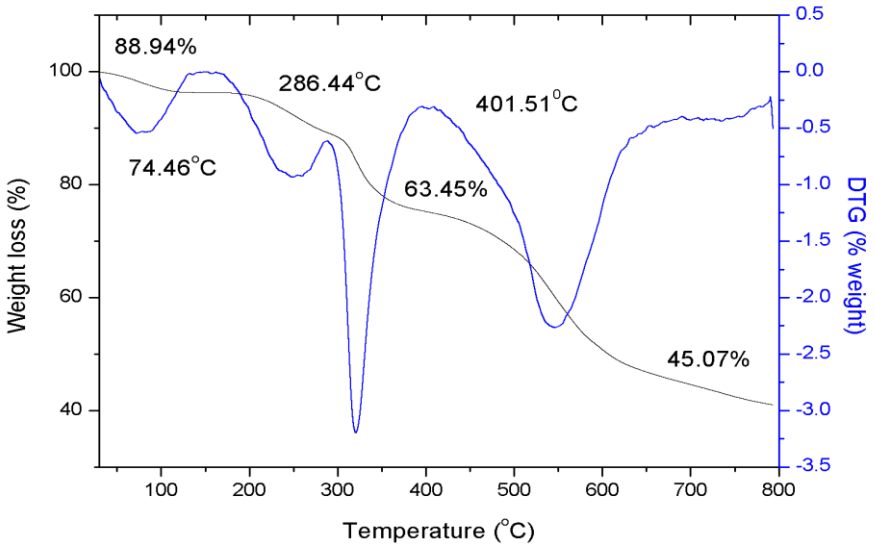
Concentration/ Time relationship

4. Thermal Analysis

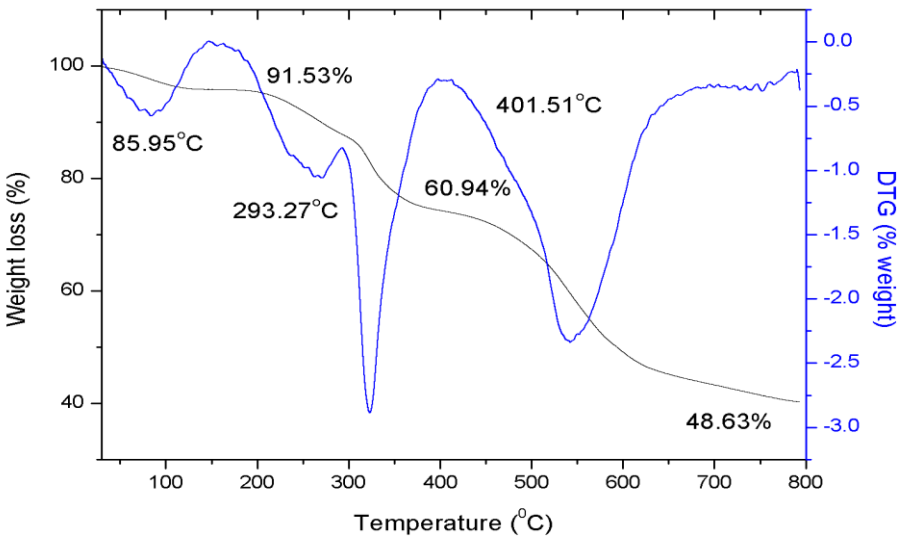
The SPEEK nanocomposite membranes were analysed to evaluate their thermal stability by the TGA. All the SPEEK/$TiSiO_4$ nanocomposite membranes showed good stability up until a temperature of 400ºC. For a DMFC operating at a temperature of 80 ºC, the decomposition temperature of 400 ºC is quite high.



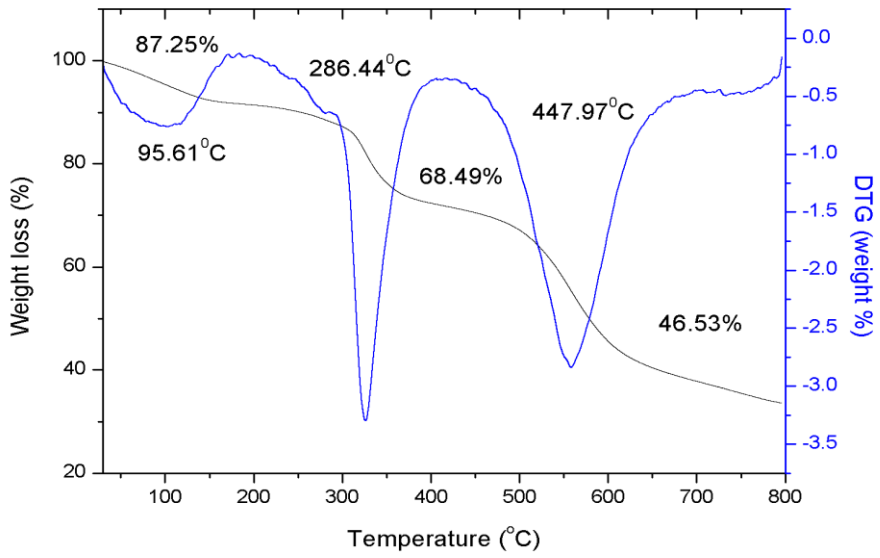
1.0wt% SPEEK/$TiSiO_4$ nanocomposite membrane



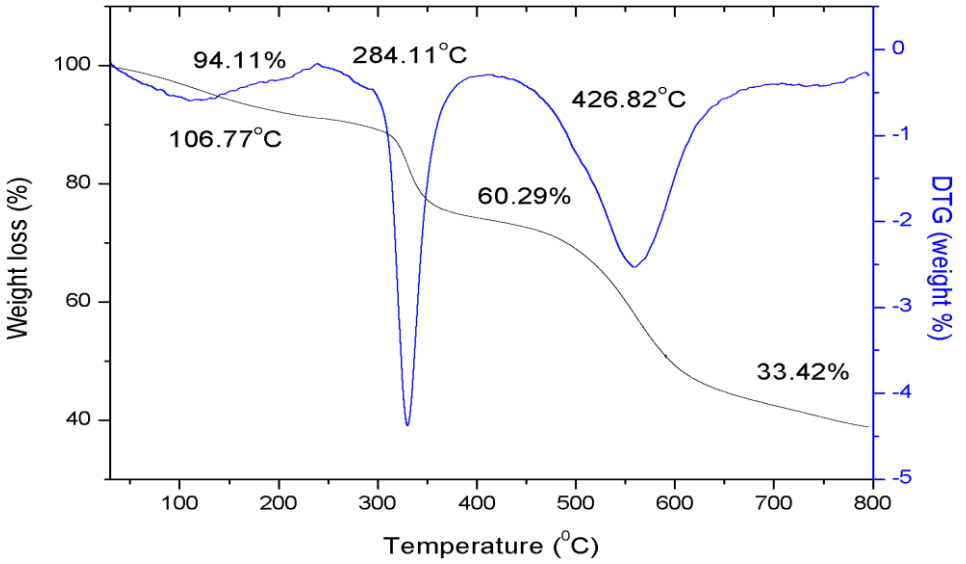
1.5wt% SPEEK/$TiSiO_4$ nanocomposite membrane



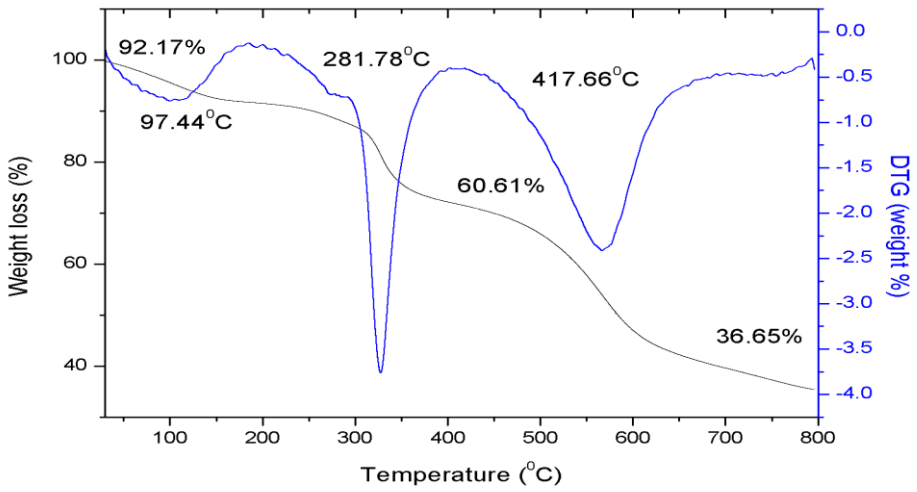
2.5wt% SPEEK/$TiSiO_4$ nanocomposite membrane



1.0wt% SPEEK/$s-TiSiO_4$ nanocomposite membrane



1.5wt% SPEEK/$s-TiSiO_4$ nanocomposite membrane



2.5wt% SPEEK/$TiSiO_4$ nanocomposite membrane