

H₂SO₄ stability of PBI-blend membranes for SO₂ electrolysis

**Dissertation in partial fulfillment of Master of Science in
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Potchefstroom campus of the North-West University**

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Abstract

Alternative energy sources are needed if the current use of energy is to be sustained while reducing global warming. A possible alternative energy source that has significant potential is hydrogen. For hydrogen to become a serious contender for replacing fossil fuels, the production thereof has to be further investigated. One such process, the membrane-based Hybrid Sulphur (HyS) process, where hydrogen is produced from the electrolysis of SO_2 , has received considerable interest recently.

Since H_2SO_4 is formed during SO_2 electrolysis, H_2SO_4 stability is a prerequisite for any membrane to be used in this process. In this study, pure as well as high and low temperature blended polybenzimidazole (PBI), partially fluorinated poly(arylene ether) (sFS) and nonfluorinated poly(arylene ethersulphone) (sPSU) membranes were investigated in terms of their acid stability as a function of acid concentration by treating them in H_2SO_4 (30, 60 and 90wt%) for 120h at 1bar pressure. The high temperature blend membranes contain the basic polymer in excess (70 wt% basic PBI and 30wt% acid sPSU/sFS polymer) and require acid doping in order to conduct protons. In the doped state they are able to conduct protons up to 200°C. The low temperature blend membranes are also composed of the same PBI polymer used in the high temperature membranes, as well as the same acidic polymers with one of the membranes containing a fluorinated polymer and the other a non-fluorinated polymer (sFS or sPSU) in excess. These membranes do not require any acid doping to conduct protons but they are only stable at temperatures below 80°C.

High temperature blend membranes were characterised using through-plane conductivity, GPC and IEC, whilst low temperature membranes were characterised using in-plane and through-plane proton conductivity, weight change, TGA, GPC, SEM, EDX and IEC techniques. The conductivity determination techniques (especially the in-plane technique) proved to be cumbersome, whilst all the other analysis techniques were deemed appropriate.

H_2SO_4 exposure had a destabilising effect on the PBI membrane which presented as weight gain at the 30 and 60wt% H_2SO_4 concentrations due to salt formation and dissolution at the 90wt% acid treatment due to sulphonation. In the sFS membrane dissolution was observed at 30 and 60wt% as a result of oligomer loss that occurred during the post treatment washing process and partial dissolution, as a result of sulphonation, at the 90wt% treated

membrane. The sPSU membrane showed great stability at 30 and 60wt%, though dissolution was observed at 90wt% because of membrane sulphonation due to a lack of fluorination. The sFS-PBI membrane blend proved to be stable with only slight degradation taking place at 90wt% treatment due to sulphonation. Similarly the sPSU-PBI blend membrane showed great stability at the 30 and 60wt% H_2SO_4 treatment concentrations however total dissolution occurred at 90wt% treatment again due to a lack of fluorination. Although both the low temperature blended membranes showed superb stability to H_2SO_4 concentrations expected in the SO_2 electrolyser (30-40wt%), the low temperature blended sFS-PBI membrane seemed slightly more stable over the H_2SO_4 treatment concentration range (30-90wt%), due to the protective role of the fluorinated polymer. The superior acid stability of this membrane could prove vital for proper SO_2 electrolysis, especially for prolonged periods of operation

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Chapter 1: Introduction

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1 Background

With the world drive for green energy, pressure has increased to develop alternative energy sources. Conventional energy sources such as fossil fuels, oil and gas are non-renewable and their consumption contributes to the release of carbon dioxide (CO₂) into the atmosphere. The role of CO₂ and the contribution thereof to global warming is a well documented and intensely researched field. In conferences like the 2009 Copenhagen Climate Change Conference the need for better greenhouse gas control was clearly emphasised¹. Nuclear energy (also a conventional energy source) has long been hailed for its potential to produce large amounts of energy on small amounts of fuel and its relatively low green house emissions (from processing stages up and downstream from the plant²). However recent events in Japan's Fukushima reactor have raised fears concerning nuclear energy and has reminded us of the significant and long-term destruction that is possible when nuclear accidents take place.

At this stage about 78% of the global energy consumption is derived from fossil fuels (Figure 1). However, alternative energy sources are needed if the current use of energy is to be sustained while reducing global warming. A possible alternative energy source that has significant potential is hydrogen. Not only is hydrogen a clean source of energy, but it also has a high energy per mass ratio³. Furthermore it is one of the most abundant elements in the universe⁴.

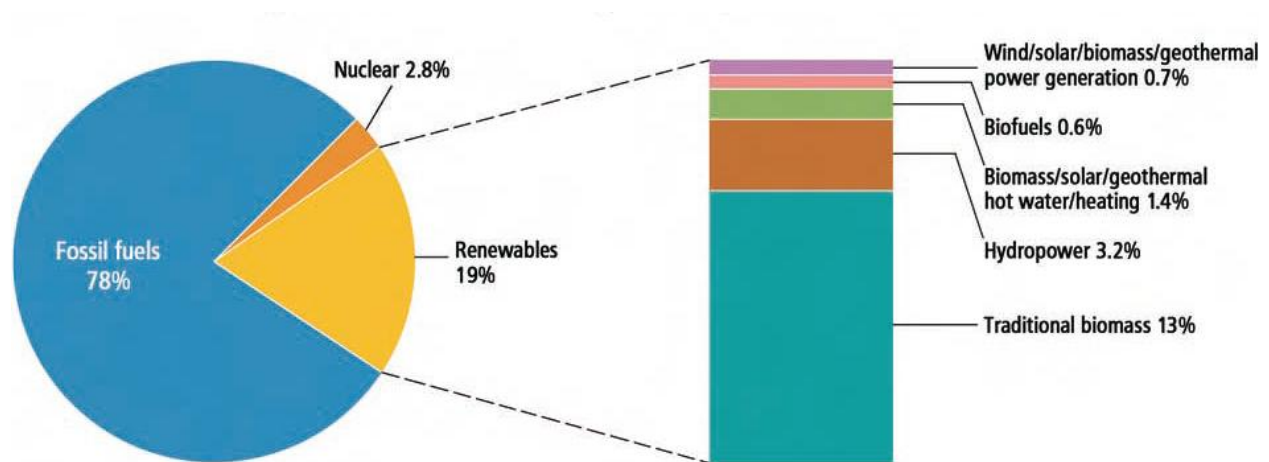


Figure 1.1: Fossil fuels energy share of the global energy consumption⁵

1.1 Sources of hydrogen

Hydrogen can be generated from a variety of energy sources, such as gasoline, natural gas, methanol, solar and wind energy. Currently approximately 96% of the world's hydrogen demand is produced from greenhouse gas emitting fossil fuels⁶ (Figure 2). The rest (approximately 4%) is produced by water electrolysis. As there is only a restricted fossil fuel supply remaining, the focus will ultimately have to shift from these limited supplies to water electrolysis or similar techniques to produce a viable alternative source of hydrogen.

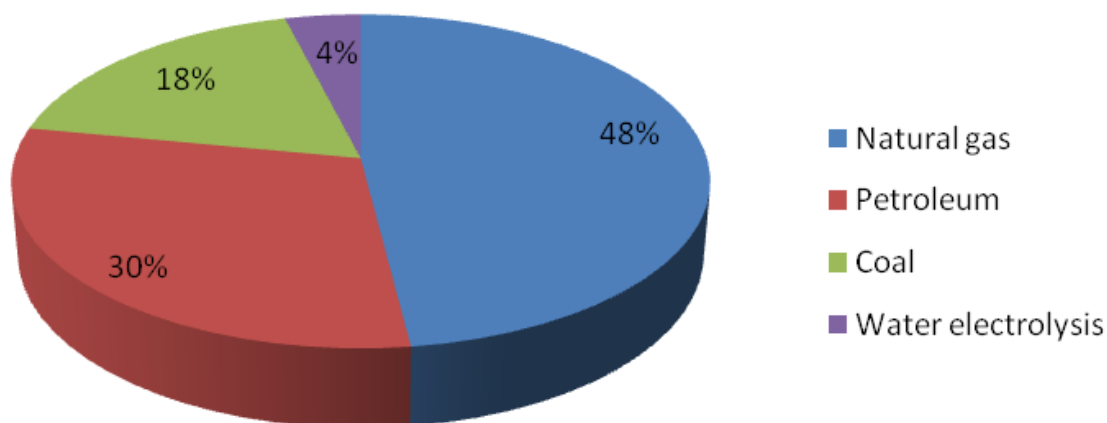


Figure 1.2: The estimated world production of hydrogen

1.2 Production of hydrogen

While hydrogen can be produced by an array of different methods, the most important processes are listed below.

1.2.1 Hydrocarbon steam reforming

The most common method used for the production of hydrogen is steam reforming. The process involves the production of hydrogen from fossil fuels such as natural gas⁷. Methane (the principal component of natural gas) exposed to high temperature steam produces carbon monoxide and hydrogen. Regrettably the formed carbon monoxide (Reaction 1)⁷ also contributes to the elevation of green house gases⁸.



Additional hydrogen can then be produced using the so called gas shift reaction (Reaction 2)⁹, which however also produces CO₂ as pollutant.



Another disadvantage of steam methane reforming is related to its high cost⁷.

1.2.2 Steam gasification

Gasification is the process by which materials rich in carbon such as coal, petroleum, biomass and biofuels are transformed into gaseous fuels through the use of gasifying agents such as high temperature steam, oxygen, carbon dioxide or a mixture of any two or more¹⁰. Steam gasification is used extensively to produce hydrogen using Reaction 3¹⁰. As can be seen from the reaction, this method also produces green house gases.



1.2.3 H₂O electrolysis

Water electrolysis entails a process by which hydrogen and oxygen is produced by means of the decomposition of water through the use of an electric current¹¹. While environmentally friendly, hydrogen production through the use of H₂O electrolysis has a much lower cost efficiency compared to the fossil fuel based processes¹² and is mainly used where electricity can be obtained relatively cheaply, for example by using hydroelectric systems⁷.

1.2.4 Thermo-chemical cycles

One significant disadvantage of H₂O electrolysis is the high voltages required for the dissociation. The recent interest in thermo-chemical cycles is related to the substantial reduction in the potential required for these processes. Although there are numerous possible thermo-chemical cycles that can be used to produce hydrogen (for instance the CuCl, Sulphur iodine,

CaBr, HBr and HyS cycles), there are a few leading candidates including the chloride-based cycles and the sulphur-based cycles, of which the Hybrid Sulphur (HyS) process is a prime contender. For the purpose of this study only the latter will be briefly elucidated.

1.2.5 The HyS process

The Hybrid Sulphur process (Figure 3) was first developed by Westinghouse Electric Corporation in the 1970`s¹³. The cycle comprises the thermodynamic splitting of H_2SO_4 at approximately 800 °C to produce $\text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$ ¹⁴. After removal of the O_2 , the SO_2 and H_2O are sent to the anodic side of the membrane electrode assembly (MEA), inside the SO_2 electrolyser to produce clean hydrogen and H_2SO_4 . The hydrogen produced in this manner uses much less energy than that of hydrogen obtained from the thermodynamic splitting of H_2O . The HyS process requires approximately 0.158 volts¹⁴ to produce H_2 , compared to water electrolysis that requires approximately 1.23 volts¹⁵. The HyS process hence uses less electrical energy and is therefore an appealing cycle to use.

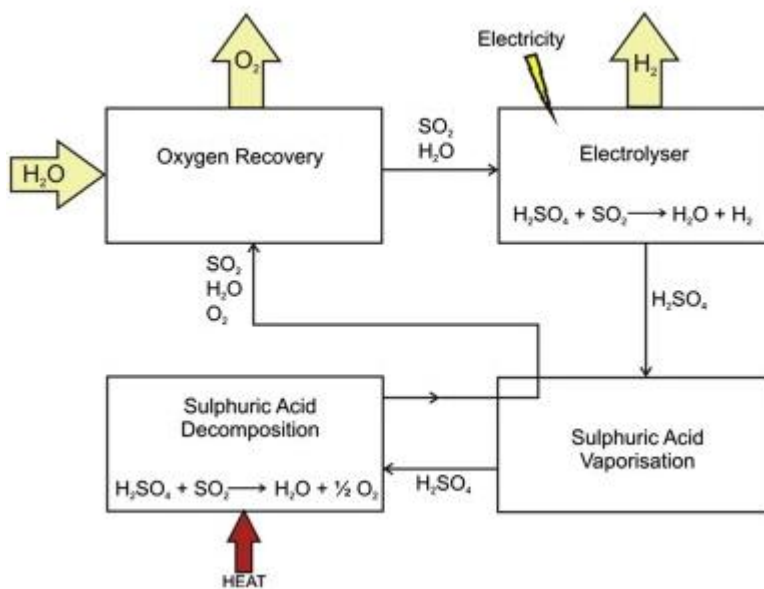


Figure 1.3: The HyS cycle¹⁶

1.3 Problem statement

One of the potential problems with the HyS process however is that it creates a different environment than the one that is found in fuel cells or H_2O electrolyzers, mainly due to the

presence of both SO_2 and H_2SO_4 . The possible changes in the stated membranes due to the H_2SO_4 environment have not been sufficiently studied and thus little is known on their stability in this acidic environment.

1.4 Aim and objectives

It is therefore the aim of this study to obtain a better understanding of the influence of the H_2SO_4 environment on membrane stability.

To attain this aim, the objective entails the exposure of specific polybenzimidazole (PBI) blend membrane to various H_2SO_4 environments. After exposure the membranes will be characterised by proton conductivity (four-probe in-plane as well as two-probe through-plane), weight change, TGA, GPC, SEM-EDX and IEC techniques.

2 Outline of thesis

Chapter 1: Introduction

In the introduction, I gave a short overview on the current energy challenges facing us and possible alternative sources and processes of obtaining energy, with a specific focus on the HyS process. I have subsequently elaborated on the possible use and problems facing the use of conventional membranes in the SO_2 electrolyser leading to the aim and objectives of this study.

Chapter 2: Literature study

In the light of the aim of this dissertation, Chapter 2 will serve as a background to explain different aspects pertaining to this study giving an overview of membrane-based energy use, membrane-based energy production, PEM characterisation, proton transport through a PEM and finally the membrane materials that were used.

Chapter 3: Experimental

In Chapter 3, the experimental set-up is explained both for the H_2SO_4 membrane treatment as well as the characterisation techniques that were used to test the stability of the exposed membranes.

Chapter 4: Results and discussion

In Chapter 4, the results obtained through the different set-ups and techniques presented in Chapter 3 will be demonstrated, described and discussed, in an attempt to correlate the membrane material to the H_2SO_4 stability.

Chapter 5: Evaluation and recommendations

In Chapter 5, a critical evaluation will be presented on this study elucidating to which extent the aim and objectives in Chapter 1 have been attained. Based on this evaluation, recommendations will be presented on possible future research that might be necessary to obtain a better understanding of membrane stability in H_2SO_4 .

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Chapter 2: Literature study

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1 Introduction

Due to the increase in world consumption of limited, carbon dioxide producing fossil fuels, alternative sources have to be sought to sustain the world's energy demands. One possible solution to the growing energy needs can be found in the usage of hydrogen, which is CO₂ neutral while having a high energy to mass ratio¹. Hydrogen can be produced and subsequently converted to energy using various routes. In view of the scope of this study, only membrane-based processes will be discussed briefly in Section 1.1, before focusing on proton exchange membranes (PEM's) in Section 1.2. To my knowledge no literature concerning the stability of the tested membranes in H₂SO₄ is available and therefore this could not be included in the literature study.

1.1 Membrane-based energy use

Fuel cells are often used to generate electrical energy through the use of specific supplied fuels. The most widely used fuel cells are currently the proton exchange membrane fuel cells (PEMFC's), alkaline fuel cells (AFC's), phosphoric acid fuel cells (PAFC's), molten carbonate fuel cells (MCFC's) and solid oxide fuel cells (SOFC's)², though at present the most popular fuel cell is said to be the PEMFC². PEMFC's generate power through the reaction of hydrogen and oxygen yielding water vapour as the only byproduct (Figure 2.1). Hydrogen is supplied to the anodic side of a membrane electrode assembly (MEA) inside the fuel cell, whilst oxygen is supplied to the cathodic side of the MEA. The protons migrate through the proton exchange membrane (PEM) situated between the two electrodes. The electrons, which are unable to pass through the membrane, move through an outer circuit resulting in an electric current. On the cathodic side of the MEA, the protons and electrons reunite and in the presence of the supplied oxygen, form water as a byproduct. It is interesting that a PEMFC is basically a H₂O electrolyser in reverse, i.e. where the PEMFC uses H₂ and O₂ to make H₂O and energy, the H₂O electrolyser uses energy and H₂O to create H₂ and O₂^{3,4}. Using this reverse process, electrolyzers can be used to produce hydrogen, which in turn can be used as a possible fuel in fuel cells.

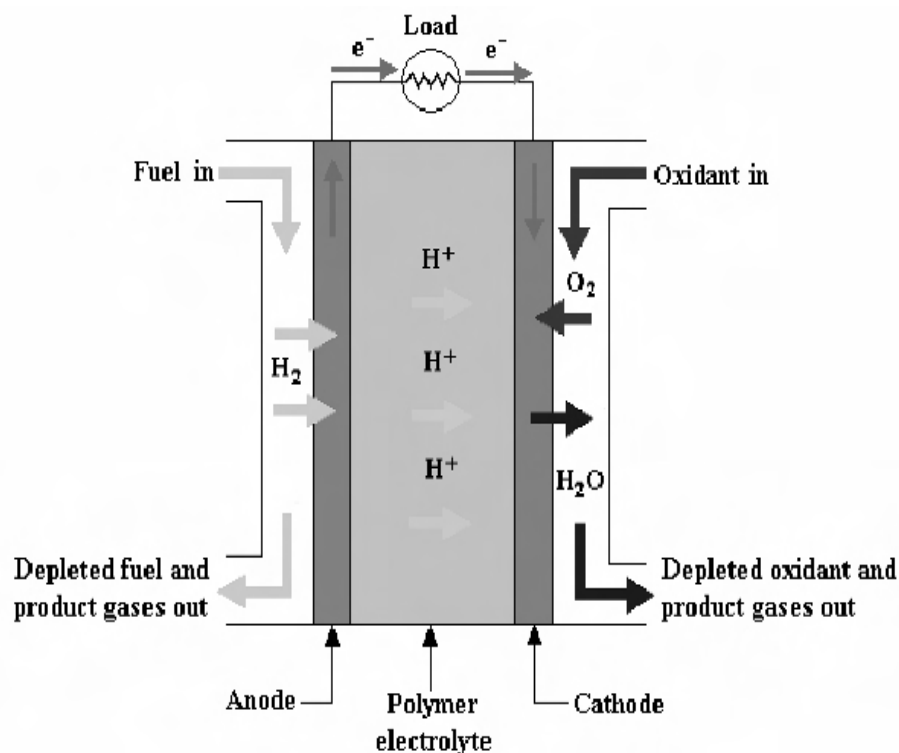


Figure 2.1: A schematic diagram of a proton exchange membrane fuel cell (PEMFC)

1.2 Membrane-based hydrogen production

Before discussing SO_2 electrolysis (Section 1.2.2) and the components of the SO_2 electrolyser (Section 1.2.3), a brief introduction is given in terms of the most commonly used membrane-based electrolyser process, i.e. H_2O electrolysis.

1.2.1 H_2O electrolysis

Electrolysis is the term given to a process where a compound is decomposed, when in solution, by means of an electric current. Electrical energy is thus converted to chemical energy⁵. Since the process does not occur spontaneously, it requires an external driving force, such as an electrical overpotential. This can be exemplified in terms of H_2O electrolysis, where the external driving force is supplied in the form of electrical energy. It is clear that the higher the electrical energy that is required, the higher the cost of the produced hydrogen. One of the major disadvantages of using specifically H_2O electrolysis is the high voltage (above 1.23V) required for the process^{6,7}. This high voltage is the most important reason for the study on SO_2

electrolysis. Whilst SO_2 electrolysis also requires overpotential for the reaction to occur, the overpotential is only approximately 0.17 volts⁸.

1.2.2 SO_2 electrolysis and the HyS process

Sulphur based cycles are said to have the best overall energy efficiency compared to other thermodynamic cycles⁶. One of these sulphur-based cycles is the HyS or Hybrid Sulphur process which was first developed by Westinghouse Electric Corporation in the 1970's⁸. The HyS cycle has the advantage over other sulphur-based cycles, for example the sulphur iodine cycle, that it requires fewer reagents to produce the required hydrogen⁹. The HyS cycle entails the thermodynamic splitting of H_2SO_4 to produce $\text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O}$ ¹⁰ at temperatures above 800 °C. The produced SO_2 and H_2O are then fed to a SO_2 electrolyser (Figure 2.2) where the $\text{SO}_2 + \text{H}_2\text{O}$ migrate through a flow field to a gas diffusion layer, from where they diffuse to the anodic side of the membrane electrode assembly (MEA). On the anodic catalyst-coated electrode, the oxidation of SO_2 occurs (Reaction 1)¹¹. Since the electrons that are obtained from Reaction 1 cannot flow through the membrane (refer to the section on PEMs), their only available option is to follow the outer pathway, which leads to the cathodic side of the MEA¹¹. The produced protons, which are able to migrate through the PEM, react with the electrons provided by the outer circuit on the cathodic side of the MEA resulting in the production of hydrogen (Reaction 2)^{10,12}, which is subsequently flushed away by a connected water supply. Since the sulphur containing compounds are recycled, the HyS process is regarded as a source of clean hydrogen^{8,11}.



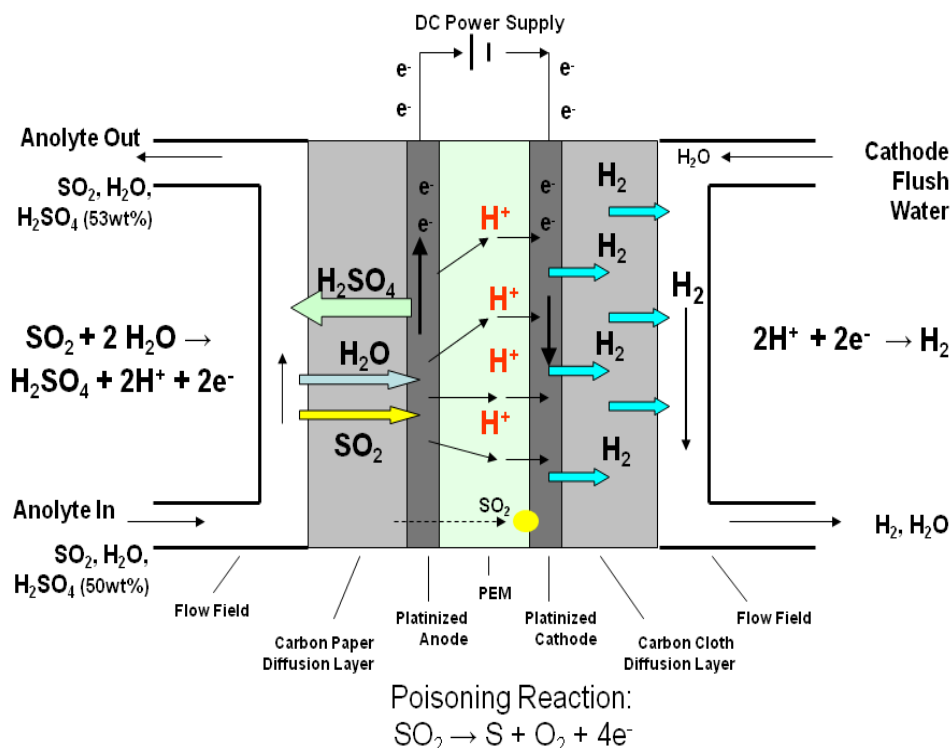


Figure 2.2: A schematic diagram of a SO₂ electrolyser

One possible problem with SO₂ electrolysis is the occurrence of SO₂ poisoning reactions on the cathodic catalyst¹². For these reactions to occur, SO₂ has to cross the PEM along with the protons giving rise to sulphur-based side reactions on the cathodic side of the MEA, which increase the internal resistance of the MEA resulting in more energy being required to maintain the same hydrogen production. The poisoning reaction consequently reduces the efficiency of the SO₂ electrolyser.

A further potential problem is the possible degradation of the MEA/PEM due to the high H₂SO₄ environment (see Reaction 1). The effect of the H₂SO₄ environment on PEMs is largely unknown, because H₂SO₄ is not found in fuel cells and therefore its effects have not received significant attention to date.

1.2.3 Electrolyser components

The earliest electrolyser consisted of two compartments separated by a membrane¹². The substitution of this two compartment system, illustrated in Figure 2.3, with a MEA transformed the sulphur depolarised electrolyser (SDEs) by i) allowing for smaller SDEs to be built, which is

a major benefit when building electrolyzers on a commercial scale, and ii) reducing the overall cell resistance within the electrolyzers^{10,12}.

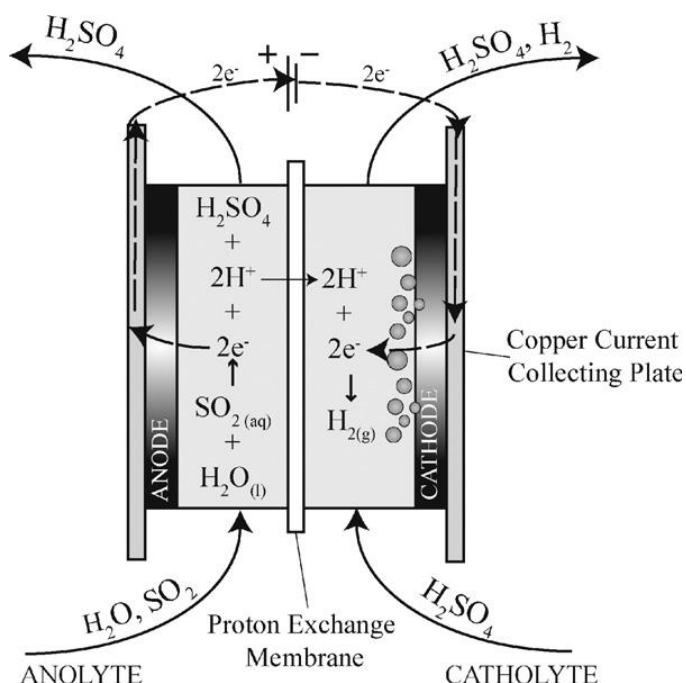


Figure 2.3: An example of an original two compartment set-up¹²

The MEA, illustrated in Figure 2.4, is the most important part of the modern SO₂ electrolyser¹³. This is the site where sulphuric acid and the hydrogen producing reactions occur and thus without a proper functioning MEA, the electrolyser would be useless. As the name entails, the MEA consists of two parts, firstly the two electrodes that each have a catalyst coating (usually a noble metal) and secondly, situated between the two electrodes, is the proton exchange membrane (PEM).

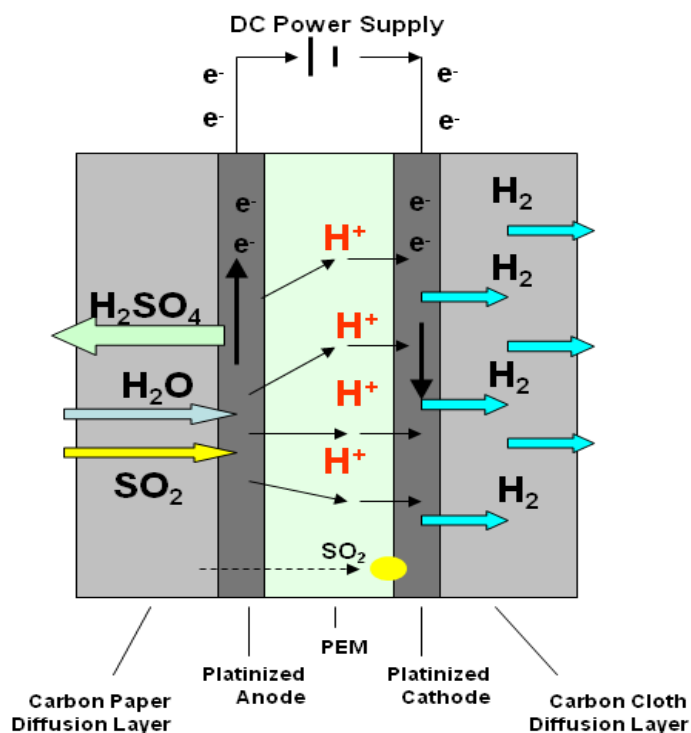


Figure 2.4: An MEA with adjacent diffusion layers

The gas diffusion layers (GDL) are situated next to the MEA both on the anodic and cathodic side. The main purpose of the GDL is to disperse evenly the inward bound gaseous substances. It is important to note that the catalyst layer can either be coated on the membrane or on the GDL. When the catalyst layer is coated on the GDL, it is known as a gas diffusion electrode (GDE)¹⁴.

The catalytic layer is the site in the electrolyser where the electrochemical reactions occur and it is thus a component of vital importance. The catalyst layer is almost always made up of noble metals or noble metal combinations, which results in the high cost of the catalyst. Both the catalyst and the catalyst loading should thus be carefully considered. The loading of the catalyst layer has a significant effect on the system, as illustrated in Figure 2.5, especially at catalyst loadings below 0.1 mg Pt/cm^2 , where a significant increase in overpotential is observed. Above 0.1 mg/cm^2 , the effect of catalyst loading on the observed overpotential decreases significantly¹⁵.

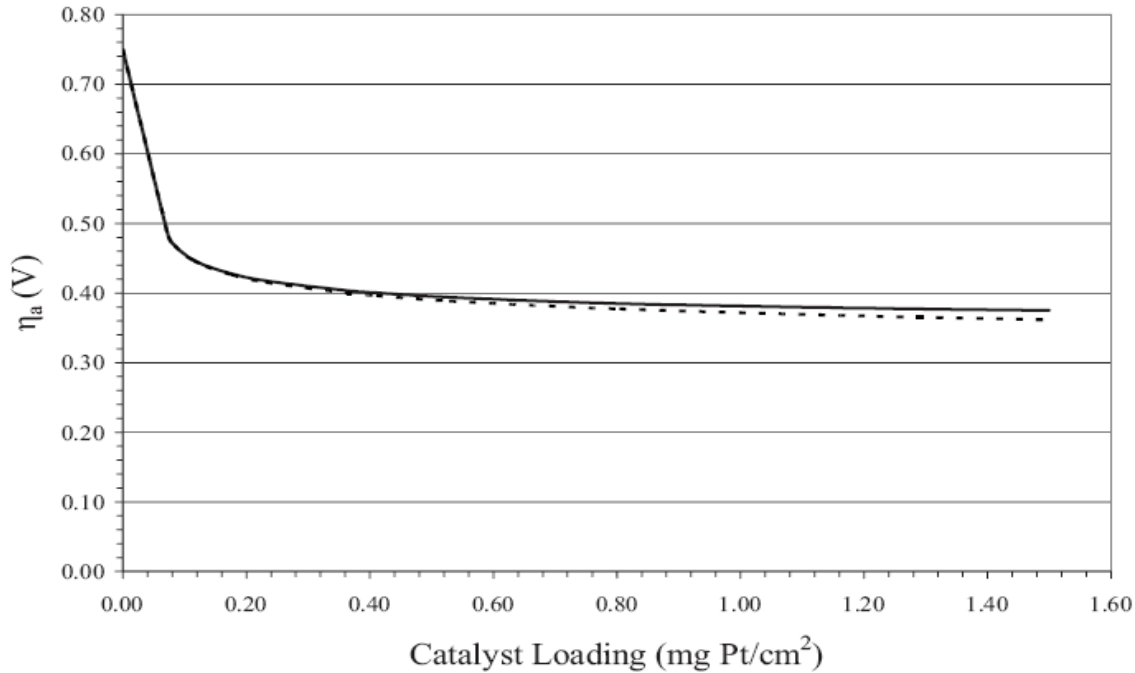


Figure 2.5 Overpotential as a function of catalyst loading¹⁵

Adjacent to the GDL`s are the bipolar plates that sandwich, the GDL`s, the catalyst layers and the MEA`s between them as illustrated in Figure 2.6 using a fuel cell stack. The reason for the sandwiching by the bipolar plates is i) to allow for the uniform distribution of reagents and products over the active areas, ii) to remove heat from the active area, iii) to conduct the current from cell to cell and finally iv) to prevent leakage of gasses and coolant¹⁶. This is obtained through flow fields that can occupy the inner space of the bipolar plates (Figure 2.6). While the flow field channels can have a range of designs, the most commonly used designs are pin, serpentine or straight designs¹⁷.

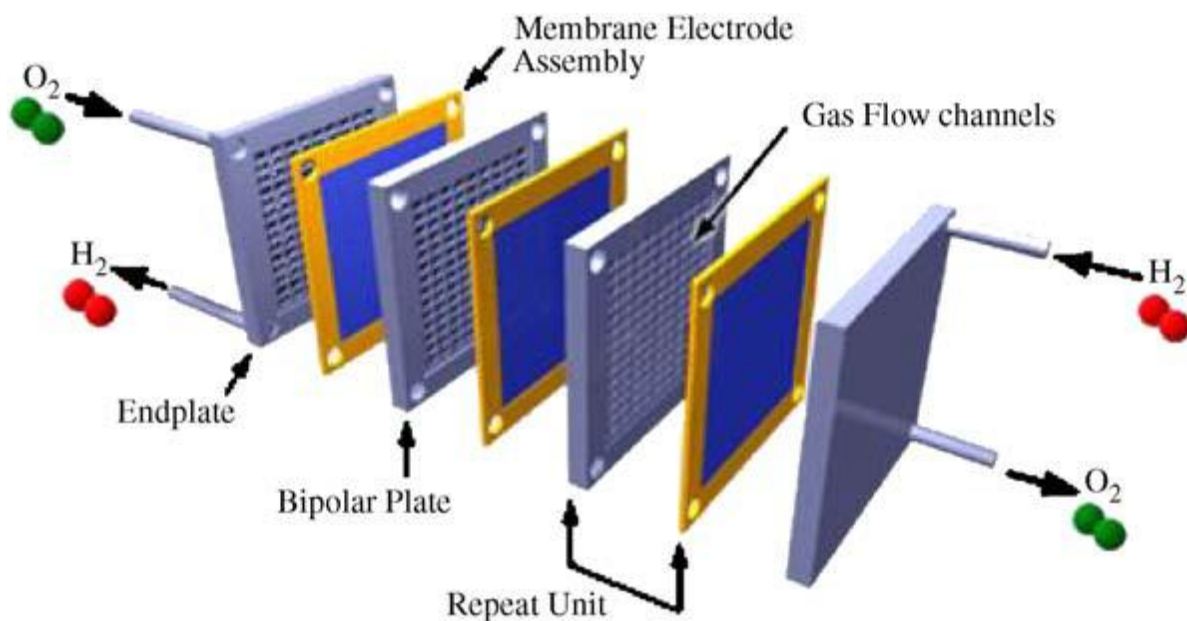


Figure 2.6: An example of bipolar plates in a fuel cell stack¹⁷

2 PEM

2.1 Introduction

As discussed above, the PEM is central to the MEA. The PEM has a variety of functions in SO_2 electrolyzers, most notably to allow unrestricted transport of protons across the membrane, while impeding the flow of SO_2 , which is responsible for poisoning the electrodes during SO_2 electrolysis as mentioned in Section 1.2.2, whilst remaining chemically and mechanically intact¹⁸. To determine the suitability of the membranes for PEM application, various characterisation techniques have been developed of which the most important are presented in Section 2.2. In the remainder of this chapter, the membrane materials of importance for this study (Section 2.3) will briefly be introduced.

2.2 PEM characterisation

2.2.1 Proton conductivity

One of the most important PEM characterisation techniques is the determination of the proton conductivity of a membrane usually through the use of impedance spectroscopy. The proton

conductivity, which measures the migration rate of protons, is directly related to the rate of hydrogen produced, which is ultimately the main purpose of electrolyzers.

As the name entails, proton conductivity refers to the ability of a membrane to transport protons across different layers. On the anodic side of the MEA, H_2O and SO_2 combine to form $\text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^-$ (see Section 1.2.2). The produced H^+ has to be transported across the membrane, as protons are unable to follow the outer MEA pathway followed by the electrons. Two conductivity measuring techniques are generally used, in-plane and through-plane conductivity (Section 2.2.1.1) using either a two- or four-probe method (Section 2.2.1.2).

2.2.1.1 In-plane vs. through-plane conductivity

Protons migrate either through the membrane (through-plane conductivity) or across the surface of the membrane (in-plane conductivity) as illustrated in Figure 2.7. Similarly, the measurement of proton transport can be done using either the in-plane, or the through-plane conductivity measurement technique. The results are similar as long as the membrane is isotropic. However, if the membrane is anisotropic, the in-plane and through-plane conductivities could differ^{19,20}. Although through-plane is of more relevance in terms of the actual functioning of an electrolyser, the disadvantage of using the through-plane-set-up is that the relatively small resistance of the membrane may be overwhelmed by the larger interfacial resistance between the probe and the membrane, which may lead to conductivity errors. Subsequently, the in-plane measurements are often preferred by researchers¹⁹. Problems arising with the in-plane conductivity measurements are usually related to errors occurring in the calculation of the membrane thickness, because of swelling of the membrane as a function of %RH, which influences the obtained resistance of the membrane¹⁹.

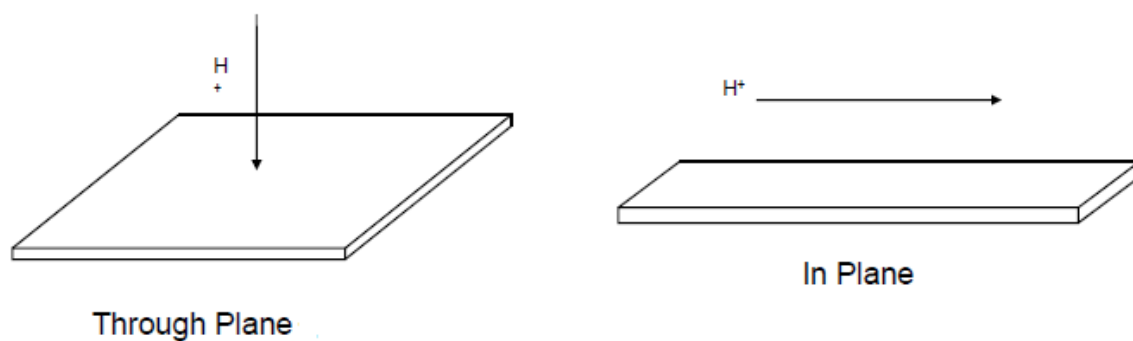


Figure 2.7: Through-plane transport of protons vs. in-plane transport of protons¹⁹

2.2.1.2 Two-probe vs. four-probe method

The in-plane and through-plane conductivities can both be measured using either a two-probe or a four-probe method¹⁹. In the two-probe method, two probes are used to measure the resistance of the membrane (see Figure 2.8 and 2.9), each probe measuring the current as well as the voltage and thus the interfacial impedance passing through the membrane¹⁹.

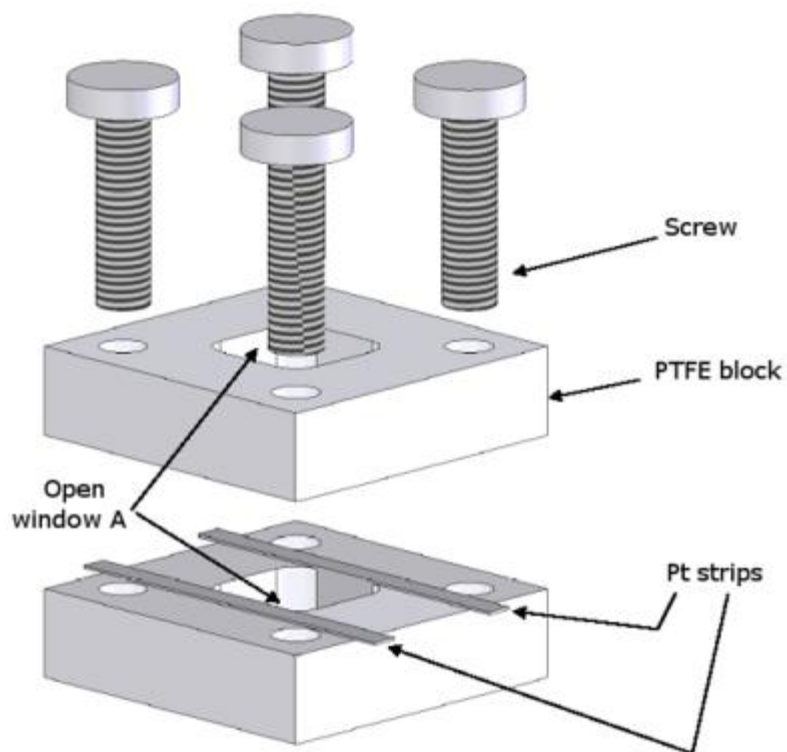


Figure 2.8: An example of in-plane two-probe meter¹⁹

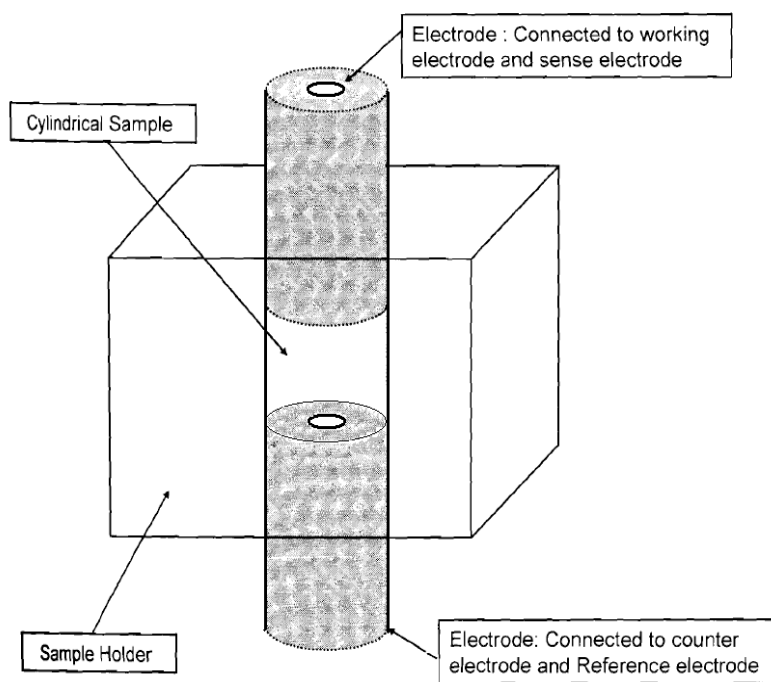


Figure 2.9: An example of through-plane two-probe meter²¹

In the four-probe method, four probes are used to measure the resistance of the membrane (see Figure 2.10 and 2.11). In this design, the current and voltage measuring probes are separated and thus interfacial impedance is not measured¹⁹. Therefore, in theory the four-probe method is more accurate than the two-point method¹⁹.

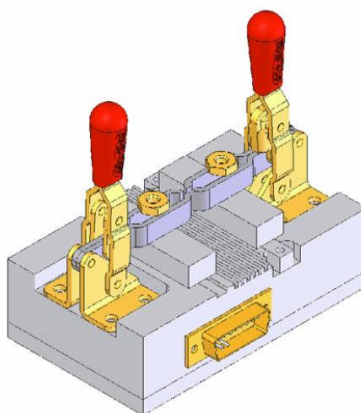


Figure 2.10: An example of an in-plane four-probe meter supplied by Giner, Inc.²²

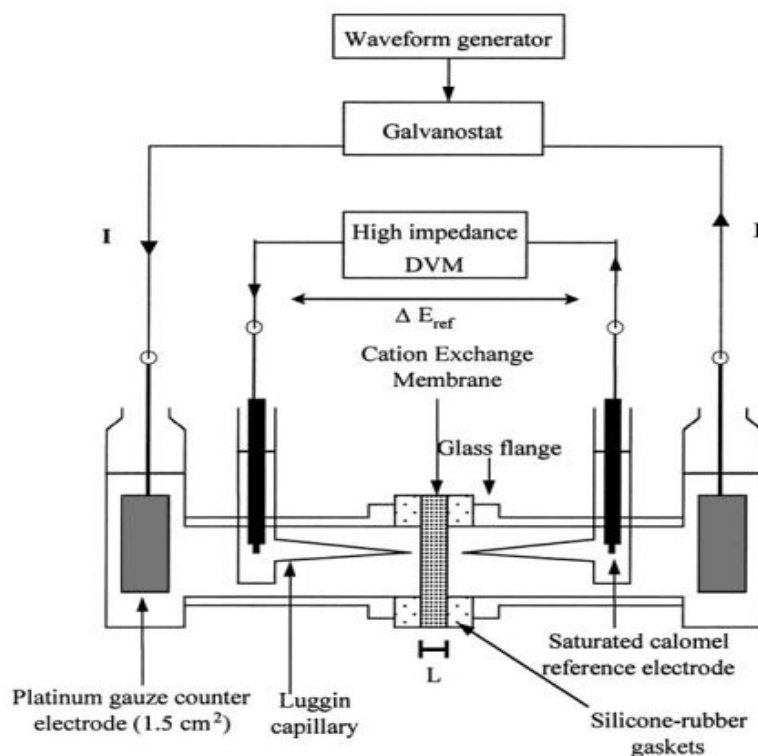


Figure 2.11: An example of an in-plane four-probe meter²¹.

2.2.1.3 Conductivity determination and calculation

For both the two-probe and four-probe set-up, AC impedance spectroscopy (IES) is generally used to obtain the impedance/resistance of the membranes^{23,24}. From the resistance, it is possible to calculate the membrane's conductivity. The standard technique used to acquire the impedance measurements is by means of a potentiostat containing a frequency response analyser (FRA)². An alternating current or potential is sent through the measured membrane over a wide range of frequencies². After this, the amplitude and phase acquired from the membrane response to the AC signal are measured and interpreted at each frequency². Different frequencies relate to different impedances of different parts of the system. AC impedance spectroscopy is usually used at relatively high frequencies when testing the resistance of membranes.

When attaining the impedance data through an AC current, the data are usually plotted on either a Nyquist or a Bode plot. The disadvantage of using a Nyquist plot is that some information, for example frequency, is lost which is available when using the Bode plot²⁵. When applying a DC current (through a potentiostat) one can also use linear polarisation. When using this method, a VI curve is plotted and by calculating the slope of the obtained line, it is possible to obtain the resistance of the membrane using the following equation

$$\rho = Rwd/l^{26,27} \quad (3)$$

ρ = Resistivity ($\Omega \cdot \text{cm}$)

w = Width of the membrane (cm)

d = Thickness of the membrane (cm)

l = Distance between voltage measuring wires (cm)

R = Resistance obtained through impedance spectroscopy (Ω)

From this resistance, the proton conductivity can be determined, where

$$\sigma = 1/\rho \quad (4)$$

σ = proton conductivity ($\text{S} \cdot \text{cm}^{-1}$)

2.2.1.4 Proton transport through a PEM

There are two major transport mechanisms proposed for the migration of protons through a membrane. The first is the vehicular transport mechanism²⁸ illustrated in Figure 2.12. In the vehicular mechanism, the protons react with the water in the membrane to form hydronium ions (H_3O^+). The water then facilitates the transport of the hydronium ions across the membrane through the diffusion of the hydronium ions from a high proton concentration region on the one side of the PEM to a low proton concentration on the other side of the PEM²⁹.

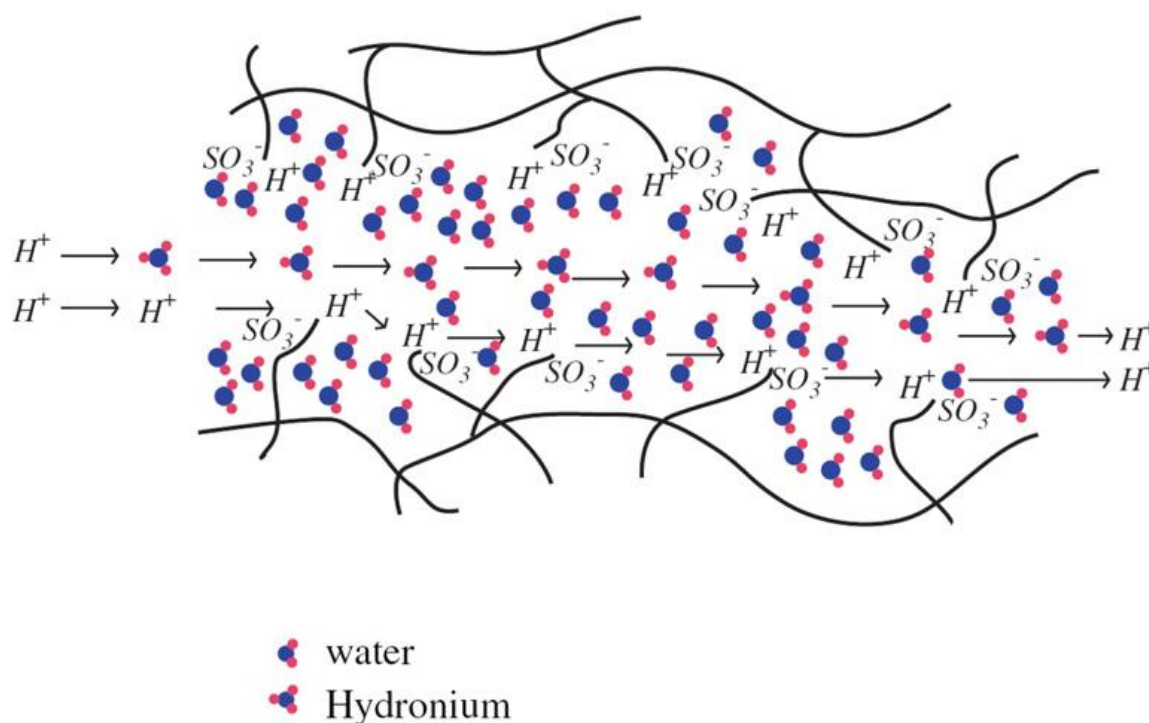


Figure 2.12: The vehicular mechanism for the transport of protons through a PEM²⁸

The Grotthuss mechanism shown in Figure 2.13 also involves the reaction of H^+ with H_2O to form a hydronium ion (H_3O^+). However instead of this hydronium ion having to diffuse through the membrane on its own, protons are passed along from one water molecule to another water molecule forming temporary hydronium ions³⁰. This mechanism relies on the forming and breaking of hydrogen bonds to form Zundel and Eigen-complexes³⁰.

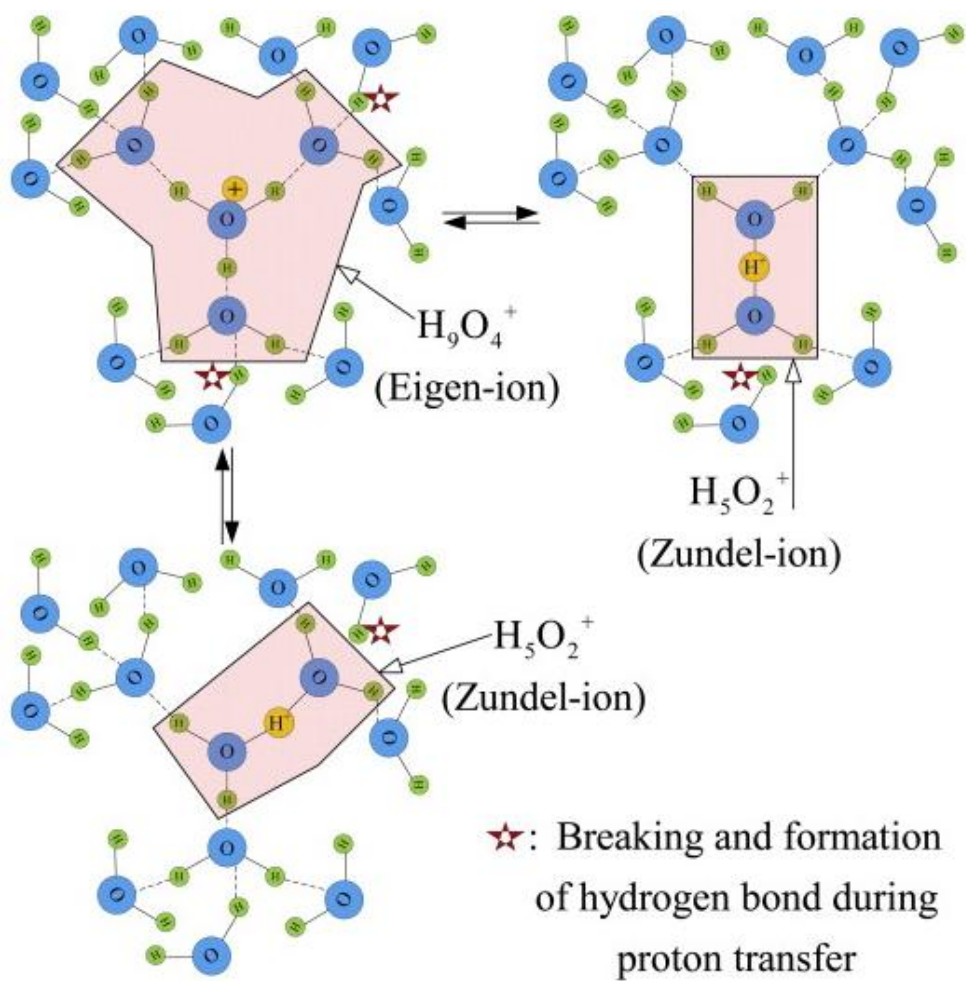


Figure 2.13: The Grotthuss mechanism for the transport of protons through a PEM²⁹

A third less common mechanism, the direct transport mechanism, has also been proposed (see Figure 2.14). It entails the direct transport of protons from one SO_3^- polymer chain to the next. This mechanism however only takes place at very low membrane water concentrations resulting in low proton conductivities.

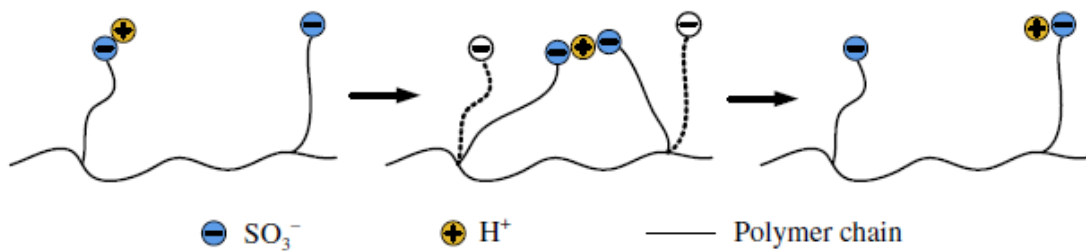


Figure 2.14: Direct proton transport at low membrane water concentrations²⁹

2.2.2 Weight change

The weight change of a membrane is used to determine which membranes remained stable after H_2SO_4 treatment and conversely which membranes degraded through weight comparisons with untreated samples.

2.2.3 TGA

Thermogravimetry (TGA) can be used to determine the thermal stabilities of selected samples through continuously recording mass changes of the tested sample as a function of temperature and time.

2.2.4 GPC

GPC or gel permeation chromatography can be used to separate polymer samples on the basis of their molecular weight. This technique can be used to gather data on the weight distribution of tested membranes and to compare the effect of different conditions on membrane degradation.

2.2.5 SEM-EDX

Scanning electron microscopy (SEM) is used to obtain a magnified three dimensional image of a required object. When used in membranes, SEM can give a visual image of possible damages to a membrane for example due to the exposure to H_2SO_4 during SO_2 electrolysis. EDX refers to energy dispersive X-ray spectroscopy analysis which attached to the SEM, can be used to determine the elemental composition of a specimen². When used to analyse membranes treated in acid, this technique can offer insight into possible raised sulphur levels relative to other commonly found elements such as carbon within the membrane.

2.2.6 IEC

The IEC or ion exchange capacity values are useful to reveal the number of $-\text{SO}_3\text{H}$ groups per gram of membrane. The number of $-\text{SO}_3\text{H}$ groups is usually directly related to the amount of conductivity that is expected. IEC values are often determined using acid-base titrations^{31,32}.

2.3 Membrane materials

2.3.1 Introduction

In 1959 GE manufactured phenolic membranes through polymerisation of phenol-sulphonic acid with formaldehyde, which was one of the first steps towards PEM development for ultimate use

in fuel cells³³. The membranes themselves were however not suitable for use in fuel cells, because of short lifetimes and weak mechanical stabilities³³. Between 1962-1965, these membranes were improved to such an extent that they were used on board of the NASA's Gemini flights even though they could only provide power densities of about $0.4\text{--}0.6\text{ kW m}^{-2}$ ³³. Further attempts were made to improve these membranes, but the inherent problem with all these membranes was the fact that insufficient proton conductivities were obtained³³. This remained a challenge until the 1970s when Du Pont developed the well-known perfluorinated membranes called Nafion[®]. What made this membrane unique was the fact that it attained higher conductivities and it also showed a remarkable extension in the membrane lifetime³³. With the established use of the membrane technology ranging from PEMFC to H₂O electrolyzers, the use of a PEM in SO₂ electrolyzers was a small step. Therefore, Nafion[®] remains the benchmark membrane both in PEMFC³³ as well as in SO₂ electrolyzers¹⁰.

2.3.2 Nafion[®]

Nafion[®] membranes consist of a hydrophobic tetrafluoroethylene (TFE) backbone with side chains of perfluorinated vinyl ethers. At the end of these side chains there are -SO₃H ion-exchange groups³⁴ as shown in Figure 2.15.

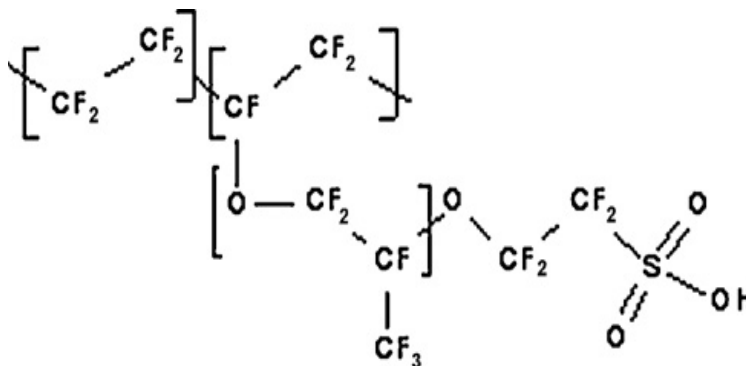


Figure 2.15: Nafion[®] structure¹⁰

A Nafion[®] membrane consists of three parts, a hydrophobic poly- backbone, and a hydrophilic phase consisting of water, ions and -SO₃H anion groups and finally an intermediate phase³⁵. It is this water located in the hydrophilic phase of the membrane that allows the H⁺ to form a hydronium ion and thus enables the Grotthuss or vehicular transport mechanism to take place. However at low membrane water concentrations, direct proton transport takes place through

passing protons from one -SO_3^- group to another -SO_3^- group as previously shown in Figure 2.14.

As stated previously, Nafion[®] membranes are currently the benchmark membranes because of their excellent chemical stability and high proton conductivity^{10,36}. Therefore, they are widely used in fuel cells, and in water electrolyzers. However their possible use in SO_2 electrolyzers has received little attention to date. Even though Nafion[®] is the benchmark membrane, it tends to become less effective at temperatures above 80 °C³⁷, because of water loss and mechanical weakening of the membrane. Research is therefore still continuing to develop better membranes, or to improve on currently available membranes.

2.3.3 High temperature polybenzimidazole (PBI) blends

The high temperature phosphoric acid doped blend membranes consist of a polybenzimidazole or PBI polymer (in this case the PBI-OO polymer) combined with an acidic polymer, which was either a sulphonated fluorophenyl sulphone (sFS) or a sulphonated polyphenyl sulphone (sPSU) polymer. The sFS polymer is a partially fluorinated acidic polymer while the sPSU polymer is a non-fluorinated acidic polymer. Since both of these high temperature membranes contain the basic polymer in excess, they do not have an ion-exchange capacity. All sulphonic acid groups of the acidic blend component are bound to PBI in acid-base bonds. Proton conduction of such blends only takes place if the membranes are protonated, for example in phosphoric acid. Both the sFS and sPSU based membranes can only be used at low RH conditions as the possible condensation of water will cause the leaching of phosphoric acid. In the doped form these membranes are able to conduct protons up to 200 °C.

2.3.3.1 High temperature PBI + sFS001

The high temp PBI and sFS001 blends contain a composition of PBI (Figure 2.16) and a partially fluorinated acidic polymer formed from the sulphonation of a PFS001 polymer with 60% oleum (Figure 2.17)³⁸. The blend used in this study contains 70wt% of the PBI and 30wt% of the acidic sFS001 polymer.

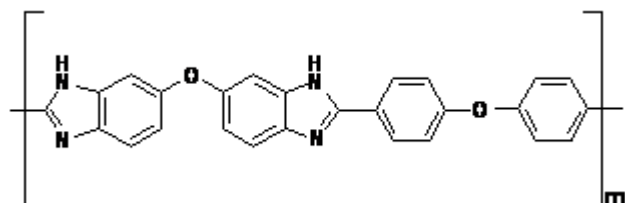


Figure 2.16: Basic PBI structure³⁹.

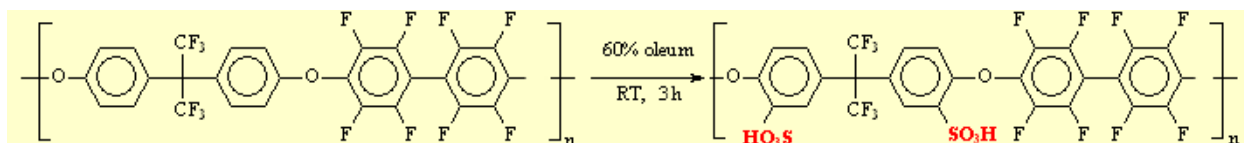


Figure 2.17: Structure of sFS membrane⁴⁰

2.3.3.2 High temperature PBI + sPSU-BP-50

As was the case with the high temp sFS-PBI membranes, these membranes also contain PBI, but this time the PBI is combined with a sulphonated polyphenyl sulphone non-fluorinated acidic polymer, shown in Figure 2.18, with the blend containing 70wt% of PBI-OO and 30wt% of the acidic polymer.

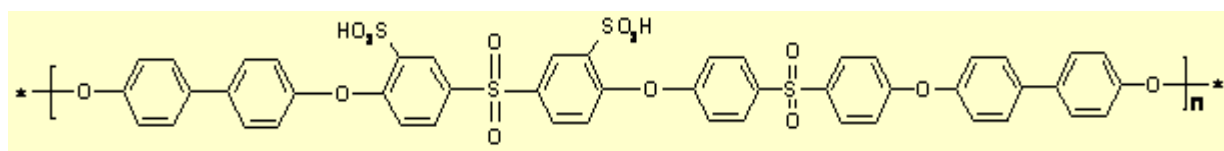


Figure 2.18: Structure of sPSU-BP-50 membrane⁴⁰

Both these membranes need to form hydronium ions in order to be able to conduct protons⁴¹. The pretreatment of these membranes in phosphoric acid increases the number of hydrogen atoms in the structure and thus enables the membranes to form hydronium ions, which in turn enables them to conduct protons. The binding of phosphoric acid to the PBI can be seen in Figure 2.19. Phosphoric acid, bound to the membrane, interacts with the heated water vapour that is present in the electrolyser environment giving rise to reaction 3:



It is this formed H_3O^+ that allows the conductivity to take place through the Grotthuss mechanism⁴².

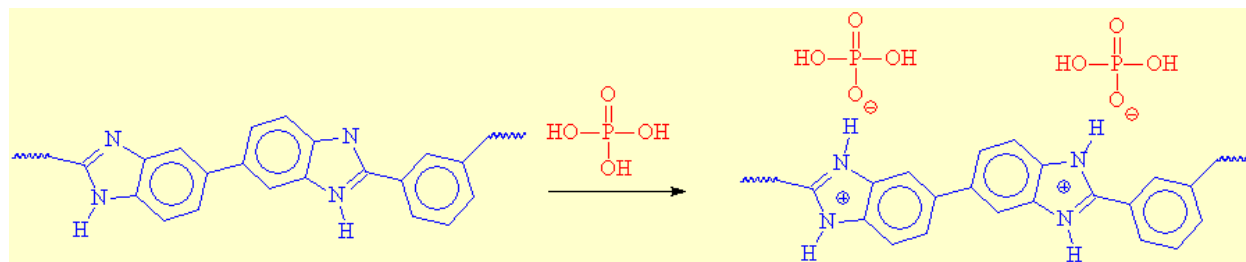


Figure 2.19: Structure of doped PBI⁴⁰

2.3.4 Low temperature PBI blends

The low temperature blend membranes used in this study are also composed of the same PBI polymers used for the high temperature membranes, as well as the same acidic polymer with one of the membranes containing a fluorinated polymer and the other a non-fluorinated polymer. These membranes are used at temperatures lower than 80 °C and no doping in phosphoric acid is needed for the membrane to be able to conduct protons, which allows these membranes to operate at high relative humidities. The difference to the high temperature PBI blends is attained by varying the ratios of the blends.

2.3.4.1 Low temperature sFS-PBI

Just like the high temperature PBI + sFS001 membranes, these membranes also consist of a blend of a partially fluorinated acidic polymer with a theoretical IEC of 1,35 meq $\text{SO}_3\text{H}/\text{g}$ membrane⁴³. In these membranes however, 3g (85.47 wt%) of the polymer was blended with 0.51g (14.53 wt%) of the PBI. The molecular weight of each blend membrane is approximately 780.1 g/mol. The formula for the equivalent weight (EW) is seen below.

$$\text{EW} = 1000 / \text{IEC}^{44} \quad (6)$$

Accordingly the EW for this membrane is 740g/mol

2.3.4.2 Low temperature sPSU-BP-50 + PBI

These membranes are a blend of a sulphonated polyphenyl sulphone non-fluorinated acidic polymer and PBI with a theoretical IEC (ion exchange capacity) of 1,35 meq $\text{SO}_3\text{H}/\text{g}$ membrane. In these membranes 3g of the polymer was blended with 0.235g (7.26 wt%) of PBI (92.74 wt%). The molecular weight of each blend membrane is approximately 468.6 g/mol. The EW of this membrane is also 740 g/mol.

The $-\text{SO}_3\text{H}$ groups in the low temperature membranes facilitate the transport of protons in the same fashion as Nafion[®] membranes do, i.e. either through the Grotthuss or the vehicular mechanism.

3 Conclusions

The worlds growing energy demands together with diminishing fossil fuels and growing concern over global warming, are forcing scientists and the governing bodies that fund them, to look at other possible energy sources. One of the most attractive alternative energy sources is hydrogen, which can be produced by many different methods. While most of these methods also make use of fossil fuels, there are techniques available that do not require fossil fuels, for example hydrogen production by means of water or SO_2 electrolysis.

Over the last few decades major advances have been made to improve electrolyzers and their components, from the earlier two compartment parallel-plate technique developed in the 1970`s, to the modern day MEA containing electrolyzers. However, although these developments have improved the efficiency of the electrolyzers considerably, there are still some difficulties in terms of efficiency, for example the high potentials required for H_2O electrolysis. An alternative technology, SO_2 electrolysis, requires a lower potential, where SO_2 and H_2O is fed to produce H_2 and H_2SO_4 . This technology however also faces its unique challenges including SO_2 crossover and subsequent sulphur deposition on the MEA cathode as well as the high acidity environment within the SO_2 electrolyser and its possible effect on the stability of the PEM, MEA and other components. The stability of the PEM can be tested by many characterisation techniques, including the percentage water uptake, weight loss, SEM-EDX, TGA-FTIR, GPC, IEC and proton conductivity techniques.

To conclude, SO_2 electrolysis holds significant potential in alleviating at least some of the world's energy needs as well as its possible application in other fields. However, in order to advance SO_2 electrolyzers, more research has to be done, especially on areas of the electrolyser that still remain challenging. This includes, for example the stability of the PEM's in the H_2SO_4 environment, which therefore forms the basis of this study.

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Chapter 3: Experimental

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1 Introduction

In this chapter the experimental procedures used to obtain the required results for the treatment of the selected membranes in accordance with the aim and objectives of the project, i.e. to determine the stability of various membranes in the presence of H_2SO_4 , as well as a description of the design and manufacture of the in-house build conductivity set-up are described.

2 Membrane selection

The four (low and high temperature, sFS-PBI and sPSU-PBI) blend membranes were obtained from the group of Dr Kerres and co-workers (University of Stuttgart Germany). Nafion[®] 115, which was used for comparative purposes, was purchased from Ion Power Inc, a distributor of Du Pont[™] Nafion[®] products.

3 Membrane treatment

3.1 Pre-test

Before any membranes were treated a pre-test was done to determine if the baseline membrane, Nafion[®] 115, which is known to be relatively stable, would be able to withstand the harsh H_2SO_4 environment.

Four samples (approximately 2cm^2) of Nafion[®] 115 were placed in four Petri dishes, each containing different concentrations of sulfuric acid. H_2SO_4 (30wt%, 60wt% 80wt% and 90wt%) was added to the four Petri dishes. The membranes were kept in the acid for 5 days at ambient temperature (25°C) and pressure (1bar). After observing adequate stability the tests with the PBI based blend membranes were commenced.

3.2 H_2SO_4 treatment

Before acid treatment, the membranes were weighed after drying in a vacuum oven (over phosphorous pentoxide powder) at 90°C for 12 hours. Membrane samples of size 2cm^2 were subsequently placed in a Teflon coated stainless steel autoclave containing either 30, 60 or 90wt% H_2SO_4 (the high temperature membranes were only treated in 30 and 60wt% H_2SO_4). The autoclave was placed inside a digital oven (Figure 3.1) where the membranes were exposed to H_2SO_4 at 1bar and 80°C for 120 hours. The pressure and temperature within the autoclave were monitored using a pressure gauge and thermocouple respectively.

The pressure was provided using N₂. The membranes with their respective compositions exposed to H₂SO₄ are presented in Table 3.1.

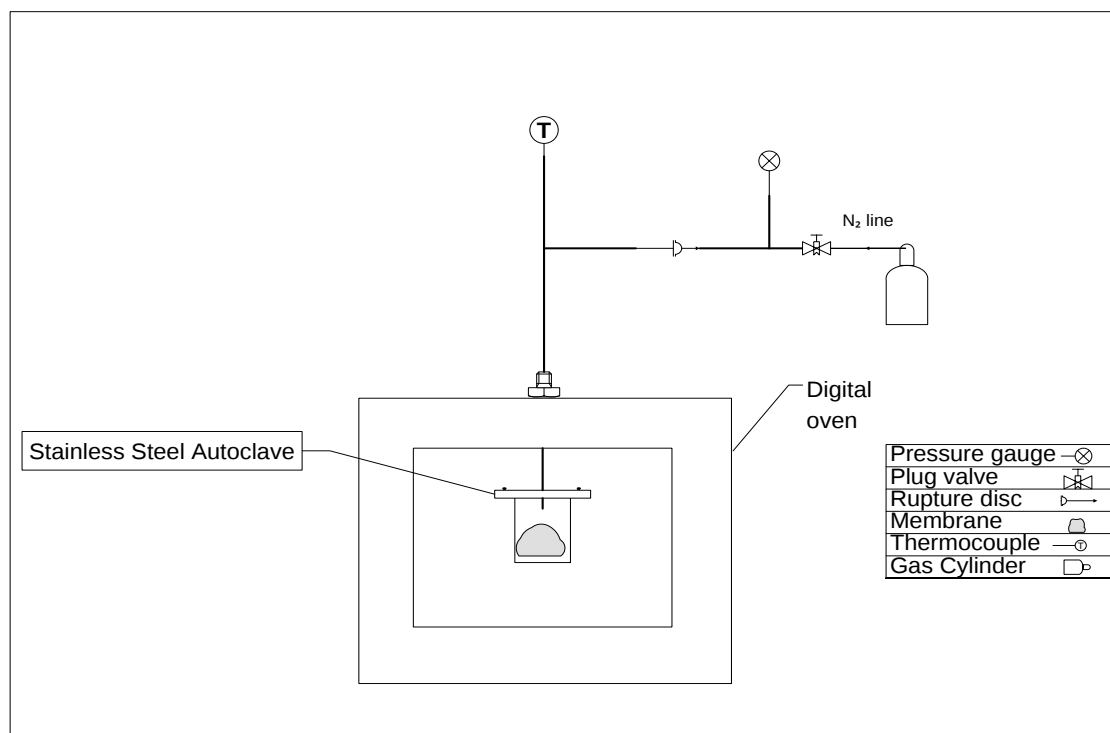


Figure 3.1: A schematic drawing of the membrane treatment set-up

Table 3.1: Composition (wt%) of PBI, sFS, sPSU, as well as the low and high temperature sFS-PBI and sPSU-PBI blend membranes.

Membrane type	Number	PBI (wt%)	sFS (wt%)	sPSU (wt%)
PBI	1	100%	-	-
sFS	2	-	100%	-
sPSU	3	-	-	100%
Low temp sFS-PBI	4	14.53%	85.47%	-
Low temp sPSU-PBI	5	7.26%	-	92.74%
High temp sFS-PBI	6	70%	30%	-
High temp sPSU-PBI	7	70%	-	30%

After acid treatment, the membranes were rinsed in de-ionised water for 5 minutes, which was followed by boiling in approximately 100ml of de-ionised water for 10 minutes. Finally they were again rinsed in de-ionised water for 5 minutes. This washing was necessary to rid the membranes of any residual H₂SO₄ that could affect the outcome of some of the characterisation results. After washing, the membranes were stored in de-ionised water in air tight bags at 25 °C.

Membranes that dissolved during the acid treatment (specifically at 90wt% H₂SO₄) were first dialysed to obtain the purified polymer. The dissolved polymer was placed in a 10000 Dalton molecular weight cut off (MWCO) dialysis tubing (supplied by separations) which was placed in 2l de-ionised water filled glass beakers. The water was changed regularly. After 3 days the acidity of the polymer suspension inside the tube was determined using litmus paper. Once neutral the solution was emptied into a 1l glass beaker. This beaker was placed in an oven at 90 °C in order to dry the polymer suspension.

4 Post-treatment characterisation

All the characterisation methods, except SEM/EDX and conductivity were adapted from Kerres et al^{1,2,3}. While the in-plane conductivity method was adapted from Ramani et al⁴, the through-plane conductivity set-up was adapted from Lee et al⁵, while the method used was obtained from Kerres et al^{1,2}.

4.1 In-plane conductivity

In Figure 3.2, a drawing is presented of the in-house developed in-plane conductivity meter set-up. This set-up was build to allow for proton conductivity measurements under SO₂ electrolyser simulated conditions. The set-up consisted of two hydrogen gas lines, one line to provide “dry” hydrogen gas which flowed directly to the stainless steel (SS) container and one line of H₂O saturated hydrogen gas that flowed via a saturator, thus obtaining humidified H₂ gas, to the container. By varying the ratio of gas supply to each line, using rotameters (supplied by Swagelok South Africa) the percentage relative humidity (RH) in the SS container was controlled. To measure the percentage RH accurately, a Vaisala INTERCAP® HMP60 Humidity and Temperature Probe (which is able to measure the percentage RH as well as the temperature) was inserted into the SS container. The flow rate of hydrogen was kept at 150ml/hour. The H₂ from the SS container was released into a fume hood. The SS container also contained a four-point-probe conductivity meter (obtained from Giner, Inc, Massachusetts, USA), which in turn contained the membranes for testing. As shown in Figure 3.2, the complete system including the hydrogen lines, humidifier and SS container was placed in an oven to be able to control the temperature. The mentioned four-point-probe meter was connected to a computer as well as a FRA containing Bio-Logic HCP-803 potentiostat for collection of impedance measurement data.

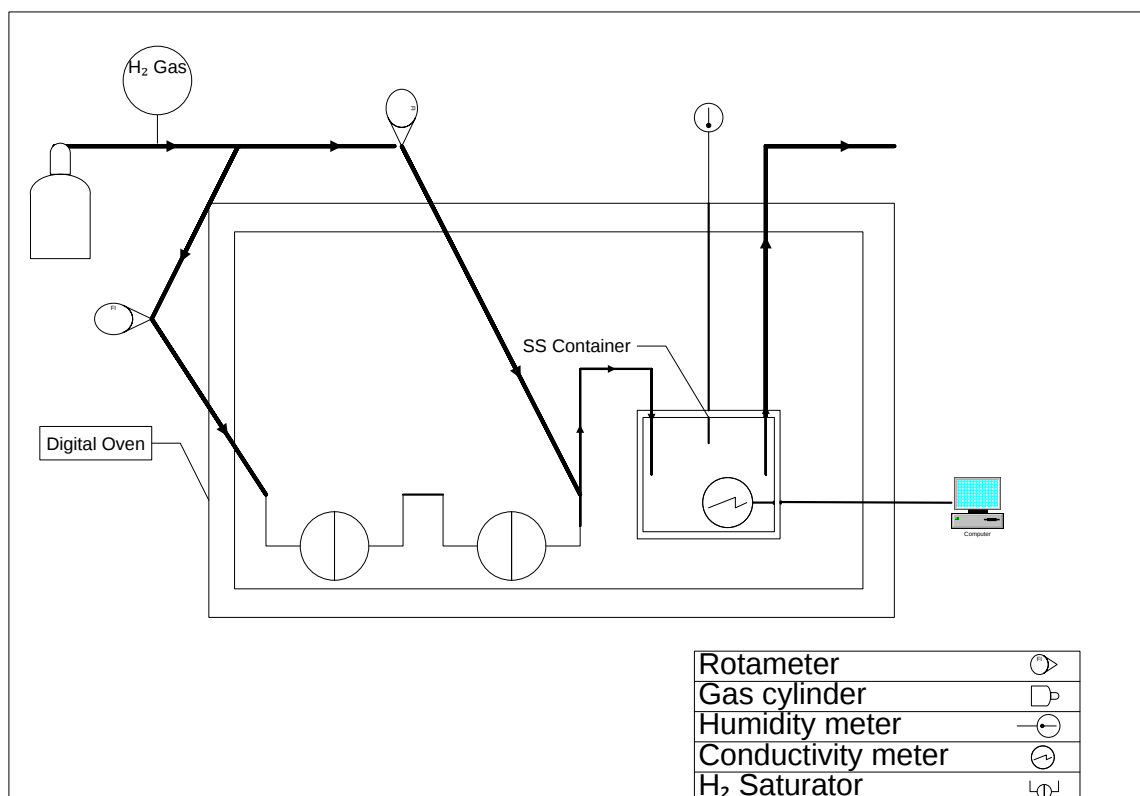


Figure 3.2: A drawing of the conductivity meter set-up

To acquire the resistance of the membrane, a DC current was measured by monitoring the current as the potential between the inner reference electrodes was swept between -0.25 V to 0.25 V vs. the reference electrode. A plot of current (I) vs. Potential (E) yielded a straight line and the slope of this line yielded the reciprocal of the resistance. EC lab express was the software that was used to gather the data.

4.2 Through-plane conductivity

The specific through-plane resistance of the membranes was determined *via* impedance spectroscopy using a Zahner elektrik IM6 impedance spectrometer. The samples were measured in through-plane mode, as shown in Figure 3.3, in a frequency range of 200 KHz – 2 MHz with an amplitude of 5 mV. We used a 0.5 N H_2SO_4 environment, for the measurements where better reproducibility was obtained, compared to measurements done in water. The conductivity was obtained using the conductivity formula ($\rho = R_{wd}/l^{6,7}$) discussed in Chapter 2.

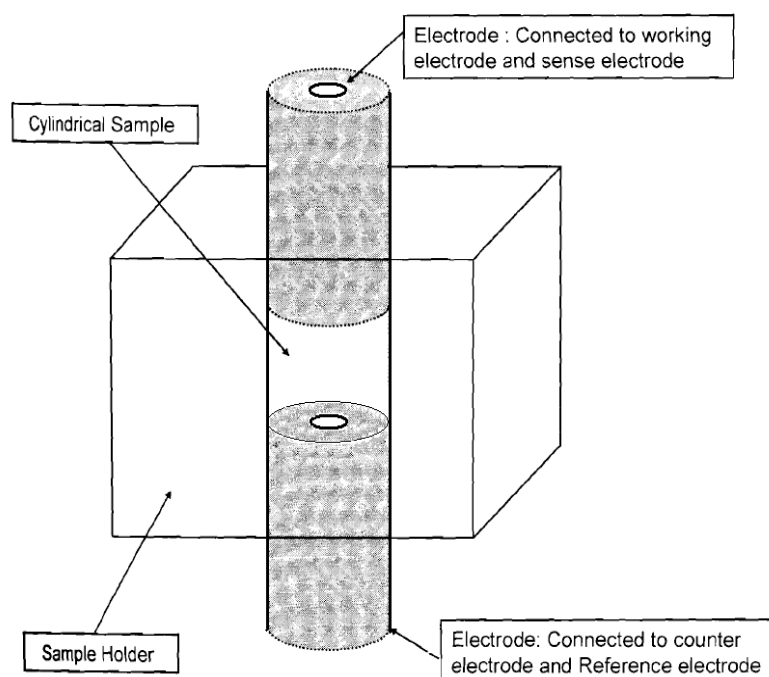


Figure 3.3: An example of a through-plane conductivity meter

4.3 Weight loss

The dry weight of the samples before treatment was compared to the dry weight of the samples after treatment. The membranes were dried through placement in a phosphorous pentoxide powder containing vacuum oven at 90 °C for 12 hours, subsequently the membranes were weighed to note their dry weight.

4.4 GPC

The molecular weight distribution of the membranes was determined by GPC, which was performed at 50 °C on a polymer standards service (PSS) system equipped with an Agilent 1200 series refractive index detector, PSS SLD 7000 multiangle-lightscattering detector and a ETA2010 viscometer detector, PSS 30 and 3000 Å columns, and an Agilent 1200 series pump using polystyrene standards for calibration. As eluent, DMAc containing 5 wt% LiBr was used to increase the solubility of the ionic polymer and to reduce the interaction between solutes and packing materials. The blend membrane and polymer solutions were injected with a concentration of 2 g/l. The obtained curves were integrated to ascertain the molecular weight distribution of the polymers and blend membranes.

4.5 TGA

The thermal stabilities of the blend membranes were determined by thermogravimetry (TGA, Netzsch, model STA 449C) with a heating rate of 20 °C/min under a 65-70% O₂ atmosphere.

4.6 SEM-EDX

A FEI Quanta 200 ESEM with integrated Oxford INCA X-sight EDS system was used to investigate the visual membrane surfaces and cross-sections as well as the elemental composition before and after H₂SO₄ treatment. SEM was also used to investigate possible visual mechanical degradation that may have occurred.

4.7 IEC

The ion exchange capacity (IEC) of the membranes was obtained by titrating a sample of a membrane with HCl. The dry membranes were weighed and immersed in 25ml of standardised 0.1M NaOH, to which 75ml of de-ionised water was added. Subsequently, the solution was stirred for 24h at 25 °C. After 24h, 8 drops of bromothymol blue were added to serve as an indicator. Thereafter, the exchanged protons were determined by titration with 0.1M of standardised HCl to the equivalent point. The equivalent point was shown by a colour change from blue to yellow. The IECs were calculated using the following equation:

$$IEC = (V_{total} * C_{total} - V_{used} * C_{used}) * 1000 / m \quad (1)$$

V_{total} : Volume of the original solution (L)

V_{used} : Volume of titration solution used (L)

m : Weight of the membrane (g)

C_{total} : Molarity of the original solution (mol/L)

C_{used} : Molarity of the solution used for titration (mol/L)

Since IECs are usually measured in milli-equivalents, the amount of moles obtained from the above equation was multiplied with 1000 to give milli-equivalents per gram of membrane.

5 References

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- ⁵ LEE, S.W. 2008. Studies on polymer electrolyte membrane degradation. Illinois Institute of Technology. (Masters.) 1-77p.
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- ⁷ JUNG, G., WENG, F., SU, A., WANG, J., LEON YU, T., LIN, H., YANG, T. & CHAN, S. 2008. Nafion®/PTFE/silicate membranes for high-temperature proton exchange membrane fuel cells. *International journal of hydrogen energy*, 33(9):2413-2417.

Chapter 4: Results and discussion

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1 Introduction

The following chapter describes the results obtained from the experimental procedures described in Chapter 3, followed by a detailed discussion on the interpretation of the acquired results in an attempt to correlate the membrane material to the H_2SO_4 stability. During a pre-test, the Nafion[®] 115 membranes remained visually stable after H_2SO_4 exposure, paving the way for the PBI-based membrane evaluation. In Section 2, the preliminary study done on the high temperature sPSU-PBI and sFS-PBI blend membranes is presented. However, the current emphasis within the broader research group at the North-West University is on low temperature SO_2 electrolysis¹. Therefore, at present, and hence in this dissertation, the focus was on the characterisation of the low temperature membranes, while the high temperature membranes for SO_2 electrolysis will be investigated at a later stage. Subsequently the bulk of this chapter (Section 3) will present an in depth analysis and discussion on the acid stability of the low temperature membranes.

2 High temperature membranes

2.1 H_2SO_4 treatment

Visually both sPSU-PBI and sFS-PBI membranes remained stable during the 30wt% and the 60wt% H_2SO_4 treatments as seen in Figure 4.1 and 4.2.



Figure 4.1: The fluorinated sFS-PBI membrane after treatment in 60wt% H_2SO_4



Figure 4.2: The non-fluorinated sPSU-PBI membrane after treatment in 60wt% H₂SO₄

2.2 Post-treatment characterisation

For the preliminary study on the high temperature PBI-blend membranes, only through-plane conductivity, GPC and IEC measurements were used for characterisation purposes.

2.2.1 *Through-plane conductivity*

Since the high temperature blended membranes have few sulphonic acid groups in their composition and as mentioned earlier (Chapter 2) these groups are bound to PBI through acid-base bonds, their ability to conduct protons is drastically reduced. Therefore, phosphoric acid treatment is required to enable the membrane to conduct protons (see Chapter 2). Proton conduction of such blends could take place without phosphoric acid treatment in a HyS electrolyser, with the sulphuric acid partially bound to the basic PBI imidazole sites via acid-base interaction and hydrogen bridges². In the absence of H₂SO₄ or SO₂ however no detectable through-plane conductivity was observed irrespective of the H₂SO₄ concentration confirming the absence of any sulphonation during H₂SO₄ treatment.

2.2.2 GPC

a) sFS-PBI membrane blend series

According to Figure 4.3 no weight loss or gain occurred during the H₂SO₄ treatment which implies that the membrane remained stable throughout the treatment.

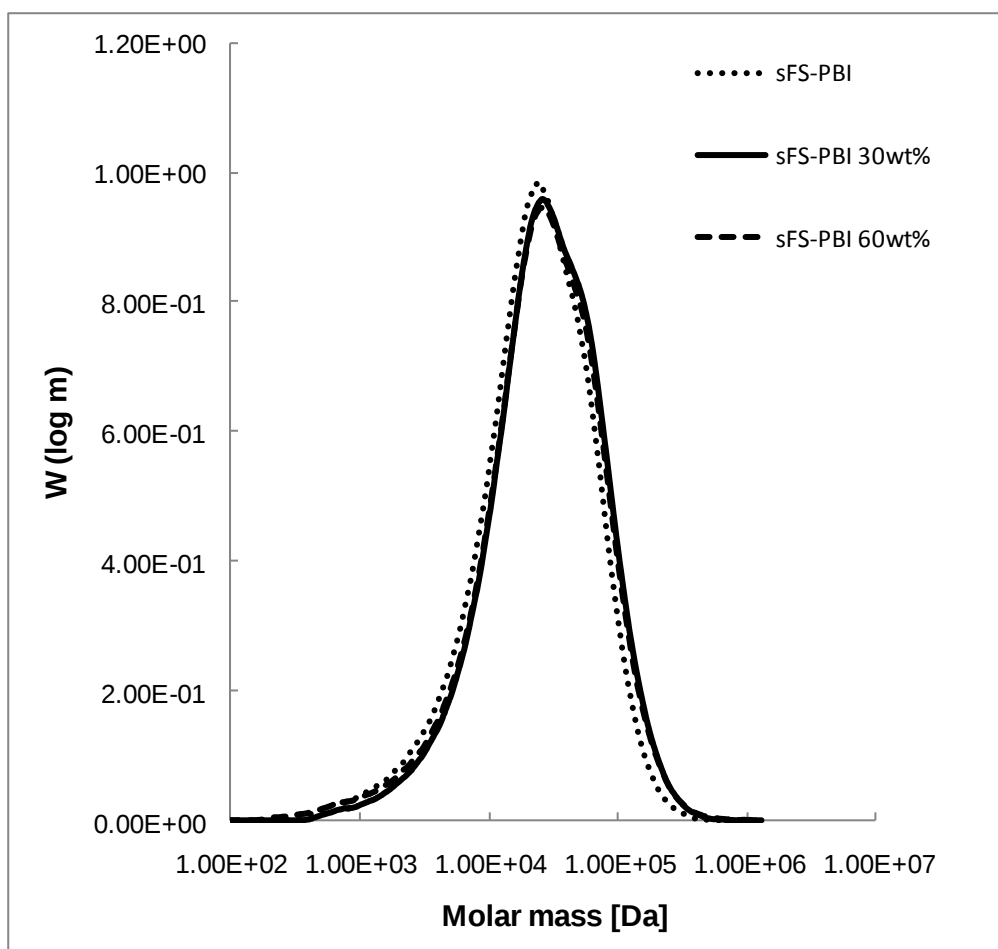


Figure 4.3: GPC values for high temperature sFS-PBI membranes after exposure to H_2SO_4 at 1bar and 80 °C.

b) sPSU-PBI blend membrane series

Figure 4.4 shows the comparable stability of the sPSU-PBI membrane at both the treatment concentrations as no weight loss or gain on the molecular level was observed.

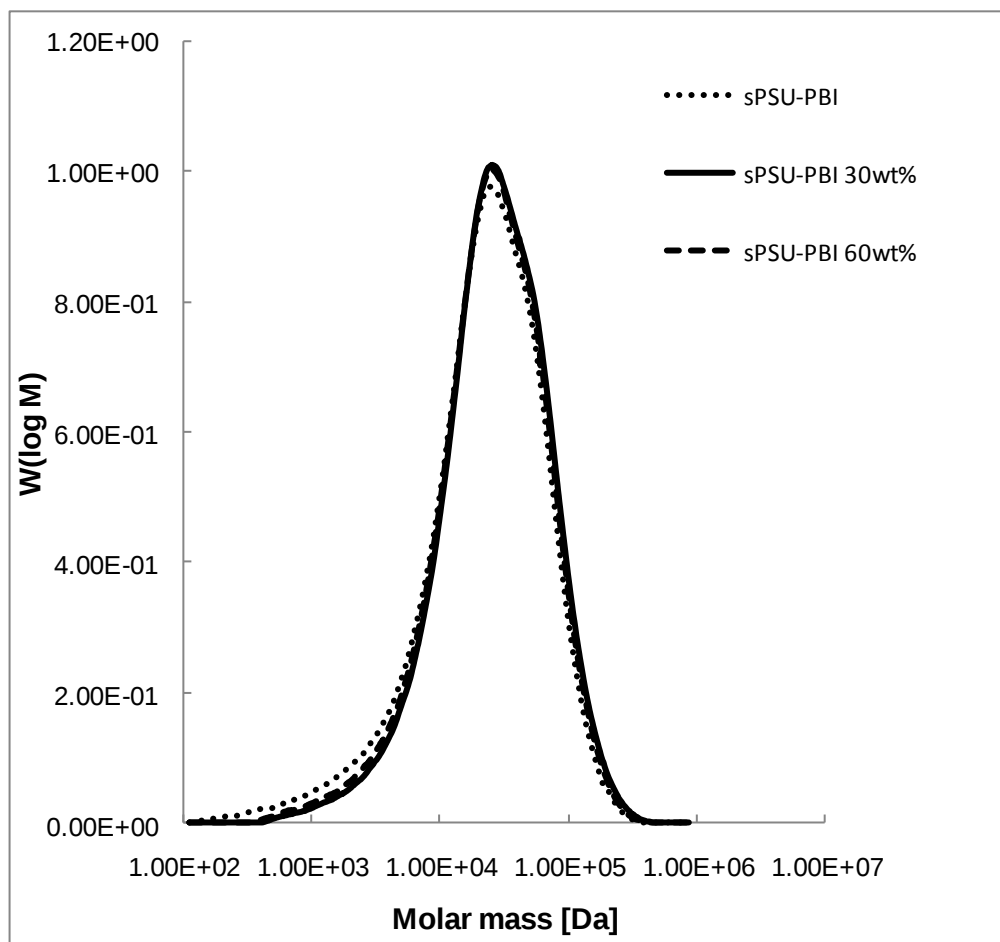


Figure 4.4: GPC values for the high temperature sPSU-PBI membranes after exposure to H_2SO_4 at 1 bar and 80 °C.

2.2.3 IEC

Since the high temperature membranes contain the basic polymer in excess (70 wt% basic PBI and 30 wt% acid sPSU/sFS polymer as seen in Figure 4.5), they have low ion-exchange capacities. This is due to the sulphonic acid groups of the acidic blend component being bound to PBI through acid-base bonds². The membranes IEC's were analyzed to determine possible IEC increases which would be indicative of sulphonation due to the H_2SO_4 treatment.

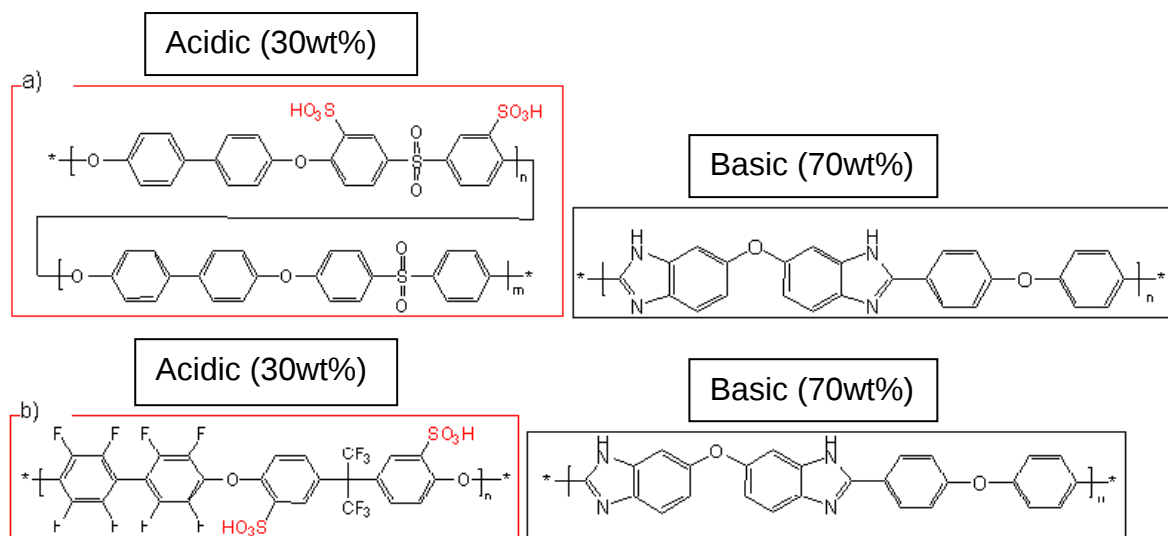


Figure 4.5: Structure of high temperature a) sPSU-PBI and b) sFS-PBI membranes³

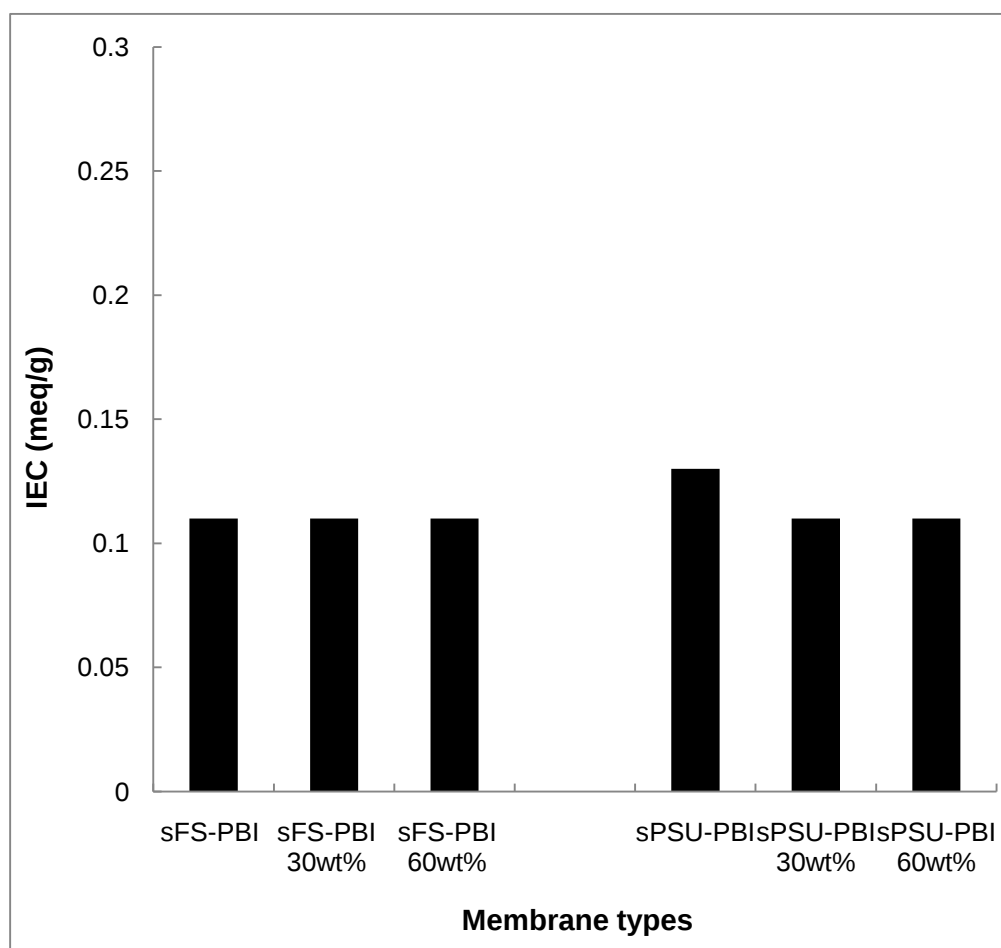


Figure 4.6: IEC change due to H₂SO₄ treatment.

As can be seen from Figure 4.6, no increase in the membrane's IEC values was found, and thus no sulphonation was observed up to 60wt% H₂SO₄. The slightly higher IEC values in the untreated sPSU-PBI membrane can be explained by the very low IEC levels obtained

(seen in the context of the IEC levels in Figure 4.27) and thus the larger margin for error. A 10% experimental error was detected.

3 Low temperature membranes

3.1 H₂SO₄ treatment

Visually all membranes remained stable during the 30wt% and 60wt% H₂SO₄ treatment. At 90wt%, the fluorinated sFS-PBI blend membrane dissolved partially (Figure 4.7), whilst the non-fluorinated membranes (PBI, sPSU and sPSU-PBI blend) dissolved completely (Figure 4.8) showing that the fluorination does contribute to the stability of the membranes at 90wt% H₂SO₄.



Figure 4.7: sFS-PBI blend membrane before (left) and after (right) treatment in 90wt% H₂SO₄.



Figure 4.8: The non-fluorinated sPSU-PBI blend membrane after treatment in 90wt% H₂SO₄.

3.2 Post-treatment characterisation

3.2.1 In-plane conductivity

Unfortunately the results obtained from the in-house build through-plane conductivity meter were inaccurate and hence of little value for the understanding of the membrane degradation during H_2SO_4 treatment. However, for the sake of completeness they were included. Figure 4.9 shows data obtained when measuring the in-plane conductivity as a function of RH for the sFS-PBI membrane. It is clear that the data are incorrect since an increase in the percentage RH should cause an increase in the proton conductivity due to an increase in membrane water content (See Chapter 2). Subsequently the significant decrease in conductivity at 94% cannot be correct. Conversely, the conductivities obtained at 90% RH are excessively high. In spite of repeating the in-plane conductivity experiments several times, no coherent data were obtained irrespective of the membrane under investigation suggesting a functional flaw in the design of the measuring technique. Further studies are currently underway to resolve this problem.

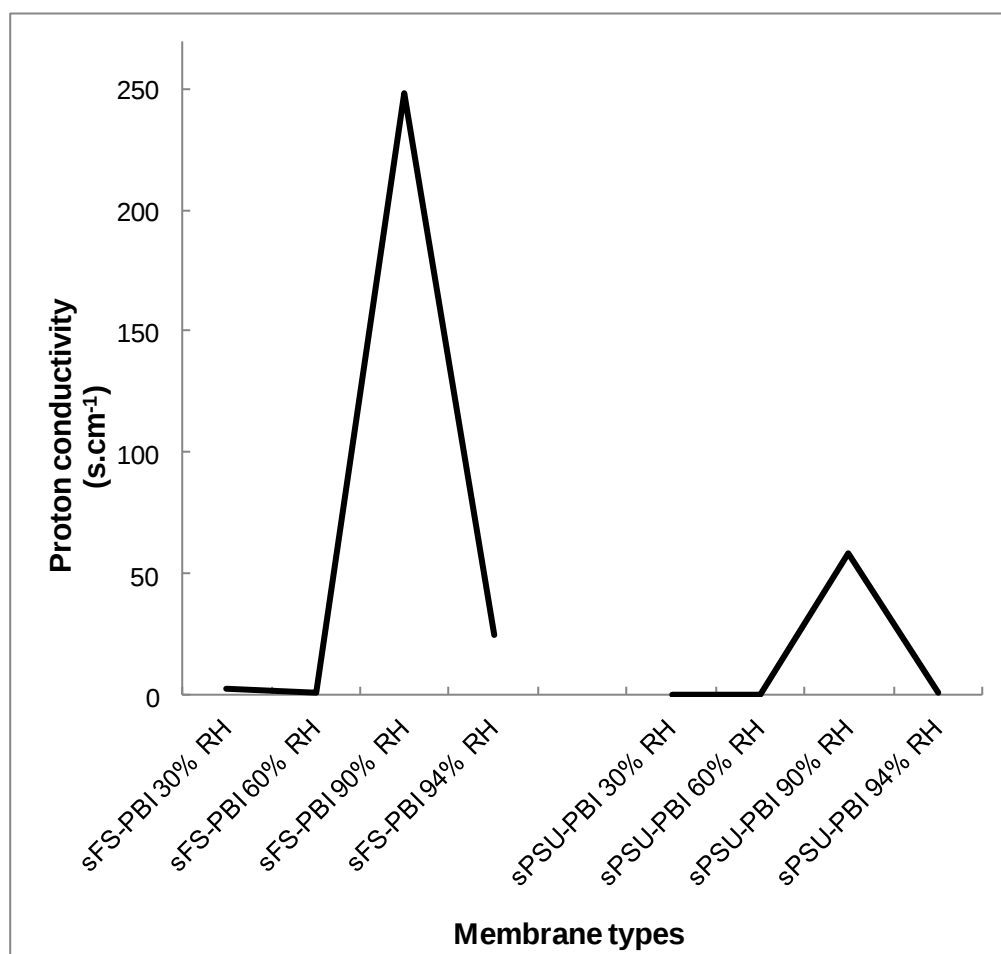


Figure 4.9: In-plane conductivity as a function of relative humidity

3.2.2 Through-plane conductivity

The through-plane proton conductivity results of the 30 and 60wt% H_2SO_4 treated sFS-PBI membranes (Figure 4.10) indicate almost no increase in conductivity from that of the untreated membranes and closely resembled those measured by Katzfuß et al⁴. There is however an increase in proton conductivity at 90wt% H_2SO_4 treated sample. This is due to more $-\text{SO}_3\text{H}$ groups that are present in the membrane because of the slight sulphonation that occurred, which might prove beneficial for the proton conductivity required for SO_2 electrolysis⁵.

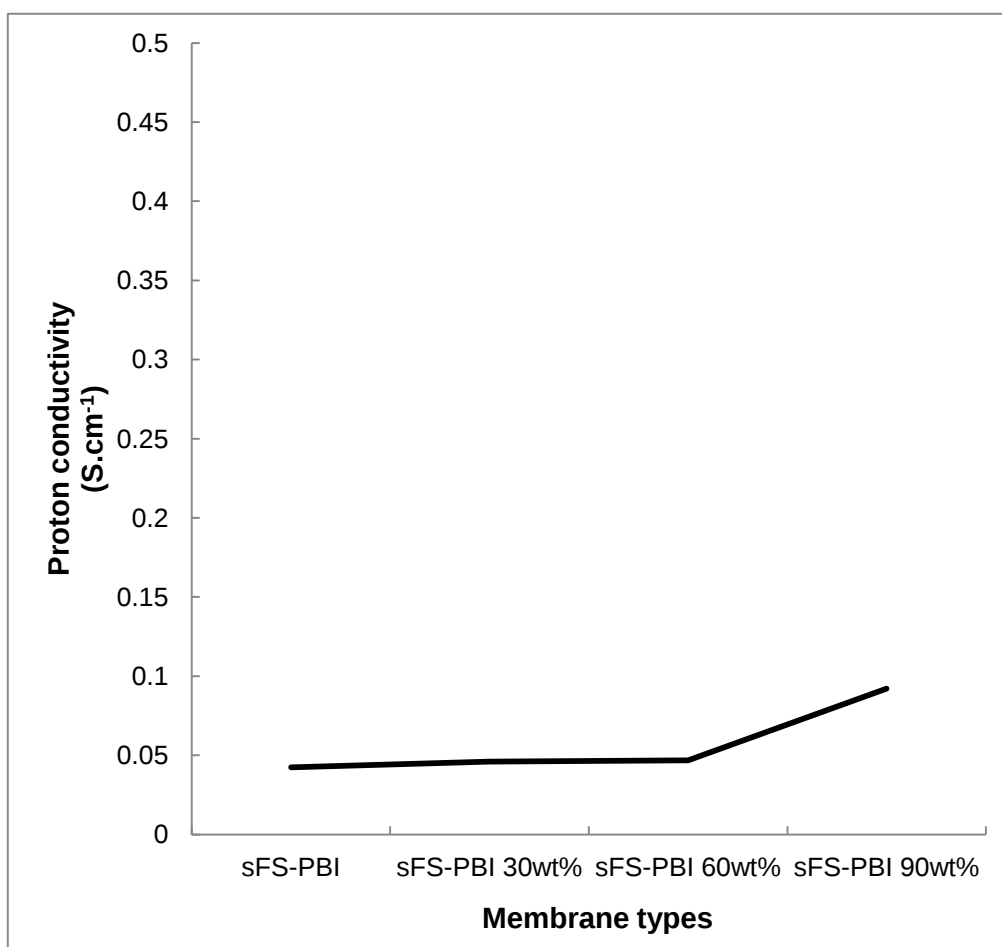


Figure 4.10: Through-plane proton conductivity change due to H_2SO_4 treatment in SFS-PBI membranes.

Figure 4.11 shows almost no increase in proton conductivity from the untreated sPSU-PBI membrane to the 30 and 60wt% H_2SO_4 treated membranes. This result confirms the absence of sulphonation (which would have caused more protons to be conducted) at the 30 and 60wt% treatments. It was however, not possible to evaluate the dissolved 90wt% treated membrane. The conductivity results also closely resemble those measured by Katzfuß et al⁴.

The dissolution at 90wt% H_2SO_4 can be ascribed to the excessive sulphonation as confirmed by the other techniques presented hereafter. Even at 60wt%, the sulphonation has increased more for the sPSU-PBI than for the sFS-PBI under the same acid treatment conditions.

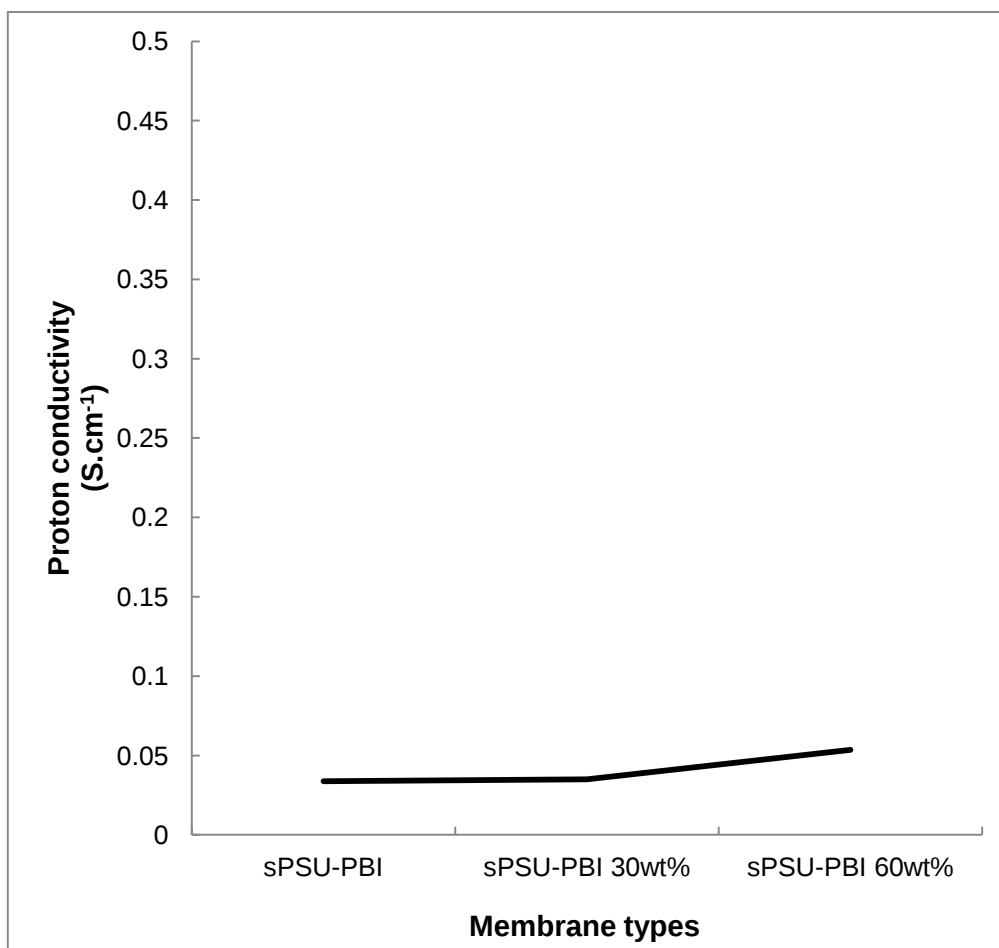


Figure 4.11: Proton conductivity change due to H_2SO_4 treatment in sPSU-PBI membranes

3.2.3 Weight change

In Figure 4.12, the weight changes before and after acid treatment is shown for all the membranes evaluated. A brief discussion for each membrane type follows.

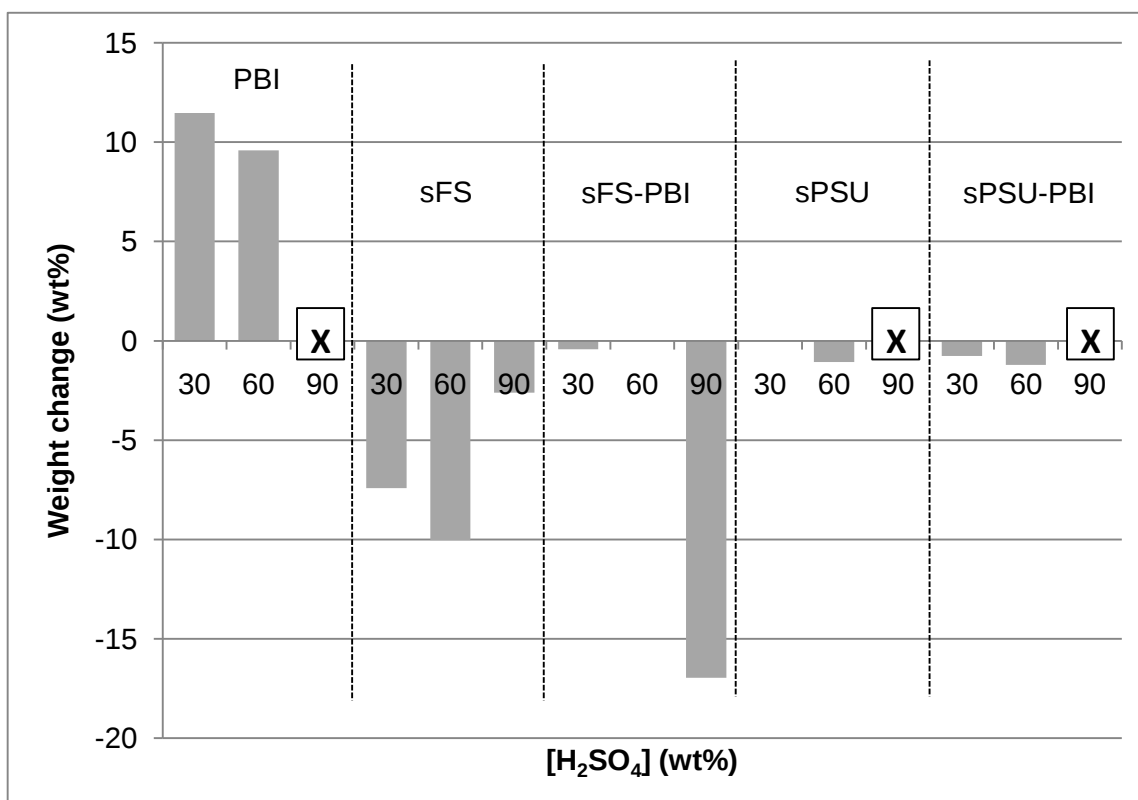


Figure 4.12: Weight change due to H₂SO₄ treatment.

a) The PBI series

The increased dry weight observed for the PBI membrane shown in Figure 4.12 at 30 and 60wt% H₂SO₄ is probably due to hydrogen sulphate salts that have formed as a result of H₂SO₄ exposure. The formed salt is relatively stable as it was not removed by the H₂SO₄ post treatment washing steps. This salt formation can be expressed by the following reaction equation²



(Im = imidazole group of PBI)

In the presence of 90wt% H₂SO₄ however the PBI membrane dissolved completely. In addition to the salt formation described above, it is likely that the strong electrophilic properties of the 90wt% H₂SO₄ were able to sulphonate the membrane backbone directly leading to the proposed structure shown in Figure 4.13.

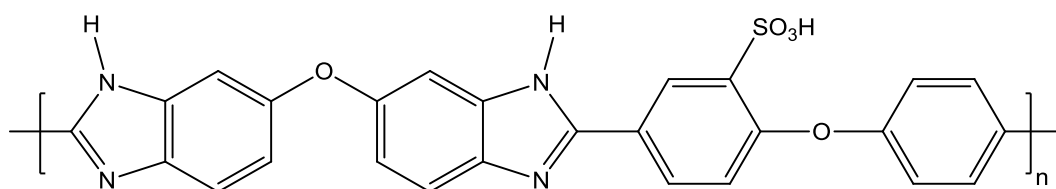


Figure 4.13: Probable structure of sulphonated PBI².

b) The sFS series

According to Figure 4.12, the sFS membranes underwent weight loss during acid treatment, which could be attributed to a loss of oligomers (low molecular weight fractions), which are always present in polyarylene condensation polymers⁶, during the post treatment washing process. In addition, all the sFS membranes were brittle and wrinkled after acid treatment, which could have contributed to possible weight losses during handling and washing. This brittleness could be due to the bisphenol A unit of the membrane, which is known to be potentially acid sensitive⁷.

c) The sPSU series

No significant weight changes were observed for the sPSU membranes exposed to 30 and 60wt% H_2SO_4 , which implies that no significant degradation or sulphonation occurred at these concentrations. However, during the 90wt% H_2SO_4 treatment the membranes dissolved, which can probably be ascribed to sulphonation. The sPSU membrane comprises an ion-exchange capacity (IEC) of 3.5 meq $\text{SO}_3\text{H}/\text{g}$ polymer after treatment in 90wt% H_2SO_4 , which translates into a sulphonic acid content of 1.9 $-\text{SO}_3\text{H}$ groups per repeat unit. Since the $-\text{SO}_3\text{H}$ group content of sPSU prior to the H_2SO_4 treatment was 0.86 $-\text{SO}_3\text{H}$ groups per repeat unit, one can conclude that roughly 1 further $-\text{SO}_3\text{H}$ group was introduced per repeat unit by the 90 wt% H_2SO_4 treatment².

It is well known that polyethersulphones can easily be sulphonated by electrophilic sulphonation agents such as H_2SO_4 or ClSO_3H at the aromatic position ortho to the ether bridge in the biarylene ether portion of the PSU repeat unit^{8,9}. This asserts our proposed sulphonation mechanism of the sPSU membranes in 90wt% H_2SO_4 , as shown in Figure 4.14.

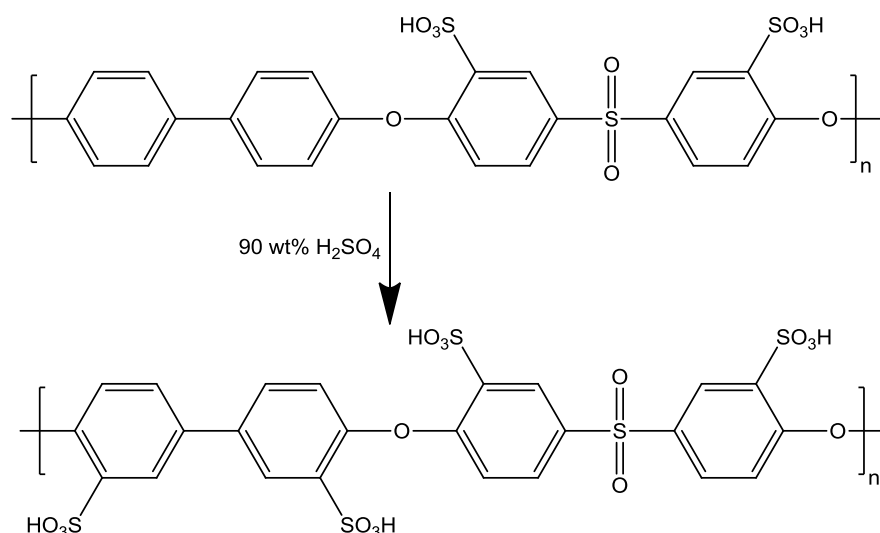


Figure 4.14: Proposed sulphonation of the sPSU membrane during the 90wt% H_2SO_4 treatment².

d) The sFS-PBI blend membrane series

The sFS-PBI blend membranes showed no significant weight change at 30 and 60wt% H_2SO_4 treatment. It is interesting to note that while the pure PBI showed an increase in weight, the pure sFS showed a decrease in weight after H_2SO_4 treatment at these conditions (Figure 4.12). This could mean that the PBI and sFS in the sFS-PBI blend membrane had a weight gain and loss respectively, resulting in the observed constant weight. On the other hand it could also imply that by combining the sFS and PBI that a stable blend membrane was obtained. While the TGA data (Section 3.2.4d) did not show any change at 30 and 60wt%, the GPC data (Section 3.2.5d) did show some increase in molecular weight which was however ascribed to salt formation rather than degradation. It therefore seems more likely that the sFS-PBI blend membrane was more stable than the stability of the pure component membranes.

Moderate weight loss (17%) did occur at 90wt% treatment, even though the membrane did not dissolve completely, as seen in Figure 4.7. The weight loss could be attributed to the complete sulphonation of the PBI (which comprises 14.5% of the membrane) and thus its dissolution from the blend, as well as partial sulphonation of the sFS and/or oligomer dissolution as described in Section 3.2.3 b.

e) The sPSU-PBI blend membrane series

The sPSU-PBI blend membrane displayed a similar stability than the pure sPSU membrane, i.e. a non significant weight decrease at 30 and 60wt%, but a complete dissolution at 90wt% H_2SO_4 . Since both the pure PBI and sPSU dissolved at 90wt% H_2SO_4 , it is only understandable that the sPSU-PBI blend membrane also dissolved at 90wt% probably

through the sulphonation of both blend components under these conditions (see Section 3.2.3a & c), leading to dissolution.

3.2.4 TGA

a) The PBI series

From Figure 4.15 it is clear that the untreated membrane had an excellent thermal stability, since considerable degradation only started at about 450 °C. The 30 and 60 wt% H₂SO₄ treated membranes show slightly less thermal stability, which could be explained by the formation of the salt groups described in Section.3.2.3a as these groups start to decompose at temperatures between 300 and 450 °C through the following proposed initiatory dehydration step of the HSO₄⁻ salt

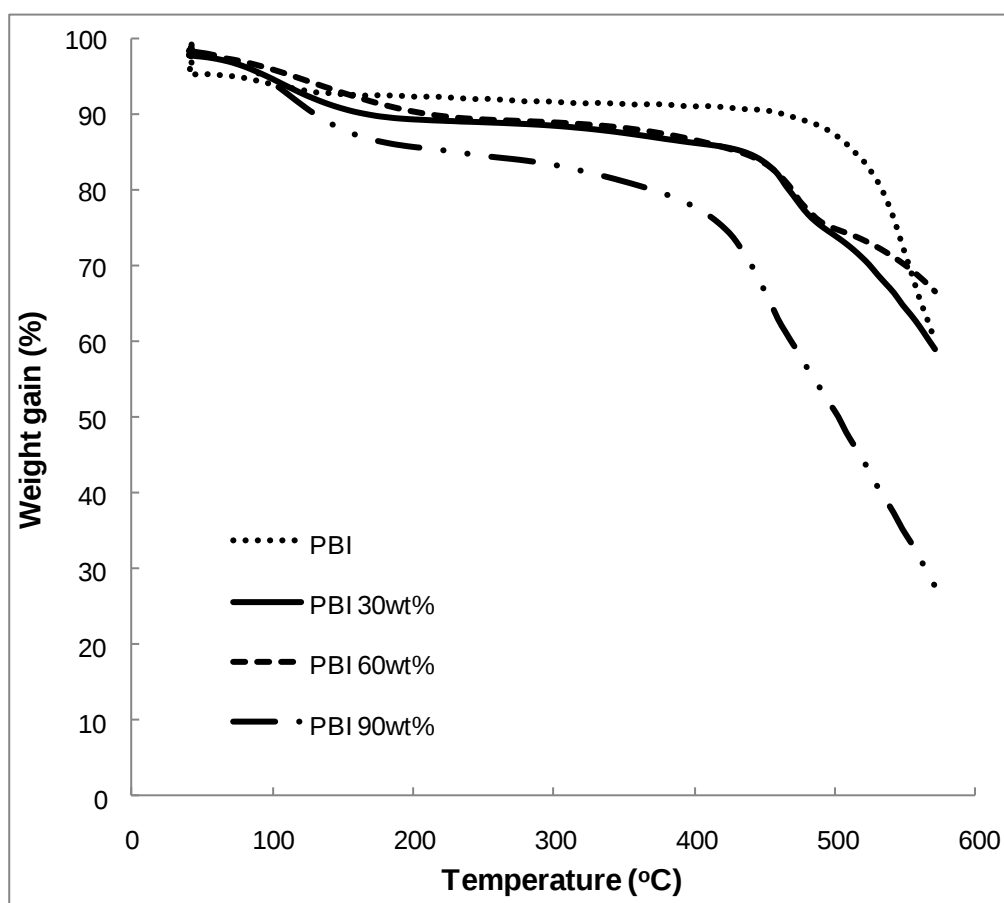


Figure 4.15: Thermal degradation of PBI membranes as a function of H₂SO₄ treatment.

At 90wt% H₂SO₄ treatment there was a sharp decrease in the TGA traces indicating the direct sulphonation occurring on the PBI aromatic rings as described in Section 3.2.3a which

would lead to a decrease in thermal stability as is seen in Figure 4.15. The weight loss between 150 and 400 °C amounts to roughly 8% compared to the untreated PBI which indicates a sulphonation degree of approximately 0.45 sulphonic acid groups per PBI repeat unit during the 90wt% H₂SO₄ treatment.

b) The sFS series

According to Figure 4.16, the sFS membranes remained stable at treatment concentrations of 30 and 60wt%, indicating that no polymer degradation has occurred. This confirms that the weight loss measured (Section 3.2.3b) was probably due to the difficulty in handling these membranes after treatment and/or the oligomer loss. At 90wt% H₂SO₄ there is a marked decrease in the TGA traces, as was observed for the other pure membranes. This decrease could be due to partial sulphonation of the membrane, yet the shape of the TGA trend line remains intact thus suggesting that the backbone of the membrane was not sulphonated, which was confirmed by the comparatively small weight loss (Figure 4.12) observed for the sFS membranes.

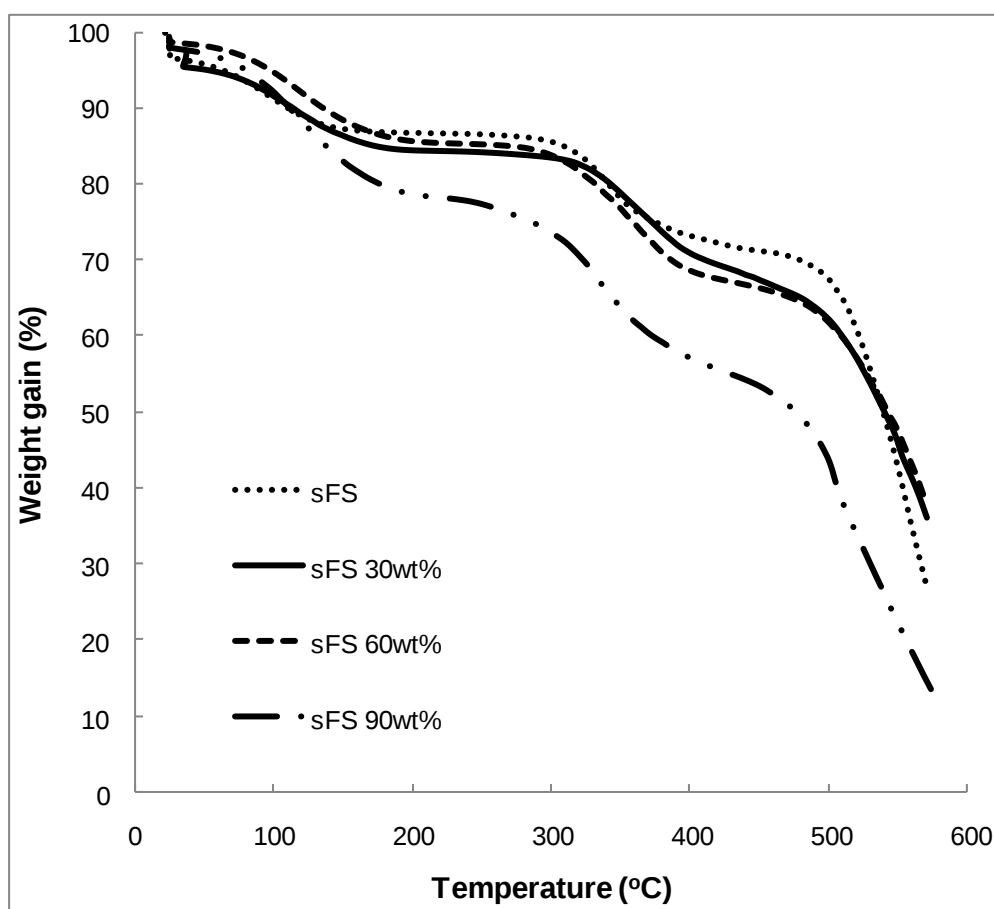


Figure 4.16: Thermal degradation of sFS membranes as a function of H₂SO₄ treatment.

c) The sPSU series

From Figure 4.17 it is clear that the membrane remained stable at the 30 and 60wt% H_2SO_4 concentrations, which was probably due to the lack of sulphonation strength of the H_2SO_4 to sulphonate the biphenol portion of the membrane, which is confirmed by the lack of weight loss at these concentrations described in Section 3.2.3c. The large drop in the TGA traces of about 23% between 150 and 320 °C confirms the suspected occurrence of sulphonation at 90wt% H_2SO_4 , which lead to the dissolution of the membrane.

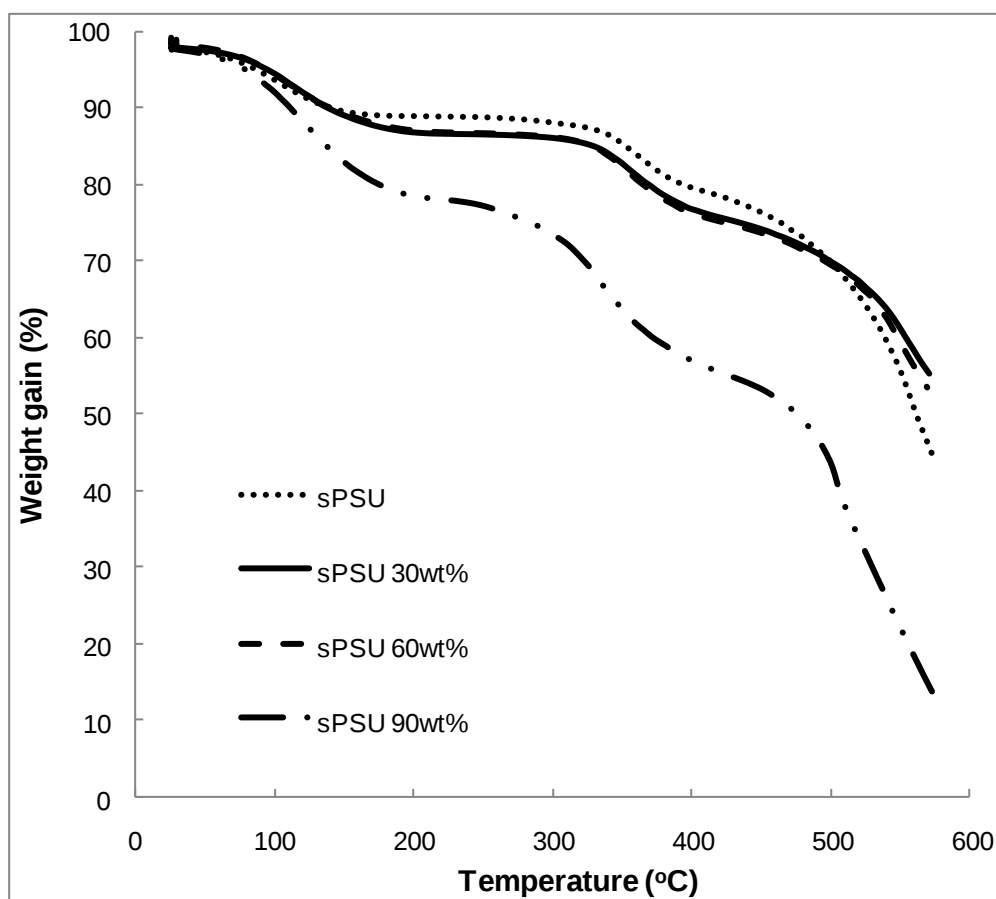


Figure 4.17: Thermal degradation of sPSU membranes as a function of H_2SO_4 treatment.

d) The sFS-PBI blend membrane series

According to Figure 4.18 the TGA traces of the sFS-PBI membrane before and after 30 and 60wt% H_2SO_4 treatment are almost identical which testifies to the membrane's stability which correlates with the observed lack of weight loss of these membranes at the same concentrations. The TGA traces at 90wt% H_2SO_4 treatment show only a slight decrease in stability at about 280 °C which could be due to the sulphonation of both the PBI as well as the sFS backbone structures. This blended membrane however did display a smaller TGA

deviation at 90wt% H_2SO_4 than either of the pure PBI or sFS membranes from which the blend was formed.

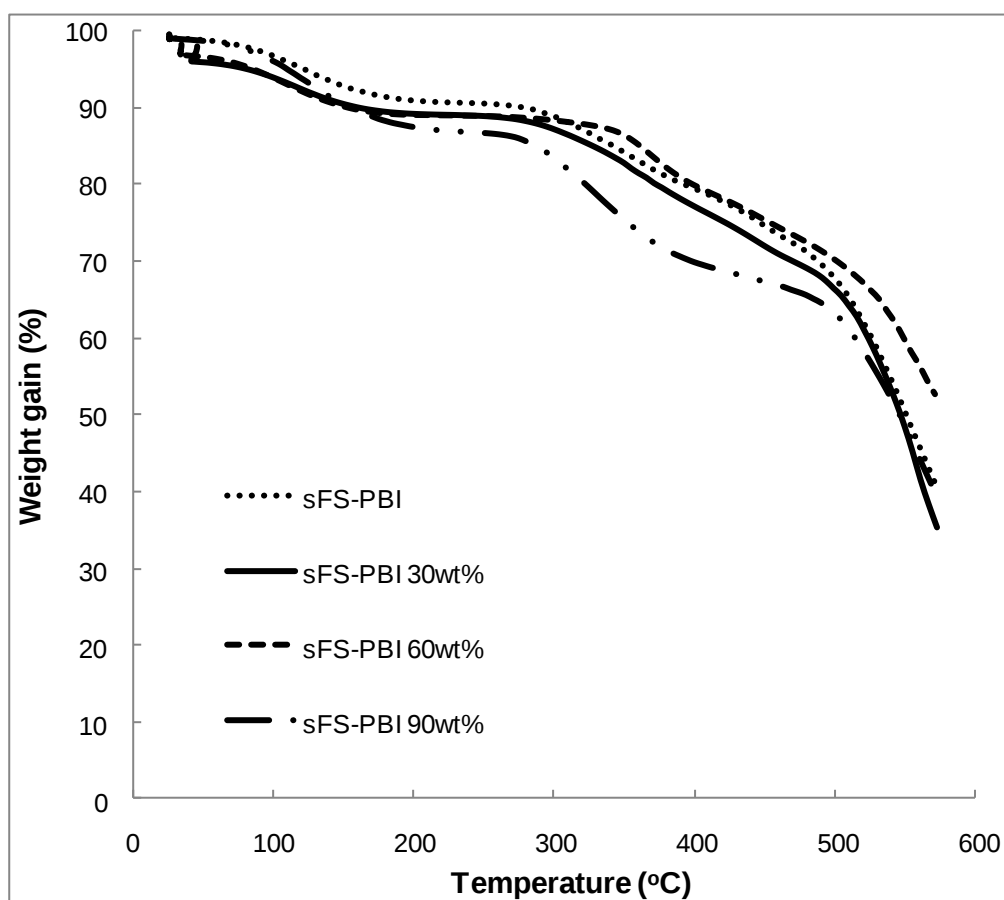


Figure 4.18: Thermal degradation of sFS-PBI membranes as a function of H_2SO_4 treatment.

e) The sPSU-PBI blend membrane series

From the TGA traces presented in Figure 4.19 it is clear that H_2SO_4 treated sPSU-PBI blend membranes remained stable at concentrations of 30 and 60wt%, which is in line with the observed constant weight before and after treatment (Section 3.2.3e). In much the same way as the pure sPSU membrane, a steep decrease in the TGA traces occurred at 90wt% H_2SO_4 treatment due to sulphonation resulting in the complete dissolution of the membrane when treated with 90wt% H_2SO_4 (see Figure 4.8).

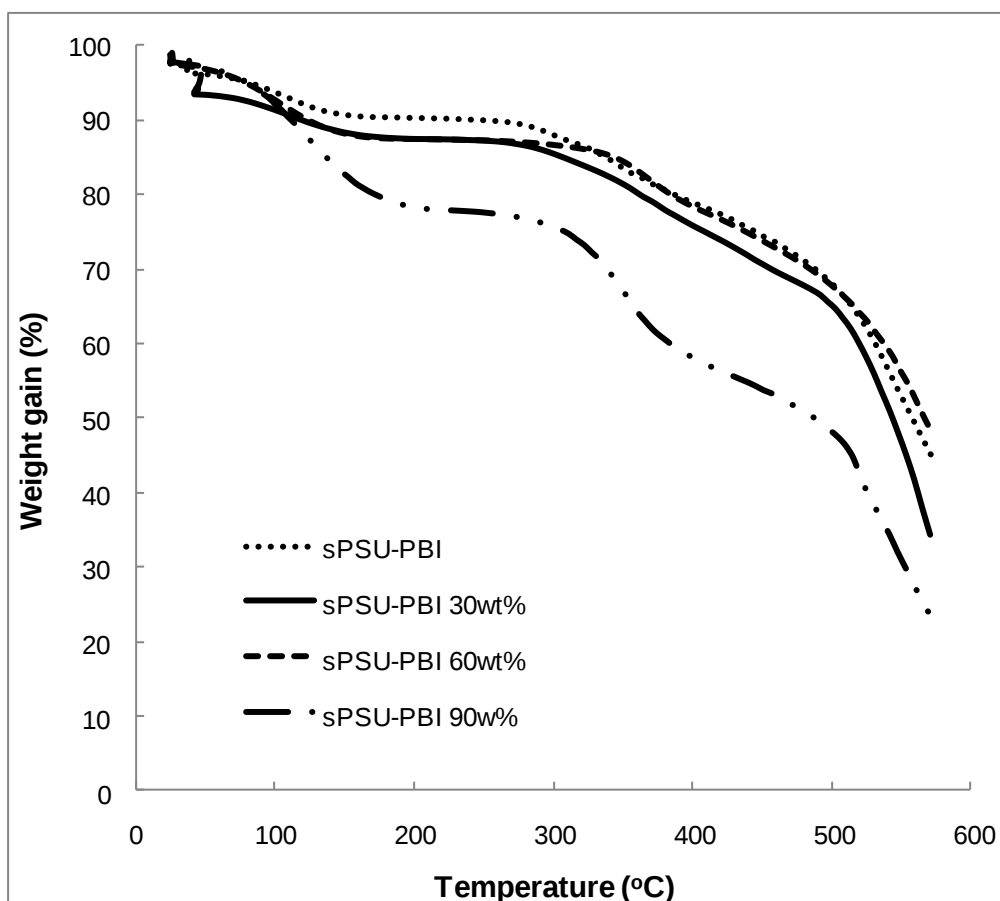


Figure 4.19: Thermal degradation of sPSU-PBI membranes as a function of H_2SO_4 treatment.

3.2.5 GPC

a) The PBI series

The weight distribution of the membranes treated in 30 and 60wt% H_2SO_4 remained relatively constant as can be seen in Figure 4.20. The increase in the membrane weight at 60wt% H_2SO_4 can be explained by the formation of the hydrogen sulphate salts as discussed in Section 3.2.3a. Regrettably the GPC curves of the 90wt% H_2SO_4 treated membrane could not be determined as the membrane was not soluble in the required GPC solvent (DMAc). Due to the excessive sulphonation the membrane became too hydrophilic in DMAc. This inability to dissolve in DMAc has previously been seen in a highly sulphonated poly phenylphenylene phosphinoyl polymers^{10,11}. These results support the discussions on weight loss and TGA data for the 90wt% treated PBI membranes.

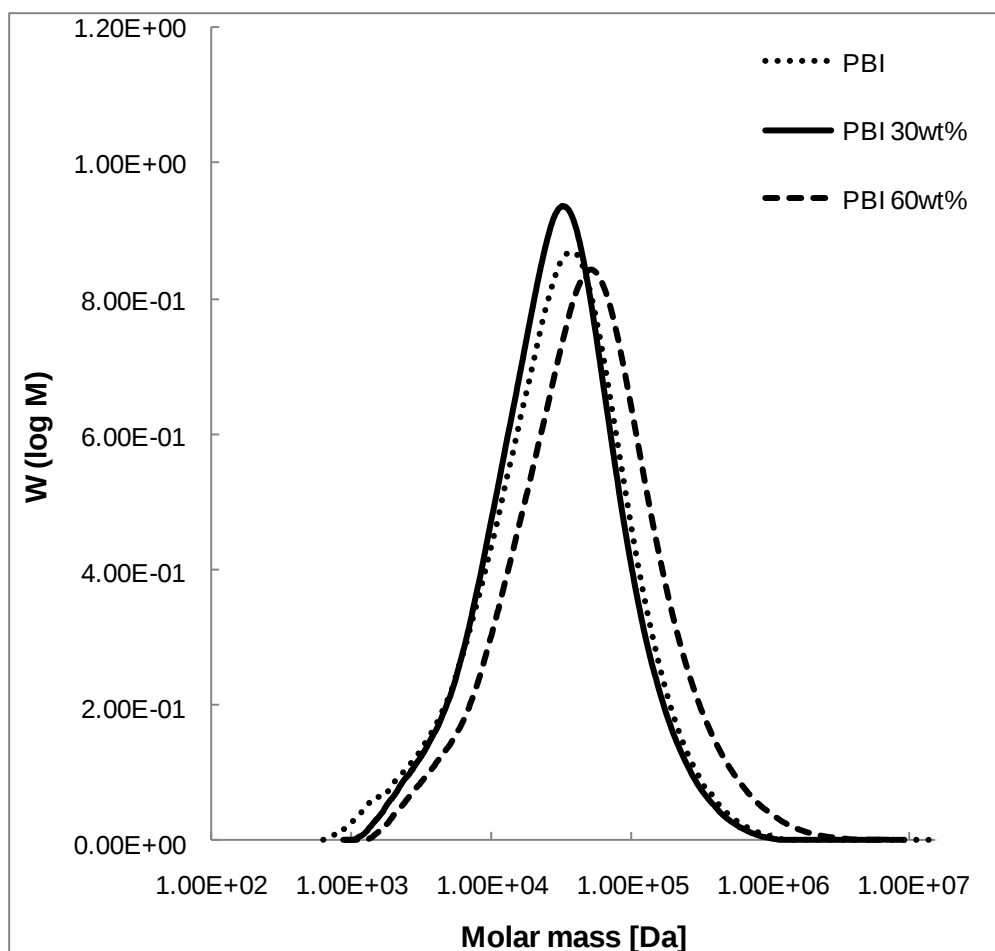


Figure 4.20: GPC traces as a function of H_2SO_4 treatment for PBI membranes.

b) The sFS series

According to Figure 4.21, a weight shift to higher molecular weights is observed regardless of the concentration of the H_2SO_4 treatment compared to the sFS membrane that has not been treated in H_2SO_4 . This could be either due to low molecular weight oligomer loss or slight sulphonation, but is most probably a combination of both these factors (oligomer loss at 30, 60 and 90wt% and slight sulphonation at 90wt%) when considering the discussions on the weight loss and TGA data.

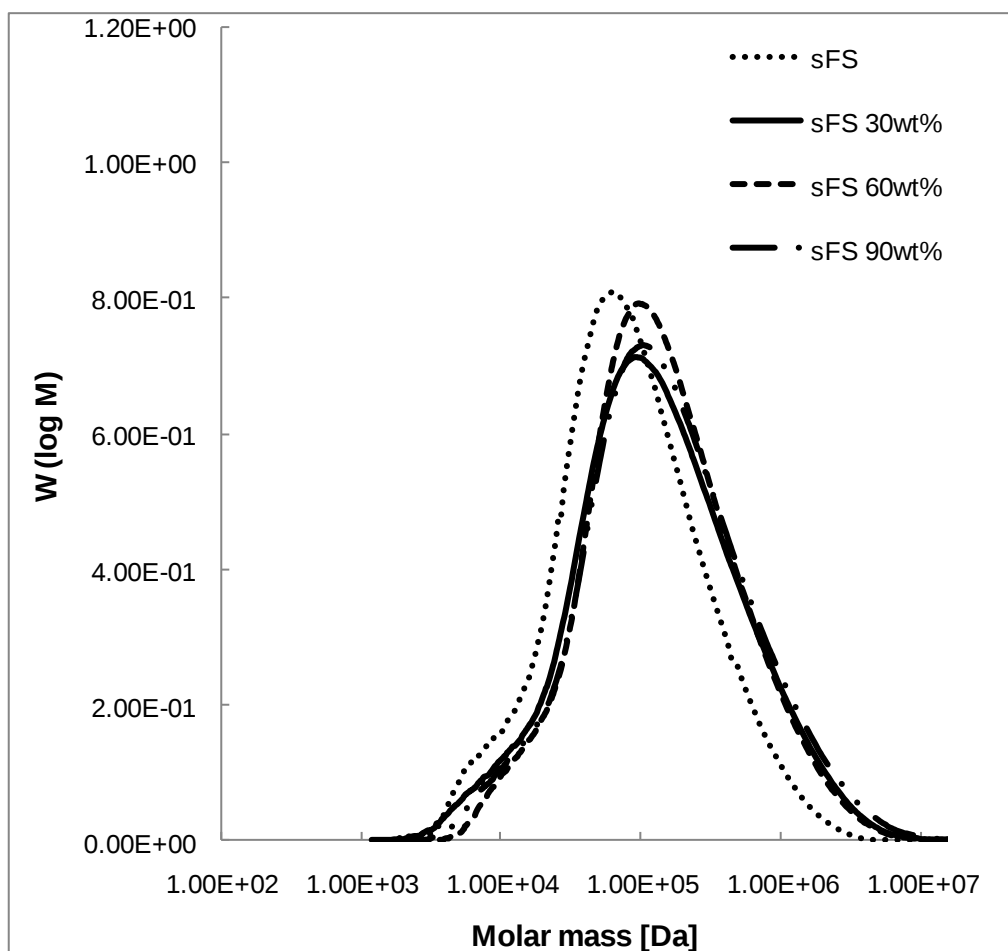


Figure 4.21: GPC traces as a function of H_2SO_4 treatment for sFS membranes.

c) The sPSU series

The increase of the molecular weight in the 30 and 60wt% H_2SO_4 membrane as seen in Figure 4.22 can be explained by oligomer dissolution during the post treatment washing step, which led to an increase in the average molecular weight of the remaining polymers. At 90wt% H_2SO_4 a further increase in the molecular weight shift is observed, due to sulphonation of the membrane (See Section 3.2.3c and 3.2.4c). In addition a smaller fraction of the polymers might have been washed out during the dialysis step required for the dissolved membrane.

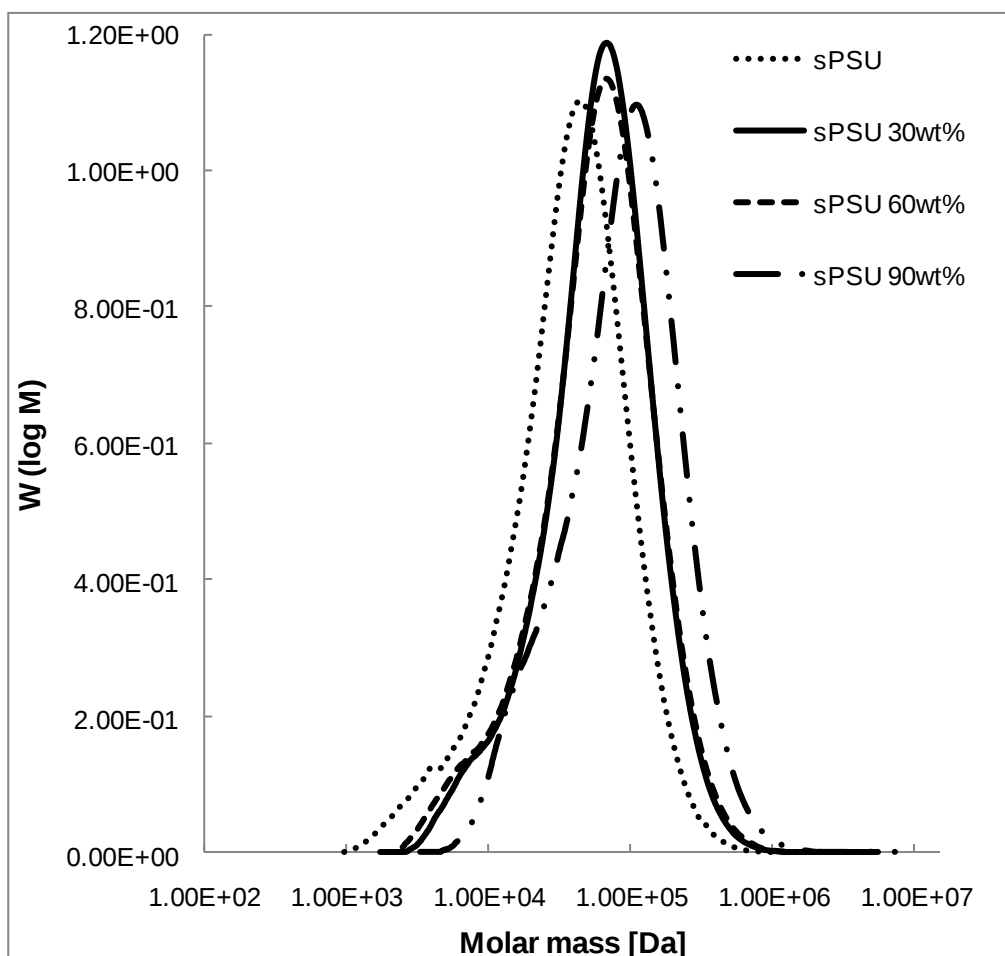
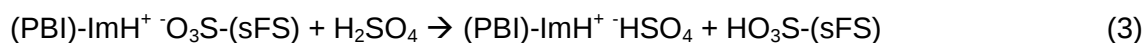


Figure 4.22: GPC traces as a function of H_2SO_4 treatment for sPSU membranes.

d) The sFS-PBI series

According to Figure 4.23 a weight shift to higher molecular values was observed. Within the blend membrane, this can be explained by a partial imidazolium sulphate salt formation through the splitting of acid-base cross-links by the highly protic H_2SO_4 according to reaction 32, leading to the ultimate increase in the molecular weight values.



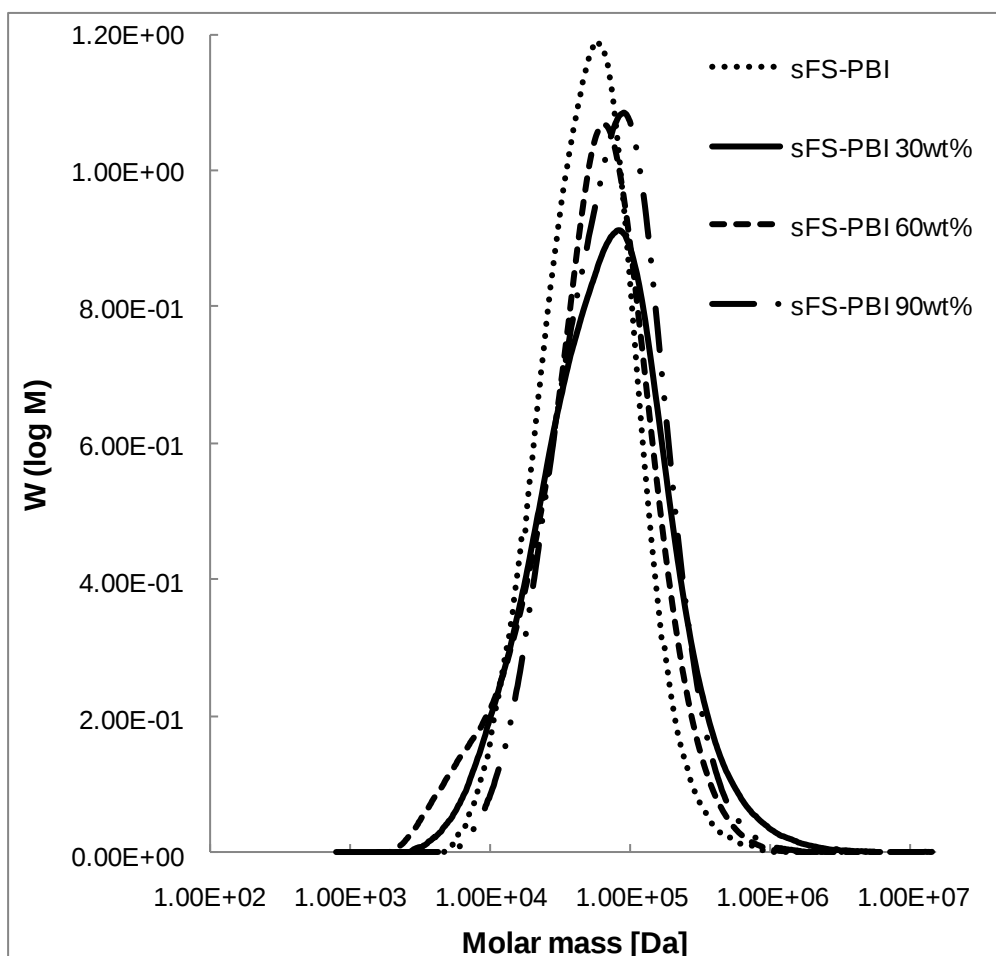


Figure 4.23: GPC traces as a function of H_2SO_4 treatment for sFS-PBI membranes.

e) The sPSU-PBI series

At H_2SO_4 concentrations of 30 and 60wt%, there was again a shift to higher molecular weight values as seen in Figure 4.24, which can again be explained by partial splitting of the acid-base ionic cross-links due to the H_2SO_4 and the subsequent inclusion of HSO_4^- anions into the blend membrane. The 90wt% H_2SO_4 treated membrane is not shown in Figure 4.24 as it was unable to dissolve in the DMAc solvent which again confirms the occurrence of sulphonation in the membrane.

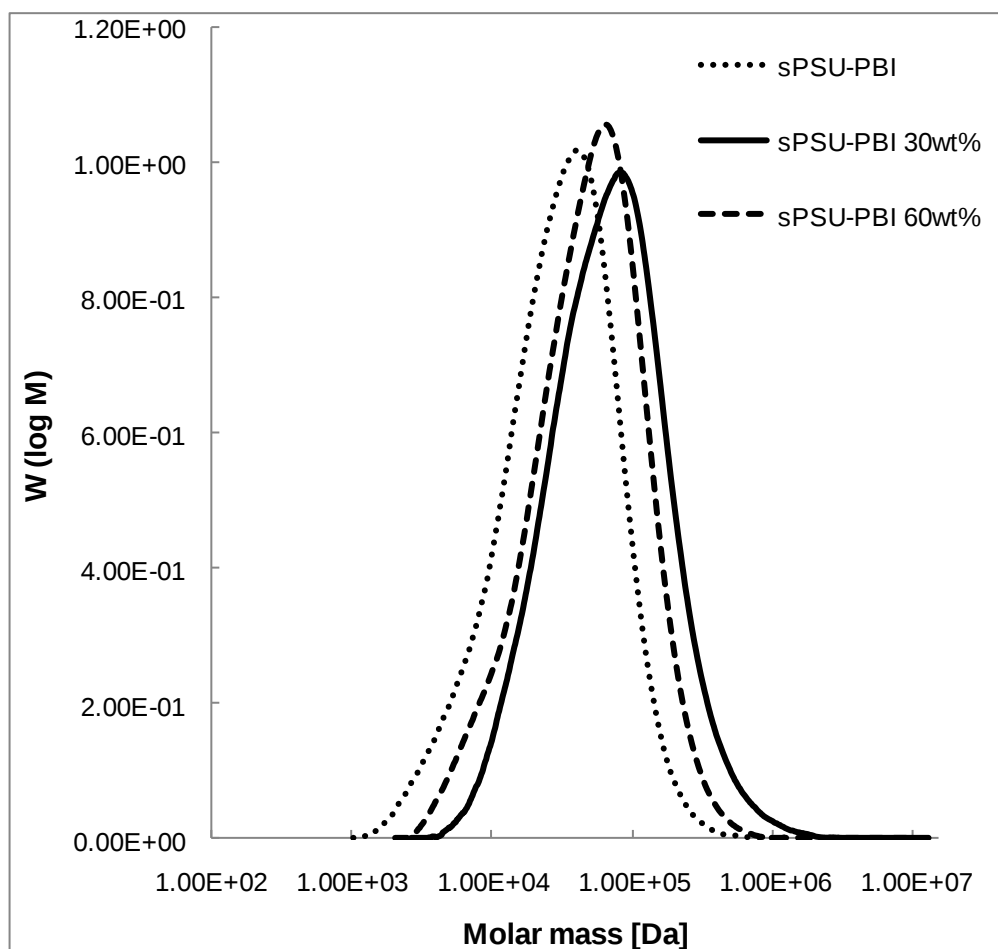


Figure 4.24: GPC traces as a function of H_2SO_4 treatment for sPSU-PBI membranes.

3.2.6 SEM and EDX

The PBI, sFS and sPSU membranes as well as the sPSU-PBI blend membrane showed no visual change under SEM, irrespective of the H_2SO_4 concentration used. It was of course not possible to evaluate the completely dissolved membranes (PBI, sPSU and sPSU-PBI at 90wt% H_2SO_4).

For the sFS-PBI membrane however a change was visible between the untreated and the 90wt% treated membrane (Figure 4.25). From Figure 4.25b it seems that micro cracks have formed in the membrane. This seems to confirm that the 90wt% treated membrane was perceived to be more brittle than the untreated membrane, which can again be contributed to the increased sulphonation observed.

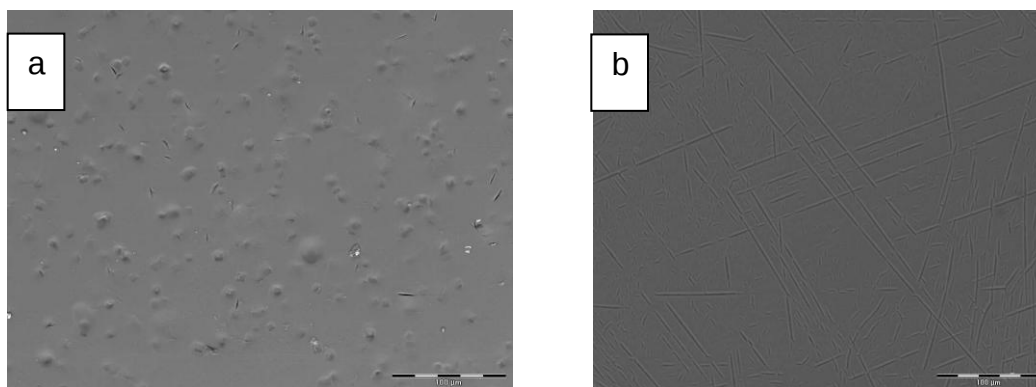


Figure 4.25: A SEM photo of sFS-PBI membrane a) before treatment and b) after the 90wt% H_2SO_4 treatment.

In Figure 4.26, the sulphur levels for the various membranes as obtained using SEM-EDX are presented as a function of the concentration of the H_2SO_4 treatment. Note should be taken that each membrane was washed repeatedly after the acid treatment to ensure that all loose surface sulphur in the presence of H_2SO_4 had been removed.

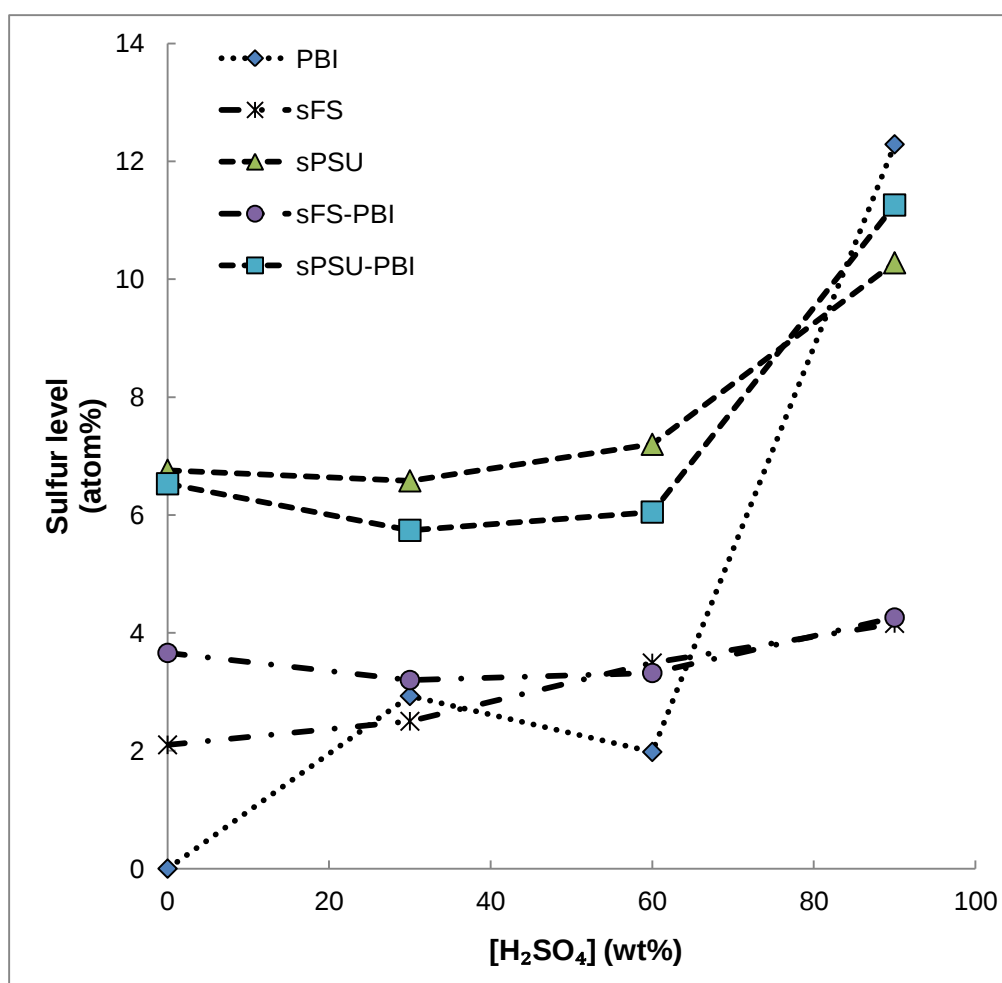


Figure 4.26: The effect of H_2SO_4 treatment on sulphur levels in the membranes according to surface EDX.

a) The PBI series

The untreated PBI showed no sulphur, which is correct according to its polymer structure. Upon H_2SO_4 treatment however the sulphur levels increased in the membrane remaining near constant for the 30 and 60wt% H_2SO_4 treatment confirming the formation of the hydrogen sulphate salts discussed in Section 3.2.3a. At 90wt% H_2SO_4 , there was a substantial 6 fold increase in sulphur levels confirming sulphonation as the most probable cause of the rapid membrane dissolution observed at this concentration.

b) The sFS series

The sFS membrane showed only a slight increase in sulphur levels as the treatment concentration increased, confirming that sulphonation was the most probable cause for the slight changes discussed previously.

c) The sPSU series

The sulphur levels remained relatively constant for the untreated and the 30 and 60wt% H_2SO_4 treated membranes. However during the 90wt% H_2SO_4 treatment, the sulphur level in the membrane shows a marked increase confirming sulphonation as the cause of dissolution.

d) The sFS-PBI blend membrane series

The sFS-PBI membrane trend line correlates well with that of the sFS membrane suggesting that the pure membrane behaved similar to the blend membrane. Although the sFS-PBI blend membrane showed a marked weight loss at 90wt% H_2SO_4 , the sulphur levels remained similar both to the sFS as well as the untreated sFS-PBI membrane. This is in spite of the fact that the blend membrane contains the highly sulphonatable PBI membrane. The sFS therefore partially protected the PBI from sulphonation.

e) The sPSU-PBI blend membrane series

For the sPSU-PBI membrane the sulphur content was similar to the sulphur content of the sPSU membrane. Both pure and blended membranes show a marked increase in sulphur content after 90wt% treatment due to sulphonation. It is interesting to note that at 90wt% the increase in the sulphur level was higher than the increase observed for the pure sPSU membrane showing the additional and increased sulphonation of the PBI fraction in the blended membrane.

3.2.7 IEC

Since the blended membranes showed the highest stability towards H_2SO_4 , only these membranes were analyzed by IEC as shown in Figure 4.27. The IEC's of both the untreated membrane blends should be close to 1.35meq/g ,¹² in spite of this and in spite of the fluctuation in data, certain trends are observable.

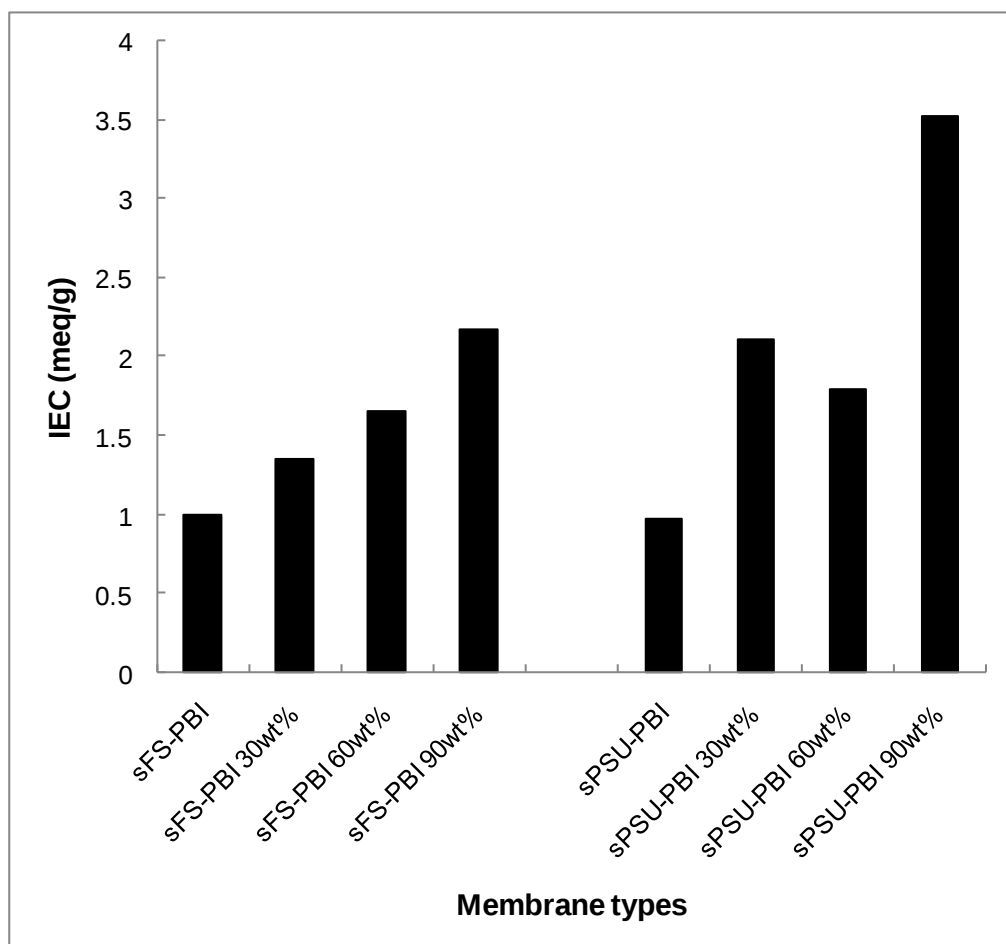


Figure 4.27: IEC change due to H_2SO_4 treatment

a) sFS-PBI

In Figure 4.27, a linear IEC increase is observed with an increase in the H_2SO_4 treatment concentration for the sFS-PBI membranes. However, this increase is small, in fact so small that its impact was largely unnoticed by weight changes and TGA (except of course for the 90wt% treatment). This slight gradual increase in sulphonation could however be correlated to the slight increase in the molecular weight changes shown by GPC.

b) sPSU-PBI

The IEC values of the sPSU-PBI membrane show a small increase at 30 and 60wt% which again correlates to the data observed with the weight changes, GPC and TGA results. At 90wt% H_2SO_4 , there is however a significant increase in the IEC value confirming the observed sulphonation previously discussed, leading to the dissolution of the membrane at 90wt% H_2SO_4 .

The IEC increase of the sFS-PBI at 30, 60 and 90wt% is moderate and comparable to the increase in sPSU-PBI IEC values at 30 and 60wt%. This seems to show that sulphonation occurred to a lesser degree in the sFS-PBI membrane than in the sPSU-PBI membrane. This also explains why the 90wt% H_2SO_4 treated sFS-PBI membrane dissolved only partially, whilst the sPSU-PBI membranes dissolved completely.

4 Conclusion

In this study two high temperature blend membranes, two low temperature blend membranes and their three pure membranes were subjected to H_2SO_4 treatment in order to determine their stability for their application in a SO_2 electrolyser. The high temperature membranes were treated in 30 and 60wt% H_2SO_4 characterised. Both membranes showed excellent stability at both these concentrations.

After treatment at 30, 60 and 90wt% H_2SO_4 , the membranes were characterised using various techniques. The non-fluorinated membranes (PBI, sPSU and sPSU-PBI) showed excellent stability at 30 and 60wt% H_2SO_4 . However, at 90wt% H_2SO_4 , sulphonation occurred resulting in the dissolution of the membranes. Fluorination of the membranes (sFS and sFS-PBI) seemed to improve the membrane's stability in H_2SO_4 in view of the improved resistance observed especially at 90wt% H_2SO_4 . Even though the membranes were tested in concentration of up to 90wt% H_2SO_4 , SO_2 electrolyzers rarely exceed concentrations of 30-40wt% H_2SO_4 , which implies that the blend membranes are stable in the acid environment found during SO_2 electrolysis.

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Chapter 5: Evaluation and recommendations

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1 Introduction

In this chapter the research presented in this study is reviewed and summarised, by identifying the main methods used and giving a summarised evaluation thereof. This chapter is concluded with some recommendations for future studies.

The purpose of this study was to investigate the acid stability of various PBI based membranes, in view of the acidic environment created by the SO₂ electrolyser and the possible detrimental effect that this would have on the stability and efficacy of novel PBI membrane blends earmarked for future use in SO₂ electrolyzers. The evaluation was achieved by characterising the treated membranes using proton conductivity (four-probe in-plane as well as two-probe through-plane), weight change, TGA, GPC, SEM-EDX and IEC techniques before and after exposure of the membranes to 30, 60 and 90wt% H₂SO₄ for 120h at 80 °C and 1 bar pressure.

2 High temperature blend membranes

The two PBI excess high temperature resistant PBI blend membrane samples were treated in H₂SO₄ concentrations of 30 and 60wt% for 120h at 80 °C and 1bar pressure. No sulphonation was observed in either of the tested membranes implying that the membrane remained stable at the tested conditions.

As previously mentioned, the current emphasis within the broader research group at the North-West University is on low temperature SO₂ electrolysis¹, and hence in this dissertation, the main focus was on the characterization of the low temperature membranes, while the high temperature membranes for SO₂ electrolysis will be investigated at a later stage.

3 Low temperature blend membranes

Three single component membranes (PBI, sFS and sPSU) as well as the two low temperature PBI membrane blends (sFS and sPSU excess) were treated in 30, 60 and 90wt% H₂SO₄ for 120h at 80 °C and 1bar pressure. Before evaluating the actual acid stability of the membranes, the suitability of the analytical techniques will briefly be discussed.

3.1 Evaluation of analytical technique

Numerous techniques were used to evaluate the low temperature membranes before and after treatment. One testing technique that proved to be challenging was the membrane

proton conductivity determination both with the in-plane and the through-plane technique. The through-plane proton conductivity data presented in this study was only obtained after numerous runs before repeatable results were obtained. The in-plane data remained inaccurate regardless of the number of runs. According to literature, the accuracy and repeatability of proton conductivity measurements remains a challenge².

A technique used in this study that was easy to use while providing important information, was the weight change technique which is a simple yet effective way to indicate membrane degradation (weight loss) or salt formation (weight gain). Similarly the TGA technique, which can give an indication of the mechanical stability of the membrane, proved to be a repeatable technique from which accurate information was derived. Although some fluctuations were observed with the GPC technique, ample information regarding sulphonation, salt formation and dissolution was obtained. Since the SEM analysis is a simple and crude method of determining visual degradation, it was only suitable in determining degradation in partially dissolved membranes. EDX was useful by providing a concrete method to confirm the presence of membrane sulphur, as postulated according to the results obtained by the other methods. Although the IEC technique also showed some fluctuations in data, the trends obtained confirmed that sulphonation increased as the treatment concentration increased, which correlated well with the other sulphonation indicating analytical techniques, for example through-plane proton conductivity, TGA and EDX.

Whilst some of the analytical techniques were more suited for the determination of either sulphonation, salt formation or dissolution, none of the techniques used were able to indicate all of these effects on their own. Thus, in order to obtain a full understanding of the effects occurring in the membrane, all these techniques should be viewed comparatively. Therefore, the analytical techniques used for the membrane characterization were both suitable and necessary providing multiple sets of data which combined, confirmed individual test results ultimately enabling us to meet the objectives set out in Chapter 1.

3.2 H₂SO₄ effect on PBI blend membranes

From the results obtained in Chapter 4, it seemed that H₂SO₄ treatment had mainly three types of effects on the membrane during treatments, which are sulphonation, salt formation and dissolution. Examples of sulphonation³ and salt formation³ are shown in Figure 5.1 and 5.2 respectively, whilst dissolution simply refers to the leaching of low molecular weight fractions, called oligomers, from the membrane as confirmed by the shift in GPC curves

observed after H₂SO₄ treatment. Sulphonation shown, in Figure 5.1, occurs when -SO₃H groups are incorporated into the membrane aromatic rings due to H₂SO₄ exposure. Conversely, the salt formation shown in Figure 5.2 occurs when hydrogen sulphate salts are incorporated to increase swelling.

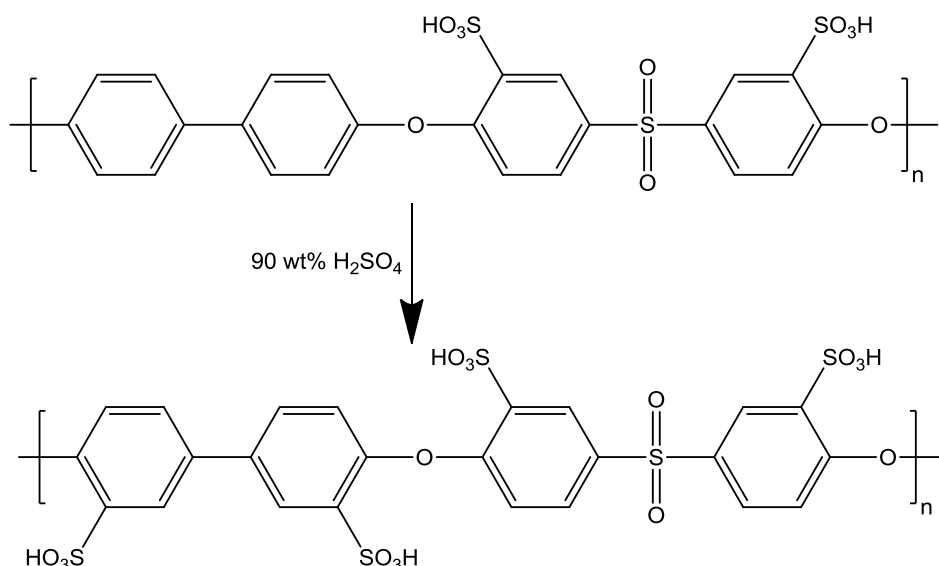


Figure 5.1: An example of sulphonation as proposed for the sPSU membrane treated with 90wt% H₂SO₄.

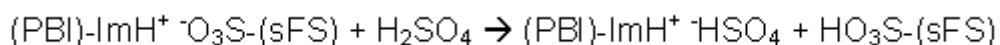


Figure 5.2: Proposed reaction illustrating the salt formation of the PBI membrane during H₂SO₄ treatment.

In Table 5.1, an attempt was made to correlate the various effects that H₂SO₄ had on the various blend membranes as well as the analytical technique from which these effects were derived. In the PBI membranes for example, salt formation was observed in the 30 and 60wt% treated membranes (attained with the weight change, TGA, GPC and EDX techniques) as well as sulphonation in the 90wt% treated membranes (attained with the weight change, TGA, GPC and EDX techniques). Accordingly, significant degradation only took place in the 90wt% treated membrane.

Table 5.1: Effect of H₂SO₄ on tested membranes as observed per analytical technique

Effect of H ₂ SO ₄	Membranes affected	Analytical technique
Sulphonation	PBI 90wt%	Weight change, TGA, GPC, EDX
	sFS 60wt%	EDX
	sFS 90wt%	TGA, GPC, EDX
	sPSU 90wt%	Weight change, TGA, GPC, EDX
	sFS-PBI 30 and 60wt%	IEC
	sFS-PBI 90wt%	Through-plane conductivity, weight change, TGA, SEM, EDX, IEC
	sPSU-PBI 90wt%	Through-plane conductivity, weight change, TGA, GPC, EDX, IEC
Dissolution	sFS 30wt%	Weight change, TGA, GPC, EDX
	sFS 60wt%	Weight change, TGA, GPC
	sPSU 30 and 60wt%	GPC
Salt formation	PBI 30wt%	Weight change, TGA, EDX
	PBI 60wt%	Weight change, TGA, GPC, EDX
	sFS 60wt%	EDX
	sFS-PBI 30 and 60wt%	GPC
	sPSU-PBI 30 and 60wt%	GPC, IEC

According to the results confirmed by most of the techniques used, the change observed in the 30 and 60wt% sFS membrane was due to oligomer dissolution. However, according to EDX, the 60wt% treated membrane did undergo slight sulphonation or salt formation. Similarly, the analytical results confirmed that the 30 and 60wt% treated membrane

remained stable, whilst the 90wt% treated sFS membrane underwent slight sulphonation according to TGA, GPC and EDX results.

According to various analytical techniques (TGA, GPC, SEM and EDX), the 30 and 60wt% sPSU membranes remained stable, although the GPC results did indicate some weight loss which was ascribed to oligomer loss occurring during the post treatment washing. The 90wt% treated membrane clearly underwent sulphonation as confirmed by weight change, TGA, GPC, SEM and EDX techniques.

In the sFS-PBI blend membrane, all the analytical techniques excluding GPC and IEC showed that the 30 and 60wt% membranes remained stable during H_2SO_4 treatment. The variation observed by GPC as well as the IEC results was ascribed to slight salt formation and not sulphonation, since sulphonation would have caused an increase in the proton conductivity, which was not observed. The through-plane conductivity, weight change, TGA, SEM, EDX and IEC results all indicate that sulphonation at the 90wt% treated membrane did occur.

According to all analyses, the 30 and 60wt% sPSU-PBI membranes remained stable, with slight salt formation illustrated by GPC and IEC. The 90wt% treated membrane on the other hand was sulphonated as confirmed by the observed through-plane conductivity, weight change, TGA, GPC, EDX and IEC results.

In summary, both the membrane blends (sFS-PBI and sPSU-PBI) showed superb stability to H_2SO_4 concentrations expected in the SO_2 electrolyser (30-40wt%) implying that both are suitable for use in a SO_2 electrolyser. The sFS-PBI membrane blends seemed slightly more stable than the sPSU-PBI membrane blends over the tested H_2SO_4 treatment concentration range (according to the weight change, TGA, EDX and IEC results), which could be ascribed to the protective role of the fluorinated polymer. The superior acid stability of this membrane could prove vital for SO_2 electrolysis, especially for prolonged periods of operation. Since this membrane also showed higher proton conductivity it can therefore be concluded that the sFS-PBI membranes is the best suited membrane for application in a SO_2 electrolyser.

4 Recommendations

This section is divided into recommendations regarding the proton conductivity set-up and the membranes in general.

Recommendations regarding the proton conductivity set-up.

- The proton conductivity techniques (both through-plane and in-plane) are time consuming and not standardised. Usually membrane proton conductivity is measured using a range of techniques chosen on the basis of availability and convenience². Since in-plane and through-plane conductivity should closely resemble one another, it is recommended that future proton conductivity tests should be done using a Scribner conductivity test system. This system allows for accurate, rapid through-plane membrane conductivity testing as a function of RH and temperature. This would assure testing which is accurate, repeatable and standardized.

Recommendations regarding membranes.

- Longer exposure tests should be done to determine the duration of membrane efficacy due to the continues exposure to H_2SO_4 . These extended tests are necessary to ensure long term SO_2 electrolysis stability of the membrane.
- Since the PBI membrane was found to be the weakest pure membrane, future studies should be done on a PBI blend membrane where the PBI part is fluorinated or partially fluorinated.
- Additional tests should be done on the low temperature PBI membrane blends at higher pressures. The in-house developed membrane treatment set-up was specifically designed for this purpose as higher pressures are believed to increase the efficacy of the electrolyser.
- Further tests should also be done on the high temperature membrane blends, for future application in a SO_2 electrolyser at 120 °C where the electrolyser has decreased cell resistance and improved performance⁴. It is even possible that the membranes will conduct more protons at this temperature during H_2SO_4 exposure leading to increased protonation. If this turns out to be the case, phosphoric acid treatment of the high temperature membrane blends will be rendered needless. In addition, as the name suggests, the high temperature blend membranes have the advantage of increased temperature stability (>100 °C) favouring improved SO_2 electrolysis.
- In future, nuclear magnetic resonance (NMR) could be included as an analytical technique to be used to determine the degree of sulphonation of a membrane after H_2SO_4 exposure. In addition infrared spectroscopy (IR) could also be used to further distinguish between sulphonation and salt formation when testing novel membranes.

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