MONASH University

CATION SELECTIVE SULFONATED POLY(ETHER ETHER KETONE) NANOCOMPOSITE ION EXCHANGE MEMBRANES

Thesis in the fulfillment of the requirement for the degree of
Doctor of Philosophy in Chemical Engineering

by

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Notice 1

Notice 2

Summary

The importance of water management recognized over past decades has seen a significant drive to develop efficient and sustainable water treatment systems. Ion exchange membranes are a promising technology that can be utilized in clean and sustainable separation processes. The adoption of these membranes for industrial wastewater treatment is limited by the significant costs of currently available commercial membranes. The focus of this research project has been to develop a unique, high performing and monovalent cation selective membrane that can be produced with relatively low material and synthesis costs. Several SPEEK based nanocomposite membranes have been established as promising cost-effective ion exchange membrane candidates for use in wastewater treatment systems. These are promising materials that will reduce the cost of membrane systems and promote sustainable water management in industrial applications.

A systematic study of SPEEK sulfonation and casting conditions investigated the influences of sulfonation time and temperature on membrane properties. Optimal preparation conditions were established for the production of suitable and reproducible SPEEK membranes. This material is a high performing SPEEK polymer matrix that can be used as a base for developing nanocomposite membranes with improved ion transport performance and mechanical stability. Inorganic

nanoparticles were integrated into nanocomposite SPEEK membranes with distinctive and novel characteristics. Surface functionalization of the fillers was found to modify the microstructure of the polymer membrane. Amine surface modification introduced a basic surface charge to spherical silica and titania nanoparticles, limiting the passage of multivalent cations and producing promising monovalent selective SPEEK membranes. Both amine and sulfonic surface groups showed particular promise for improving the thermal and mechanical stability of the nanocomposite while also increasing ion transport.

This work provides a comprehensive understanding of the structural influences of the polymer matrix on the physicochemical and electrochemical properties of fabricated SPEEK nanocomposite membranes. Monovalent cation selective membranes were designed and characterized using a novel and reproducible quantitative approach. These robust and cost-effective membranes have significant potential to be commercialized in wastewater treatment systems or other separation processes that require cation selective membranes.

Declaration of Authorship

ACKNOWLEDGMENT OF CONTRIBUTION TO THE

RESEARCH WORK AND/OR AUTHORSHIP

DECLARATION

In accordance with Doctorate Regulations 17/Doctor of Philosophy Regulation 61 at Monash University the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any University or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

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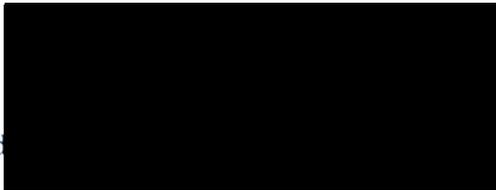
It is agreed that in terms of the overall workload for each paper the relative

contributions of each author, in percentage terms, was:

Chapter 2: Rebecca Yee (100%)

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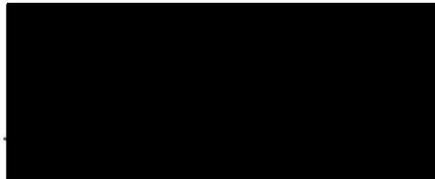
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CHAPTER 1

INTRODUCTION

1.1. Water Treatment

1.1.1 Overview

Increasing environmental consciousness in the past few decades has identified water as a significant resource. Research has seen a focus on developing new technologies for efficient and sustainable water treatment systems. However, the adoption of best practice water management in industrial sectors has been limited by significant commercial factors. Compared to energy production processes, water management projects are a low-profit margin industry that is highly driven to find cost competitive advanced wastewater treatment techniques. Many water authorities in Australia have implemented policies and legislations to encourage industrial users to recycle and reuse wastewater on site. Stringent effluent quality requirements for inland wastewater treatment plants incentivize the implementation of newer and more sustainable systems. Systems that utilize wastewater to produce usable products such as energy or chemicals are economically attractive. Developments in water management technologies allow plants to reduce their on-site footprint.

The volume and components in industrial wastewater streams varies significantly. They typically contain suspended solids, colloidal or dissolved solids in both mineral and organic form. Government restrictions on effluent

content will generally include a limit on the biochemical oxygen demand, which measures the biodegradable organic matter in wastewater. Managing water on-site where possible provides strong technical and cost benefits such as minimizing transport and downstream issues with other combined streams. Recent research has identified several approaches to treating the organic content in wastewater on-site, which allows for direct water re-use and potential recovery of valuable energy from the wastewater biomass.

1.1.2   Ion Exchange Membranes

Ion exchange membranes (IEMs) are a promising environmentally considerate technology that can be applied in many industrial separation processes. Ion exchange membranes separate electrolyte solutions in anode and cathode chambers while allowing for the transport of ions. Cation exchange membranes contain negatively charged groups such as sulfonic or carboxylic acid groups attached to a polymer network. These membranes allow free counter-ions with positive charges to pass through while excluding negatively charged species. Alternatively, anion exchange membranes contain positively charged groups. These groups repel positively charged species while allowing anionic species to travel through.

Membranes are critical components in applications such as electrodialysis or bioelectrochemical systems. Using electrodialysis, membranes can be used to treat brackish water and produce fresh water. In bioelectrochemical systems, there is potential to generate electricity using microbial fuel cells or produce hydrogen by microbial electrolysis cells[1]. This thesis will focus primarily on ion conducting membranes used in bioelectrochemical systems. IEMs are used in applications such as desalination, industrial effluent treatment, the concentration of food and pharmaceutical products, and in the manufacture or recovery of basic chemical products.

IEMs are crucial for the future development of sustainable and clean water treatment technologies. One of the significant advantages of membrane technology is the opportunity to develop novel and unique membrane materials with tailored properties required for specific applications. While significant efforts in IEM research have seen a recent increase in new commercial ventures, there are still many areas of research required to fully develop their commercial potential. Extensive opportunities for developing original membrane materials requires a thorough understanding of the fundamental relationships between preparation conditions and resulting membrane properties.

1.1.3 Bioelectrochemical Systems

Bioelectrochemical systems are promising clean technologies that use ion conducting membranes to treat water or produce energy. In water treatment, this technology allows for the separation of valuable components from effluent streams while simultaneously reducing organic loading prior to off-site disposal. Electrochemically active microorganisms can oxidize organic matter present in the wastewater. Bioelectrochemical systems take advantage of this microbial activity to directly produce energy or chemicals[1]. These systems are advantageous as feed streams do not need to be purified, ambient operating conditions are used, and the biological catalyst is self-regenerating. These systems are a promising and unique approach for cost effective commercial wastewater treatment.

In a microbial fuel cell (MFC), energy available in the organic substrate can be converted from biomass to electricity. These systems generate electricity while simultaneously treating wastewater by using bacteria to oxidize the organic matter and release electrons to the anode. Electrons then flow to the cathode to combine with oxygen and protons to form water. Electroneutrality is maintained through the transport of cations through an ion exchange membrane. MFCs are also efficiently operated at ambient temperatures. The concept of using microorganisms as catalysts in fuel cells has been explored

since the 1970s. In a microbial electrolysis cell (MEC), instead of producing electricity, a voltage can be applied to extract and separate valuable ionic species from wastewater effluents streams. Previous research has indicated how industrial wastewater can be used as a renewable resource for generating commodity products such as hydrogen or hydrogen peroxide[2-6]. Figure 1.1 demonstrates a schematic example of the use of acetate in wastewater streams to produce free H^+ cations. Driven by an applied current, a cation permselective membrane allows for the transport of cations while restricting the negatively charged bicarbonate ions. Commercially valuable hydrogen is produced at the cathode side, with treated wastewater able to be reused or benignly released to the environment.
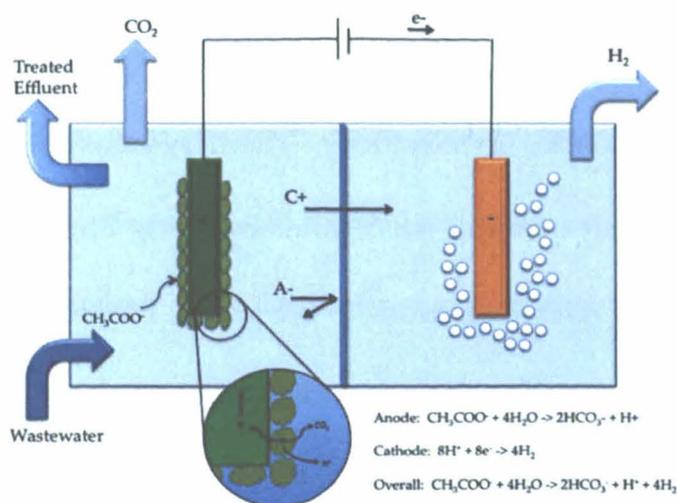
Figure 1.1: Schematic representation of microbial electrolysis cell using acetate as the organic feed substrate

Suitable ion exchange membranes for these systems must remain stable under harsh caustic conditions on the cathode side of the membrane. For long term performance and to ensure unimpeded processes at the cathode, the membrane should be highly monovalent ion selective, preferentially transporting the dominant monovalent ions in the wastewater feed while rejecting multivalent cations, such as Ca^{2+}, which can rapidly precipitate in low pH environments and cause fouling on the cathode side of the membrane[6]. Monovalent selective transport will also reduce or eliminate the transport of $Fe^{2+/3+}$ ions, a well known H_2O_2 decomposition catalyst, to prevent product loss[7].

These bioelectrochemically active systems have many advantages as a clean and sustainable technology. With small footprints, these systems can be integrated into existing industrial plants to provide on-site water treatment. This provides the option to directly reuse treated water and may simultaneously produce valuable chemical species that could also be used on site. Membrane technologies are particularly relevant for Australia, where we are faced with significant industrial water challenges in the context of delicate environmental ecosystems. With strict effluent license targets, unique climate considerations, land availability, and a relatively young existing water treatment infrastructure, there is significant potential for new membrane

technology to contribute to the responsible water management of this invaluable natural resource.

Increased recognition of the value of on-site water treatment and re-use is expected to see a significant growth in the use of membrane technology such as bioelectrochemical systems. Novel and cost-effective ion exchange membranes are being developed to promote the commercialization of these processes. Specific membranes can be produced with tailored characteristics suitable for a particular commercial process. In general, IEMs are desired to have; low ionic resistance, high transport number of counter-ions, high selectivity, and good thermal, mechanical and chemical stability in aqueous environments.

1.2. Research Motivations

1.2.1 Limitations of Current Technology

Ion exchange membranes are vital components in numerous industrial processes. They are generally applied in technologies to concentrate salts or in the separation of ionic materials. Various IEMs have been developed with characteristics tailored for different applications. In particular, IEMs prepared for electrodialysis and fuel cells have been extensively reviewed. Styrene-divinyl benzene membranes are best known in literature for applications in electrodialysis and have chemistry available for selective ion separation. However, while these membranes exhibit good electrochemical properties, they lack chemical stability, which is crucial in bioelectrochemical systems[8].

There has been insufficient development of suitable membranes for the specific conditions of bioelectrochemical systems. Available commercial membranes, such as Nafion®, are limited by high cost, restricted performance conditions at temperatures over 80°C and fouling issues. While Nafion® performs well in fuel cells, these membranes also transport cation species other than protons. In MFCs and MECs, other cation species are present and can accumulate in the cathode compartment as they are not consumed at the cathode. This increases the pH and has been shown to reduce MFC performance[9]. To avoid the pH effects, alternative membranes are desired to

be proton selective. These factors drive the development of a candidate material that is monovalent selective and can effectively be applied in bioelectrochemical systems.

1.2.1.1 High Costs

DuPont's Nafion® membranes are currently the most popular cation exchange membrane available. They are also used as a benchmark material in membrane research studies. These are made of perfluorosulfonic polymers and are stable in oxidative and reductive environments, though they are limited by high methanol crossover[10]. They also provide good conductivity properties, which is useful in polymer electrolyte fuel cells. However, perflurosulfonic acid membranes are significantly disadvantaged by the inherent safety and environmental concerns of the use of fluorinated chemicals. The high costs of Nafion® membranes, $600 – 1200 m^{-2}, is a major limitation for their use in low margin industries such as wastewater treatment[10].

There has been significant interest in developing polymer electrolyte membranes with the aim of replacing such expensive perfluorinated membranes. Poly(ether ether ketone) is a readily available thermoplastic polymer that can be produced from low cost materials. By functionalizing this

material with an acidic functional group, such as sulfonic acid, these membranes can provide conductive paths for ion transport. While aromatic polymers are a promising route for obtaining high performance polymer electrolytes because of their availability, processability, wide variety of chemical composition options and their stability in aqueous environments, excessive sulfonation of the SPEEK polymer can result in mechanical instability and extreme swelling. However, sulfonated poly(ether ether ketone) (SPEEK) is a third of the cost of Nafion® 117 and has been found to halve the cost of power in fuel cells when using SPEEK membranes compared to Nafion® 117. This promising economic benefit indicates that SPEEK has potential to be developed for commercial use if material limitations can be improved.

Ion exchange membranes are a main contributor to the capital and operation cost factor of such technologies. In a 2005 report from National Renewable Energy Laboratory of the U.S. Department of Energy, a cost analysis of polymer electrolyte membrane fuel cell systems describes the membrane as a main cost contributor to such technologies[11]. Figure 1.2 summarizes a cost breakdown of a fuel cell stack for 2001. The MEA (membrane electrode assembly) is notably the most significant contributor to cost, with a further MEA cost breakdown in Figure 1.3 showing that the membrane itself is a

significantly costly component. There are substantial economic benefits that can be derived from reducing the fundamental cost of the membrane material.
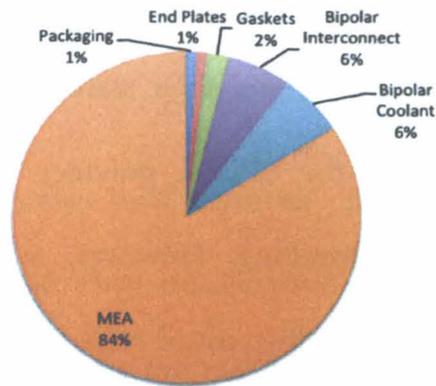
Figure 1.2: Fuel Cell Stack Cost Breakdown for 2001 System Configuration[11]

Figure 1.3: (a) Membrane Electrode Assembly Cost Breakdown for 2001 System Configuration[11], (b) Membrane Cost Breakdown[11]

Currently available commercial membranes are expensive due to their fluorinated backbone. Using non-fluorinated polymer electrolytes can provide significant economic savings as well as environmental benefit by

reducing the use of fluorinated species. Membrane cost reduction is essential for wide commercialization of membrane water treatment systems as the cost of currently available ion exchange membranes is prohibitive for use in these low margin industries. In comparison to valuable consumer power industries, water treatment systems attract little public or political interest and are predominantly prioritized by environmental factors rather than financial. As such, water treatment systems must be cost effective to promote their adoption in industrial best practices.

1.2.1.2 Fouling

Membrane fouling is a significant challenge limiting the development of many membrane technologies. Fouling is the unwanted build up of material on the surface of the membrane. Scaling is a particular concern in bioelectrochemical systems where the hydroxide formation of divalent and trivalent ions produces salts that precipitate readily in caustic environments. Fouling can influence the membrane's electrochemical properties by increasing electrical resistance and decreasing permselectivity. The membrane structure can be permanently damaged as intermolecular bridges are formed through irreversible fouling within the membrane network.

In addition to separating cations and anions based on charge, membranes are desired with the ability to separate cations of different valency. Such selective membranes will have a preference for transporting monovalent cations while rejecting multivalent cations. Restricting the multivalent ions from passing through the membrane will reduce the ions available for scale precipitation[12]. Reducing fouling effects significantly improve membrane performance and operational lifespan.

1.2.2   Aims of Research

This thesis aims to design and characterize a novel ion exchange membrane material that can be developed for bioelectrochemical cell technologies. This research aims to provide a deeper understanding of membrane ion transport characteristics. In particular, experimental studies shall be used to design a suitable membrane that preferentially transports monovalent cations over multivalent species, which allows for the specific separation of ionic species based on valency. Membrane properties, including selectivity, are affected by the morphology and physicochemical structure of the material. A detailed understanding of the influences of membrane morphology on performance characteristics shall also be established.

The specific aims of this research project are summarized below.

- To identify optimal sulfonation conditions for producing suitable SPEEK membranes that can be used as a cost effective polymer base for the development of an ion exchange membrane

- To determine the water uptake and swelling characteristics of SPEEK membranes in relation to the sulfonation degree

- To establish a suitable sulfonation degree for SPEEK membranes to be used in aqueous environments

- To blend SPEEK with selected nanoparticles to produce novel nanocomposite membranes

- To surface functionalize nanoparticles and determine the loadings suitable for embedding into SPEEK membranes

- To determine the influence of nanoparticle surface functionalization on the water uptake, thermal stability, ion exchange capacity, and ion transport performance of nanocomposite SPEEK membranes

- To establish a SPEEK based nanocomposite membrane material that can be utilized in bioelectrochemical systems with the following characteristics:

  o Thermally stable at operating temperatures of 50 – 120°C

  o Stable under operation of high current densities particularly in caustic conditions

  o Provides an adequate barrier between anode and cathode compartments

  o Ion exchange capacity of 1 – 2.5 meq/g

- o Ionic conductivity >0.01 S cm^{-1}
- o High selectivity that promotes the permeability of monovalent cations over multivalent cations
- To establish a consistent and quantitative method for comparing the permeation rates of cations of different charges transported through ion exchange membranes

1.3. Thesis Structure

This thesis presents a comprehensive report of the theoretical and experimental studies conducted during this PhD candidature.

Chapter 1: This introductory chapter outlines the prominent challenges of sustainable water management and the promising fields of membrane technology. Current limitations are described to explain the motivations for developing novel membrane materials. The specific aims of this research project are presented and the thesis structure outlined here.

Chapter 2: The literature review presented in this chapter provides background of ion exchange membranes and their material composition. Applications for this technology are also described. A previously published patent review is integrated into this chapter to outline the commercial context for the membranes developed in this research project. Ion transport phenomena will also be established to provide rationale in designing experimental methods for synthesizing, producing and characterizing unique high performing membranes.

Chapter 3: A previously published journal article has been integrated into Chapter 3 to describe the synthesis and preparation conditions of SPEEK

membranes. Their properties were systematically studied to optimize a SPEEK membrane suitable for use as a polymer matrix base for further study. This chapter discusses the correlation between preparation conditions and resultant material characteristics.

Chapter 4: A high performing SPEEK membrane is used as a supporting network for the integration of nanoparticles in Chapter 4. The synthesis, functionalization and characterization of silica and titania nanoparticles is examined. Various surface modifications are investigated. The influence of these inorganic additives on the physciochemical properties of the SPEEK membranes is investigated.

Chapter 5: Chapter 5 presents a comparative electrochemical study of the SPEEK and SPEEK nanocomposite membranes. Electrochemical impendence spectroscopy is applied over several unique cells to determine the influence of nanoparticle functionalization and loading content on the resultant hybrid membrane morphology and corresponding membrane performance. A novel, consistent and reproducible method for determining cation selectivity is described. A detailed discussion of the surface modified nanoparticles influence on membrane morphology is also presented.

Chapter 6: This concluding chapter summarizes the significant findings from this research. Major contributions of the nanocomposite SPEEK membranes are described in relation to their performance. This section gives a detailed understanding of the ion transport phenomena of these unique membrane materials. Future studies are also recommended for several of the novel nanocomposite SPEEK membranes produced. Several promising and high performing selective membranes are also discussed for potential commercialization.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter examines recent literature published in relation to ion exchange membranes. The fundamentals of IEM materials and ion transport phenomena through these thin films will be discussed as background for this research project. To gain greater insight into the economic challenges of membrane technology, a previously published review of commercialized membrane materials will be presented in edited form to provide a practical context for industrial membrane applications. Polymer composite membranes will also be discussed in reference to previous designs. Strategies for fabricating selective membranes for cation separation from the literature will also be evaluated.

2.2 Fundamentals of Ion Exchange Membranes

Ion Exchange Membranes are thin films that contain anionic or cationic charged groups fixed to a polymer network. IEMs have received considerable research attention over the past several decades due to their low footprint and sustainable contributions to separation technologies. These have been successfully applied in desalination, industrial effluent treatment, concentration of food and pharmaceutical products, and in the manufacture or recovery of basic chemical products[1]. IEMs have been shown to improve the energy efficiency and sustainability of fuel cell applications[2].

IEM performance is correlated to a membrane's physical and chemical structure. Studies have found homogeneous membranes to have good electrochemical properties, while heterogeneous membranes having good mechanical strength have comparatively poor electrochemical performance[3]. Understanding the relationships among the material's microscopic structure, physicochemical and electrochemical properties is crucial in developing novel membranes with properties that can be tailored for specific industrial and commercial requirements.

Types of IEMs are defined according to the charged functional groups fixed to the polymer network in the membrane structure. Free ion species with the

opposite charge to the fixed ions are able to pass through the membrane, while like-charged co-ionic species are rejected, as represented in Figure 2.1. Cation exchange membranes (CEMs) contain negatively charged functional groups that allow cationic species to pass through the membrane while rejecting anionic species. The opposite situation applies for anion exchange membranes (AEMs). The exclusion of certain charged species is known as Donnan exclusion, which depends on parameters such as the concentration of the fixed ions, the concentration of the electrolytes, and the interactions among the fixed charges in the membrane matrix and their counter-ions[4].
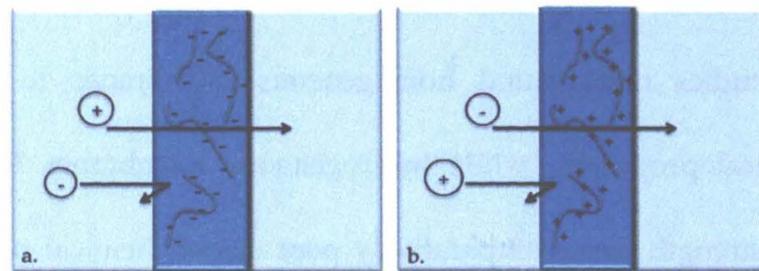
Figure 2.1: Schematic representations of ion transport and rejection for a. cation exchange membrane and b. anion exchange membrane

2.2.1 Applications for Ion Exchange Membranes

Many diverse processes utilize ion exchange membranes. They can be applied to desalination or the separation of ionic species from non-ionic materials[5-7]. They can also be used in the electrodialytic concentration of seawater to produce edible salt[1]. Membranes have demonstrated the potential for producing fresh water from brackish water through electrodialysis[8,9]. In diffusion dialysis, IEMS can also recover acid and alkali from waste solutions[10,11]. Electrodialysis can also be applied to cheese whey demineralization, fruit juice deacidication, blood plasma protein recovery, or in the recovery of electrolytes such as producing edible salt from seawater[12].

With increasing demand for sustainable energy technologies, significant research has been developed on IEMs used in power generation systems such as fuel cells or reverse electrodialysis[13-15]. Membrane technology provides opportunities for efficient electricity generation using the energy from mixing solutions of different salinity[13,16,17]. Reverse electrodialysis has been shown to use the ionic flux through IEMs to generate energy from these salinity gradients[18]. This process uses natural seawater and river water, where the presence of multivalent ions is inevitable and currently limits the performance of such systems. Membranes for this application are desired

with selectivity for monovalent ions to overcome this limitation. Such technologies can potentially generate power densities higher than 6 Wm^{-2} [13].

Fuel cells are a promising clean energy technology with significant commercial potential for portable power storage[19]. These electrochemical devices couple the oxidation of a fuel (hydrogen, methanol, ethanol, or formic acid) in the anode compartment with the reduction of an electron acceptor (typically oxygen) in the cathode compartment. As electrons flow via an external connection from the anode to the cathode, cations must also be transported to maintain electroneutrality. The ion exchange membrane is a critical component for separating the electrolytes in the anode and cathode chambers while allowing for proton permeation. There are several types of fuel cells, but ion conducting membranes are being predominantly presented in literature for polymer electrolyte membrane fuel cells that operate at 60 – 100 °C and direct methanol fuel cells that operate at 50 – 120 °C.

Microbial fuel cells are a development of fuel cell technology that takes advantage of microbial content active in the feed stream to either generate electricity directly or produce fuels such as hydrogen or other gases[20]. These systems are advantageous as the fuel supplies do not need to be purified, operation is at ambient temperatures[21], and the biological catalyst is self-regenerating[22]. MFCs can assist in the purification of wastewater streams

while simultaneously generating electricity or recovering valuable chemical species. Current densities achieved in MFCs are typically 10^3 to 10^4 times lower than those achieved in PEMFCs. Ion exchange membranes for such systems have less demands for cation transport. These electrochemical systems are a promising approach to anaerobic wastewater treatment as they simultaneously generate valuable outputs.

Bioelectrochemical systems are being increasingly developed with potential for sustainable commercial production of energy and chemicals[20,23]. BESs can be divided into electron-producing microbial fuel cells (MFCs) or electron-consuming microbial electrolysis cells (MECs). This thesis will focus on the development of IEMs applied in such technologies. The theoretical cell voltage of the overall reaction in a bioelectrochemical system can be determined to assess the electricity generated or required for operation. This electromotive force (*emf*) can be calculated from the Gibbs free energy of the process.

Equation 2.1:

$$emf = \frac{\Delta G}{nF}$$

Where *emf* is the electromotive force (V), ΔG is the Gibbs free energy of the reaction (J/mol), *n* is the amount of electrons involved in the reaction (mol), and *F* is Faraday's constant. In an MFC, the Gibbs free energy of the reaction is negative and the *emf* is positive, implying that the system can directly produce electricity. If the Gibbs free energy is positive and the *emf* is negative, electricity is required to drive the system. In such a case, the system is known as a Microbial Electrolysis Cell and can be used to generate valuable chemicals from the organic material in wastewater effluents[8]. For economic feasibility, a MEC should operate under an internal resistance of <80 mΩ m^{-2} with a current density of ~20 A m^{-2} and for MFCs, the internal resistance should be <40 mΩ m^{-2} and a current density of ~25 A m^{-2}[23]. While MECs have a minimum cost at a certain current density, the costs for MFCs will decrease with increasing current density. Schematic representations of hydrogen fuel cells, microbial fuel cells and microbial electrolysis cells are presented for these system variations in Figure 2.2.

a.

b.

c.

Anode: $CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + H+$

Cathode: $8H^+ + 8e^- \rightarrow 4H_2$

Overall: $CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + H^+ + 4H_2$
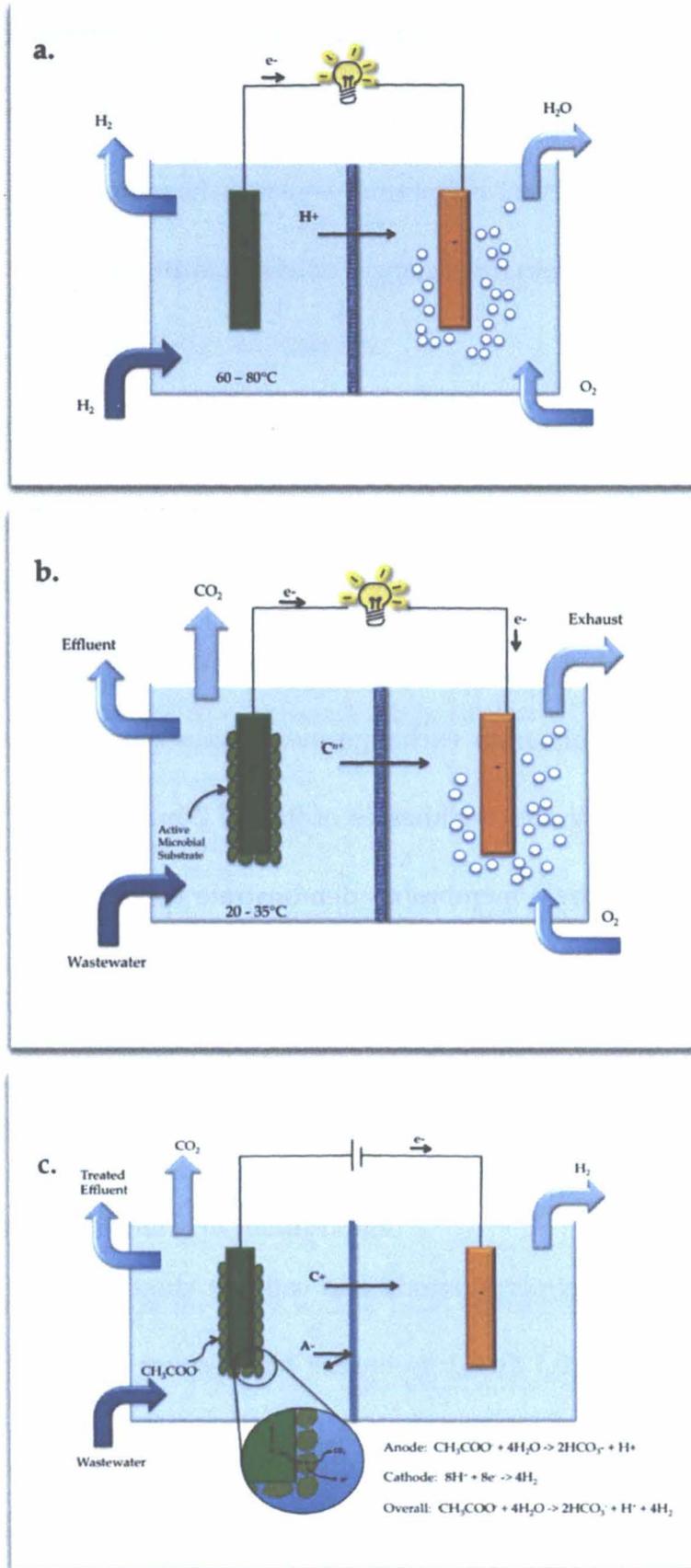
Figure 2.2: Schematic representations of a. hydrogen fuel cell, b. microbial fuel cell, and c. microbial electrolysis cell with acetate as organic feed substrate

The use of membranes is essential to achieve high Coulombic efficiencies and to recover pure product streams. IEMs add an additional internal resistance to these systems. However, membrane research has shown it is possible to achieve acceptable internal resistances of less than 10 mΩ m^{-2} [23].

Specific membrane properties can vary depending on the intended application and performance requirements. Commercial membranes are generally desired to have low ionic resistance, high permselectivity and selectivity, and good thermal, mechanical and chemical stability. Currently available commercial cation exchange membranes have IEC values ranging from 0.9 – 2.7 meq/g and thicknesses of 0.1 – 1.2 mm[24]. At 30 °C and 100 % relative humidity, these membranes demonstrate conductivities in the range of 0.007 – 0.03 S/cm^2.

Table 2.1 summarizes several of the desired membrane properties for use in fuel cells and electrodialysis. For fuel cells, the combined area-specific resistivity of the electrolyte, anode and cathode should be below 0.5 Ωcm^2, ideally approaching 0.1 Ωcm^2, to ensure high power densities[24]. The power densities of membranes for fuel cell applications has been continuously improved since the 1950s[2]. Power densities of 1 kW dm^{-3} and 1 kW kg^{-1} are considered as targets for viable transport applications, with high power densities potentially reducing cost[12]. There has been significant interest in

developing cation exchange membranes as an alternative to Nafion®, which

has reduced performance at temperatures above 80 °C, and is also limited by

significant methanol crossover and cost[25]. For direct methanol fuel cells, a low

methanol crossover of $<10^{-6}$ mol min^{-1} cm^{-1} or a low methanol diffusion

coefficient of $<5.6 \times 10^{-6}$ cm^2 s^{-1} is desired[26].

Table 2.1: Desired cation membrane properties for fuel cell and electrodialysis applications

	Temperature range	IEC	Conductivity	Thickness
Fuel Cells	60 - 100°C for polymer electrolyte membrane 50 – 120°C fuel cells, direct methanol fuel cells, 200°C for phosphoric-acid fuel cell[24-26]	~1.9 meq/g to provide conductivities close to 0.1 S/cm in water at 30°C.	Area specific resistance of 0.02 Ω cm^2 Proton conductivity 0.1 S/cm[25]	Self supported structure with thickness ~150μm[24]
Electrodialysis	20 – 50 C[12,27]	1.2 – 2.0 meq/g[28]	Area specific resistance of 0.82 Ω cm^2 [16]	~110μm[12]

2.2.2 Polymer Electrolyte Materials

2.2.2.1 Perfluorosulfonic acid membranes

Nafion® membranes are the most widely used commercial membrane for ion

conducting applications. These are also used as benchmark materials for

comparison in membrane research studies. Flemion®, Aciplex®, Aquivion®,

and Fumion® are also commercially available membranes. These membranes

are perfluorosulfonic polymers, with very high hydrophobicity in the

perfluorinated backbone. Perfluorosulfonic acid membranes are highly stable in oxidative and reductive environments and can be produced with high proton conductivity, which is useful in polymer electrolyte fuel cells.

Perflurosulfonic acid membranes have several significant disadvantage that limit their use particularly in wastewater treatment processes. Manufacturing safety is a concern with the use of fluorinated chemicals, operating temperature range is limited for such materials, high methanol crossover can cause material damage and, most notably, the high costs of Nafion® membranes limits their use in low margin industries such as wastewater treament[2]. Significant global research into alternative membrane materials, such as high performance polymer electrolyte membranes based on hydrocarbon polymers, show promising properties for separation applications while being more cost-effective and environmentally benign than perfluorosulfonic acid materials[29].

2.2.2.2 Grafted and Block Copolymers

There are several approaches to developing polymer IEMs. These can involve the synthesis of new ionic random and block copolymers, graft copolymerization of ionic polymers on hydrophobic membranes, blending of ionic and non-ionic polymers, or the synthesis of interpenetrating networks of

ionic and non-ionic polymers[30].

Several papers have reported grafting of hydrophobic polymers, using base polymers such as poly(ethylene-tetrafluoroethylene), poly(vinylidene fluoride), or low-density poly(ethylene)[31-33]. Grafting is typically carried out by exposing the hydrophobic polymer membrane to a radiation source, which promotes the formation of radicals and functional groups on the membrane.

Other methods have been reported in the development of block copolymer membranes[34,35]. Block copolymers are chemically attractive because they hold both ionic and non-ionic monomers on the same polymer backbone in an ordered sequence[36]. Block copolymers provide a unique template, where microphase separation occurs on a nanometer scale due to the thermodynamic instability between the different blocks[34]. These regions can form a variety of morphologies that influence membrane transport properties.

2.2.2.3 Sulfonated Aromatic Polymers

Aromatic polymers are a promising route to obtain high performance polymer electrolytes because of their availability, processability, wide variety of chemical compositions and their potential stability in fuel cell environments. These polymer electrolytes can be produced from low cost materials, have high proton conductivities, good water uptake and are

durable[29]. Specifically, poly(arylene ether) type polymers such as poly(arylene ether ether ketone)s (PEEKs), poly(arylene ether sulfone)s, polysulfones, polyimides, polybenzimidazoles and derivatives of these are currently under investigation[2,30].

From recent literature, novel functionalized aromatic polymers are being developed with comparable performance to the more expensive Nafion® membranes. Polyethersulfone (PES) membranes have been modified using a layer-by-layer technique to assemble charged polyelectrolytes by electrostatic adsorption directly onto an ultrafiltration membrane without prior surface treatement[37]. This multi-layered surface produces membranes with a denser active layer compared with the open structure of unmodified PES membranes. PES can also be sulfonated and has been demonstrated by various research groups to have suitable electrochemical and mechanical properties comparable to Nafion® membranes[38,39]. Crosslinked ionmer membranes based on sulfinated and sulfonated poly(ether sulfone) were directly compared to Nafion® 117 and found to be more compact and with conducting paths of a smaller dimension than the Nafion membrane[10].

Aromatic polymers are known to have high oxidative and hydrolytic stability under harsh conditions, making them attractive for use in bioelectrochemical

systems[6,11,12,23-25]. Modification of aromatic polymers typically occurs by electrophilic aromatic sulfonation. Aromatic polymers are easily sulfonated using concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, or sulfur trioxide. Several examples of hydrocarbon polymers functionalized with sulfonic acid are presented in Figure 2.3. Sulfonic acid groups are highly hydrophilic and can assist the transport of cations through the membrane structure[40,41]. Blends of semi-homogenous sulfonated poly(phenylene sulfide) and poly(ether sulfone) have also been developed as effective cation exchange membranes[42].
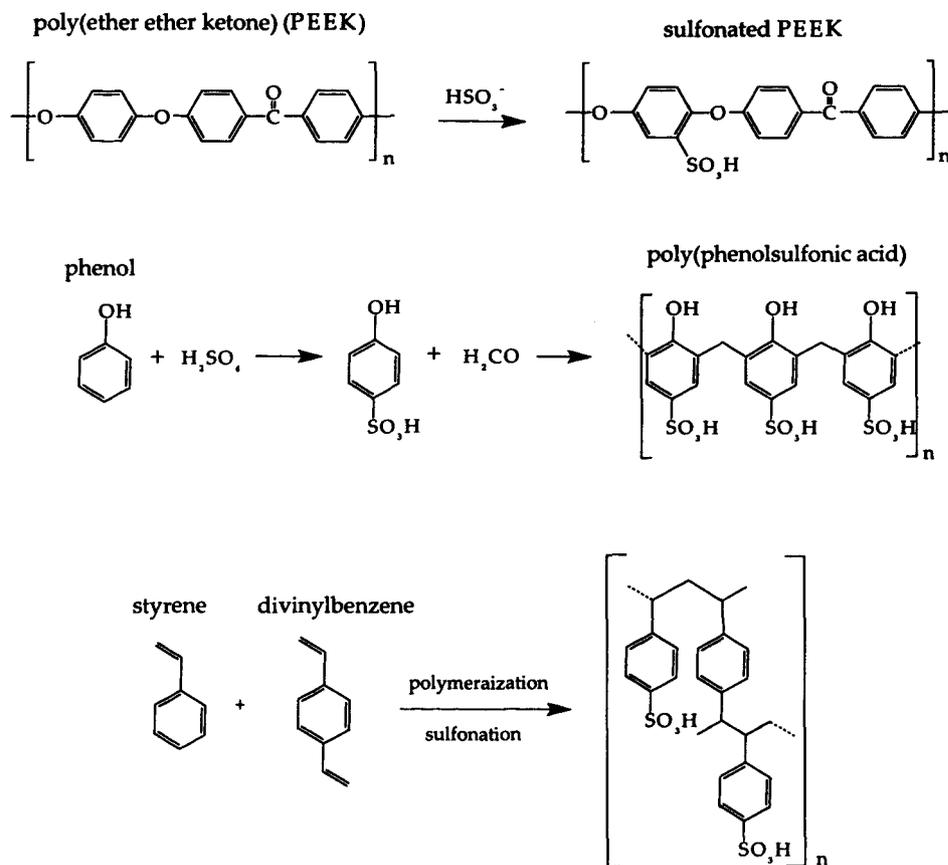
Figure 2.3: Chemical structures of sulfonated polymer electrolyte materials with hydrocarbon backbones

Poly(aryl ether ketone)s (PEEKs) have been extensively studied and determined as a viable candidate material for developing selective and robust CEMs[21,43,44]. The sulfonation of PEEK is shown in the first reaction presented in Figure 2.3. Poly(ether ether ketone) is a readily available commercial polymer and multiple researchers have investigated the properties of sulfonated PEEK (SPEEK) membranes[42,45-47]. The proportion of sulfonated repeat units is described as the degree of sulfonation (DS) SPEEK membranes

with a sulfonation degree of around 90% exhibits a high ion exchange capacity of 2.48 meq/g, and with similar proton conductivity of Nafion® membranes[48]. However, SPEEK with excessively high degrees of sulfonation exhibits poor dimensional stability particularly in aqueous environments[49]. Previous literature notes that a critical point for water uptake of membranes occurs at sulfonation degrees above 0.8[50,51]. Above this level of sulfonation, membranes readily lose integrity in water. Therefore, research efforts have focused on strategies that can maintain the mechanical integrity of the material while enhancing the electrochemical properties. Blending SPEEK with other polymers, crosslinking either by reaction bonding, thermal bonding or thermal treatment, or integrating new materials into the SPEEK matrix can improve the thermal and mechanical stability of SPEEK membrane[45,52,53].

SPEEK is a high performing alternative to costly Nafion® 117. Modified SPEEK membranes can have good hydrophilic properties and proton conductivity. They can also be designed with uniquely tailored properties. The cost of Nafion® 117 is almost three times higher than that of SPEEK[54]. In fuel cell units, the cost of power produced using SPEEK membranes is 50% less than that using Nafion® 117[54]. As such, SPEEK membranes offer a cost effective alternative for commercial separation applications.

2.2.3 Ion Transport Kinetics

The movement of ions through a membrane is influenced by the membrane's physical and chemical structure. For example, morphologies with closed cell pores or open interconnected pores will differ in their ion transport properties[55]. Understanding the fundamental principles for ion movement through a membrane is essential to develop membranes with suitable ion transport properties.

2.2.3.1 The Donnan Membrane Principle

The Donnan membrane equilibrium arises from the inability of certain ions to diffuse through a semi-permeable membrane in aqueous polar environments[56]. The charged particles will distribute unevenly on either side of the membrane as some charged species are unable to pass through the membrane[4,57]. As the uneven charge distribution arises due to the Donnan principle, an electrical potential known as the Donnan potential will develop across the membrane.

Non-diffusible fixed charges in the membrane phase can affect the distribution of free ions, which influences the separation efficiency or product recovery of certain species. In SPEEK cation exchange membranes, fixed negative charges of sulfonate groups ($-SO_3^-$) are covalently attached to the

polymer. The distribution of these fixed charges throughout the membrane matrix will affect the diffusion of ions through the thin film[56].

2.2.3.2 Electrochemical Transport

For a system with uni-directional flux from the anode to the cathode, the ion transport across the membrane-solution interface is considered irreversible. Ion flux is better described by kinetic parameters as equilibrium laws no longer apply. Ion movement can be driven by an applied current or a concentration gradient between the membrane separated compartments. The net flux of a species can be written in relation to the gradient in the chemical potential. In ion exchange membranes, the chemical and electrical potential act simultaneously, and can be combined into an electrochemical potential. The electrochemical potential, η_i, can be described for species i, where μ_i represents the chemical potential, z_i is the charge of the species, and ϕ indicates the local electrostatic potential.

Equation 2.2:

$$\eta_i = \mu_i + z_i e \phi$$

For a one-dimensional case, the electrochemical potential gradient can be expressed as;

Equation 2.3:

$$\frac{d\eta_i}{dx} = \frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx}$$

This describes the mass transport process of a charges species through the membrane.

Under a potential gradient force, P_i, a flux density of species i, develops proportional to the self-diffusion coefficient, D_i. Assuming the potential acting is the electrochemical potential, the following flux equation can be obtained.

Equation 2.4:

$$j_i = \frac{-D_i c_i}{kT}\frac{dP_i}{dx} = \frac{-D_i c_i}{kT}\frac{d\eta_i}{dx} = \frac{-D_i c_i}{kT}\left(\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx}\right)$$

Using the Nernst-Einstein equation, random diffusivity can be substituted with conductivity to obtain the following expression for flux density under an electrochemical potential.

Equation 2.5:

$$j_i = \frac{-\sigma_i}{(z_i e)^2}\left(\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx}\right)$$

For a charged species, the flux density for species, i, gives rise to the partial current density, i_i;

Equation 2.6:

$$i_i = z_i e j_i = \frac{-\sigma_i}{(z_i e)^2}\left(\frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx}\right)$$

Using the definition for total conductivity, $\sigma_{tot} = \Sigma_k \sigma_k$, and the definition of transport number, $t_k = \frac{\sigma_k}{\sigma_{tot}} = \frac{\sigma_k}{\Sigma_k \sigma_k}$, an expression can be derived that relates the electrical potential gradient to the total (net, external) current density, the total conductivity, and the transport number and chemical potential gradient of all the charge carriers. The flux equation for species, i, can then be expressed as follows.

Equation 2.7:

$$\frac{d\phi}{dx} = -\frac{i_{tot}}{\sigma} - \Sigma_k \frac{t_k}{z_k e}\frac{d\mu_k}{dx}$$

If there is a net current, a flux density of species, i, will be set up proportional to the total current density and the transport number, t_i, divided by the

species' charge. The flux density of an individual species in the company of many other species can be written by the general expression;

Equation 2.8:

$$j_i = \frac{t_i i_{tot}}{z_i e} - \frac{\sigma_i}{(z_i e)^2}\left(\frac{d\mu_i}{dx} - z_i \Sigma_k \frac{t_k}{z_k}\frac{d\mu_k}{dx}\right)$$

In general cases, Fick's 1st Law of Diffusion expresses the concentration gradient in relation to the chemical diffusion coefficient.

Equation 2.9:

$$j_i = -\widetilde{D}_i\frac{dc_i}{dx}$$

Diffusion can occur under a chemical potential or concentration potential. Fick's 2nd Law can be expressed for situations where the material takes up or contributes matter to the system, leading to changes in the concentration of the species with time.

Equation 2.10:

$$\frac{dc}{dt} = -\frac{dj}{dx} = \frac{d(D\frac{dc}{dx})}{dx}$$

If D is independent of c, and subsequently x and t, this expression can be simplified and used into solve for electrical conductivity situations.

Equation 2.11:

$$\frac{dc}{dt} = -\frac{dj}{dx} = D\frac{d^2c}{dx^2}$$

For ion transport through IEMs, the Nernst-Planck flux equation describes transport phenomena in both solutions and the IEM. This assumes the independent migration of cations and anions in the solution and membranes. Under equilibrium conditions (ie. no net flux), the Nernst-Planck equation can also be simplified to give the Nernst equation.

Equation 2.12:

$$V_n = \frac{RT}{z_n F} \ln \frac{c_n^0}{c_n^i}$$

This gives the value for the membrane potential, V_n, at which a given ion n is in steady-state equilibrium. It must be noted that the Nernst-Planck model neglects the interactions among different ions and solvent in real situations.

2.3 Review of Commercialized Cation Exchange Membranes

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A previously published review paper is included here in edited form to discuss the current state of commercially available CEMs. This provides context for the commercial applications available for the novel membranes to be developed in this research project.

2.3.2 Introduction

Ion exchange membranes are highly efficient for use in separation applications, providing cleaner and more energy-efficient alternatives in applications such as water treatment and power generation.[1] Over the last 50 years, ion exchange membranes have progressed from laboratory scale to applications in commercial industries such as fuel cells.[2,58] In addition to lowered operational costs and energy demands, environmental and safety issues are pushing more industries towards membrane technology.

A focus on the cost reduction of membrane materials is essential for developing economically competitive technologies that are more

environmentally conscious. A continual challenge in this field is to find lower cost membranes with the desired properties for ion exchange applications. A significant reduction in the capital costs of these membranes without sacrificing performance is essential for new technologies to become commercially competitive on an industrial scale.

There has been significant interest in developing commercial polymer electrolyte membranes with the aim of replacing high cost ion exchange membranes such as Nafion®, Flemion® and Aciplex®. These perfluorinated polymer electrolytes are currently the most commercially utilized electrolyte membranes for polymer electrolyte fuel cells, with high chemical stability, proton conductivity and strong mechanical properties. While perfluorinated polymer electrolytes have satisfactory properties for fuel cell applications, they limit commercial use for water treatment systems because of their significant high costs. 2012 costs of Nafion® membranes are summarized in Table 2.2.

Table 2.2: - 2012 Cost of Nafion® Membranes

Membrane Classification	Cost ($USD)	Normalised Cost ($USD/cm²)
Nafion® NRE212 Membrane 100cm²	$24	$0.24
Nafion® NRE212 Membrane 900cm²	$130	$0.14
Nafion® 115CS Membrane 100cm²	$30	$0.30
Nafion® 115CS Membrane 900cm²	$175	$0.19
Nafion® 117CS Membrane 100cm²	$35	$0.35
Nafion® 117CS Membrane 900cm²	$200	$0.22
Nafion® N115 Membrane 900cm²	$282	$0.31
Nafion® N117 Membrane 900cm²	$340	$0.38
HYDRion™ N115 25cm² Electrolysis Membrane	$103.50	$4.14
Nafion® N117 Membrane 900cm²	$221	$0.25
HYDRion™ N117 25cm² Electrolysis Membrane	$117	$4.69

These membranes are used in fuel cells, such as proton exchange membrane fuel cells, which are a promising technology for use in transportation because of their high efficiency and environmentally friendly solution to energy conversion. A proton exchange membrane (PEM) separates the fuel and oxidizer, simultaneously facilitating the transport of positive charges from the anode to cathode to compensate for the transport of current electrons. A promising approach to obtain high performance proton-conducting polymer electrolyte membranes is through the use of hydrocarbon polymers. Inexpensive and efficient materials with high thermal and chemical stability,

high ionic conductivity, miscibility with other polymers, and good mechanical strength are reviewed in this paper. Though it is difficult to evaluate the true cost of a product based on preliminary research, this section will examine several of the more promising materials available as low cost alternatives for ion exchange membranes. These alternative membranes represent a new generation of cost effective electrolytes that can be used in various ion exchange systems. This review will cover recent and significant patents regarding polymer electrolytes suitable for ion exchange membrane applications. Promising candidates for commercial applications will be discussed and the future prospects of cost effective CEMs will be presented.

PEMs are typically based on polymer electrolytes having acidic functional groups attached to the polymer backbone. The efficiency of these fuel cells is highly dependent on their ability to minimize ionic and electronic resistivity. The polymer electrolyte membrane acts as an electrolyte, providing ionic transport between the anode and cathode while separating the reactant gases and performing as an electronic insulator.

Polymer electrolyte fuel cells offer a promising alternative for portable electronic power using solid polymer membrane direct methanol fuel cells (DMFCs). DMFCs are capable of producing up to 500W power and have the potential to replace batteries in portable devices such as laptops, phones and

cameras[59]. The higher energy density in liquid methanol fuel over batteries is a strong advantage but is offset by several electrokinetic issues such as methanol crossover. Where methanol molecules are transported through the membrane from the anode to the cathode, this methanol crossover leads to a reduced potential at the cathode and lowers the overall fuel cell voltage. To manage these inefficiencies, the DMFC operating temperature is increased to more than 150°C. Operation from 100°C to 200°C is termed as high temperature operation and can reduce the effect of performance limitations. At these conditions, robust membranes are required to achieve long-term stability. Currently, membranes for fuel cells are typically made of perfluorocarbon-sulfonic acid iononmers. These copolymers are formed from tetrafluorethylene and various perfluorosulfonate monomers.

Membranes used in these electrochemical systems require good mechanical and chemical stability in harsh chemically oxidative and physical environments, high proton conductivity and high permselectivity. The development of membranes must also address issues of low cost, automated processing, performance and reliability.

Bioelectrochemical systems are a promising technology for water treatment and purification systems. These systems utilize membranes to provide a novel and promising biotechnological approach for the production of renewable

energy or commodity chemicals from wastewater[8]. Based on the current costs of materials used, the capital costs of full-scale electrodialysis cells and BESs are orders of magnitude higher than those of current conventional wastewater treatment systems. The most common of bioelectrochemical systems involve microbial fuel cells (MFCs). MFCs are attractive as technologies for off-grid rural or remote power applications in developing countries.

Up until 2003, materials and designs employed for BESs were based on similar membranes as used for ion exchange fuel cells, such as Nafion® 117, which has the equivalent weight of 1100 meq/g and is 0.17mm thick[20]. However, further research into more optimal materials for these systems has resulted in several cost effective membrane materials more suitable to these specific environments and operational requirements.

Developments are being investigated to produce alternative, low-cost, polymer-based electrolytes with good chemical resistance, good mechanical stability and sufficient proton conductivity. The U.S. Department of Energy has set the following technical targets, as shown in Table 2.3, for proton exchange membranes and can be used as a general guide to determine the practical viability of newly developed membranes[43]. Currently, ionic

conductivity comparable to Nafion® membranes of 10^{-3} to 10^{-2} S/cm is sought

after for maintining viable and cost effective alternative membranes.

Table 2.3: Technical Targets of Proton Exchange Membranes set by the U.S. Department of Energy

Conductivity (S/cm)	Operating temperature (°C)	Area-specific resistance (Ω cm²)	Cost ($/m²)	Durability with cycling (hours)
0.07 (at room temp.)	≤120	0.02	40	5000 (at ≤80°C)
0.01 (at -20°C)				2000 (at >80°C)

2.3.3 Currently Available Commercial Membranes

2.3.3.1 Fluorinated Membranes

Currently, the most commercially applied cation exchange membranes are

based on perfluorinated or partially fluorinated materials. Membranes most

commonly used in PEMFCs are perfluorosulfonic polymers, such as Nafion®

developed from two patents in 1966 and 1982 and assigned to the then Dow

Chemical Company[60,61]. These membranes are classified as perfluorosulfonate

ionomer membranes where the fluoropolymer backbone is bonded with

sulfonic acid groups.

Nafion® membranes are commonly used commercial membranes in ion

conducting applications or in strong oxidizing environments such as in

chloro-alkali plants[5]. The previous generation of cation exchange membranes

used in PEMFCs are based on these sulfonated perfluoropolymers. Perfluorinated membranes have a strong stability in oxidative and reductive environments due to the polytetrafluoroethylene backbone structure and their strong proton conductivity. However, at elevated temperatures, above 80°C, these membranes decrease in performance.[58] When operating at temperatures of around 100°C, perfluorinated membranes lose their mechanical properties and have lowered swelling properties. They are also limited by low proton selectivity, relatively low mechanical stability, high methanol crossover, low conductivity at a low humidity or a high temperature, and, most significantly, high cost[59]. The Nafion series membranes are expensive due to the fluorochemistry involved in synthesis. At costs of US$700/m², these membranes limit broader commercial applications when compared with other current technologies[2,20]. The basic structure of the Nafion membranes is shown in Figure 2.4.
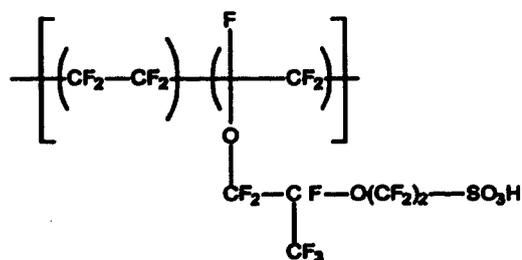
Figure 2.4: Chemical structure of Nafion®

Well established commercial membranes can also be found with trade names of Flemion® (manufactured by Asahi Glass Co., Ltd.) and Aciplex® (Asahi Kasei Co., Ltd.). Though not as widely used as Nafion®, these membranes also have the proton conductivity and chemical stability required for an electrolyte membrane, but are similarly limited by high cost. Modified composites of these commercial membranes have shown improved performance and properties, however, little progress has been made to significantly reduce manufacturing or materials costs[58].

In addition to cost and performance limitations, safety during manufacture and operation, as well as environmental considerations regarding disposal render any fluorinated membranes less appealing. Safety concerns derive from the toxic intermediates and corrosive gases released above 150°C[2]. These materials will remain inherently costly due to the use of fluorine and the severe reaction conditions needed to prepare these polymers. They also cause considerable environmental concern with regard to disposal of halogenated materials. Decomposition of the fluorinated material is also of concern and limits the recycling options of this material. At high temperatures (>90°C) and low relative humidity, performance and conductivity of these materials are compromised. In addition to high cost and high methanol permeability, these limitations are crucial to be addressed for commercial viability.

Gore and Associates Inc. are developing novel fluorinated ionomer membranes based on polytetrafluorehylene (PTFE). This membrane provides good resistance to tear, dimensional stability, low membrane resistance and durability under fuel cell operation for vehicle applications [58]. This membrane is a composite based on PTFE porous sheet reinforcement and is trademarked under the name Gore-Select®[62,63]. With a lower shrinkage rate upon dehydration, higher mechanical strength and more effective water management, Gore-Select® is a reasonable alternative to Nafion® in fuel cell applications. Gore-Select® with PTFE reinforcement has been shown to outlast Nafion® commercial membranes three times its thickness and can also provide significantly higher power density[58]. These factors indicate Gore-Select® may be a more durable alternative to Nafion® when considering capital and operational cost aspects.

2.3.3.2 Partially Perfluorinated Membranes

An alternative family of materials that can be used for ion exchange membranes involves partially perfluorinated polymers. A sulfonated copolymer incorporating α,β,β-trifluorostyrene monomers has been patented under Ballard Advanced Materials 3rd Generation (BAM3G) from Ballard Advanced Materials and have been recognized as membranes suitable for PEMFC applications. BAM3G is a partially fluorinated polystyrene-like

electrolyte membrane where the C-F bonds are substituted at the benzylic position, as shown in Figure 2.5.
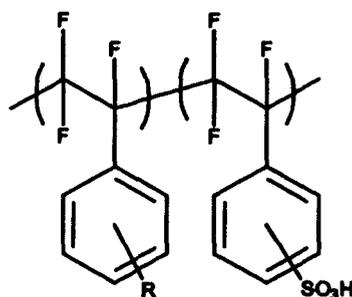
Figure 2.5: Chemical structure of BAM3G, where R = alkyls, halogens, alkoxy, CF=CF$_2$, CN, NO$_2$, or OH

The presence of the electron-withdrawing group (-CF-) on the aromatic ring renders the sulfonic acid group a stronger acid. These membranes have shown superior PEFC performance than that of conventional fluorinated membranes[58]. BAM3G is considered a promising membrane in terms of performance and stability.

The high cost and limited availability of trifluorostyrene monomers used to produce BAM3G limits the practical application of this material in commercial membranes. Subsequently, BAM3G composites have been investigated where a porous substrate has been impregnated with a polymeric composition comprising of various combinations of the following:

i. sulfonated α,β,β-trifluorostyrene and *m*-trifluoromethy-α,β,β-trifluorostyrene;

ii. sulfonated polymer of α,β,β-trifluorostyrene;

iii. copolymer of α,β,β-trifluorostyrene, *m*-trifluoromethyl-α,β,β-trifluorostyrene and *p*-sulfonyl fluoride-α,β,β-trifluorostyrene;

iv. sulfonated copolymer of α,β,β-trifluorostyrene and *p*-fluro-α,β,β-trifluorostyrene;

v. copolymer of α,β,β-trifluorostyrene, *p*-fluoro-α,β,β-trifluorostyrene and *p*-sulfonyl fluoride-α,β,β-trifluorostyrene

These modifications can further improve the mechanical strength of the material in the dry state and its dimensional stability when wet. The modified composites of BAM3G have reduced costs compared to the initial membrane material[58]. These composite materials are still in early stages of development and have not yet been patented for commercialization. A further study of the chemical and mechanical properties of these materials is recommended to determine if these are viable membranes for commercial applications.

The use of fluorinated materials in developing new membrane materials increases costs of production. Non-fluorinated materials may be capable of controlling methanol crossover but are only now being developed in research capacities with sufficient proton conductivity to act as replacements for

fluorinated membranes. These materials may also be subject to chemical degradation in strong acidic and oxidative conditions due to the -C-H- bonds within these materials. Partially fluorinated materials show excellent resistance to acids, low methanol crossover and high proton conductivity. However, these are still unable to produce low-cost membranes due to their use of expensive fluorinated materials.

2.3.4 Non-fluorinated hydrocarbon membranes

The most promising alternative materials that are capable of producing low cost membranes are non-fluorinated polymers or acid-base blends. Other materials such as composite membranes also show significant promise. Hydrocarbon membranes provide distinct advantages over perfluorinated membranes in terms of reducing cost and allowing for easier manufacture by eliminating fluorinating steps. Reducing the content of fluorinated species reduces manufacturing costs, and improves environmental viability by minimizing the use of halogenated materials.

Low cost cation exchange membranes can be produced from functionalized polymers, which are readily available or able to be produced from inexpensive materials. In order to enhance stability at higher temperatures, aromatic hydrocarbons can be incorporated directly to the hydrocarbon

polymer backbone. Due to these inflexible and bulky aromatic groups, polyarylenes are stable at high temperatures of more than 200°C[15]. Aromatic rings also allow for electrophilic as well as nucleophilic substitution. Functionalization is typically by sulfonation or phosphonation, either directly or by polymerizing functionalized monomers. These reagents are inexpensive and readily available[39].

Earlier sulfonation treatments mainly focused on improving the hydrophilicity of membranes. Concentrated sulfuric acid and chlorosulfonic acid are typically employed as sulfonating agents. It is known that chlorosulfonic acid is a stronger solvent due to the weaker Cl-S bond. This causes the sulfonation reaction to be less controllable, with side reactions often occurring. Sulfonation is an electrophilic substitution reaction, with the active site for substitution determined primarily by electron density, preferably taking place on the aromatic ring.

Thermoplastic polymers such as polystyrenes, polyethersulphones, polyetherketones, and polybenzimidazole have been proposed as substitutes of perfluorinated materials, provided an acidic functional group has been introduced to the unit structure. For cation exchange materials, it is preferable that the solid electrolyte has an acidic functional group, with sulphonic acid

most commonly used, phosphonic acid, carboxylic acid or phosphoric acid groups are also currently being investigated[64].

2.3.4.1 Polystyrene membrane materials

Polystyrene is a very low cost thermoplastic and is readily available for large-scale commercial uses[65]. Membranes developed from sulfonated polystyrene can be composed of hydrogenated and sulfonated styrene copolymers, obtained by sulfonating styrene-(ethylene-butylene)-styrene (SEBS) copolymer[66]. However, at higher sulfonation levels, the strength of these membranes decreases when they become hydrated.

A proton exchange membrane with improved stability has been developed with a sulfonated and phosphonated polystyrene material having a covalently bonded tertiary hydrogen replacement group[65]. The base structure of this polymer is shown in Figure 2.6, where the Y is a covalently bonded group and R is a group of $-SO_3H$, $-PO_3H_2$, or mixtures thereof. The produced membrane has high chemical and mechanical stability suitable for use in fuel cells.
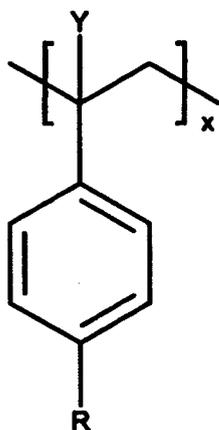
Figure 2.6: Structure of modified polystyrene

Further improvements to the selectivity of polybenzoxazole membranes have used poly(styrene sulfonic acid) polymers as a polymer backbone[67]. These membranes are prepared from aromatic polyimide membranes for gas, vapor, and liquid separations. Thermally treating these membranes with poly(styrene sulfonic acid) polymer showed 95% improvement in selectivity for CO_2/CH_4 and H_2/CH_4 separations[67].

Typical polystyrene contains phenol groups distributed randomly along the hydrocarbon chain. Syndiotactic polymers are ordered, with phenol groups alternating on each side. Syndiotactic polystyrene (s-PS) is a commercially available and inexpensive engineering plastic. Several sulfonation synthesis techniques have been investigated based on polystyrene materials[43].

A polyelectrolyte material comprising a syndiotactic polystyrene configuration was patented as a suitable membrane for fuel cell use or wastewater treatment[68]. This inexpensive membrane material also exhibits good long-term stability. Typical sulfonated styrene resins are copolymerized with divinylbenzene to maintain the film configuration when hydrated, however, this resin has poor long-term stability[68]. Previously published syndiotactic configurations of polystyrene have low sulfonation degrees of up to 6.3mol%. When formed into electrolyte membranes, this gives a maximum ion exchange capacity of only 0.6meq/g if all sulfonic groups are effectively functioning. This performance of such materials leaves them as insufficient for use in industrial fuel cells. However, when blended, the sulfonated polystyrene (s-PS) can effectively form pores in the resin. The preferred styrene polymers include polystyrene, poly(p-methyl styrene), poly(m-methyl styrene), poly(p-tertiary-butyl styrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), hydrogenated polystyrene and copolymers containing these constituting units. The membrane blends retained their configuration due to the good crystallizabilty of s-PS, while also having high sulfonation from resins more readily sulfonated than polystyrene. The resulting membrane showed good electric conductivity, low water-permeability and good retention of the film's configuration in water and is ultimately inexpensive.

Simplified processing methods also assist in reducing the overall cost of a membrane. Several methods have been presented for post-sulfonation of aromatic polymers via transition metal-catalyzed polymerization followed by post-sulfonation[43]. This novel synthesis procedure is more cost effective, though less controllable, than methods where the monomer is pre-sulfonated. The presence of the electron-withdrawing group enhances the polymerization rate and increases the molecular weight of the polymer, while also making the sulfonic acid group a stronger acid. The mix of meta- and para- configurations also provides for improved solubility and easier film processing.

Recently, the use of sulfonated polystyrene grafted to a polyethylene backbone has shown promise for low cost membranes for DMFCs. Baglio et al. (2010) recently produced a low cost fluorine-free proton conducting polymer electrolyte for application in DMFC mini-stacks[32]. This membrane material was based on sulfonated polystyrene grafted onto a polyethylene backbone. The mini-stack structure improves the utilization of this fluorine-free membrane. A power density of 18 mW cm^{-2} was achieved and, while low compared to Nafion 117® of 31 mW cm^{-2}, the fluorine-free membrane showed good characteristics for application in DMFCs especially with regard to significant cost reduction.

2.3.4.2 Poly(arylene ether sulfone) membranes

Poly(arylene ether)s are promising candidates for ion exchange membranes due to their outstanding chemical and thermal stabilities, high glass-transition temperature, as well as their good solubility in dipolar aprotic solvents for film forming[39]. Sulfonated poly(arylene ether sulfones) in random copolymer form is a highly promising material being investigated[69]. Sulfonated arylene-main-chain polymers such as poly(ether sulfone)s and poly(etherketone)s are the next preferable materials as they show the best chemical stability compared to Nafions and are relatively cheaper[10].

Victrex Manufacturing Ltd has examined sulfonated polyarlyethersulfones as ion conducting membranes for PEMFC, although greater ion exchange capacities are needed to achieve similar conductivities to perfluorosulfonic acid Nafion polymers.

Hibino et al. (2006) discusses a method to provide a solid electrolyte that can be formed into an electrolyte membrane that has restricted fuel crossover even at high ion exchange capacity. The solid electrolyte displays the structure shown in Figure 2.7, where the functional group -SO_3H is bound to any position of the benzene ring. This three armed, trifunctional compound structures allows for control of the cross-linking density and cross-linking positions in solid electrolyte to restrict fuel crossover[70].
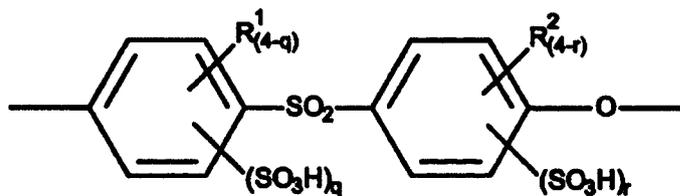
Figure 2.7: Chemical structure described by Hibino et al. (2006)

Cooray et al. (2009) describes an electrolyte composed of a sulfonic acid group-containing polymer having at least one structure unit of those shown in Figure 2.8. These membranes are cross-linked by irradiation treatment and can be used in DMFCs as they are stable in strong acid environments, give low methanol crossover and have high proton conductivity[71].
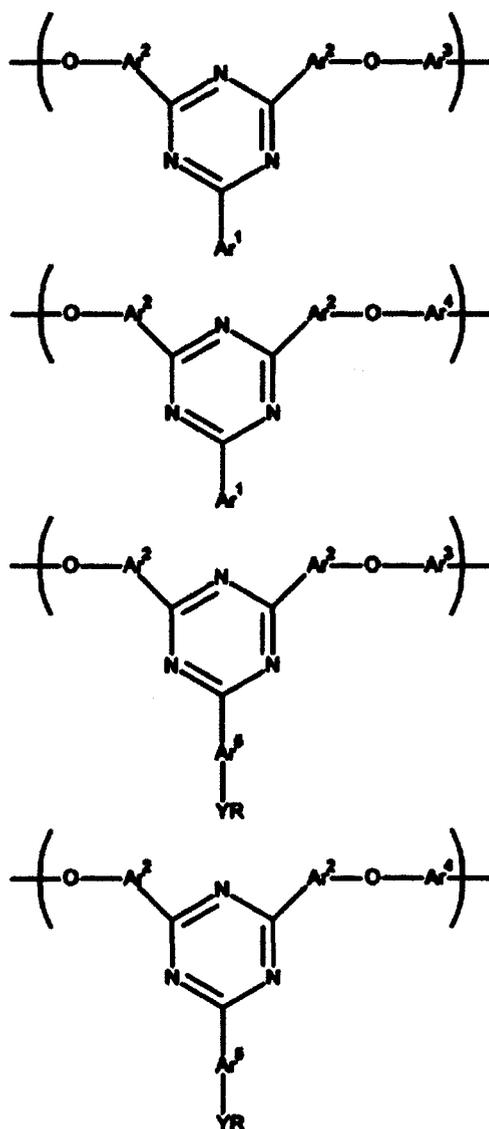
Figure 2.8: Chemical structure of polybenzimidazole

2.3.4.3 Poly(arylene ether ketone) Membranes

Poly(arylene ether ketones)s (PAEKs) are regarded as high performance engineering thermoplastics due to their good solvent resistance, high thermooxidative stability and excellent mechanical properties[72]. Depending on the sequences of ether and ketone units, this class of materials can include

various types of polymers such as PEK, PEEK, PEKK and PEEKK. The sulfonated derivates of these polymers are low cost alternatives to Nafion® membranes that may also help reduce problems with high methanol crossover[73]. SPEK materials are inexpensive and are environmentally friendly alternatives to fluorinated materials[15]. For such materials, it is crucial to achieve a balance between high proton conductivity and the degree of sulfonation, which in turn affects the mechanical strength of the polymer.

Sulfonated PEEKs can be prepared via modification, where a sulfonating agent incorporates sulfonate groups onto the polymer chains. Alternatively, direct copolymerization of pre-sulfonated monomers enables easier control of the degree of sulfonation by controlling the ratio of the sulfonated monomers. This method also avoids cross-linking and other side reactions associated with post-sulfonation that can reduce thermal and mechanical stability. Several papers have described this direct sulfonation technique and the subsequent polymerization to attain SPEEK polymers[72,74-79].

Sulfonated aromatic polyether ketone has been produced where the ratio of sulfonated monomer to non-sulfonated monomer was varied from 0.2 to 1[80]. Subsequently, a homogeneous polymer alloy comprising of SPEK and at least one aromatic polysulfone was identified as suitable for electrochemical cells

at operating temperatures above 100°C[81]. By copolymerization, properties of the polymer materials can be improved or controlled.

While the direct synthesis of SPEEK from sulfonated monomers has been shown to be more advantageous from a materials perspective than that of post-sulfonation, the simplicity and lower cost of post-sulfonation is preferable for ease of large-scale commercialization[74]. Despite the limitations of cross-linking, mechanical and thermal degradation, the post-sulfonation procedure described in various reports provides for a noticeably much simpler and hence, more cost effective, method for SPEEK synthesis[42,44,48,82-89]. The differences with regard to the mechanical and transport properties of hydrated perfluorinated polymers such as Nafion® and low cost sulfonated polyaryls has been previously described[73].

SPEEK polymer membranes are characterized by lower permeability to water, methanol, O_2 and H_2 when compared to Nafion®[90]. They also present good chemical, high thermal resistance and mechanical stability[15]. These materials have high heat resistance, excellent hydrophilicity and good solubility in organic solvents, which allows them to be cast into thin film membranes. SPEEK membranes show promise as commercial ion-exchange membranes with sufficient stability in many processes[10].

Conventional sulfonation processes for polyether ketones are described by numerous papers[21,45,46,48,78,91]. Under mild conditions, the sulfonation reaction proceeds very slowly, while under vigorous conditions sulfonated products are difficult to obtain pure, with high degrees of cross-linking or decomposition of the polymer main chain. Helmer-Metzmann and Schneller (2000) describe a process that permits the rapid and mild post-sulfonation of aromatic PEK[92]. The manufacture and casting of SPEK thin films has also been described[93].

More recently, various synthesis techniques that provide SPEEK membranes with reduced methanol crossover for use in direct methanol fuel cells have been reported[74,85]. These show much lower methanol diffusion coefficients than the currently used Nafion®. The ion exchange capacities and proton conductivities of these alternative membranes shows good potential for use in proton exchange membrane fuel cells.

Recent inventions have allowed for homogenous SPEEK electrolyte membranes to be developed by organic solvent casting. Reduced methanol permeability down to a tenth that of Nafion has been achieved while still maintaining ion conductivity. These membranes act as effective alternatives to more expensive commercial membranes[94]. Variations on these materials

such as SPEEKK have also been prepared using inexpensive commercially available monomers[95].

Other recent patents have investigated modifications of SPEKs that contain cycloalkenyl groups as candidates for PEMFCs[53]. Composite polymer electrolyte membranes have recently been produced which show significant promise as inexpensive materials for use in such applications as PEMFCs. These include a blend of PEEK and poly(amide imide)s giving reduced methanol permeability while maintaining good proton conductivity[96]. A monomer comprising of phthalazinone and a phenol group has also been used to produce a sulfonated poly(phthalazinone ether ketone) membrane that can be used particularly for direct methanol fuel cells[97]. A composite material comprising of silica dispersed in a polymer matrix based on poly(aromatic ether ketones), poly(benzoyl phenylene) or derivatives of these have also been characterized with good water retention capabilities, good impermeability to the gas and liquid fuels commonly used in fuel cell technology, obtained due to the presence of silica particles. Good mechanical properties of this composite allows for straightforward casting into thin films, suitable for use as proton exchange membranes for fuel cells[98].

2.3.4.4 Acid-doped Polybenzimidazole Membranes

Polybenzimidazoles (PBI) refer to aromatic heterocyclic polymers containing benzimidazole units as shown in Figure 2.9, that may provide a low cost alternative as a base for composite membranes.
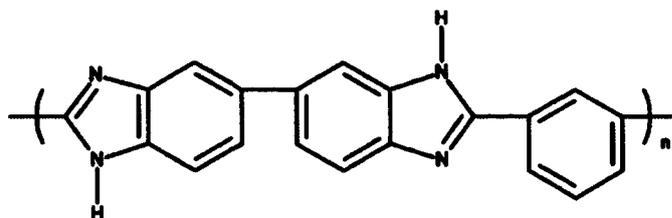
Figure 2.9: Structure of phosphoric acid-doped poly(benzimidazole)

Acid-base complexation is an effective method for the development of proton conducting membranes as the basic polymer acts as a proton acceptor, where an ion pair can be formed. With a lower permeability for hydrogen, they also retain high temperature oxidative stability, good chemical and mechanical properties as well as high ionic conductivity when acid-doped[58]. PBIs doped with high acid concentrations can result in high ionic conductivities of 2×10^{-3} and 6×10^{-2} Scm^{-1}. These conductivities are comparable with commercial Nafion® 117, while being significantly more cost effective than perfluorinated options.

Doped PBI shows great potential for fuel cells operating at moderate temperatures. A review by Smitha et al. (2005) looks at several journal articles that examines the potential of doped PBI membranes to replace commercial Nafion® in DMFCs as they are known to have lower methanol permeability. The ease of fabrication of such composites membranes is also increasingly appealing for low cost membrane production. While these materials are promising, they are relatively novel and require further studies into long-term stability and reliability if they are to be commercialized. Several journal articles have examined these materials but there have been few patents relating this material to commercial applications[99,100].

The first patent filed regarding doped PBI membranes was by Savinell and Litt (1996), after which numerous patents on PBI membranes and fuel cells have been issued to Savinell's group[101], Hoechst Celanese and Aventis[102-104] and Honda among others[105,106].

Modified PBI membranes have high ionic conductivity and are suitable for solid polymer electrolytes in electrochemical applications. Phosphoric acid-doped polybenzimidazole membranes have been shown to be highly successful in PEMFCs, with demonstrated performance and high ionic conductivity at temperatures up to 200°C[107]. PBI membranes doped with phosphoric acid have insufficient proton conductivity to replace Nafion®

membranes, novel polybenzimidazole-benzamide copolymer are instead proposed for fuel cell use with higher proton conductivity than conventional PBI polymer electrolyte membranes[108]. The polymer electrolyte composed of repeating benzimidazole and benzamide units has improved proton conductivity and excellent mechanical strength, as compared with conventional polybenzimidazole membranes. High thermal and chemical stability was also shown under operating capacities in a wide temperature range. Further improvement to PBI membranes can be made on the thermal and chemical stability of the polymer[107].

2.3.4.5 Poly(vinyl chloride) Membranes

Ion exchange membranes are also relevant for electrodialysis applications. Anion exchange membranes Neosepta AMX and cation exchange membranes Neosepta CMX have been used[13]. These membranes are homogeneous ion-exchange membranes based on poly(vinyl chloride) and are manufactured commercially by Tokuyama Soda Co. (Japan). Neosepta AMX contains quaternary ammounium groups as fixed charges while Neosepta CMX contains sulfonic acid groups. The anion and cation membranes are stacked in pairs, separated by spacers.

2.3.5 Future Progress of Commercial Ion Exchange Membranes

Non-fluorinated membrane materials offer a competitive alternative to current high cost ion exchange membranes. Developments in hydrocarbon membranes show promise to produce economically viable membranes for ion separation processes. Appropriate membrane materials are sought with key factors involving appropriate conductivity, thermal, mechanical and chemical stability as well as low cost manufacturing ability. Polymer membranes offer opportunities to readily tailor membrane properties for optimal performance. In particular, poly(aryl ether)s are promising candidates due to their chemical and thermal stabilities. These materials are also readily available and can be functionalised and easily cast to specific parameters. Improvements to ion exchange capacities will make these materials highly competitive to current high cost membranes. Given the steadily improving performances documented by recent literature and patents, these materials show strong potential to replace fluorinated materials as PEMs.

With the fuel cell market rapidly developing, demand for inexpensive membrane materials is also expected to boom. Growing technologies such as electrodialysis and bioelectrochemical systems are also encouraged by the commercialisation of viable membrane alternatives. Rikukawa and Sanui (2000) suggest that in order to produce materials that are less expensive than

Nafion, some sacrifice in material lifetime and mechanical properties may be acceptable, provided the cost factors are commercially realistic. Hence the use of hydrocarbon polymers, even though they had been previously abandoned due to low thermal and chemical stability, has attracted renewed interest.

Other promising polymers that may be considered for porous polymeric support membranes include polysulfone, polyethersulfone, poly(ether sulfone ketone), poly(ether ethyl ketone), poly(phthalazinne ether sulfone ketone), polyacrylonitrile, polypropylene, cellulose acetate, and cellulose diacetate or cellulose triacetate. These polymer materials have high potential for developing competitive membranes with high thermal, mechanical and chemical stability.

Many promising materials for future investigation and commercialisation also involve composite materials. Cheap proton conducting composite membranes offering stability up to 150°C can allow for promising developments in upcoming comercial areas such as fuel cell technology, electrodialysis and water treatment[58]. Recent patents describing solid acid polymer electrolyte membranes using carbon nanotubes have been employed for use in fuel cells[109]. Further patents for similar materials are desired to promote the commerical capability of polymer membranes.

Despite increasing patents for such materials, these membranes still face some commercial limitations. These membranes are typically in the demonstration phase of the commercialization progress with these new materials needing to demonstrate performance on par with current Nafion® membranes in large scale systems. The water industry has been most successful in implementing these low cost alternative membranes in water purification and treatment systems. This is primarily due to the low profit margins of these industries, causing increased demand for novel, low cost technologies. Commercial markets in fuel cells and electrodialysis industries are further expected to develop with demonstrated pilot scale results, technological advances and as economies of scale reduce to competitive levels.

2.4 Polymer Composite Ion Exchange Membranes

In the last few decades, there has been considerable development in the field of ion conductive composite polymers[52,110-113]. Their unique properties allow membranes to be tailored with desirable qualities for specific commercial applications[1]. Inorganic-organic composite materials are viable cost-effective alternatives to currently expensive perfluorinated membranes used in commercial applications. The organic component offers the benefits of convenient processing and structural flexibility, with opportunities for chemical modifications. The inorganic compounds provide the potential for improved thermal and mechanical stability as well as increased conductivity. In addition, new phenomena may also arise as a result of nanoscale interactions between the organic and inorganic components.

Composites have been proposed to improve water retention and, subsequently, improve proton transport[110]. In general, the addition of inorganic fillers increases conductivity at temperatures higher than those allowed by pure polymer IEMs[114]. These have also seen a reduction in methanol permeability, beneficial for fuel cell systems[115-118]. Integrating hydrophilic inorganic fillers into the organic polymer matrix influences the microstructure and charge distribution of the membrane[112,119]. The effect of

these embedded particles can depend on the type of nanoparticle used,

particle size, distribution, surface charge and the loading content of the

additives.

2.4.1 Polymer composite membranes

A large variety of fillers such as silica, zeolites, titania, or zirconia can be

incorporated into polymer membranes[55,91,114,115,118,120-127]. Composite membranes

also show promise in selective separation of cations by valency, though

further work is needed to identify suitable membranes and to understand the

mechanisms of ion transport[48]. Examples of previously studied polymer

composite membranes are summarized in Table 2.4 below.

Table 2.4: Examples of polymer composite membranes

Ref.	Membrane	Properties
128	SPEEK/clay-SO3H	Sulfanilic acid grafted to clay and embedded in SPEEK with different weight contents of clay-SO3H. The performance of the hybrid membranes was improved for direct methanol fuel cells. The introduction of clay and clay-SO3H resulted in increased water uptake but lowered conductivity.
91	SPEEK/SiO2 and SPEEK/SiO2-SO3H	Additive loadings of 5% and 10% of both SiO2 and SiO2-SO3H were studied. A decrease in water uptake was observed in the composite membranes compared to the pure SPEEK membranes. However, proton conductivity was found to increase. This was attributed to the

		additive particles retaining water even under dry conditions. Little difference was observed between the SiO_2 and SiO_2-SO_3H composites as significant agglomeration was observed by SEM, consigning most of the additional sulfonic acid groups to the bulk of the additive rather than the surface.
110	SPEEK/Laponite and SPEEK/Montmorillonite	Layered silicates incorporated into SPEEK polymer membranes helps to reduce swelling and decrease methanol permeability. Thermally stable to 240°C with 3-3.5 x 10^{-3} S cm^{-1} proton conductivity at room temperature. Methanol crossover is reduced compared to pure SPEEK without significant reduction in proton conductivity.
129	SPEEK/Silicotungstic acid impregnated onto K10 montmorillonite	Water uptake and swelling ratio increased with increased loading of STA. The resulting composite membranes resulted in lower methanol permeability than Nafion® 112, making it a promising as a composite membrane for DMFC applications.
113,130	SPEEK/Heteropolyacids	Heteropolyacids (HPAs) are highly conductive inorganic solid electrolytes. When appropriately embedded in a hydrophilic polymer matrix, the hydrated HPAs endow the composite membrane with the high proton conductivity of the additives while retaining desirable mechanical properties of the polymer film. Incorporation of HPA fillers increases glass transition temperature and enhances membrane hydrophilicity and conductivity compared to pure SPEEK membranes. Potential for use in fuel cells, but limited by leaching of the HPAs in aqueous environments.
131	SPEEK/Heteropolyacids	Incrased proton conductivity was found with increased loadings of heteropolyacids. Leaching from these

	(tungstophosphoric acid and molybdophosphoric acid) loaded onto a MCM-41 silica molecular sieve	composites was negligible and allows for almost complete loading of heteropolyacids. With high conductivity, these solid proton conducting composites may also be used in developing membranes for direct methanol fuel cells.
85	SPEEK/Sulfonated poly(ether sulfone) with a 0 – 90% SPEEK ratio	The range of SPEEK content in the blend from 50 – 60% provided selective separation of monovalent ions from bivalent ions. Below this loading, not all ion exchange groups were available for ion transport due to the high SPES content. Above this range, the SPES content was too low to provide the physical cross-linking required for a reduction of water content.
132	SPEEK/ZrO$_2$	The incorporation of ZrO$_2$ pretrated with n-propylamine and polybenzimidazole produced composite membranes with decreased water swelling, proton conductivity and permeability towards methanol and water. The morphological stability of the membranes was improved for DMFC applications at temperatures up to 90°C.
121	SPEEK/TiO$_2$	The titania network was dispersed in SPEEK by sol-gel processes. Syntheses by non-hydrolytic and hydrolytic sol-gell process were studied, with both routes giving flexible membranes with improved mechanical and thermal properties and hydrolytic stability.
133	SPES/TiO$_2$	Fouling-resistant nanocomposite membranes were prepared via electrostatic self-assembly between TiO$_2$ nanoparticles and sulfonic acid groups on the membrane surface. The SPES membranes were prepared by the phase inversion method and dipped in the TiO$_2$ nanoparticle solution. The results showed that the amount and rate of membrane fouling decreased in the nanocomposite membranes compared to the straight

		polymer membranes.
134	Nafion®/ TiO₂-RSO₃H	An organically modified ceramic material (TiO₂-RSO₃H) used as a filler in Nafion-based membranes. Propylsulfonic acid groups were covalently grafted onto the surface of the TiO₂ nanoparticles. The hybrid membranes resulted in higher ion exchange capacity and proton conductivity. The highest conductivity value was obtained for the composite membrane containing 10%w/w of TiO₂-RSO₃H. Membranes tested in a DMFC single cell indicated that the presence of the filler resulted in a general enhancement in the cell response, in terms of both higher power density and lower methanol crossover with respect to pure Nafion membrane.
123	SPEEK/TiO₂-NH₂	Grafting amine groups onto the titania fillers increased the content of facilitated transport sites in the membrane, increasing both gas permeability and selectivity. Mechanical and thermal stabilities of the membranes were also enhanced compared to pure SPEEK membranes.
135	Poly(benzyl acrylate)/TiO₂ functionalized with 1-decylphosphonic acid and diethyl undec-10-enyl phosphonate	Rutile titanium dioxide nanoparticles were surface functionalized with 1-decylphos-phonic acid and diethyl undec-10-enyl phosphonate in a two-stage process. Nanocomposite poly(benzyl acrylate) films with TiO₂ loadings of up to 30%w/w showed a high light transmittance of around 90% at wavelengths above k = 400 n.
136	Block copolymer of polysulfone and poly(phenylene sulfide sulfone) (SPSf-co-PPSS)	Composite membranes were found to have reduced water swelling at elevated temperatures. These also resulted in improved mechanical properties and good anti-oxidative stability. TPA loading of 4.3% for SPSf-co-

	blended with tungstophosphoric acid (TPA) and SPEEK/TPA.	PPSS membranes showed optimal properties with proton conductivity of 6.3 x 10-2 S cm^{-1} and water uptake of 23.9%.
137	SPEEK/boron phosophate (BPO$_4$)	BPO$_4$ was introduced into SPEEK by a sol-gel process. Composite membranes had higher water uptake but controlled swelling. A six-fold increase in conductivity for 30%w/w BPO$_4$ composites membranes was found compared to that of pure SPEEK. The uniform dispersion of BPO$_4$ was attribute to the improved continuity of conduction pathways in the composite membranes.
114	SPEEK/zeolite beta	Proton conductivity was improved by the addition of the aluminosilicate, zeolite beta, with the fillers comprised of various SiO$_2$/Al$_2$O$_3$ ratios. The composite membranes were hydrodynamically stable and performed better in fuel cell tests than pure SPEEK membranes.
138	SPEEK/polymer carboxylic acid spheres (PCASs)	Composite membranes showed improved performance, where the PCASs were homogenously embedded and provided new bathways within the bulk membrane for proton conduction. The more tortuous pathways also provided greater resistance for methanol crossover, with composite membranes containing 15%w/w PCAS having four times the methanol selectivity (proton conductivity over methanol crossover) than pure SPEEK membranes.

Most investigations looked at reducing the methanol crossover of membranes used in DMFCs. From this summary, it was noted that HPAs have issues with

leaching in aqueous environments. Polymer blending provides crosslinking that may improve the physical structure of the membrane and reduce methanol crossover, but has not been seen to specifically influence electrochemical characteristics. It is noted that the use of nanoparticles is the most favorable composite pathway to tailor selective electrochemical properties with possibly improved mechanical and thermal stability.

2.4.2 Preparation methods for composite membranes

Composite ion exchange membranes can be prepared by several routes such as sol-gel process, blending, in-situ polymerization, or molecular self-assembly[26]. Figure 2.10 shows the physical blending and sol-gel routes that are most commonly used for the synthesis of nanocomposite materials. The sol-gel method offers better interconnection between the two phases of the membranes as the processing of the nanoparticles inside the polymer dissolved in solution results in the formation of interpenetrating networks between the inorganic and organic components[121].
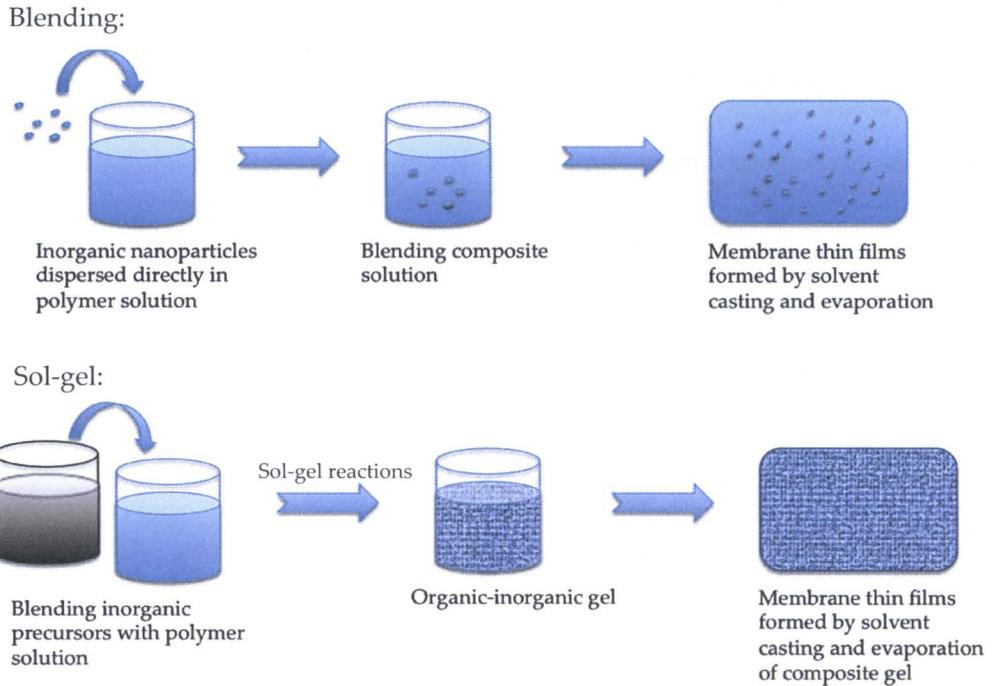
Figure 2.10: Commonly used blending and sol-gel preparation methods to produce composite membranes

2.4.3 Stabilizing nanoparticles in suspension

To achieve stable suspensions of nanoparticles in the casting solutions, zeta potential is commonly used to assess the stability of the colloidal system[139]. Combining the effects of van der Waals attraction and electrostatic repulsion, DVLO theory gives an indication as to the stability of a particle in solution dependent on the total potential energy function;

Equation 2.13:

$$V_T = V_A + V_R + V_S$$

Where V_S is the potential energy caused by the solvent, which is only a marginal contribution compared to the more significant attractive (V_A) and repulsive (V_R) potential forces.

This expression denotes an energy barrier resulting from the repulsive forces preventing the particles from adhering together. However, if the particles collide with sufficient energy to overcome this barrier, the attractive forces will pull them into contact where they may irreversibly aggregate.

For a colloidal system to be stable, the repulsive forces between the nanoparticles must be dominant to resist flocculation. There are two mechanisms that affect dispersion stability[139]. Polymers added to the system can adsorb onto the particle surfaces, creating steric repulsion between the polymer layers with sufficient separation. Altering the concentration of ions in the system can also influence the electrostatic charges within the membrane. Dissociation of acidic groups on the surface of a particle will give rise to a negatively charged surface while a basic surface will take on a positive charge. The magnitude of the surface charge depends on the strength of the acid or base surface groups and the pH of the solution. The pH of a suspension, such as the casting solutions for SPEEK nanocomposite membranes, can be adjusted to achieve suitable dispersion.

2.5 Membrane Selectivity

In PEMFCs, protons are the only cation species present and will be the only cation species transport through the ion exchange membrane. However, when focusing on bioelectrochemical systems, other cation species such as Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+} are present at up to 10^5 times the concentration of protons[140]. Using Nafion® 117 in MFCs has shown that this membrane transports these cation species as well as protons. These species accumulate in the cathode chamber as only proton is consumed in the cathode reaction. Consequently, an increased pH in the cathode compartment decreases the MFC performance[140]. In addition to separating cations and anions based on charge, membranes are also desired with the ability to separate cations of different valency[141].

Preferential selectivity also helps to avoid fouling issues. Where the anode or cathode solutions contain ionic species such as bicarbonate, fouling by scale formation is also a significant issue. This hydroxide formation of divalent and trivalent ions produces calcium salts such as $CaCO_3$ and $CaSO_4$ with low solubility[85,142]. Fouling increases cell resistance, decreases permselectivity and can permanently alter the membrane structure[143,144].

To minimize these effects, it is useful for membranes to have a higher preference for transporting monovalent cations rather than multivalent ions (such as Ca^{2+}). These monovalent cation selective membrane separate ions of the same charge but different valences, improving the performance of existing processes without the addition of surface-active agents or polyelectrolytes in the solution[145].

A selective membrane minimizes the effects of fouling while also enabling the recovery of reusable monovalent species such as H^+, K^+ and Na^+. A focus of this research project is to develop suitable membranes with such selective properties for preferential transport of monovalent cations over multivalent cations.

In previous literature, membrane selectivity has been inconsistently defined and measured. Membrane selectivity has been used to refer to actual permselectivity, which is a measure of how easily counter-ions migrate through an ion exchange membrane compared to co-ions that have the same charge as the fixed species[146]. The permselectivity of a given cation M^{n+} is defined in relation to the transport number of cation M^{n+} relative to that of sodium ions[146].

Equation 2.14:

$$P_{\text{Na}}^{M} = \frac{t_M / t_{\text{Na}}}{C_M / C_{\text{Na}}}$$

Where t_M and t_{Na} are the transport numbers of ions M^{n+} and Na^+ in the membrane phase, and C_M and C_{Na} are the concentrations of M^{n+} and Na^+ at the membrane surface.

Analysis of the transport numbers of different species does give an indication of the transport rates of certain conductive species across a membrane compared to the overall conductivity. The transport numbers of membranes can be compared to give an indication as to the relative rates of transport of different ionic species[147,148].

Some areas of membrane research involved in fuel cell applications have also focused on methanol selectivity, which defines the permeation of methanol over conductivity[52,148]. In this work, we identify membrane selectivity as a direct reference to the concentration of transported cation species in relation to the concentration of a reference monovalent cation through a membrane. Typically, a reference monovalent cation such as Na^+ or H^+ is used to provide a change in concentration ratio, which gives a quantifiable measure of membrane cation selectivity performance[149,150].

Membrane properties, including selectivity, are affected by the morphology and physicochemical structure of the material. These characteristics are controlled by precursors used in the synthesis of the membrane material as well as by reaction and preparation conditions. Understanding the relationships between these parameters and resulting membrane performance is essential in designing and developing a suitably robust and selective membrane. This work will investigate the development of a novel and consistent measure for this definition of selectivity.

2.5.1 Fabricating Selective Membranes

In unmodified ion exchange membranes, cations migrate across the thin film at different rates influenced by ion valency, size or the level of hydration of the membrane. Due to higher electrostatic attraction, divalent cations are preferred for transport by unmodified IEMs. To obtain IEMs that are preferentially selective to monovalent cations, there are several approaches that can be used. The two main fabrication methods that have been previously researched can be generalized as:

1. Manufacturing a suitable membrane by adjusting fabrication parameters

2. Depositing a thin anion-exchange layer with positively charged fixed groups at the surface of the IEM, introducing a slight electrical repulsion barrier to limit the penetration of multivalent cations.

The formation of a thin charged layer on the surface of the main cation exchange membrane has been reported as an effective method for separating ions by valency[142,145,151,152]. Monovalent cation selective ion-exchange membranes have been industrially used in the electrodialytic concentration of seawater to produce edible salt in Japan and other countries[146,153]. Sata has developed a material able to sieve sodium ions from multivalent cations using a tight polypyrrole layer. The presence of positive charges within the membrane results in limited multivalent ion transport as the electrostatic repulsion is greater for multivalent cations. Membranes capable of divalent ion repulsion have also been produced by depositing a thin permselective polymeric layer on both sides of the membrane[154]. Coating a layer of SPEEK onto the surface of a positively charged nanofiltration membrane can produce a nearly neutrally charged membrane with a surface charge that creates a repulsive charge and rejects multivalent ions[145]. The neutrally charged membrane was found to reject multivalent ions more efficiently (>95%) than monovalent ions (80%) with a rejection sequence of $CaCl_2 \approx MgSO_4 \approx Na_2SO_4 >$ NaCl.

Modifying the polymer matrix of an ion exchange membrane is a promising concept for improving membrane selectivity. One method aims to increase the cross-linkages within the membrane, altering the pore sizes of the membranes and affecting the transport of bulkier molecules and smaller molecules[155-159]. Increased crosslinking has been found to enhance the selectivity of the membrane, but is also known to increase the membrane's electrical resistance. Introducing additional fillers to the membrane matrix may compensate for this limitation. Examples of covalently crosslinked SPEEK modified with tungstophosphoric acid were found to feature good electrochemical characteristics such as high proton conductivity and ion exchange capacity[160,161].

Ion specific selectivity is related to the membrane surface charge density, porosity, and the hydrophilic and hydrophobic domains in the membrane. To reduce the transport of multivalent ions compared with monovalent ions, the introduced particles in composite membranes may effect the electrostatic repulsion, hindering multivalent ions to pass through the membrane. Organic-inorganic composite membranes have been previously developed with the aim of improving membrane selectivity[162]. Additives may influence the hydrophilicity of membranes, affecting the ionic interactions and surface charge density of the composite matrix. To achieve selective and cost-effective membranes, composites may be a suitable route for this material development.

2.5.2 Measuring Membrane Selectivity

There are several bioelectrochemical and electrodialysis applications that require specific ions to be concentrated or separated by valency[48,85,163-166]. Ion exchange membranes with specific selectivity for particular ions based on valency are known as monovalent permselective ion-exchange membranes. There have been several approaches to measuring the cation selective properties of ion exchange membranes. In a previous study, composite membranes have been prepared using sulfonic acid groups introduced into the organic segment[162]. These membranes were designed for the specific separation of Na^+ from Ca^{2+}, Mg^{2+}, and Fe^{3+}. Using a two-compartment cell, the electro-transport efficiency, η, is measured for different counter-ions by:

$$\eta = \frac{z_i m F}{MQ}$$

Where z_i is the valence of the studied cation, m is the weight of the electrolyte transported across the membrane, F is Faraday's constant (96480 C/mol), M is the molecular weight of the electrolyte passed through membrane, and Q is the number of coulombs delivered across the membrane.

Defining membrane preference for transporting a particular species is best described by comparing ionic flux through the membrane. Flux models of kinetic and equilibrium controlled mechanisms have been described in previous literature[11,145,154]. Separation tests by electrodialysis have also been described where an electrochemical cell of four distinct compartments was used to test the ability of Nafion® and sulfonated polyimide membranes in separating H^+ and Cu^{2+} ions[150]. The transport of the different ions under an applied potential difference is illustrated in Figure 2.11.
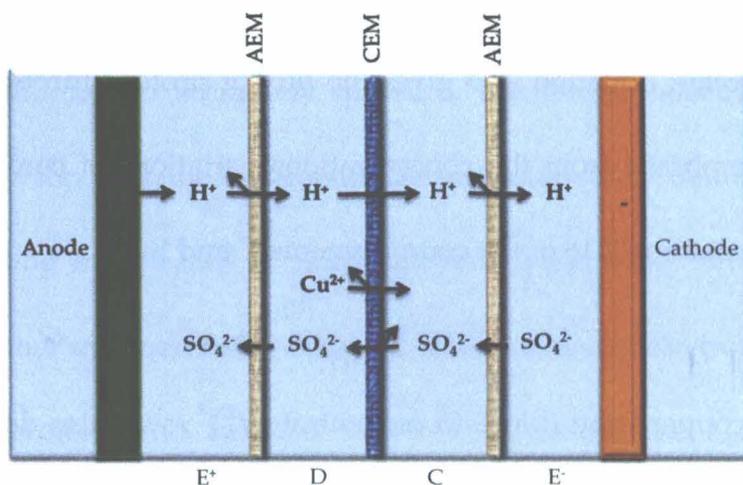
Figure 2.11: Electrodialysis cell for separation tests (E+ and E-: electrode compartments; C: concentrate; D: dilute).

The volumes of the compartments were measured with time and used to calculate the amount of species present. The moles of H^+ and Cu^{2+} ions were determined by acid-base titration using 0.01 M NaOH and by UV-Vis

spectroscopy, respectively. The flux of protons from the dilute to the concentrate compartments can be written as:

Equation 2.15:

$$\left(J_{DC}^{H^+}\right)' = -\left[\frac{\Delta n_{H^+}}{\Delta t}\right]_D - \left[\frac{\Delta n_{H^+}}{\Delta t}\right]_{E+} + \frac{1}{F}$$

Equation 2.16:

$$\left(J_{DC}^{H^+}\right)'' = \left[\frac{\Delta n_{H^+}}{\Delta t}\right]_C + \left[\frac{\Delta n_{H^+}}{\Delta t}\right]_{E-} + \frac{1}{F}$$

Where F is the Faraday constant and Δn is the change in moles of the subscript species. Equation 2.15 gives the flux of protons through the cation exchange membrane from the concentrations variations of compartments D and E^+, and equation 2.16 of the compartments C and E^-.

The flux of copper from dilute to concentrate, $J_{DC}^{Cu^+}$, was also derived in this study.

Equation 2.17:

$$\left(J_{DC}^{Cu^+}\right)' = -\left[\frac{\Delta n_{Cu^{2+}}}{\Delta t}\right]_D$$

Equation 2.18:

$$\left(J_{DC}^{Cu^+}\right)'' = \left[\frac{\Delta n_{Cu^{2+}}}{\Delta t}\right]_C$$

To evaluate the modified membranes, the transport number, t_i, of species i was used to compare ion transport efficiency.

Equation 2.19:

$$t_i = z_i F \frac{J_{DC}^i}{I}$$

Where z_i is the valency of the species i and I is the applied current.

Volume is difficult to accurately measure. Membrane selectivity is better described by ion flux measurements. A previous study demonstrates this approach using membranes of sulfonated poly(ether ether ketone) blended with poly(ether sulfone). Tests were performed in binary electrolyte solutions containing protons and calcium ions[48]. To measure the Ca^{2+} flux, a 2 compartment cell was used with Ag/AgCl electrodes. The electrode reactions for this process are:
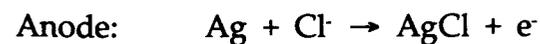
Cathode: $AgCl + e^- \rightarrow Ag + Cl^-$

Anode: $Ag + Cl^- \rightarrow AgCl + e^-$

The following binary solutions were placed in the anode compartment with 0.01M HCl solution in the cathode compartment.

- 0.025M $CaCl_2$/0.075 M HCl;

- 0.05M $CaCl_2$/0.05 M HCl;

- 0.075M $CaCl_2$/0.025 M HCl.

Under a constant current density of 30 mA/cm², the ions were driven through the test membranes. Ca^{2+} concentrations were determined by elemental analysis (atomic absorption spectroscopy) and the corresponding Ca^{2+} flux ($J(Ca^{2+})$) through the membrane was calculated.

Equation 2.20:

$$J(Ca^{2+}) = \frac{V \frac{dC_{Ca^{2+}}}{dt}}{A}$$

Where V is the volume of the circulated solution, A is the membrane area and $\frac{dC_{Ca^{2+}}}{dt}$ is the concentration change in time in the cathode compartment. For homogenous structure membranes, the flux can be normalized by the wet membrane thickness and compared to give a quantifiable metric for comparing membrane selectivity.

Equation 2.21:

$$J_N(Ca^{2+}) = J(Ca^{2+})d_{wet}$$

These researchers have investigated the flux of binary systems. Proton transport is compared directly with Ca^{2+} and Cu^{2+} transport. Further work is required to evaluate multi-ion systems and to provide a reproducible quantitative analysis of membrane selectivity performance. A direct approach to measuring the flux of individual cation species is necessary for further developments into cation selective membrane materials.

2.6 Conclusions

Ion exchange membranes are a promising technology that can be applied to many industries and separation processes. Used to separate electrolyte solutions, they enable the transport of species of the opposite charge while rejecting like-charged species. IEMs are crucial for the development of sustainable and clean water treatment and fuel cell technologies. A cross-disciplinary field, IEMs can be tailored to have specific physicochemical and electrochemical properties. In recent developments, IEMs have been designed and prepared by multiple strategies, such as through polymer modifications or tailoring the architecture of composite materials. However, unique membrane technologies drive further investigation into membranes that can be produced at lower cost and with improved properties such as higher thermal stability and lower methanol crossover. Ion exchange membrans are also desired to be selective of same charged species of different valancy.

To develop suitable IEMs, it is crucial to understand the fundamental relationships between preparation conditions and resulting membrane properties. Membranes intended for bioelectrochemical systems require high conductivity, high ion exchange capacity and must be robust in the caustic aqueous environment in the cathode compartment. Sulfonated PEEK is a viable thermoplastic polymer candidate that is readily available and offers a

cost effective alternative to expensive Nafion® membranes. Blending SPEEK with other polymers, crosslinking either by reaction bonding, thermal bonding or thermal treatment, or integrating new materials into the SPEEK matrix can produce membranes with tailored mechanical, physicochemical and electrochemical properties.

While significant efforts in IEM research have seen an increase in new commercial ventures in this field, as demonstrated by a sharp increase in patents, there are still many areas of research necessary to fully develop the potential of ion exchange membranes. The extensive opportunities for developing novel materials requires detailed study of the preparation, structure and properties of new membranes. In addition to material research, bioelectrochemical system design and operation must also be further developed for IEMs to reach their potential.

In particular, a suitable membrane that preferentially transports monovalent cations over multivalent species is still lacking. To develop appropriate synthesis routes for the production of such a selective membrane, the ion transport phenomena through the material must be understood. Such membranes can be utilized in many practical applications such as in bioelectrochemical systems to enable the specific separation of ionic species

based on valency as well as charge. This research project will identify suitable

synthesis and preparation conditions for developing such membranes.

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CHAPTER 3

THE EFFECTS OF PREPARATION

CONDITIONS ON SPEEK ION

EXCHANGE MEMBRANE PROPERTIES

3.1.   Introduction

This chapter is based on a previously published journal article. Methods of sulfonation of poly(ether ether ketone) are examined and an optimized synthesis procedure established. An effective ion exchange membrane is produced from a cost-effective polymer. In this study, the influences of sulfonation time and temperature on the polymer's degree of sulfonation were systematically explored. A SPEEK membrane with suitable characteristics was designed as a base matrix for future membrane tailoring.

Ion exchange membranes have been extensively developed for use in fuel cells, with most commercially available membranes consisting of expensive perfluorinated materials. Membrane materials with good ion exchange properties are desired for use in wastewater treatment systems such as microbial bioreactors. However, the high cost of currently available membranes limits the industrial development of membrane technologies. Aromatic polymers are alternative materials that can be sulfonated to improve the ion exchange capabilities of new membranes.

Current commercial ventures have predominantly employed Nafion® 117. However, perfluorinated Nafion® membranes are too costly for large-scale use in low profit margin wastewater treatment systems[1]. Aromatic polymers are considered to be one of the most promising routes to obtain high performance polymer electrolytes because of their availability, processability, wide variety of chemical composition and potential stability in fuel cell environments. PEEK is a high performance engineering thermoplastics that has good solvent resistance, high thermo-oxidative stability and excellent mechanical properties. The sulfonated derivatives of PEEK produce random copolymers with sulfonic acid substituted directly to the aromatic backbone[2]. The aromatic backbone helps maintain thermal and mechanical stability, as well as allowing for chemical modification such as through simple electrophilic substitution by sulfonation.

In this paper, a suitable ion exchange membrane is produced from a cost-effective polymer, PEEK. Cation exchange membranes are desired to be cation selective, and stable under operation of high current densities in caustic conditions. To increase the hydrophilicity of PEEK materials, charged groups are introduced using sulfuric acid. This functionalization enables the polymer chains to transport cations. The sulfonate groups ($-SO_3H$) can be introduced into the PEEK polymer chain using several methods. A sulfonating agent can incorporate sulfonated groups onto the polymer chains, either directly or by

polymerizing functionalized monomers. The degree of sulfonation and the correlating ion exchange capacity can be controlled by reaction time and temperature[3].

Previous research on SPEEK membranes has focused on reducing methanol crossover for fuel cell applications[4,5]. However, few works have concentrated on the use of PEEK as a polymer matrix to achieve improved properties by optimization of synthesis conditions. For bioelectrochemical wastewater treatment systems, ion exchange membranes with conductivities in the range of 3 – 5 mS/cm and ion exchange capacities in the range of 1 – 2 mol/kg are desirable[11]. There has been limited publications focusing on the relationship between SPEEK preparation conditions involving synthesis and membrane formation, and the resulting membrane structure and properties.

Pre-sulfonation process offers better control of sulfonation degree by being able to vary the ratio of modified monomers in the final polymer and has been examined for producing SPEEK membranes for fuel cells[6-11]. However, this method of modification is not very reproducible and the complexity of synthesis is impractical for large-scale commercial application. Post-sulfonation is more widely used due to its simplicity and low production costs[7,12-15].

The sulfonation of PEEK is a second order electrophilic subtitution reaction that attaches the charged sulfonic groups onto polymer chains, making them capable of ion transport. The addition of the fixed charged groups depends on the substituents present in the aromatic ring[16,17]. Electron-donating substituents will favor reaction whereas electron-withdrawing groups will not. In PEEK, the hydroquinone unit between the ether bridges can be sulfonated under relatively mild conditions[3]. Substitution takes place preferentially on the aromatic ring between two ether (-O-) links, as demonstrated in Figure 3.1. At higher temperatures, substitution of the other aromatic rings is also possible.
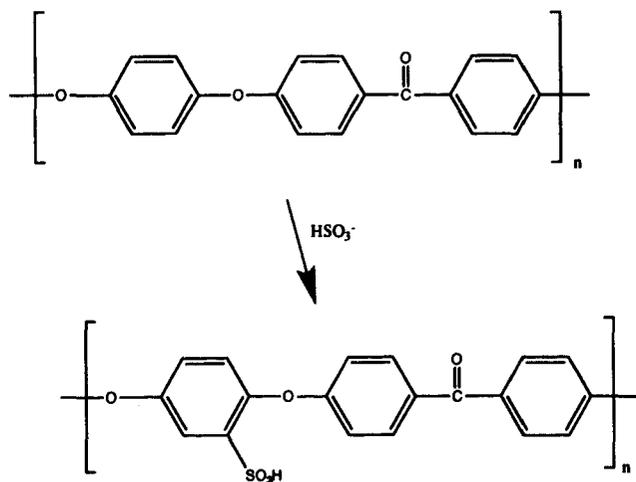

Figure 3.1: Typical sulfonation schematic of poly(ether ether ketone) to sulfonated poly(ether ether ketone)

Several methods for the sulfonation of SPEEK have been previously described[5-7,16,18-20]. Table 3.1 summarizes the properties found for SPEEK materials and comparative membranes.

Table 3.1: Summary of SPEEK and SPEEK based membrane properties compared with Nafion® 117 membrane reference from previous literature

Ref.	Membrane Material	IEC (meq/g)	Water Uptake	Conductivity
21	Nafion ® 115	0.92	30%	0.11 S/cm
21	SPEEK	1.51	89%	
21	SPEEK/sulfonated polyethersulfone (40/60 blend)		36%	0.09 S/cm at 30°C
12	SPEEK (DS 83%)	2.21	114%	
12	SPEEK (DS 61%)	1.74	60%	0.0034 S/cm
22	SPEEK (DS 80%)	2.29		
23	SPEEK (DS 83%)	2.36	45%	
16	SPEEK (DS 100%)	2.56		

It is a challenge to achieve sulfonation conditions that produce consistently sulfonated PEEK. To develop commercially appropriate membranes with reliable DS, SPEEK membranes must be effectively reproducible. The time and temperature of the sulfonation conditions significantly affects the resulting membrane properties. Sulfonation conditions used in previous SPEEK studies have not previously been studied by any systematic approach. This paper tests an extensive array of membranes produced at specific reaction times and temperatures in order to thoroughly establish a consistent combination of variables that will facilitate synthesis of appropriate

membranes for future large-scale development. Membrane casting and preparation conditions also affect the performance of produced SPEEK membranes. The effects of drying on membrane structure has also been investigated on materials such as sulfonated PES[24].

The aim of this chapter is to systematically determine the effects of sulfonation, casting and drying conditions on SPEEK membrane performance. These optimal production conditions will be used for future development of SPEEK membranes with tailored characteristics for cation selectivity. These results will be used as a base to design new polymer membrane materials with high performance characteristics for bioelectrochemical wastewater treatment.

3.2. Synthesis of SPEEK and Membrane Casting

3.2.1 Synthesis of Sulfonated Poly(ether ether ketone)

3.2.1.1 Sulfonation of monomers and post-polymerization

The direct synthesis of polymers from sulfonated monomer units provides the opportunity to tailor polymer compositions with controlled distributions of the ionic functional groups along the polymer backbones. This allows for finer tuning of both microstructure and properties of the ion exchange membrane. It has been indicated in literature that post-functionalisation of the polymer can be difficult to control and can lead to side reactions, degradation and crosslinking via the condensation of sulfuric acid group[10]. Alternatively, copolymerization of pre-sulfonated monomers enables easier control of the degree of sulfonation by controlling the ratio of the sulfonated monomers. This method has potential problems with side reactions associated with post-sulfonation that can reduce thermal and mechanical stability.

Several papers have described this direct sulfonation technique and the subsequent polymerisation to attain SPEEK polymers for fuel cell applications[6,8-10,19,25,26]. SPEEK membranes have been produced via direct sulfonation intended for use in proton exchange membrane fuel cells[19]. This paper focused on reducing the methanol diffuson coefficient, a significant

issue for fuel cell membranes. These membranes show comparable water swelling, proton conductivity and thermal stability to Nafion, but with significantly reduced methanol diffusion coefficients. Several studies have investigated the influence of ratios of sulfonated and non-sulfonated monomers on the membrane's affinity towards water over methanol at high temperatures[4,9].

Monomers with benzene rings are particularly useful for sulfonation due to their stability. As such, materials such as bis(4-chlorophenyl) (BCPS) and 4,4'-difluorobenzophenone (DFBP) have been studied, with their structures shown in Figure 3.2 and Figure 3.3, respectively. The monomer Bisphenol A shown in Figure 3.4 is also used in the polymerization process.
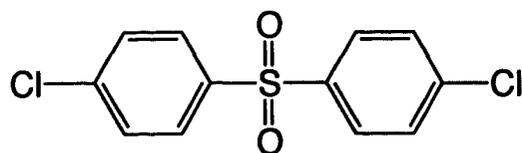

Figure 3.2: Bischlorophenyl Sulfone (BCPS)
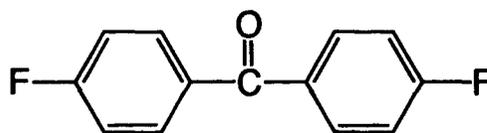
Figure 3.3: Difluorobenzophenone (DFBP)
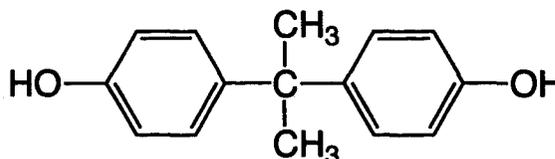
Figure 3.4: Bisphenol A

Sulfonation is a versatile method for modifications and is a common method for functionalizing monomers[27]. An optimized method for the sulfonation of BCPS was derived from descriptions by Harrison *et al* (2003), Li *et al* (2005), Kim *et al* (2004) and Gohil *et al* (2006)[6,10,28,29]. A typical procedure was performed as follows. 3g of BCPS was dissolved in 6mL of concentrated sulfuric acid. The solution was heated and stirred for 6 hours at 100°C. This was then cooled and poured into 40mL ice water. 18g sodium chloride was added to the resulting suspension, producing a white precipitate. This was filtered under vacuum and the thin needle-like crystals redissolved in 40mL deionised water. The pH was reduced to 6 – 7 by addition of 2N sodium hydroxide. 18g of excess sodium chloride was then added to salt out the sodium form of the disulfonated monomer. The white precipitated crystals

were filtered and recrystallised from a heated mix of methanol and water at a

7/3 volume to volume ratio. The solution was left to cool slowly overnight

and filtered to give fine white flake-shaped crystals consistent with that

described in literature. This product structure, as shown in Figure 3.5, was

then dried in a vacuum oven at 80°C for 2 days.
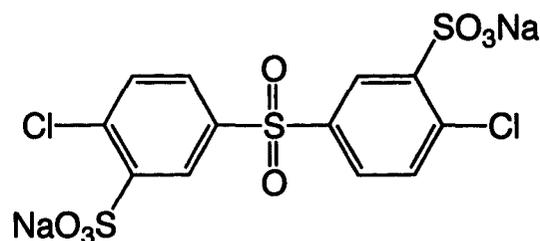
Figure 3.5: Disodium Salt of S-BCPS

The sulfonation of DFBP was similar to that described for the synthesis of S-

BCPS. The product was recrystallised from isopropanol and deionised water

at a 5/1 volume to volume ratio. The structure of S-DFBP is shown in Figure

3.6 with the reaction scheme for its sulfonation shown in Figure 3.7.
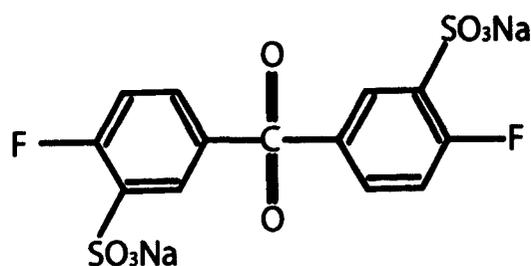
Figure 3.6: Disodium salt of S-DFBP
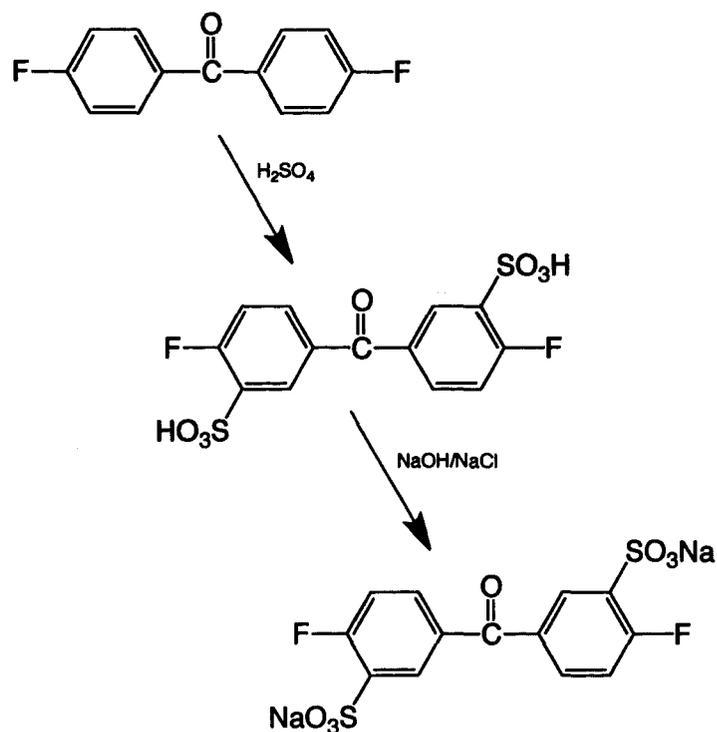
Figure 3.7: Reaction Scheme for DFBP Sulfonation

The monomers of S-DFBP and DFBP were then polymerised to produce sulfonated poly(ether ether ketone). Polymerisation also consumed bisphenol A (BPA) and phenolphthalein. SPEEK/PEEK copolymers were produced using varying ratios of DFBP, S-DFBP, BPA and potassium carbonate as a catalyst. DFBP/S-DFBP ratios of 0/100, 20/80 and 40/60 were used. The polymerisation procedure was attempted as follows with the schematic depicted in Figure 3.8.

1. Appropriate quantities of DFBP and S-DFBP were added to a 3-necked round bottom flask at the desired molar ratio. The 3-necked round bottom flask was attached to a Dean-Stark trap and condenser

2. 10mmol of bisphenol was added, with 15 mol% excess of potassium carbonate used as a catalyst

3. DMSO (dimethyl sulfoxide) was used as a solvent in a 2:1 ratio with toluene to azeotrope the water by-product

4. A Dean-Stark apparatus was used to reflux the solution under nitrogen at 140°C for 4 hours

5. The temperature was raised to 175°C for 16 - 24 hours and then left to cool to room temperature

6. The viscous product was diluted with NMP (N-methyl-2-pyrrolidone) and precipitated in excess water while vigorously stirred

7. The precipitate was filtered and dried in a vacuum oven overnight

Figure 3.8: Synthesis route of SPEEK polymerisation

Initial experiments looked at the independent sulfonation of difluorobenzophenone (DFBP) and bischlorophenyl sulfone (BCPS) monomers, and subsequent post-polymerization to form SPEEK. Unfortunately, polymerization was difficult to control and the SPEEK produced through post-polymerization methods was inconsistent. The product could not be used to cast appropriate membranes and this approach was discarded in favour of direct post-sulfonation of PEEK. Direct sulfonation of PEEK was found to produce more consistent SPEEK membranes. Direct sulfonation of the readily available PEEK polymer is more feasible for developing large-scale membranes for commercial use.

3.2.1.2 Direct post-sulfonation

The direct polymerization from monomer units offers some advantages on the precise control of the sulfonate groups on the aromatic rings of the polymer backbones, and the feasibility to tune the molecular weight of the polymer, thus leading to the polymer with better stability and processibility. While the direct synthesis of SPEEK from sulfonated monomers has been shown to be advantageous from a materials perspective[19], the simplicity, reliability and lower cost of post-sulfonation is preferable for ease of large-scale membrane commercialisation. Despite the limitations of cross-linking and potential structural degradation, the post-sulfonation procedure

described in various papers provides for a noticeably simpler and hence, more cost effective, method for SPEEK synthesis[4,12,14,17,18,23,29-33]. Hence, the post-sulfonation of PEEK is considered as a vastly favourable method in terms of ease of manufacture and subsequently to maintain low production costs.

In post-sulfonation, the PEEK polymer chains are directly sulfonated with concentrated sulfuric acid (>95%) used as the sulfonating agent. This produces simple reactions and is known to produce polymers free from degradation or cross-linking reactions that can occur when using 100% H_2SO_4 or cholorosulfonic acid.

5 g of PEEK was gradually added to 50 mL sulfuric acid (95-98 wt%) in a three-necked round-bottomed flask. The flask was fitted with a mechanical stirrer and a condenser. The reaction mixture was heated in a water bath to the desired sulfonation temperature for the desired time while being vigorously stirred. The dissolved PEEK was a dark red, highly viscous solution. The PEEK was sulfonated at 40 °C, 50 °C, 60 °C and 70 °C for reaction times of 2, 3, 4, 5 and 6 hours.

The sulfonation reaction was terminated by precipitating the polymer in cold water. The precipitated SPEEK formed white noodle-like strands. These were

soaked in water overnight and washed until the pH was neutral. The SPEEK

polymer was dried at room temperature overnight and then in a vacuum

oven at 60 °C for 24 hours or longer as required to a consistent weight.

3.2.2   Casting SPEEK Membranes

Membranes were prepared using the solvent evaporation technique. In a

typical procedure, 3 g of SPEEK polymer was dissolved in DMAc (dimethyl

acetamide) and cast on a glass substrate. A doctor blade was used to control

the nominal membrane thickness. Cast membranes were dried in a

temperature and humidity controlled oven and then placed in a vacuum oven

for 24 hours to ensure all residual solvent was removed. The membranes were

immersed in water and peeled from the glass, then stored in deionized water

before use.

Homogenous films were prepared with varying DMAc concentration, casting

thickness, drying temperature and drying humidity. Membranes were cast

with nominal (wet) thicknesses ranging from 200-400 μm, DMAc

concentrations of 10-30% and dried at temperatures of 40-80 °C. Drying

humidity was originally varied from 50-90%, however, it was quickly

determined that 60% was optimal for producing defect-free membranes, and

was used for all subsequent experiments.

To determine the integrity of the membranes in different environments, 1 g samples of the dried membranes were placed in 100 mL of the following solvents and stirred for 4 hours.

- Room temperature water

- Hot water (~50 °C)

- Methanol

- Aprotic solvents (DMAc, DMSO, NMP)

- Concentrated sulfuric acid (>95%)

3.2.3   Characterization of SPEEK Membranes

3.2.3.1 Ion Exchange Capacity

One of the most crucial parameters of ion exchange membranes is the ion exchange capacity. The ion transport properties of a membrane is primarily dependant on a combination of the interrelated effects of the ion exchange capacity, cross-linking and water sorption[34]. Ion exchange capacity (IEC) is the number of fixed $-SO_3$ charges inside the ion exchange membrane as measured per unit weight of the dry polymer. Measured in milli-moles per gram, IEC is more commonly expressed in milli-equivalents per gram of dry membrane. These terms are typically equivalent where the ion exchange membrane has monovalent fixed charges. The IEC of a membrane material

depends on the molecular weight of the polymer as well as on the sulfonation

degree for membranes with fixed $-SO_3^-$ groups[29]. This provides information of

the density of ionisable functional groups present in the membrane matrix.

To determine the ion exchange capacity, a back-titration technique can be

used where the membranes in acid form (SPEEK-H+) are first converted to

sodium form by first immersing the membranes in 0.01M NaOH aqueous

solution for 3 days to form SPEEK-Na. 1M NaCl aqueous solution is used to

back titrate the exchanged H+ ions in the NaOH(aq) solution using

phenolphthalein as an indicator. The IEC can then be determined as following.

This model assumes that the ions are homogenously distributed over the

entire polymer matrix to give an average IEC value.

Equation 3.1:

$$IEC = \frac{\text{Volume of NaOH consumed} \times \text{NaOH molarity}}{m_{dry}}$$

The IEC can then be used to calculate the degree of sulfonation as shown

below. The degree of sulfonation gives the number of $-SO_3H$ groups per

repeating polymer unit. The extent of sulfonation can also be confirmed by

^{1}H-NMR[17].

Equation 3.2:

$$DS = \frac{IEC \times MW_{PEEK}}{1 - (IEC \times MW_{SO_3H})} \times 100\%$$

It is expected that with higher degree of sulfonation, ion exchange capacity is also increased, with a corresponding increase in water swelling[19]. Excessively high degrees of sulfonation allow for high levels of ion exchange capacity but may cause the material to degrade in aqueous environments. Samples of Nafion® from Du Pont have been found to provide nominal ion exchange capacity of 0.8 – 0.9 meq/g[8].

3.2.3.2 Water Uptake and Thickness

Samples of SPEEK membranes of approximately 1cm x 5cm were cut from the center of the cast polymer sheet. These were soaked overnight and wiped before being weighed and measured to determine their wet weight, wet length, and wet thickness. The wet thickness of each sample was taken from the center of the strip using a digital micrometer. At least 3 samples of each membrane were tested. These samples were then dried in a vacuum oven overnight, and the dry weight and dry length determined. The water uptake and swelling ratios were determined by the following equations.

Equation 3.3:

$$\text{Water Uptake} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100\%$$

Equation 3.4:

$$\text{Swelling} = \frac{\text{wet length} - \text{dry length}}{\text{dry length}} \times 100\%$$

3.2.3.3 ¹H-NMR

The NMR spectra of SPEEK samples sulfonated at 50 °C-2hr, 50 °C-6hr, 60 °C-2hr and 60 °C-6hr were collected using a Bruker 400 Advance II NMR spectrometer. SPEEK samples were dissolved in DMSO-d6 at concentrations of 2 – 5%w/w. The chemical shift of tetramethylsilane (TMS) was used as the internal standard reference.

Non-sulfonated PEEK is insoluble in any solvent except for strong acids, hence no 1H-NMR spectra could be recorded for pure PEEK.

3.2.3.4 SEM

Samples were coated in carbon to examine the membrane cross-sections. Images of the SPEEK membrane cross sections were taken using a Hitachi S-4800 High Resolution Scanning Electron Microscope (SEM).

3.3.   Results and Discussion

3.3.1   Material Characterizations of SPEEK Membranes

3.3.1.1 SEM

The physical morphology of SPEEK membrane cross-sections is illustrated below in Figure 3.9. These membranes were homogenous, dense and had no visible bubbles or void spaces after casting. The bulk of the membrane is highly uniform, indicating a defect-free polymer matrix structure. The different sulfonation levels made little change to the homogenous structure or cross-section morphology. The polymer with increased sulfonation time did dissolve more readily into the casting solvent resulting in a less viscous solution, which would explain the thinner membrane as this casting solution spread out further while drying.
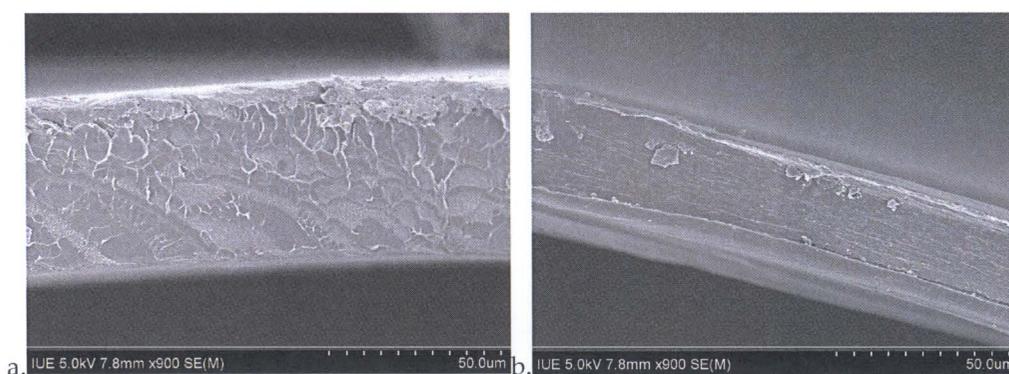
Figure 3.9: Cross-sections of SPEEK membranes sulfonated at (a) 60°C, 2hr and (b) 60°C, 15hr

3.3.1.2 FTIR

SPEEK sample membrane was dried at 100°C for 30 minutes to remove any residual moisture or solvents. The FTIR spectrum was taken over the range 600-1800 cm^{-1}. The spectrum in Figure 3.10 shows the characteristic symmetric and asymmetric stretching vibrations of the O=S=O group present in sulphonic acid. Characteristic peaks at 1016 and 1075 cm^{-1} can be assigned to the symmetric and asymmetric O=S=O stretching vibrations of sodium sulfonate groups[3]. Two bands at 1016.6 and 1219.7 cm^{-1} were shifted by sulfonic acid vibrations to lower frequencies indicating weak hydrogen-bonding interactions[35].
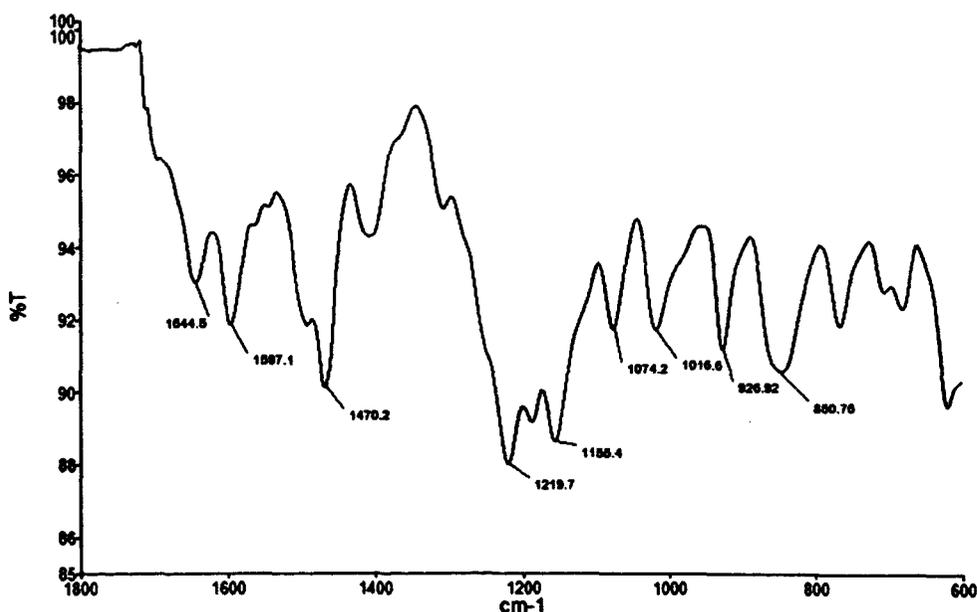
Figure 3.10: FT-IR spectra of SPEEK membrane

3.3.1.3 ¹H-NMR Structural Analysis

The structure of the sulfonated SPEEK was determined by ¹H-NMR analysis. The spectra and nomenclature of the aromatic protons for the SPEEK repeat unit is shown in Figure 3.11.

The presence of the sulfuric acid group causes a down-field shift of the hydrogen, H_E, to 7.50 ppm. The doublets at 7.15 and 7.25 can be assigned to H_C and H_D on the hydroquinone ring. When more sulfonic groups attached to the aromatic ring in the PEEK repeat unit, the intensity of the signal was enhanced as expected. In particular, the peak at 7.27 grows noticeably smaller as the degree of sulfonation increases.
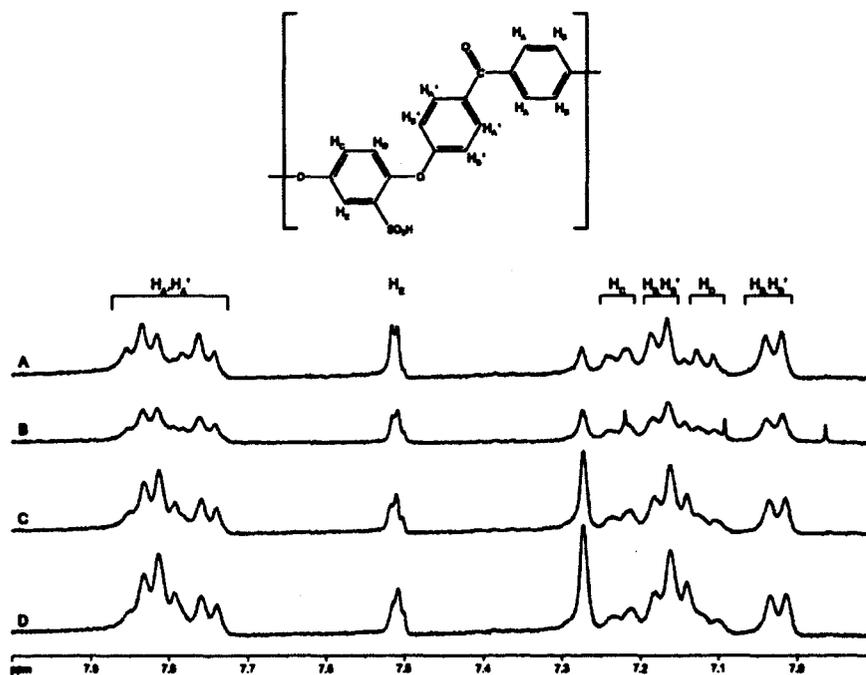
Figure 3.11: ^{1}H-NMR analysis of SPEEK membranes produced at various sulfonation

temperatures and reaction times; A) 60 °C-6hr, B) 50 °C-6hr, C) 60 °C-2hr, D) 50 °C-2hr

The intensity of the H_E signal provides an estimate of the SO_3H group content.

The ratio of the peak area of the distinct H_E (AH_E) and the integrated peak

area of the signals corresponding to all the other aromatic hydrogens

($AH_{A,A',B,B',C,D}$) can be expressed as:

Equation 3.3:

$$\frac{n}{12 - 2n} = \frac{AH_E}{\Sigma AH_{A,A',B,B',C,D}}$$

Where AH_E is the peak area of the H_E signal, and $\Sigma AH_{A,A',B,B',C,D}$ is the sum of

the peak area of the signals corresponding to all the other aromatic

hydrogens. The degree of sulfonation (DS) can be obtained from DS = n ×

100%.

3.3.1.4 Degree of Sulfonation

The DS is defined as the percentage of repeat PEEK units that have been

sulfonated. A higher degree of sulfonation indicates that more repeat units

contain sulfonate groups. The DS can be determined using either the IEC

found by the titration method or by ^{1}H-NMR spectroscopy.

Using the back-titration method to find the IEC, the degree of sulfonation can

be calculated by determining the amount of H$^+$ cations that are released from

the membrane. By measuring the amount of sulfuric acid consumed in the

titration, the molar quantity of-SO$_3$H present in the SPEEK can be

determined, where 288.30 is the molecular weight of the PEEK repeat unit

and 81.07 is the molecular weight of the -SO$_3$H group. The DS can then be

found using the following relation.

Equation 3.4:

$$DS = \frac{M_{w,p}\text{IEC}}{1 - M_{w,f}\text{IEC}}$$

Where $M_{W,p}$ is the molecular weight of the non-functional polymer repeat unit

and $M_{W,p}$ is the molecular weight of the functional group including the

counter ion (-SO₃Na).

The degrees of sulfonation found using titration and NMR are shown in Table

3.2. The results from both methods are consistent. As expected, the higher

sulfonation temperature and longer sulfonation time results in SPEEK

membranes with higher sulfonation degrees. These values are within a

reasonable range for use as ion exchange membranes in the proposed BESs.

Table 3.2: Degree of sulfonation as determined by ¹H-NMR and IEC back-titration

Sulfonation temperature (°C)	Sulfonation time (h)	Degree of sulfonation - ¹H NMR	Degree of sulfonation - IEC
60	6	0.85	0.87
60	2	0.70	0.71
50	6	0.73	0.65
50	2	0.64	0.67

3.3.1.5 Solubility and Swelling

The main purpose of sulfonating PEEK is to increase the hydrophilicity of the

membrane[3]. The charged groups cause the polymer chains to fold, as

illustrated in Figure 3.12, creating hydrophobic regions on the hydrocarbon

backbone and hydrophilic regions at the charged sites that allow for the

absorption of polar water molecules. The presence of water is known to

facilitate proton transfer and enhance the conductivity of these solid electrolytes. The presence of water molecules in the channels of the microscopic polymer structure improves the ionic conductivity of the resulting membranes due to the increased number of protonic charged sites on the $-SO_3H$ group, which provide a water-mediated pathway for ion transport[36]. However, excessive water uptake can result in undesirable effects such as excessive membrane swelling and structural instability in aqueous environments.
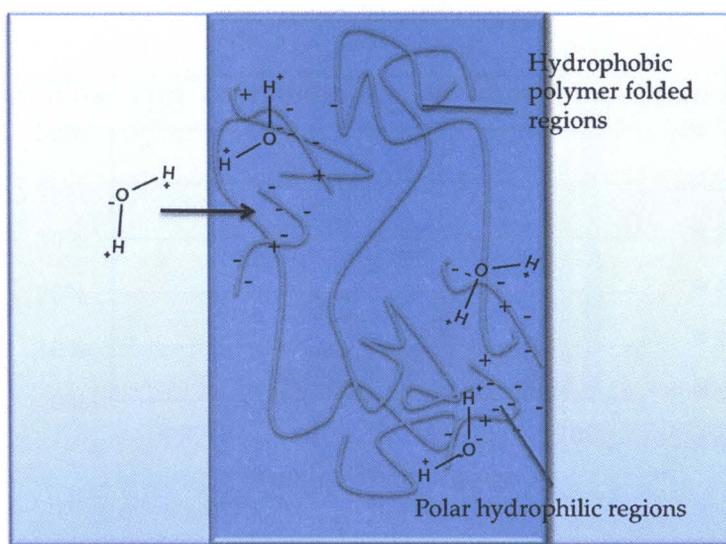

Figure 3.12: Schematic of ion exchange membrane with polymer network containing hydrophobic and hydrophilic regions.

Water uptake indicates the water content that the film is able to hold within the polymer structure. Figure 3.13 and 3.14 compare the water uptake and

swelling of membranes sulfonated at different temperatures over different times. Both water uptake and swelling were found to increase with increased sulfonation temperatures. Comparing the series prepared at 50°C and 70°C, it can be seen that longer sulfonation times also increased the water uptake and swelling of the produced SPEEK. Both water uptake and swelling showed an increase with time and temperature. This indicates that at higher temperatures and longer sulfonation times, SPEEK was able to absorb more water, which is consistent with previous studies. Sulfonation at 70°C for 5 hours showed a dramatic increase in sulfonation of the polymer chain. These conditions are considered as a limit for stable membrane manufacture as the secondary aromatic sites may be sulfonated to give sulfonation degrees higher than 100%.
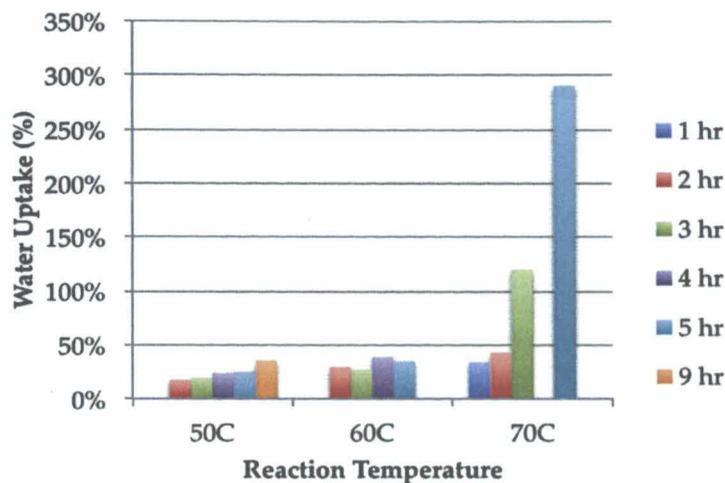
Figure 3.13: Water Uptake for SPEEK sulfonated at 50°C, 60°C and 70°C under various
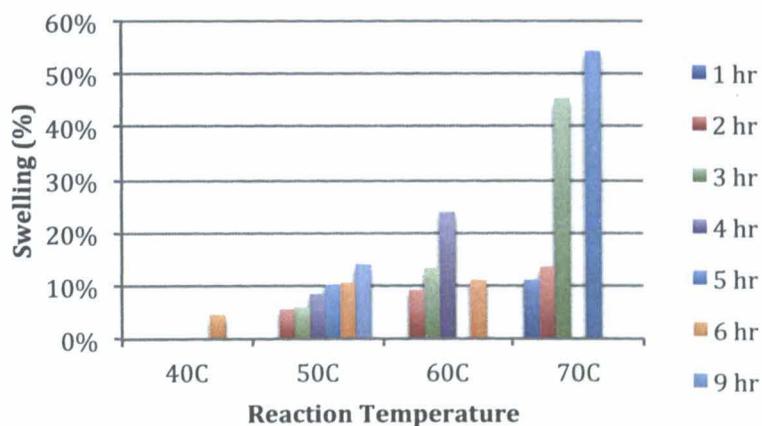
reaction times

Figure 3.14: Swelling for SPEEK membranes sulfonated at 40°C, 50°C, 60°C and 70°C under

various reaction times

The effect of sulfonation time on water uptake and swelling is directly

compared in Figure 3.15 and 3.16 for SPEEK produced at 50 and 60°C. From 2

to 6 hours, there is a reasonably steady increase in water uptake and swelling

for SPEEK sulfonated at 50°C. However, at 60°C there were no notable trends in relation to the sulfonation time.

SPEEK membranes with water uptake of 20 – 35% were found to be most flexible and robust when handled. At higher levels, the polymer began to lose integrity in the aqueous environments. All SPEEK membranes were found to be soluble in aprotic solvents such as DMAc, NMP and DMSO. At sulfonation degrees lower than 60%, SPEEK was only soluble in strong acids such as sulfuric acid. Above 80% DS, the SPEEK polymer was soluble in methanol and at 100% sulfonation, the membranes were soluble in hot water (~50°C). 60-80% was found to successfully enhance hydrophilicity while still maintaining the membrane structure in an environment. This is consistent with previous literature that identifies a DS over 80% as structurally unstable[37]. The range of DS from 60-80% resulted in water uptake between 20-40%, which is suitable to allow for reasonable levels of IEC while remaining intact when handled.
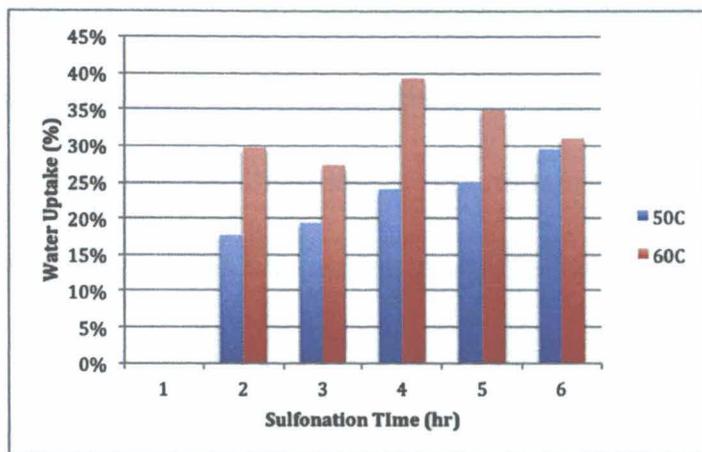
Figure 3.15: Water Uptake for SPEEK membranes sulfonated under various reaction times
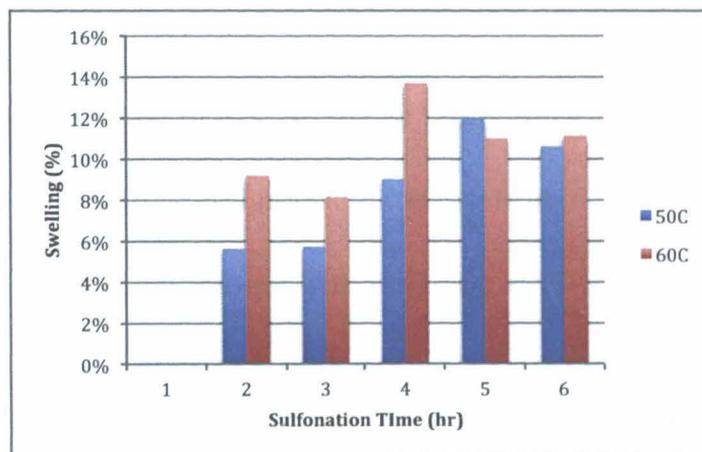

Figure 3.16: Swelling for SPEEK membranes sulfonated under various reaction times

3.3.2   Influences of Time and Temperature on the Degree of Sulfonation

Higher temperatures of sulfonation were found to correspond to an increase in the degree of sulfonation. The increased temperature would allow for faster kinetics of the sulfonation reaction. This also corresponds to the

increased water uptake and swelling of SPEEK produced at higher temperatures. This is consistent with literature as the added sulfonate groups provide for the formation of water-mediated pathways[4,18,29,32,38-40]. The influence of sulfonation temperature on the DS is shown in Figure 3.17. Sulfonation temperatures below 40 °C were too low to effectively sulfonate the PEEK polymer within a reasonable time frame. The SPEEK produced at sulfonation temperatures less than 40 °C were insoluble in DMAc or other organic solvents at room temperature.

No observable trends were found in Figure 3.18 to relate sulfonation time to the resulting DS. This indicates that a reaction time within 2 – 6 hours did not directly affect the DS. Previous literature reports sulfonation with reaction times of 24 to 112 hours required to produce membranes with reasonable IEC values of more than 1.2 meq/g[3,16-18]. This suggests that the degree of sulfonation can be more directly controlled by sulfonation temperature.

At temperatures higher than 70 °C, SPEEK was considered as over-sulfonated even after short reaction periods of 1 hour. Over-sulfonation leads to membrane deterioration in water. This is consistent with previous literature that describes membranes with a DS of 0.8 to be at a critical point where excess water can enter the hydrophilic polymer[37]. SPEEK sulfonated above

70°C had a DS of 0.8 and dissolved rapidly in weak solvents including hot water, making them impractical for membrane casting.
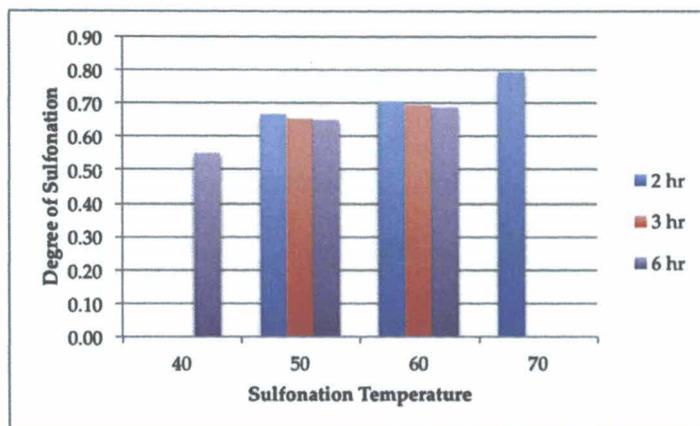
Figure 3.17: The influence of sulfonation temperature on the degree of sulfonation of SPEEK
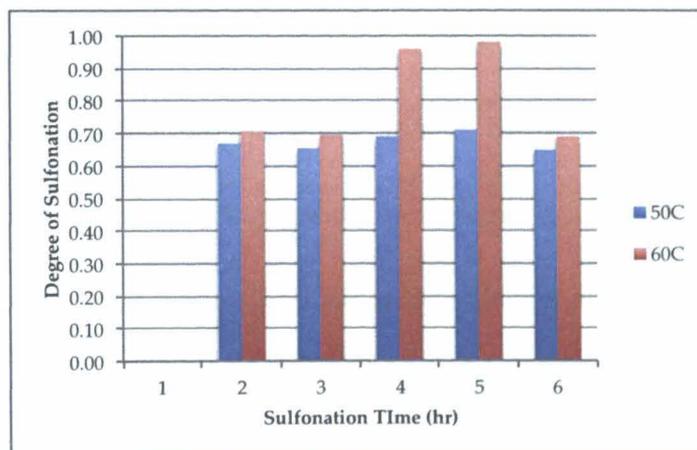
membranes

Figure 3.18: The influence of sulfonation time on the degree of sulfonation of SPEEK

membranes

A sulfonation degree in the range of 60 – 80% successfully enhanced the hydrophilicity of the SPEEK while still maintaining a robust membrane

structure that was stable when handled manually, even when wet. This range

of DS corresponded to membranes having water uptake between 20 – 40%. At

sulfonation degrees lower than 60%, SPEEK was only soluble in strong acids

such as sulfuric acid. Above 80% DS, the SPEEK polymer was soluble in

methanol and at 100% sulfonation, the membranes were soluble in hot water

(~50°C). For SPEEK membranes intended for use in bioelectrochemical

systems, an ion exchange capacity in the range of 1 – 2.5 meq/g is desired[41].

Figure 3.19 shows the corresponding IEC values to the degrees of sulfonation

in Figure 3.18. SPEEK sulfonated at temperatures of 50 – 60°C achieved

reasonable IEC values between 1.86 – 2.45 meq/g.
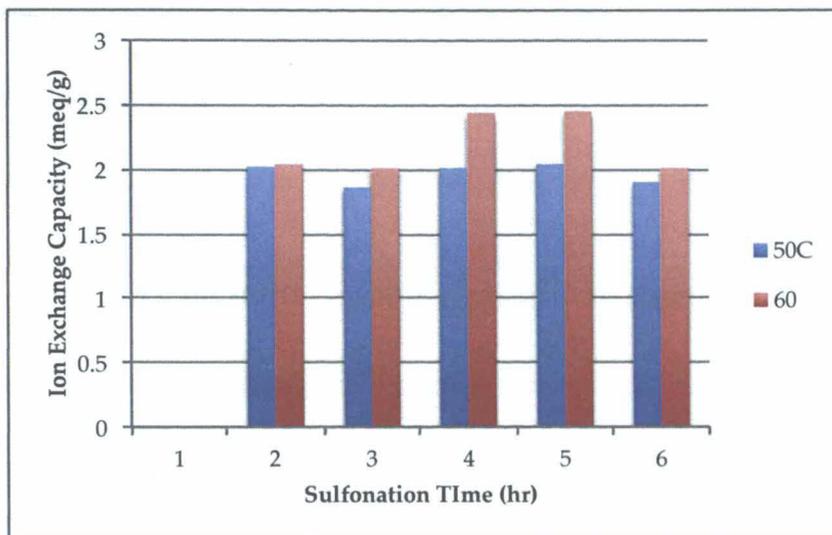
Figure 3.19: Ion exchange capacity for SPEEK membranes sulfonated at 50°C and 60°C

3.3.3   Influences of Drying Conditions

Membranes cast at thicknesses of 250 – 300μm were found to be suitably robust to withstand manual handling. It was difficult to maintain uniform thickness across the sheet for thicker membranes as the solution pooled in some areas during the drying process inside the oven. The thickness of the resulting membranes would be dependent on the DMAc solvent evaporating at different rates and potentially influencing the structure of the membrane.

The drying temperature and humidity had no notable influences on membrane swelling or ion transport properties. With higher humidity, longer times were required to remove all DMAc. It was qualitatively noted that

drying temperatures of 50 – 60 °C produced homogenous and supple membranes without requiring long drying times of more than 24 hours.

3.3.4   Influence of Casting Concentration on Thickness

The casting concentrations and resulting wet thickness of several comparable membranes are summarized in Table 3.3. The membranes were cast using a doctor blade to govern the thickness. As they were then dried at ambient pressures, the solution spread with time across the glass substrate. As such, the resulting dried membrane was significantly thinner than the cast thickness. The resulting membrane thickness was predominantly influenced by the concentration of the casting solution. As expected, higher weight percentages of SPEEK polymer in DMAc resulted in generally thicker membranes. Membranes with a resulting wet thickness in the range of 30-50 μm were found to be most resistant to tearing or breakages while still maintaining flexibility when manually handled. Thinner membranes became brittle when dried and tore easily. Thicker membranes were difficult to produce with a homogenous thickness across the cast sheet. Using this method, 15-25% casting concentrations SPEEK in DMAc were established as most suitable for producing even and robust membranes suitable for future development.

The thickness and casting solution concentration had no discernable influence on the ion transport or water uptake properties of the membranes. These properties are expected to have an impact on the selectivity of the membranes due to changes in the microscopic pore structure[17].

Table 3.3: Summary of SPEEK membranes cast in DMAc

Temp.	Time	Casting Conc.	Wet Thickness	Wet Thickness σ^2
°C	hr	%	mm	mm
40	6	10	0.025	0.007
60	6	10	0.025	0.004
60	6	15	0.034	0.004
60	6	20	0.046	0.015
60	6	25	0.037	0.004
60	6	30	0.110	0.013

3.4. Conclusions

A potentially low cost cation exchange membrane has been developed using poly(ether ether ketone) (PEEK). This material is presented as an alternative to current commercial membranes such as Nafion® 117. To increase the hydrophilicity and ion transport of the PEEK material, charged groups were introduced through sulfonation. A series of membranes synthesized under various reaction and casting conditions has been used to systematically assess the effect of sulfonation and casting conditions on membrane performance. Membrane materials were characterized by ion exchange capacity, water uptake, swelling, potential difference and NMR analysis. Optimal reaction and casting conditions were established for producing SPEEK ion exchange membranes with desirable performance characteristics. This extensive membranes series established that the most appropriate sulfonation conditions were 60 °C for 6 hours to produce membranes with 87% degree of sulfonation. For ease of handling, SPEEK membranes cast from solvent casting concentrations of 15 - 25% with a resulting thickness of 30–50 μm were also found to be most suitable.

Increased sulfonation time and temperature were noted to both increase the sulfonation degree. The DS was consistently determined using both the

titration method and the ^{1}H-NMR method, representing accurate quantification of this variable. The most appropriate sulfonation conditions were noted as being 60 °C and 6 hours to produce high ion exchange capacity membranes of 2.21 meq/g with an appropriate water uptake of 35.9%w/w.

The membrane thickness was predominantly influenced by the concentration of the casting solution. Higher weight percentages of SPEEK in DMAc resulted in thicker membranes. Membranes in the thickness range of 30 – 50 μm was found to be supple and resistant to tearing when handled. 15 – 25% concentrations should be used to produce these membranes. While the drying conditions did not have an apparent impact on the measured parameters in this study, further investigation will look at the influence of these conditions on controlling porosity and selectivity.

To obtain the most desirable membrane properties of high ion exchange capacity and cation conductivity, while still maintaining the integrity of the membrane in aqueous environments, the sulfonation and preparation conditions for SPEEK membranes has been optimized with large-scale production in mind. The findings from this study will lead to a better understanding of the effect of the polymer preparation conditions on SPEEK membrane performance. Future work will involve modifying these SPEEK membranes for improved selective ion transport performance.

3.5. References

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CHAPTER 4

PHYSICOCHEMICAL CHARACTERIZATION OF SPEEK NANOCOMPOSITE MEMBRANES

4.1. Introduction

Sulfonated polymer membranes are cost effective alternatives for use as ion exchange membranes. With increased sulfonation, SPEEK membranes have promising ion transport properties. However, the conductivity of these membranes is limited by excessive swelling and structural instability at high sulfonation degree. The integrity of the SPEEK polymer network must be improved to develop robust membranes for use in commercial wastewater treatment applications.

Modifying the polymer matrix of an ion exchange membrane by introducing additional fillers is a promising approach for improving membrane structure and can also be used to promote selective ion transport[1-5]. Inorganic-organic composite materials allow membranes to be tailored with specific and unique properties[6]. In these materials, the organic component offers the benefits of convenient processing and structural flexibility. The inorganic compounds provide the potential for improved thermal and mechanical stability as well as increased conductivity. In addition, new phenomena may also arise as a result of nanoscale interactions between the organic and inorganic components.

Novel ion exchange membranes can be developed by dispersing ionomers or inorganic solids into a conducting polymer matrix[7]. Composite ion exchange membranes can be prepared by several routes including sol-gel processing, blending, in-situ polymerization, and molecular self-assembly[8]. To achieve stable suspensions of nanoparticles in the casting solutions, the zeta potential is commonly used to assess the stability of the colloidal system[9]. Combining the effects of van der Waals attraction and electrostatic repulsion, DVLO theory gives an indication as to the stability of a particle in solution dependent on the total potential energy function;

Equation 4.1:

$$V_T = V_A + V_R + V_S$$

Where V_S is the potential energy caused by the solvent, which is insignificant compared to the contributions from attractive (V_A) and repulsive (V_R) potential forces.

This expression denotes an energy barrier resulting from the repulsive forces preventing the particles from adhering together. However, if the particles collide with sufficient energy to overcome this barrier, the attractive forces will pull them into contact where they may irreversibly flocculate.

For a colloidal system to be stable, the repulsive forces of the nanoparticles must be dominant to resist flocculation. There are two mechanisms that affect dispersion stability[9]. Polymers added to the system can adsorb onto the particle surfaces, creating steric repulsion between each other and allowing for sufficient separation in polymer layers. Altering the concentration of ions in the system can also influence the electrostatic charges within the membrane. Dissociation of acidic groups on the surface of a particle will give rise to a negatively charged surface while a basic surface will take on a positive surface charge. The magnitude of the surface charge depends on the strength of the acid or base surface groups and the pH of the solution. The pH of a suspension, such as the casting solutions for SPEEK nanocomposite membranes, can be adjusted to achieve suitable dispersion.

In this chapter, nanocomposite membranes will be developed using SPEEK as a polymer matrix base. SPEEK is a useful polymer backbone with optimized synthesis and casting conditions established in Chapter 3. This polymer provides a chemically, mechanically and thermally stable matrix suitable for developing ion exchange membranes[10]. Silica (SiO_2) and titania (TiO_2) are inexpensive and readily available mesoporous nanoparticles that have been extensively studied and used in a wide range of applications[11]. These can be functionalized and incorporated into the SPEEK matrix to create unique nanocomposite membranes. The physicochemical properties of the resulting

SPEEK composite membranes will be characterized. SPEEK is also a high performing thermoplastic that is about a third of the cost of Nafion® 117, making it highly viable as an alternative membrane in commercial separation applications[12]. As well as having the potential to reduce the cost of fuel cells and other membrane systems, composite polymer membranes can achieve improved mechanical and electrochemical properties that can be tailored for specific applications[13].

Inorganic oxides, such as silica and titania, are abundant, chemically stable, and environmental friendly with fairly benign routes for synthesis[14,15]. These inorganic poriferous materials have large surface areas that can be further modified with a variety of functional groups[8]. Functionalizing nanoparticle surfaces can affect the electrostatic interaction between the nanoparticles themselves and the polymer matrix network[16].

Composite membranes can be tailored to have unique properties influenced by the choice of functionalization group, size and shape of the particles, and their surface properties (acidic or basic). The structure and performance of composite membranes depends on the type of nanoparticles that are used, modifications to the nanoparticle, size and shape, loading concentrations and the level of interaction with the polymer matrix base. A large variety of fillers can be incorporated into polymer membranes, such as silica, titania, or

zirconia[13,15,17-30]. This study will systematically determine the influences of different functional groups on silica and titania nanoparticles embedded in SPEEK membranes. Various loadings will also be examined. This novel investigation will directly compare composite membrane properties and quantitatively identify promising candidates for possible commercialization.

Nanoparticles integrated into the organic polymer matrix will influence the microstructure and charge distribution of the membrane[1]. Membranes mixed with various fillers have been proposed to improve water retention and, subsequently, improve the membrane's electrochemical properties[3,11]. This study shall comparatively investigate the morphological effects of various nanoparticle loadings and surface functionalization. Nanocomposite membranes have seen a reduction in methanol permeability, which is beneficial for fuel cell systems[13,24,31,32]. Composite membranes also show promise in selective separation of cations by valency[33], though further work is needed to identify suitable membranes and to understand the mechanisms of ion transport. This study aims to develop nanocomposite membranes with good physicochemical properties. The influences of the nanoparticles on SPEEK membrane performance will be examined.

4.2.   Functionalization of Nanoparticles

A major challenge in designing new composite materials is to limit the aggregation of fillers and phase separation of the membrane microstructure as the casting solvent is evaporated[34]. To ensure even dispersion of nanoparticles throughout the membrane matrix, nanoparticles can be modified to enhance the covalent bonding, hydrogen bonding and electrostatic interactions between the fillers and the polymer network[35]. This improves the compatibility between the nanoparticles and the polymer network, which ensures proper dispersion throughout the membrane[36].

There are several approaches to modifying inorganic nanoparticle surfaces. Polymer molecules can be grafted by covalent bonding to hydroxyl groups on the nanoparticles[37,38]. Surface adsorption or reactions with small functional groups, such as silane coupling agents, have ready pathways for controlled particle modification[1]. Through the systematic study of silica and titania nanoparticles modified with various functional groups, this chapter will investigate the influence of different modifiers and their loadings on the properties of SPEEK nanocomposite membranes.

There are multiple options for nanoparticle modifications and their inclusion in polymer matrix membranes has been studied for several inorganic-organic

nanocomposite combinations. Inorganic oxides are of particular interest for their compatibility in polymer networks. Zirconia (ZrO_2) has been incorporated into a poly(ethylene oxide)-lithium tetrafluoroborate matrix for with enhanced electrochemical transport properties useful for lithium polymer electrolyte battery technologies[18]. Zeolites and epoxy resins have also been fixed to polymer backbones to promote ionic cross-linking in the membrane[39]. Polymer composites with TiO_2 nanoparticles have also been successfully integrated in different polymer matrixes such as polycarbonate, polyamide, epoxy, unsaturated polyester, polyacrylate, poly(methyl methacrylate), polyimide, and polystyrene[35].

Monodispersed spherical silica and titania particles have been readily modified with organic groups such as vinyl, thiol and amine functional groups[25,37,40,41]. Previous individual studies have looked at properties of singularly functionalized polymer membranes. However, electrochemical studies are difficult to replicate and varied measurement techniques have been used to characterize different composite membranes. In this work, a direct comparison of several functional groups shall be investigated. This unique systematic study will enable consistent evaluation of membrane properties as dependent on their specific structural influences. This study will focus on chemical modifications of the nanoparticle surface with silane coupling agents to assess their effects on the nanocomposite SPEEK

membranes. The silane coupling agent is adsorbed on the surface of the nanoparticle at its hydrophilic end and interacts with the pre-existing hydroxyl groups on the nanoparticle's surface[26,42]. This study will assess consistent methods for determining electrochemical properties such as conductivity, transport number and selectivity. A novel technique for determining cation selectivity shall be developed. The functional groups shall be compared to determine their unique influence on membrane structure and subsequent membrane properties. This novel contribution provides a deeper understanding of the specific structural and morphological influences associated with the distinctive nanoparticle modifications.

In addition to the type of functional group used, the size and shape of the nanoparticles also influences membrane structure and performance characteristics[43]. Inorganic nanoparticles can take the form of spheres, shells, or even nanotubes by using different synthesis routes and templates. SPEEK membranes with silica nanorods functionalized with poly(phosphonic acid) have been produced where proton conductivity was found to relate to the aspect ratio of the nanotubes[31]. An aspect ratio of 45.9 produced membranes with the highest proton conductivity of 0.1032 S/cm at 30°C. To allow for consistent comparison between the effects of different functional groups on membrane properties, this study will only focus on spherical nanoparticles. The porosity and degree of functionality on the particles will also be kept as

consistent as possible to differentiate affects derived only from the unique functional groups.

4.2.1 Functionalization of Silica

4.2.1.1 SiO_2

Unmodified silica nanoparticles can be readily synthesized through the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in a mixture of alcohol, water and ammonia[26]. The hydrolysis method is recognized as the simplest and most effective route to synthesize monodispersed silica spheres.

A seeded growth technique using TEOS as a precursor was used to ensure monodispersity of the spherical particles[44]. To minimize the formation of new nuclei and avoid the aggregation of growing silica spheres, it was necessary to first dilute the TEOS with ethanol. When the total amount of TEOS added is more than a 1:8 molar ratio to water, the hydrolization reaction speed is not fast enough to consume the TEOS. The TEOS in the seeded suspension then accumulates and new nuclei forms in the solution. This causes the silica powder to be heterodisperse, with different sized particles in the final product. 1 mL of TEOS was first diluted with 4 mL of ethanol and added dropwise to a solution of 46 mL ethanol and 10 mL ammonia. The contents were stirred for 2 hours. The solution was washed with ethanol and

centrifuged several times to remove any impurities of ammonia or unreacted TEOS. The product was dried in an oven at 60°C overnight and then ground with a motar and pestle to produce a fine white silica powder.

Silica is a useful additive to explore the influence of functional groups on SPEEK polymer membranes as it can be readily modified by a variety of functional groups[25]. For example, heteropolyacids such as tungstophosphoric acid and molybdophosphoric have been previously incorporated onto silica particles[45,46]. Benzene-silica powder was also found to result in higher proton conductivities and lower methanol crossover when added to SPEEK polymer at ~15%w/w[24].

4.2.1.2 SiO$_2$-SH

Silica nanoparticles with thiol (-SH) functional groups can be synthesized by the route as shown in Figure 4.1 through the use of 3-mercaptopropyltrimethoxy silane (MPTMS) as a precursor[25,26]. In a 100 mL round bottom flask, 0.011 mol of TEOS and 0.00046 mol of MPTMS was added to 2.2 mol of ethanol and 17.8 mol of water. The solution was vigorously stirred for 1 hour and 7 mL of 25%w/w of NH$_4$OH was added. The solution was continuously stirred for another 4 hours and the product isolated by the addition of twice excess of water. The sample was then

centrifuged and the solid washed with ethanol several times to thoroughly

remove any unreacted MPTMS. The nanoparticles were then dried overnight

at 50°C to produce silica particles with attached thiol groups. The

nanoparticles denoted as SiO_2-SH.
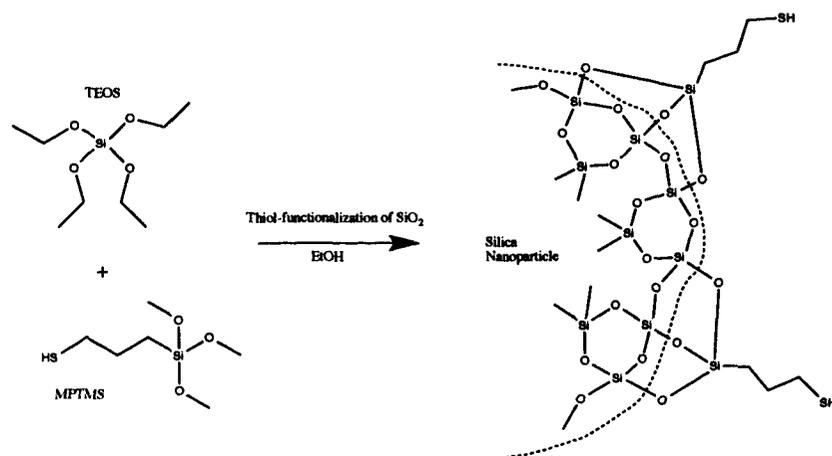
Figure 4.1: Thiol-functionalization of silica with MPTMS to synthesize SiO_2-SH

4.2.1.3 SiO₂-SO₃H

The thiol group in the previously synthesized SiO₂-SH can be readily oxidized

to a sulfonic group using a 15%w/w peroxide solution. SiO₂-SH nanoparticles

were immersed for 3 hours to produce SiO₂-SO₃H as shown in Figure 4.2.
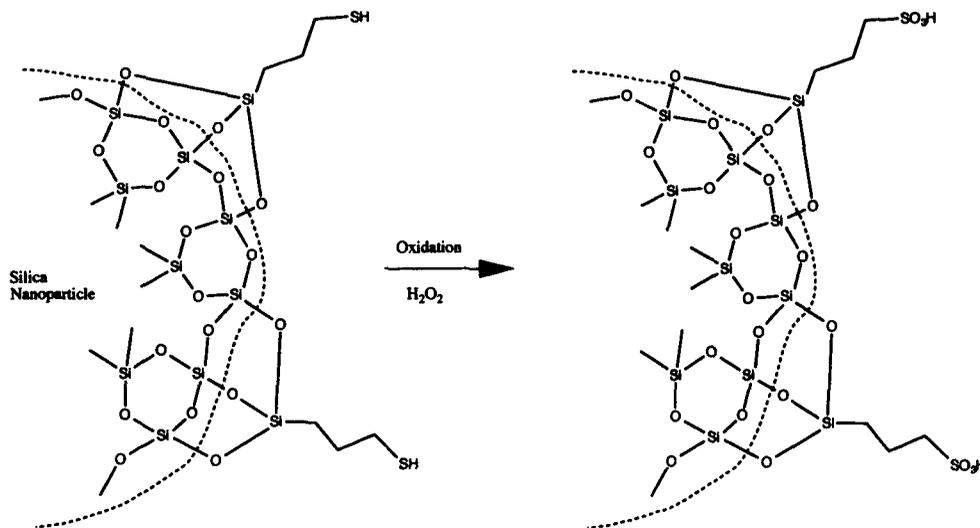
Figure 4.2: Reaction pathway to synthesize SiO₂-SO₃

4.2.1.4 SiO₂-NH₂

Amino functionalized silica was also synthesized as shown in 4.3 via the soft-

templating method using 3-aminopropyltriethoxysilane (APTMS)[43]. A TEOS

to APTMS molar ratio of 1:11 was added to 2.2 mol of ethanol and 17.8 mol of

water. The solution was stirred for 1 hour and 7 mL of 25%w/w ammonium

solution added. This was stirred for 4 hours and isolated with twice excess of

water. The precipitate was centrifuged and washed with ethanol several

times.
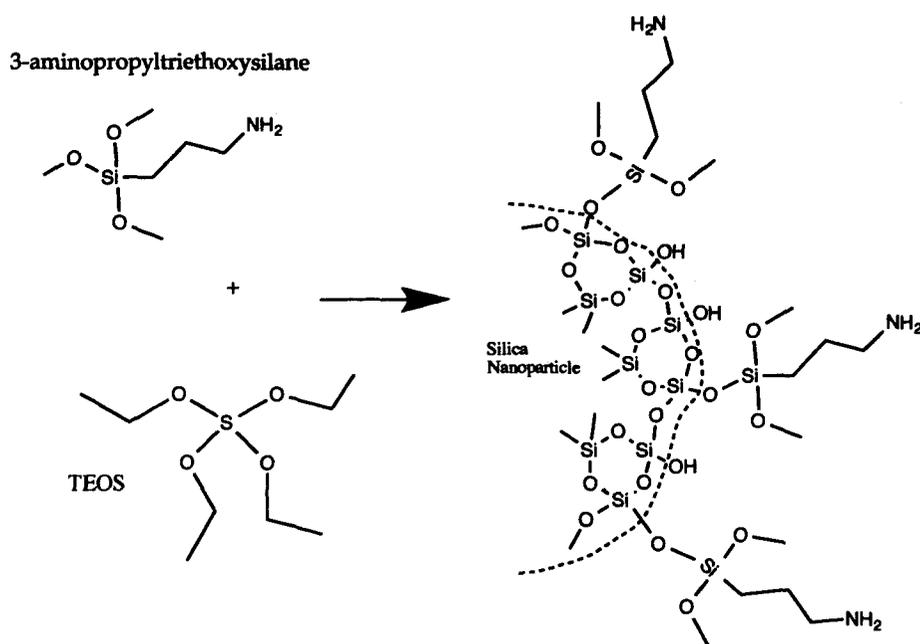
Figure 4.3: Synthesis of SiO2-NH2 nanoparticles

4.2.2   Functionalization of Titania

In previous studies, the increased content of TiO2 in hybrid SPEEK membranes increases water uptake and water retention by introducing hydrophilic regions to the membrane[47]. To synthesize titania nanoparticles by soft-templating, anhydrous TiCl4, TiOSO4, peroxytitanates, titanium ethoxide, titanium isopropoxide or titanium butoxide can be used as a suitable Ti source[15,20,48]. Figure 4.4 shows the surface functionalization of titania with amine, sulfonic and triethanolamine groups.
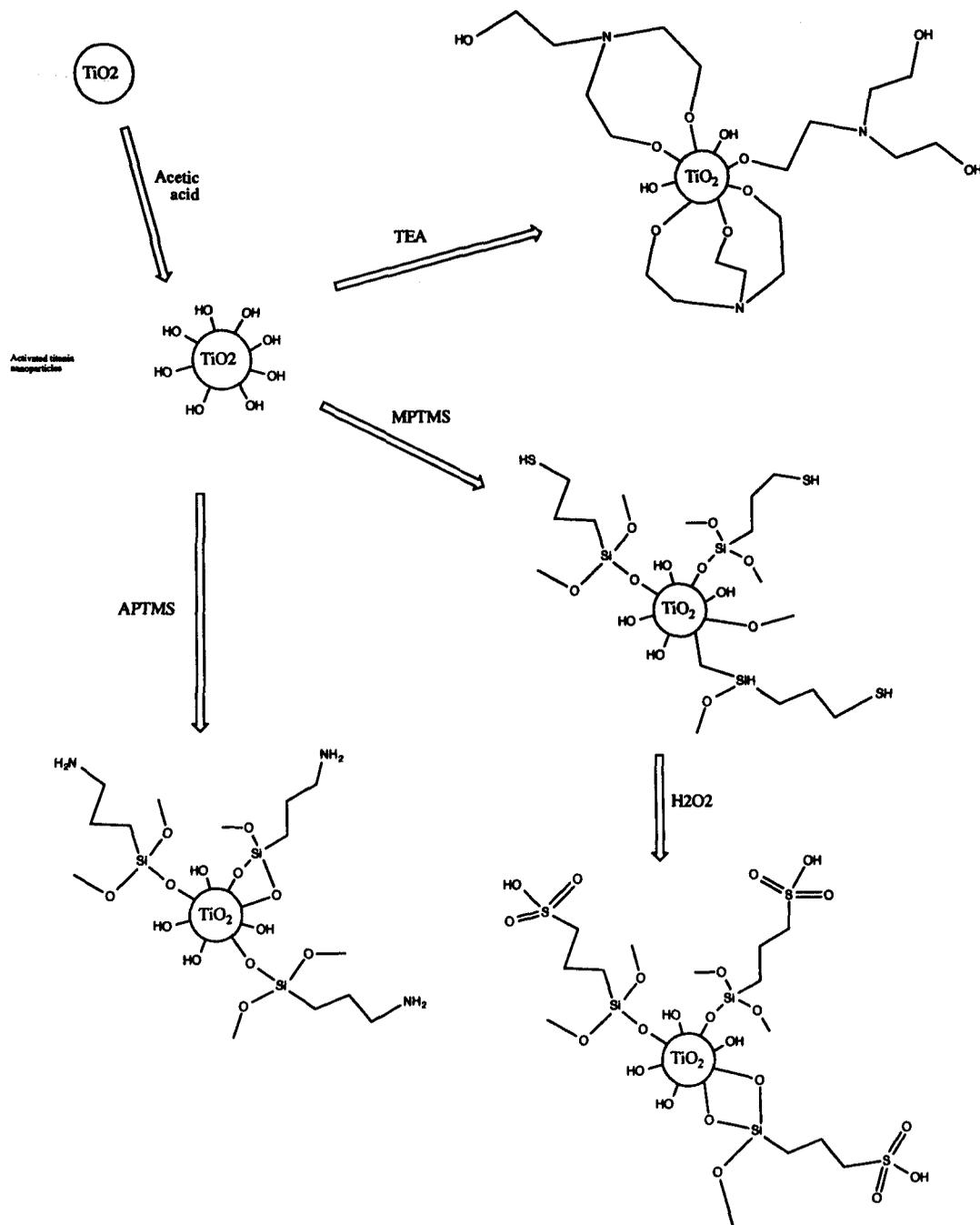
Figure 4.4: Activated titania nanoparticles functionalized with triethanolamine (TEA), 3-mercaptopropyltrimethoxysilane (MPTMS), H2O2, and 3-aminopropyltriethoxysilane (APTMS).

4.2.2.1 TiO₂

A solution of titanium butoxide (Ti(C4H9O)4) (0.11 mmol) and 2,4-pentandione (2.4 mmol) was added to 3 mL of dimethyl acetate (DMAc) and stirred. This solution was added directly to SPEEK in DMAc and stirred for 1 hour. The solution was evaporated to reduce the volume prior to casting.

4.2.2.2 TiO₂-SO₃H

To modify titania particles with sulfonic acid groups, 1 g of TiO₂ was suspended in 10 mL of toluene. 2.58 mmol (0.5g) of MPTMS was added and the solution stirred at 80°C overnight. The precipitate was centrifuged and washed with toluene twice. After drying at 60°C overnight in a vacuum oven, the product was reacted with 140mL of peroxide (40%w/w) for 6 h at 50°C under stirring to oxidize the thiol group. The final TiO₂-SO₃H particles were then separated by centrifuge and dried under vacuum for 2 h at 60°C.

4.2.2.3 TiO₂-NH₂

Amine functionalized titania was synthesized with APTMS by grafting. 1g of TiO₂ was first suspended in 50 mL of water using an ultrasonic bath at 60°C for 1 hour. 2.58 mmol of the APTMS was added and returned to the ultrasonic bath for 6 h at 60°C. The precipitate was centrifuged and washed with ethanol three times before drying in the oven overnight at 100°C.

4.2.2.4 TiO₂-TEA

Triethanolamine (TEA) functionalized titania was prepared usng a sol-gel

method[49]. The starting material of titanium butoxide was dissolved in ethanol

at a molar ratio of 1:2. Several drops of acetic acid were added to avoid

aggregation of the particles. The acid reduces the pH of the solution, and

subsequently the zeta potential, which assists in stabilizing the suspension. A

solution of ethanol and triethanolamine was mixed in an excess of water at a

molar ratio to the starting titanium butoxide of Ti(C4H9O)4:TEA:ethanol =

1:3:2. The TEA solution was added to the titanium mixture to yield a

transparent gel at room temperature. The gel was dried in an oven overnight

at 60°C and then in a vacuum oven for 6 h at 100°C.

4.3.   Casting SPEEK Nanocomposite Membranes

The SPEEK membranes described in Chapter 3 were designed with promising ion exchange capabilities. Plain SPEEK synthesized at 60°C for 6 hours with an ion exchange capacity (IEC) of 2.21 meq/g was used in this chapter as the base for composite polymer matrix membranes. The solid inorganic particles were finely ground to ensure good dispersion in the polymer solution.

Membranes cast with nanoparticle loadings higher than 10%w/w were found to result in notable aggregation of particles in the dried membrane. This is exemplified in Figure 4.5 particularly for unmodified silica and titania. To ensure good dispersion, membranes were cast with loading concentrations of 1, 3, and 5%w/w of the nanoparticles in relation to the SPEEK content. The photo shown in Figure 4.6 presents an illustration of these different membrane loadings for SPEEK-TiO$_2$-SO$_3$.

Figure 4.5: Silica in SPEEK membrane at 10%w/w
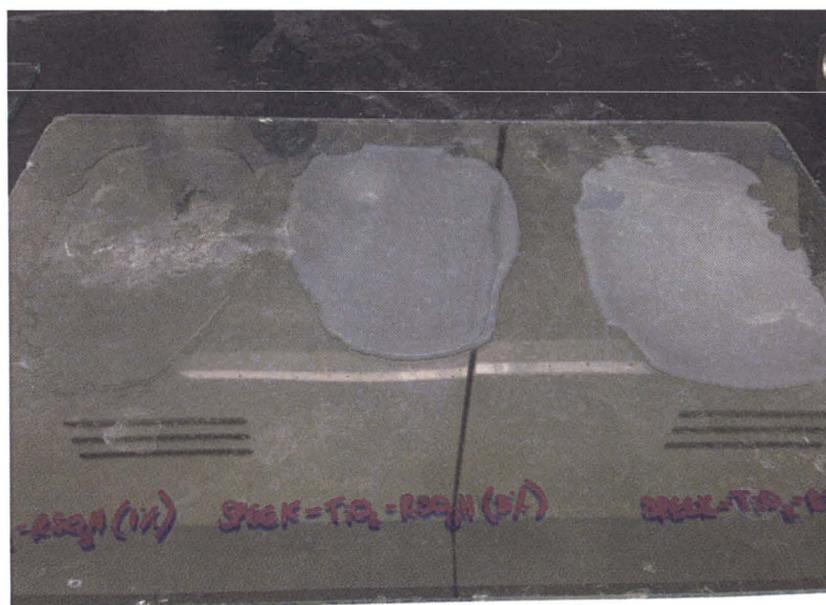
Figure 4.6: Photo of SPEEK membranes cast with 1, 3, and 5%w/w of TiO$_2$-SO$_3$H nanopartilces

Concentrations of ~15% w/w of total solid components were dissolved in DMAc and aggravated in an ultrasonic bath for an hour before casting on glass plates. The casting thickness was set with a doctor blade to 300μm. Membranes were dried in the oven at 60°C overnight and then placed in a vacuum oven at 100°C for 1 hour to ensure all solvent was removed. Nanocomposite membranes were stored in a solution of 0.5M NaCl until used in the characterization tests.

4.4.   Physicochemical Characterizations

4.4.1   FTIR

FTIR spectroscopy was used to confirm the successful incorporation of functional groups in the SPEEK and SPEEK nanocomposite membranes. Samples were dried in a vacuum oven at 110°C for 1 hour prior to direct testing with a PerkinElmer Spectrum 100 FT-IR Spectrometer. Samples and were analyzed over a range of 400-2000 cm^{-1}.

The FTIR spectrum of the pure SPEEK membrane is shown in Figure 4.7. The noticeable peak at 1596 cm^{-1} is characteristic of C-O stretching, with the shoulder at 1640 cm^{-1} indicating aromatic C-CH quadrant stretching. Bands at 1219, 1079 and 1014 cm^{-1} were also characteristic of symmetric and asymmetric O=S=O stretching vibrations present in sulfonic acid groups. There is also a noticeable absorption band of symmetric S-O stretching at 694 cm^{-1}. These bands are consistent with previous studies on SPEEK materials[46,50,51].
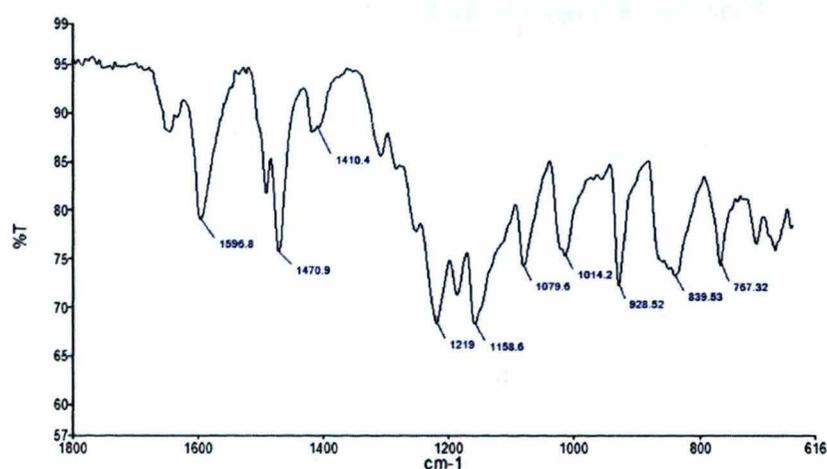
Figure 4.7: FT-IR spectra of SPEEK membrane

The spectra in Figure 4.8 of SPEEK with silica additives showed similar bands shifted to lower frequencies. This down-shifting indicates the presence of weak hydrogen-bonding interactions with the nanoparticles. The band at 467 cm^{-1} was characteristic of Si-O-Si bending in the silica. Bands at 800 and 1100 cm^{-1} is also characteristic of symmetric stretching and deformation modes in mesoporous silica[13]. For pure silica powder, an intense band at 1100 cm^{-1} represents siloxane stretching. For all silica samples, corresponding bands are represented for –Si-O-Si- linear stretching at 1030 cm^{-1}, –Si-O-Si- cyclic stretching at 1080 cm^{-1}, and –Si-O-Si- asymmetric stretching at 810 cm^{-1} [26,40,42].
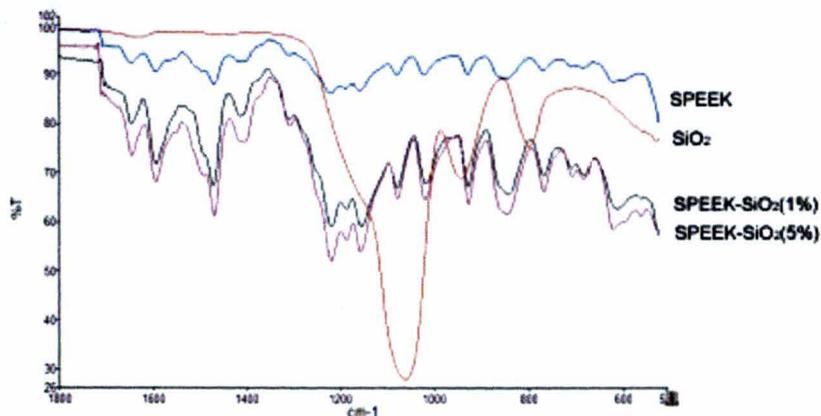
Figure 4.8: FT-IR spectra of pure SPEEK, SiO₂, and SPEEK-SiO₂ nanocomposite membranes at

1 and 5%w/w loadings

For composite membranes of silica nanoparticles as shown in Figure 4.9, bands at 1225 and 1050 cm^{-1} corresponds to the symmetric and asymmetric stretching of O=S=O on the sulfonic acid groups, confirming the attachment of sulfonic acid to the silica nanoparticles.
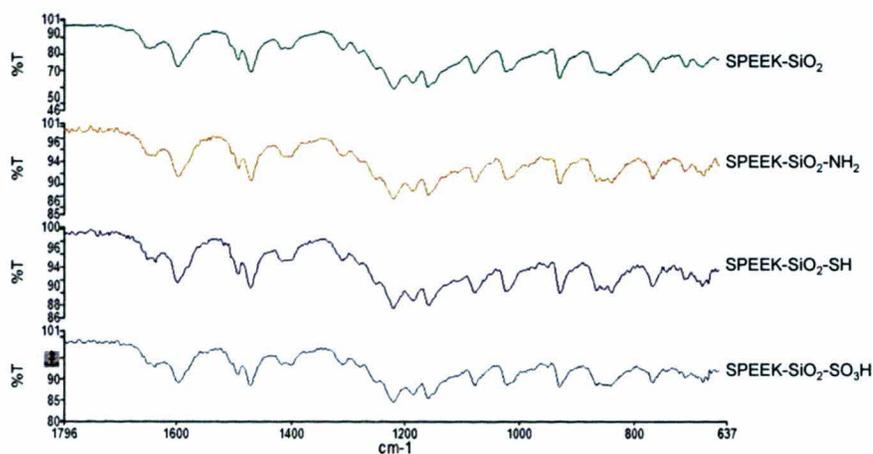
Figure 4.9: FTIR spectra of functionalized silica nanoparticles

The FTIR spectra in Figure 4.10 of TiO_2 showed a characteristic peak at 1080 cm^{-1}, which became weaker after modifications. With amine functional groups, peaks at 1540 cm^{-1} were indicative of the C-N stretching. The peak at 1635 cm^{-1} for SPEEK-TiO_2-NH_2 could also be attributed to the scissoring vibration of H-N-H bonds. Evidence of these bands proves the presence of amine functional groups on the nanoparticles.
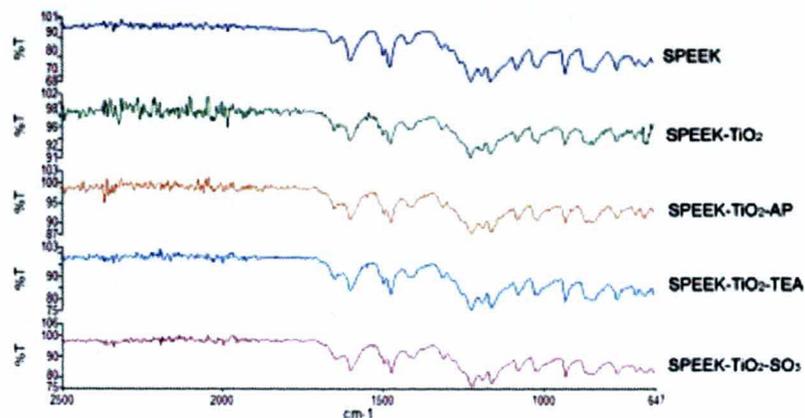
Figure 4.10: FTIR spectra of titania and functionalized titania nanoparticles

4.4.2   SEM

Scanning electron microscopy (SEM) was performed using a FEI Nova NanoSEM 450 for morphological analysis. Cross-sections of the SPEEK and SPEEK based nanocomposite membranes at 3%w/w loadings were obtained by nitrogen fracture and coated with carbon. SEM images for the nanocomposite membranes are compiled in Figures 4.11 to 4.18. Enlarged images are presented in the Appendix to provide greater detail of these images.
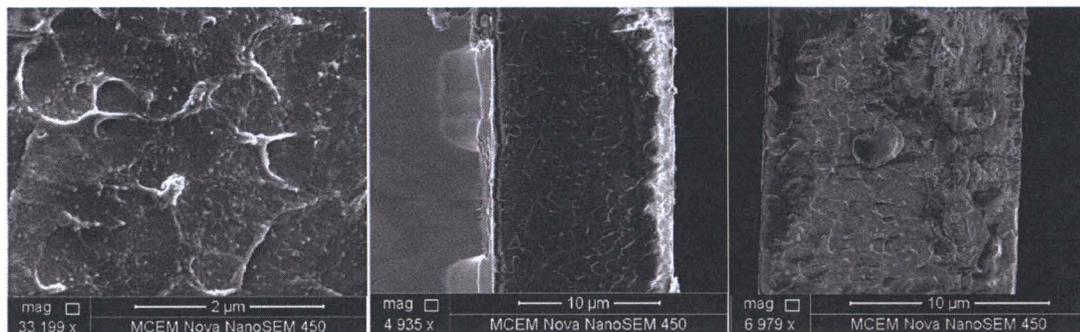
Figure 4.11: SEM image of SPEEK membrane cross-section
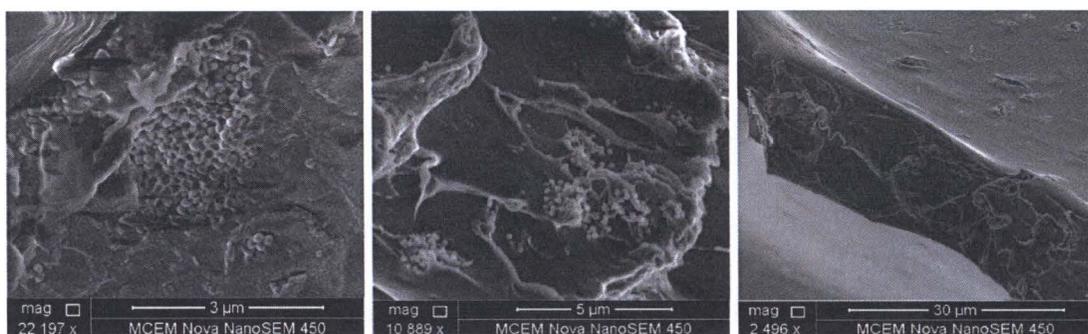
Figure 4.12: SEM image of SPEEK-SiO$_2$ membrane cross-section
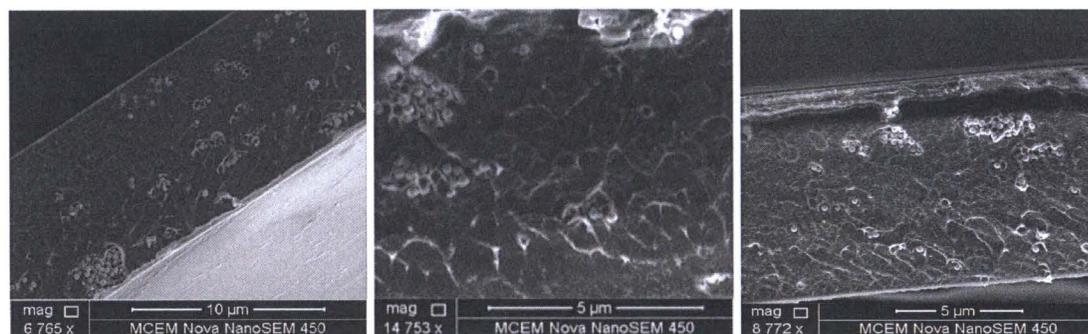
Figure 4.13: SEM image of SPEEK-SiO$_2$-SH membrane cross-section
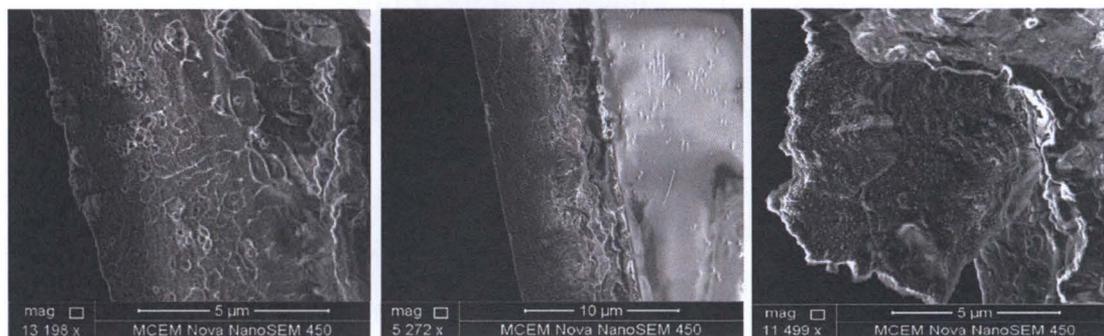
Figure 4.14: SEM image of SPEEK-SiO$_2$-SO$_3$H membrane cross-section
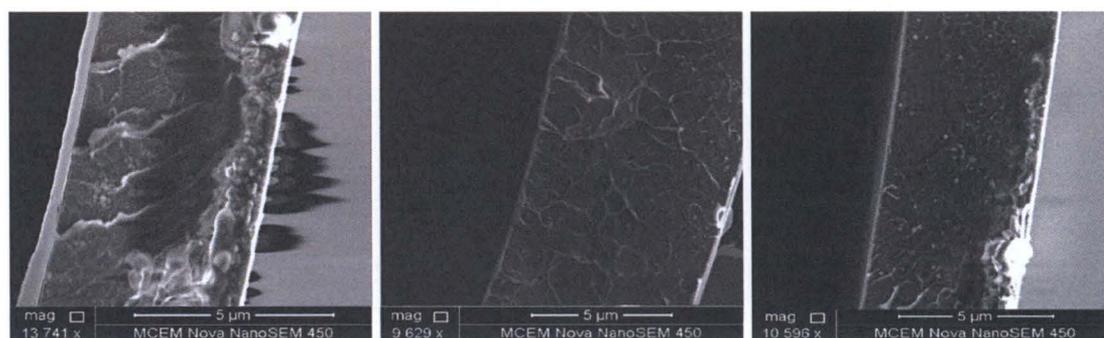
Figure 4.15: SEM image of SPEEK-SiO$_2$-NH$_2$ membrane cross-section
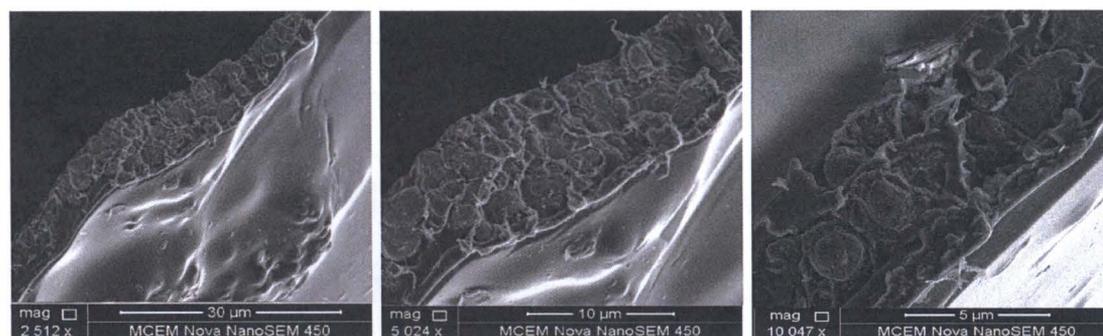
Figure 4.16: SEM image of SPEEK-TiO$_2$ membrane cross-section
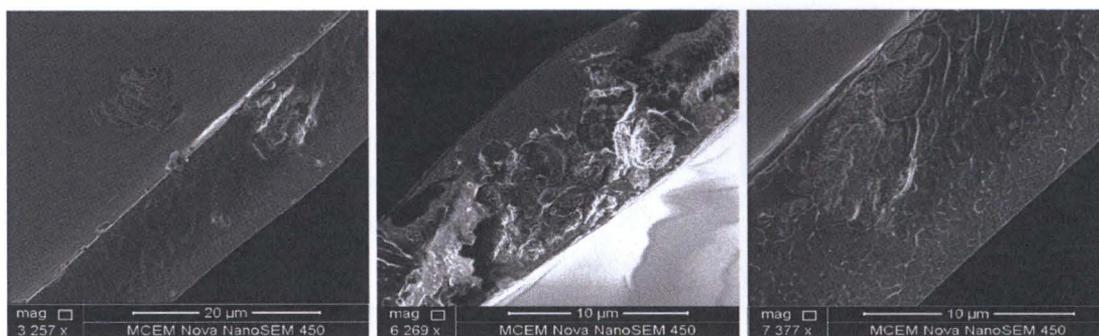
Figure 4.17: SEM image of SPEEK-TiO$_2$-NH$_2$ membrane cross-section
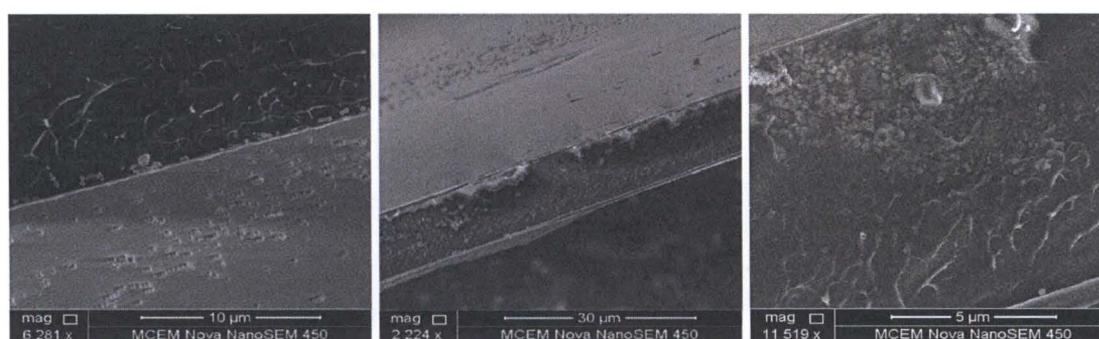
Figure 4.18: SEM image of SPEEK-SiO$_2$-TEA membrane cross-section

The SEM images of the pure SPEEK membrane in Figure 4.11 showed a smooth and homogenous cross-section measuring approximately 30 μm across. The cross-section shows different morphology of the surfaces of the membranes compared to the bulk section. As the solvent evaporates from the exposed membrane surface, a dense skin is formed on the air-facing edge. All the membranes showed these dense surface skins, with a thicker skin on the air-facing edge.

The SEM image for SPEEK-SiO_2 in Figure 4.12 revealed that spherical nanoparticles had been synthesized and were embedded in the bulk of the membrane cross-section. Large clusters were found, showing insufficient dispersion of the nanoparticles, which resulted in agglomeration as the cast membrane was dried. Similar clumping was seen in Figure 4.13 of the SPEEK-SiO_2-SH cross-sections, though with less agglomeration than the unmodified SPEEK. The SEM images in Figure 4.14 and Figure 4.15 of SPEEK-SiO_2-SO_3H and SPEEK-SiO_2-NH_2, respectively, shows improved dispersion of the particles, with individual particles diffused evenly through the bulk of the membrane cross-section.

Figure 4.16 shows SPEEK-TiO_2 membranes having extreme aggregation of the particles with the polymer spread out around the nanoparticles. The titania nanoparticles were difficult to disperse even using ultrasonic mixing, and may have continued to agglomerate while the cast membrane was drying. In previous studies, an external AC electric field was applied during solvent evaporation to prevent nanoparticles from aggregating[34]. While Figure 4.17 of the SPEEK-TiO_2-NH_2 showed improved dispersion of the modified nanoparticles, large clusters were still noticable. The –TEA modified nanoparticles in Figure 4.18 were minimally dispersed through the membane bulk and were instead found to predominantly stick on top of the dried membrane surfaces. While some particles were present in the bulk of the

membrane, most were embedded onto the surface. This may influence the membrane's integrity. Ions will also be influenced at the membrane surface before they penetrate into the membrane bulk.

4.4.3   Water Uptake and Swelling

Water plays an important role in polymer ion exchange membranes as water content directly affects ion transport across the membrane[52]. Proton conductivity is dependent on the connectivity of the hydrated domains as the protons are transported along hydrogen-bonded ionic channels. Membranes need to absorb sufficient water to allow for effective conductivity, but excessive swelling may result in poor mechanical and dimensional stability.

To evaluate the water absorption and dimensional changes, samples of approximately 1cm x 5cm of the SPEEK and SPEEK composite membranes were soaked overnight at 25°C. These were wiped down before determining the wet weight. Samples were then dried in a vacuum oven at 110°C overnight to measure the dry weight. The water uptake was then determined by the following equation.

Equation 4.2:

$$\text{Water Uptake} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100\%$$
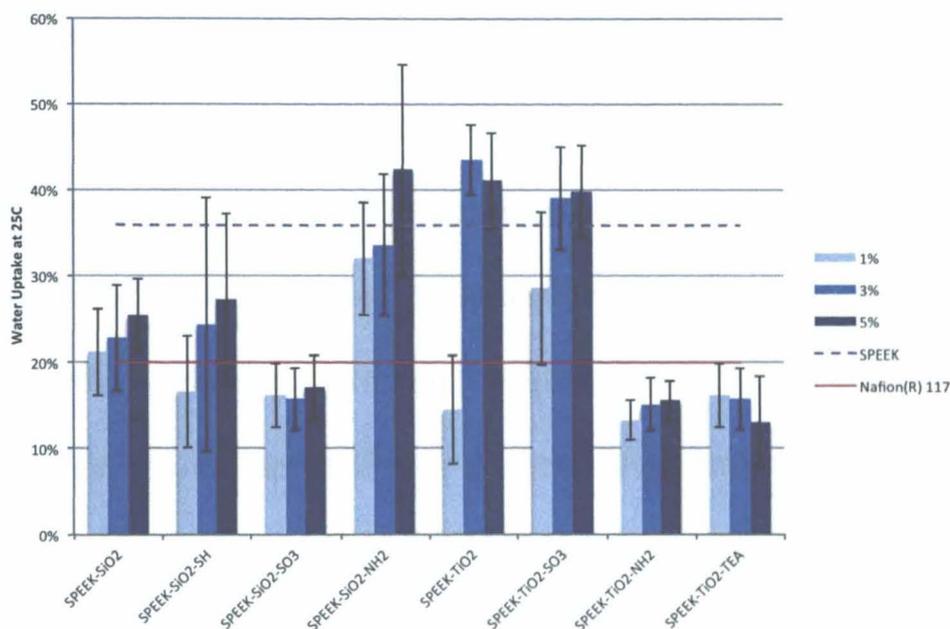
Figure 4.19: Water uptake of SPEEK and SPEEK nanocomposite membranes at 25C

The water uptake of pure SPEEK membranes is shown as a reference in Figure 4.19 by the dashed line. A sample of Nafion® 117 was shown to have a low water uptake of 14%. At least four samples of each membrane were tested to determine error bars of one standard deviation.

The nanoparticles in the polymer matrix improves structural integrity by limiting extreme swelling in the composite membranes. These nanocomposite membranes were found to have water uptake of 15-40%, suitable for use in

aqueous bioelectrochemical wastewater systems. SPEEK-SiO$_2$-NH$_2$, SPEEK-TiO$_2$, and SPEEK-TiO$_2$-SO$_3$ were found to have water uptake values similar to pure SPEEK, indicating that these nanoparticles did not affect the network structure as much as the other functionalized nanoparticles.

Nanoparticle loadings in the 1-5%w/w range were typically proportional to the increased water uptake. Integrating inorganic fillers into the organic polymer matrix can induce structural changes in the polymer matrix. The presence of acidic functional groups on the surface interacts with the sulfonic groups on the SPEEK polymer chains, potentially reducing water retention regions. SPEEK-TiO$_2$ and SPEEK-TiO$_2$-TEA were the only membranes not to show increased water uptake proportionally with nanoparticle loading content. The unmodified TiO$_2$ was seen in SEM studies to agglomerate in large clumps through the membrane. This inhomogeneity of the membrane may have resulted in inhomogeneous samples tested for water uptake. SEM also showed that the TiO$_2$-TEA nanoparticles lay on the membrane surface, rather than being embedded in the membrane bulk. Increased loadings for this nanocomposite structure would not affect the water retention capabilities in the bulk polymer network.As the particles lay on the surface, they may restrict the permeation of water into the bulk, explaining the low water uptake for SPEEK-TiO$_2$-TEA membranes.

Membranes with a water uptake of 20-40% are favourable to ensure good cohesion of the polymer matrix and nanoparticles[3]. Water uptake is beneficial for proton conducting, but excessive water uptake can result in poor mechanical performance. While higher water uptake generates a more solvated species, which is needed for high conductivity, this also produces less structurally stable membranes. The water uptake and conductivity of pure polymer membranes typically demands a tradeoff between high conductivity and good mechanical properties as both properties are most significantly dependent on the polymer sulfonation degree. Embedded nanoparticles in the polymer matrix prohibits extreme swelling of the composite membranes, which improves the hydrostability of the membranes while providing other pathways for ion transport.

4.4.4   Ion Exchange Capacity

Preliminary investigation of the ion transport properties of SPEEK and SPEEK nanocomposite membranes can provide a deeper understanding of the membrane microstructure. Ion exchange capacity (IEC) is the number of fixed $-SO_3$ charges inside the ion exchange membrane as measured per unit weight of the dry polymer. Expressed in milli-equivalents per gram of dry membrane, the IEC relates to the water uptake and conductivity properties.

To determine the ion exchange capacity, the acid-base titration technique used sodium hydroxide was performed as described in Chapter 3 by Equation 3.1.

Figure 4.20 shows the IEC results for SPEEK and SPEEK nanocomposite membranes at varied loadings. At least four samples of each membrane were titrated with the average represented by the column and one standard deviation in each direction by the error bars. The dashed line indicates the IEC of the unmodified SPEEK polymer membrane.
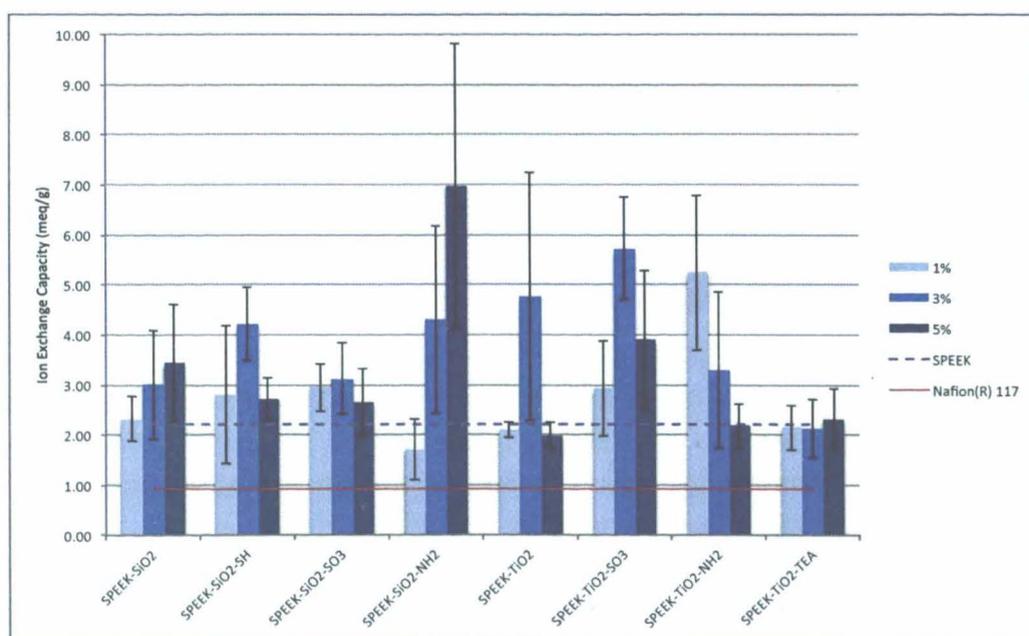

Figure 4.20: Ion Exchange Capacity of SPEEK and SPEEK nanocomposite membranes at 1, 3 and 5% w/w nanoparticleloadings

SPEEK nanocomposite membranes with loadings of 1-5% were found to exhibit IEC values close to that of pure SPEEK, with increased loading typically corresponding to increased IEC. This indicates that the nanoparticles provided provide additional pathways for ion transport other than through hydrophilic domains. These nanocomposite membranes exhibit good potential for ion transport while maintaining membrane stability in aqueous environments. While higher loadings were found to result in increased IEC for SPEEK-SiO$_2$ and SPEEK-SiO$_2$-NH$_2$ membranes, there were not noticeable trends for all the nanocomposite membranes. SPEEK-TiO$_2$-NH$_2$ showed an inverse relation between the loading concentration and IEC. The remaining membranes exhibited no clear correlation of IEC with loading, indicating that the IEC may not be significantly affected by nanoparticle concentration in the range of 1-5%w/w.

The steep increase in the IEC of the SPEEK-SiO$_2$-NH$_2$ membranes with loading concentration may be attributed to hydrogen bonds forming between the sulfonic acid group and amine groups, which is consistent with FTIR analysis. This restricts movement and swelling of the SPEEK polymer chains. These bonds strengthen the polymer matrix while providing new pathways for ion transport.

The addition of nanoparticles creates inorganic phases in the polymer matrix, increasing the ion exchange capacity of the membranes while maintaining a stable network structure as indicated by the reduced water uptake. These membranes have the potential to transport ions via alternative pathways than the pure SPEEK polymer membranes, which are typically dependent on water channels for ion conduction. As excessive water uptake results in a loss of structural integrity, these membrane materials have the potential to improve ion transport capabilities while maintaining a stable structure in aqueous enviroments.

4.4.5   Thermal Stability

A SII Nanotechnology Inc. EXSTAR TG/DTA6300 was used to study the thermal stability of the SPEEK and SPEEK nanocomposite membranes in a .

Samples were heated under nitrogen at a scanning rate of 10°C min⁻¹ from 25 – 700°C. This analysis of the mass change of the membrane sample as a function of increasing temperature provides valuable information as to the structural integrity of the membranes. Regions of thermal stability are shown in Figure 4.21 where no mass change or degradation occurs. Most polymers are known to degrade at temperatures over 250°C, and previous studies on SPEEK membranes have recorded degradation after 250°C[3,53].
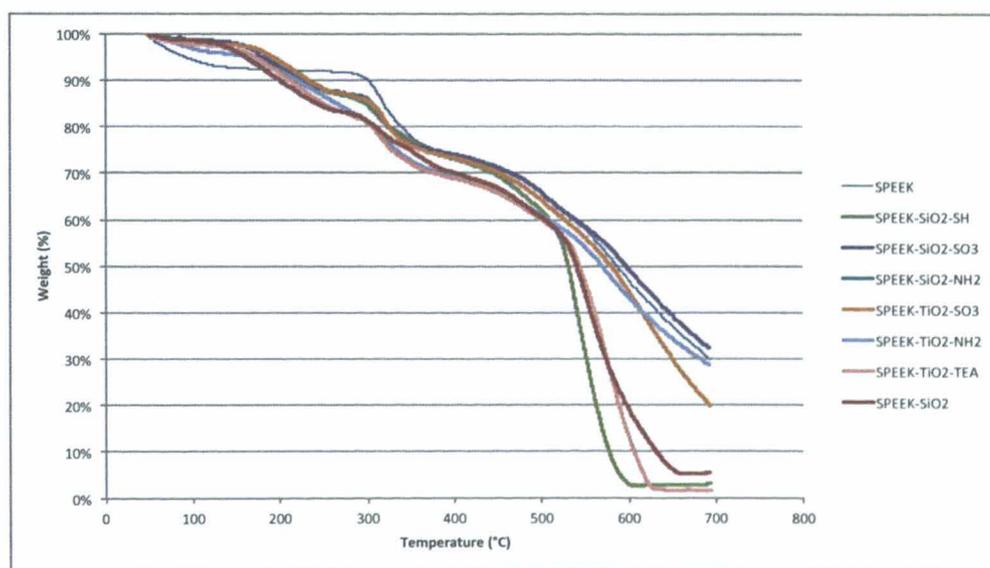

Figure 4.21: TGA spectra of SPEEK and SPEEK nanocomposite membrane samples

Figure 4.21 shows the thermo-gravimetric analysis spectra for the SPEEK and SPEEK nanocomposite membranes. The initial mass loss of all membranes is

attributed to the gradual desorption of resisdual water bonded to hydrophilic sulfonic groups. After dehydration, no further weight loss was observed until degradation of the sulfonic groups occurring at 300°C. The second weight loss observed at temperatures above 500°C represents the thermal decomposition of the main SPEEK polymer chains. At temperatures higher than 500°C, oxidation sharply increased. SPEEK-SiO_2, SPEEK-SiO_2-SH, and SPEEK-TiO_2-TEA material showed a sharp weight loss at 550°C with nearly all the polymer consumed when the temperature reaches 600°C. At 700°C, only 20% of SPEEK-TiO_2-SO_3 and 30% of the other membrane materials are still present.

Comparing the nanocomposite membranes, it is noticeable that the SPEEK nanocomposites of SPEEK-SiO_2, SPEEK-SiO_2-SH and SPEEK-TiO_2-TEA deteriorated at sharper rates after dehydration than the other SPEEK and SPEEK nanocomposite membranes. These membranes are less thermally stable than the other samples.

These TGA studies of these composite membranes reveal good thermal properties suitable for use in wastewater treatment systems typically operating at <200°C. These SPEEK nanocomposite membranes will be stable in operating conditions up to 300°C.

4.5.   Conclusions

Silica and titania nanoparticles were successfully synthesized, modified, and directly blended into SPEEK polymer matrix to form nanocomposite membranes with 1-5%w/w loadings of the nanoparticles. The functionalization of the surface properties of these additives was confirmed by FTIR spectroscopy. The SEM images of the SPEEK nanocomposite cross-sections showed the membranes to be comprised of a bulk interior with dense thin surface skins. Functionalized nanoparticles showed better dispersion through the polymer membrane compared to the unmodified SPEEK-SiO_2 and SPEEK-TiO_2, which showed highly agglomerated inorganic regions. Modified nanoparticles were generally well dispersed through the bulk of the membrane interior as surface functionalization generates repulsion between the nanoparticles. The exception of this phenomenon was noted for SPEEK-TiO_2-TEA, where the nanoparticles were found to sit on the membrane skin surface.

Functionalized composite membranes were found to exhibit lower water uptake than pure SPEEK membranes. The presence of acidic functional groups on the surface interacts with the sulfonic groups on the SPEEK polymer chains, potentially reducing water retention regions. Membranes with a water uptake of 15-40% have been reported in previous literature to be

suitable for fuel cell operation[33,54]. The thermal stability of the SPEEK and SPEEK nanocomposite membranes was also suitable for operating temperatures up to 300°C.

Preliminary ion transport studies indicate that the integration of nanoparticles results in nanocomposite membranes with good IEC values over 2.0 meq/g while maintaining structural integrity in aqueous environments. The physicochemical properties of SPEEK-SiO$_2$, SPEEK-SiO$_2$-SH, SPEEK-SiO$_2$-SO$_3$, SPEEK-SiO$_2$-NH$_2$, SPEEK-TiO$_2$-SO$_3$, and SPEEK-TiO$_2$-NH$_2$ membranes are promising for applications in fuel cells and bioelectrochemical systems. Further study of the electrochemical performance of these membranes is required to understand the structural influences on ion transport properties.

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CHAPTER 5

ELECTROCHEMICAL

CHARACTERIZATION OF SPEEK

NANOCOMPOSITE MEMBRANES

5.1.   Introduction

There has been growing demand for ion exchange membranes that are able to separate cations of different charge. Particularly for bioelectrochemical systems that can be used to recover chemicals or energy from wastewater streams that consist of varied ionic components. Microbial electrolysis cells can be used to produce valuable hydrogen peroxide from organic matter, and membranes with monovalent selective transport properties can reduce or eliminate the transport of $Fe^{2+/3+}$ ions, which is a well known H_2O_2 decomposition catalyst, and prevent product loss[1]. Scaling can also be caused by mineral build up where hydroxide formation of divalent and trivalent ions produces calcium based salts that readily precipitates out of low pH environments, such as $CaCO_3$ and $CaSO_4$[2]. In the concentration or removal of ions from a mixture such as the production of salt from seawater, electro-acidification of milk, deacidification of fruit juice, scaling can be a serious problem by effecting the formation of bivalent hydroxides, membrane poisoning and causing a decrease in membrane conductivity and permselectivity. Fouling can also permanently alter membrane structure[3,4]. Using monovalent selective membranes, which reject bivalent ions, such as Ca2+ and Mg2+, membrane fouling can be reduced[5].

In addition to separating cations and anions based on charge, membranes are desired with the ability to separate cations of different valency[6,7]. Such selective membranes are desired with a preference for transporting monovalent cations while rejecting multivalent cations[8,9]. Monovalent cation selective membranes can improve the performance of existing processes and minimize the effects of fouling[10]. They also enable the recovery of valuable species such as H^+ or Na^+ that can be used in the production of $NaOH$[9].

Membrane properties, including selectivity, are affected by the morphology and physicochemical structure of the material. These characteristics are controlled by precursors used in material synthesis as well as by membrane preparation conditions, which produces unique membrane chemistry and microstructure. It is essential to understand the relationships between these parameters and the resulting membrane performance.

In unmodified ion exchange membranes, cations migrate across the thin film at different rates according to charge, size, or the level of hydration of the membrane. Due to higher electrostatic attraction, multivalent cations are typically preferred for transport by unmodified IEMs. To obtain IEMs that preferentially transport monovalent cations, some researchers have deposited a thin anion-exchange layer with positively charged fixed groups at the surface of the ion exchange membrane[2,11-14]. This introduces a slight electrical

repulsion barrier that resists the transport of multivalent ions more than monovalent ion transport. There are challenges in maintaining cohesion between the layers and membrane lifetimes are limited by possible peeling. Internal and irreversible fouling may even form within the membrane.

To directly influence ion transport through the membrane, composite membranes can be developed by embedding nanoparticles into a polymer matrix[15-19]. Various fillers can be incorporated and selectively affects the transport pathways through the unique organic-inorganic hybrid network[20]. Inorganic silica and titania nanoparticles can improve thermal stability and water retention properties, which may be beneficial for certain applications. The modified morphology can also influence ion transport[21]. The large surface area to volume ratio inherent to nanoparticles allows for many sites for surface functionalization.

Charged nanoparticles can affect the electrostatic influences throughout the membrane. Additives can influence the hydrophilicity of membranes, which affects the ionic interactions and surface charge density of the nanocomposite matrix[22]. Nanoparticles have also been used to alter the membrane structure to improve the proton conductivity in membranes. For example, polyaniline is an electronic conductor that increases the conductivity of Nafion®-based membranes by aligning the hydropbobic backbone structure as it forms,

which has also been shown to align the hydrophilic clusters by a secondary orientation effect.[23] To achieve selective and cost-effective membranes, composites are a suitable route for further material development.

The focus of this chapter is to assess and compare the electrochemical and ion transport properties of the series of SPEEK nanocomposite membranes produced in Chapter 4. The unique series of functional groups provides the opportunity to directly compare the performance of various nanoparticle modifications on SPEEK nanocomposite properties. Membrane performance is investigated by several standard techniques used to determine the electrochemical and transport properties of IEMs. To consistently determine the cation selectivity properties of the membranes, this work will also develop a novel, quantifiable and consistent measure for comparing ion exchange membranes.

5.1.1   Measuring Membrane Selectivity

In previous literature, membrane selectivity has not been consistently defined. Membrane selectivity has been used to refer to actual permselectivity, which is a measure of how easily counter-ions migrate through an ion exchange membrane compared to ions of the same charge as

the fixed species[24]. The permselectivity of a given cation M^{n+} is defined by the transport number of cation M^{n+} relative to that of sodium ions[24].

Equation 5.1:

$$P_{Na}^{M} = \frac{t_M / t_{Na}}{C_M / C_{Na}}$$

Where t_M and t_{Na} are transport numbers of M^{n+} and Na^+ in the membrane phase, and C_M and C_{Na} are the concentrations of M^{n+} and Na^+ at the membrane surface.

Some areas of membrane research involved in fuel cell applications have also focused on methanol selectivity as the ratio of proton conductivity to methanol permeability[25-27]. In this work, we identify membrane selectivity as the concentration flux of a particular transported cation species in relation to the concentration flux of a standard monovalent cation through a membrane. A reference monovalent cation, such as Na^+ or H^+, can be used as a basis for this ratio, which gives a quantifiable measure of membrane cation selectivity performance in binary systems.

There have been several varied approaches to measuring the cation selective properties of ion exchange membranes[28,29]. Kumar (2009) describes the study

of composite membranes prepared using sulfonic acid groups introduced into the organic segment[22]. These membranes were designed for the electroseparation of Na^+ from solutions also containing Ca^{2+}, Mg^{2+}, and Fe^{3+}. Using a two-compartment cell, the electro-transport efficiency, η, was measured for different counter-ions:

Equation 5.2:

$$\eta = \frac{z_i m F}{MQ}$$

Where z_i is the valence of the studied cation, m is the weight of the electrolyte transported across the membrane, F is Faraday's constant (96480 C/mol), M is the molecular weight of the electrolyte passed through membrane, and Q is the number of coulombs delivered.

Membrane selectivity has also been previously described by comparing the flux of specific ions through the membrane as the rates can be normalized for membrane thickness. Flux models of kinetic and equilibrium controlled mechanisms have been described in previous literature[11,14,30]. These studies have looked at the mass change with time to determine membrane selectivity.

Separation tests by electrodialysis have also been studied where an electrochemical cell of two compartments and four electrodes was used to test the ability of Nafion® and sulfonated polyimide membranes in separating H^+ and Cu^{2+} ions[29]. The volumes of the compartments were measured with time and used to calculate the amount of species present. The moles of H^+ and Cu^{2+} ions were determined by acid-base titration using 0.01 M NaOH and by UV-Vis spectroscopy, respectively. The flux of protons from the dilute to the concentrate compartments can be written as:

Equation 5.3:

$$\left(J_{DC}^{H^+}\right)' = -\left[\frac{\Delta n_{H^+}}{\Delta t}\right]_D - \left[\frac{\Delta n_{H^+}}{\Delta t}\right]_{E+} + \frac{1}{F}$$

Equation 5.4:

$$\left(J_{DC}^{H^+}\right)'' = \left[\frac{\Delta n_{H^+}}{\Delta t}\right]_C + \left[\frac{\Delta n_{H^+}}{\Delta t}\right]_{E-} + \frac{1}{F}$$

Where F is the Faraday constant and Δn is the change in moles of the subscript species. Equation 5.3 gives the flux of protons through the cation exchange membrane from the concentrations variations of compartments D and E^+, and Equation 5.4 of the compartments C and E^-.

The flux of copper from dilute to concentrate, $J_{DC}^{Cu^+}$, was also derived from this study.

Equation 5.5:

$$\left(J_{DC}^{Cu^+}\right)' = -\left[\frac{\Delta n_{Cu^{2+}}}{\Delta t}\right]_D$$

Equation 5.6:

$$\left(J_{DC}^{Cu^+}\right)'' = \left[\frac{\Delta n_{Cu^{2+}}}{\Delta t}\right]_C$$

To evaluate the modified membranes, the transport number, t_i, of species i was used to compare ion transport efficiency.

Equation 5.7:

$$t_i = z_i F \frac{J_{DC}^i}{I}$$

Where z_i is the valency of the species i and I is the applied current.

Ion flux measurements have also been used to investigate membranes of sulfonated poly(ether ether ketone) blended with poly(ether sulfone) in binary electrolyte solutions containing protons and calcium ions[7]. To measure the Ca^{2+} flux, a 2-compartment cell was used with two Ag/AgCl electrodes. The electrode reactions for this process are:

Cathode: $AgCl + e^- \rightarrow Ag + Cl^-$

Anode: $Ag + Cl^- \rightarrow AgCl + e^-$

The following binary solutions were placed in the anode compartment with 0.01M HCl solution in the cathode compartment.

- 0.025M $CaCl_2$/0.075 M HCl;

- 0.05M $CaCl_2$/0.05 M HCl;

- 0.075M $CaCl_2$/0.025 M HCl.

Under a constant current density of 30 mA/cm², the ions were driven through the test membranes. Ca^{2+} concentrations were determined by elemental analysis (atomic absorption spectroscopy) and the corresponding Ca^{2+} flux ($J(Ca^{2+})$) through the membrane was calculated.

Equation 5.8:

$$J(Ca^{2+}) = \frac{V\frac{dC_{Ca^{2+}}}{dt}}{A}$$

Where V is the volume of the circulated solution, A is the membrane area and

$\frac{dC_{Ca^{2+}}}{dt}$ is the concentration change in time in the cathode compartment. For

homogenous structure membranes, the flux can be normalized by the wet

membrane thickness and compared to give a quantifiable metric for

comparing membrane selectivity.

Equation 5.9:

$$J_N(Ca^{2+}) = J(Ca^{2+})d_{wet}$$

These researchers have investigated the flux of Ca^{2+} and Cu^{2+} in binary

systems. Further work is required to evaluate multi-ion systems and to

provide a consistent, reproducible and quantitative analysis of membrane

selectivity performance. While previous methods were able to quantify

membrane selectivity, these techniques use highly customized

electrochemical cells and would be difficult to repeat. The measure of flux is a

consistent approach, and a more direct method for measuring the ratios of

transported cation species will be further developed in this work.

This chapter presents a novel method for reliably determining cation selective

properties for a unique series of SPEEK and SPEEK nanocomposite

membranes. These membranes will be characterized by electrochemical

techniques to develop an understanding of ion transport through the membrane structure. This will provide a more comprehensive model of the morphological effects on membrane performance.

5.2.   Experimental

5.2.1   Membrane Fabrication

The synthesis and casting of sulfonated poly(ether ether ketone) membranes used as the base polymer matrix has been previously described in Chapter 3. In Chapter 4, the functionalization and incorporation of silica and titania nanoparticles into SPEEK based nanocomposite membranes was described. The physicochemical properties of these nanocomposite membranes have been previously investigated and are presented in Table 5.1.

Plain SPEEK synthesized at 60°C for 6 hours with an ion exchange capacity (IEC) of 2.21 meq/g was used in this chapter as the basis for the membrane polymer matrix. Membranes were dried in an oven at 60°C overnight and then placed in a vacuum oven at 100°C for 1 hour to ensure all the solvent was removed. Nanocomposite membranes were stored in a solution of 0.5M NaCl.

The SPEEK based nanocomposite membranes samples under investigation are labeled by the format: SPEEK-nanoparticle.functional group. The functionalization pathways for the particular modified silica (SiO_2) and titania (TiO_2) nanoparticles have been discussed in Chapter 4.

Table 5.1: Physical characteristics of SPEEK nanocomposite membranes

Membrane	IEC	Water Uptake	Wet Thickness
	meq/g	%	mm
SPEEK	2.21	36%	0.032
SPEEK-SiO$_2$	3.00	23%	0.016
SPEEK-SiO$_2$.SH	4.22	24%	0.035
SPEEK-SiO$_2$.SO$_3$H	4.29	16%	0.028
SPEEK-SiO$_2$.NH$_2$	3.12	34%	0.023
SPEEK-TiO$_2$.SO$_3$H	4.76	44%	0.035
SPEEK-TiO$_2$.NH$_2$	3.29	15%	0.022
SPEEK-TiO$_2$.TEA	2.13	16%	0.034

5.2.2   Electrochemical Cell Designs

Electrochemical performance indicators of conductivity, transport number and selectivity were determined using a BioLogic Potentiostat and customized electrochemical cells. The potentiostat is high-precision instrument able to observe the response of certain electrical stimuli. Electrochemical impedance spectroscopy (EIS) is a powerful and useful method that has been used to characterize many of the electrical properties of IEMs[31]. A through-plane cell arrangement allows for an effective system to study the main parameters of SPEEK ion exchange membranes.

5.2.2.1 Conductivity

Impedance spectroscopy was used to determine the electrical through-plane resistance of membrane samples by applying an alternating potential across an electrochemical cell and measuring the resulting AC current as a function of the applied frequency. The 4-electrode cell setup is shown in Figure 5.1. Both compartments contained 0.5M NaCl separated by 1 cm² of the membrane. The schematic shown in Figure 5.2 represents the cell set up for resistance measurements across the membrane interface. The configuration allows for measurement of the liquid-liquid interface potential of the two electrolytes, E_{CE}, separated by the membrane. The membrane through-plane resistance can be determined by subtracting the resistance of a blank cell from the total cell resistance measured at the zero phase angle. Two platinum (Pt) electrodes supply a constant current across the cell and the two Ag/AgCl electrodes record the voltage drop in response. A frequency range from 1MHz to 1mHz and an AC amplitude of 10mV was applied.
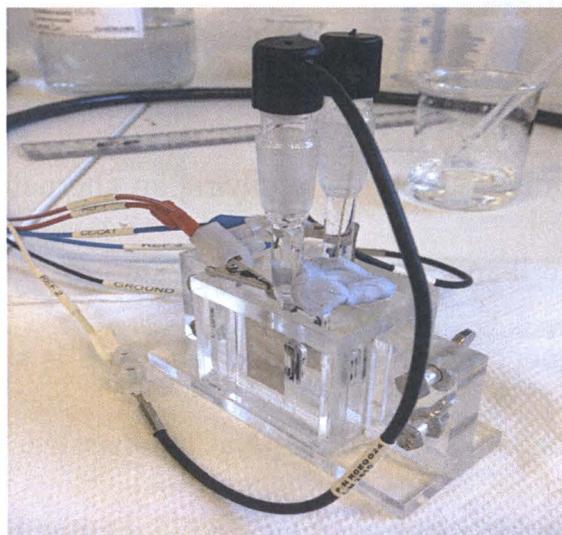
Figure 5.1: Four-electrode electrochemical cell setup for measuring cell resistance
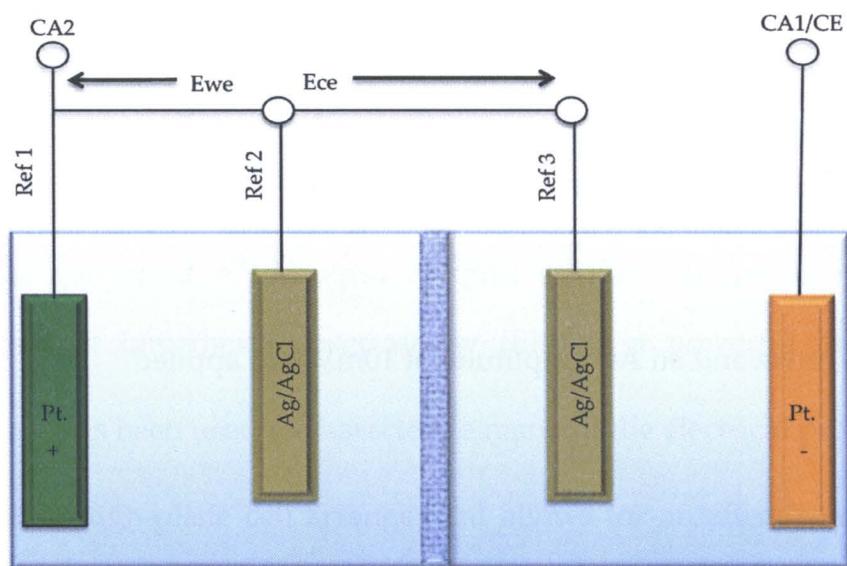

Figure 5.2 Schematic representation of cell arrangement used for resistance measurements

EIS is a useful electrochemical technique for directly determining solid-state polymer resistances[32]. Using EIS, the cell impedance can be plotted versus frequency[33]. The voltage is linked to the current through the impedance vector expressed as:

Equation 5.10:

$$Z(\omega) = Z_{Re} - jZ_{Im}$$

Where Z_{Re} and Z_{Im} are the real and imaginary parts of the impedance, respectively. The current response leads or lags in relation to the voltage by a phase angle, ϕ.The measured total impedance of the cell, Z, can be expressed as:

Equation 5.11:

$$|Z|^2 = (Z_{Re})^2 - (Z_{Im})^2$$

and the phase angle, ϕ, given by:

Equation 5.12:

$$\tan \phi = \frac{Z_{Im}}{Z_{Re}} = \frac{X_C}{R} = \frac{1}{\omega RC}$$

Where ω is the angular frequency, which is 2π times the conventional frequency in *Hz*, *R* is the resistance and *C* is the pure capacitance of the resistor. Both real and imaginary aspects of the impedance are measurable by phase angle.

Using the Bode Plot, the $\log |Z|$ and ϕ are plotted against $\log \omega$. An alternative representation can be visualized used the Nyquist plot, which displays Z_{Im} against Z_{Re} for different values of ω. As $\omega \to 0$, the plot of Z_{Im} *vs.* Z_{Re} becomes linear and the resistive component is represented by the value of the real impendance.

To establish the membrane conductivity, membrane resistance is defined as this measured cell resistance minus the average resistance taken for a blank cell with no membrane present.

Equation 5.13:

$$R_{mem} = R_{cell} - R_{blank}$$

Specific membrane conductivity can then calculated by:

Equation 5.14:

$$\sigma_{mem} = \frac{d}{RA}$$

Where σ_{mem} is the membrane specific conductivity (S/cm), d is the wet membrane thickness (cm), A is the membrane cross-section (1 cm²) of the cell, and R is the bulk membrane resistance (Ω) determined from the Nyquist plot

5.2.2.2 Transport Number

The transport number (t_+) is defined as the fraction of the total current carried through an electrolyte by a given ion[34]. For example, given a 100% permselective membrane, all of the current is carried by counter ions, and will have a membrane transport number of 1 while the co-ions will have a transport number of 0[35]. The total conductivity through the membrane can be expressed as:

Equation 5.15:

$$\sigma_{tot} = \Sigma_k \sigma_k$$

The transport number can then be defined as:

Equation 5.65:

$$t_k = \frac{\sigma_k}{\sigma_{tot}} = \frac{\sigma_k}{\Sigma_k \sigma_k}$$

In this analysis, the transport number of Na^+ was studied as the model

species. The open circuit voltage (OCV) procedure is typically used to achieve

equilibration of the electrochemical cell as a pre-conditioning method for

other EIS experiments. As such, OCV was applied on the set-up shown in

Figure 5.3 directly prior to the cation transport measurements of Na^+. A two-

compartment cell was used with two platinum electrodes to measure the

resting potential. The membrane sample was clamped between the EIS cell

with a 1cm² cross-section separating the compartments.
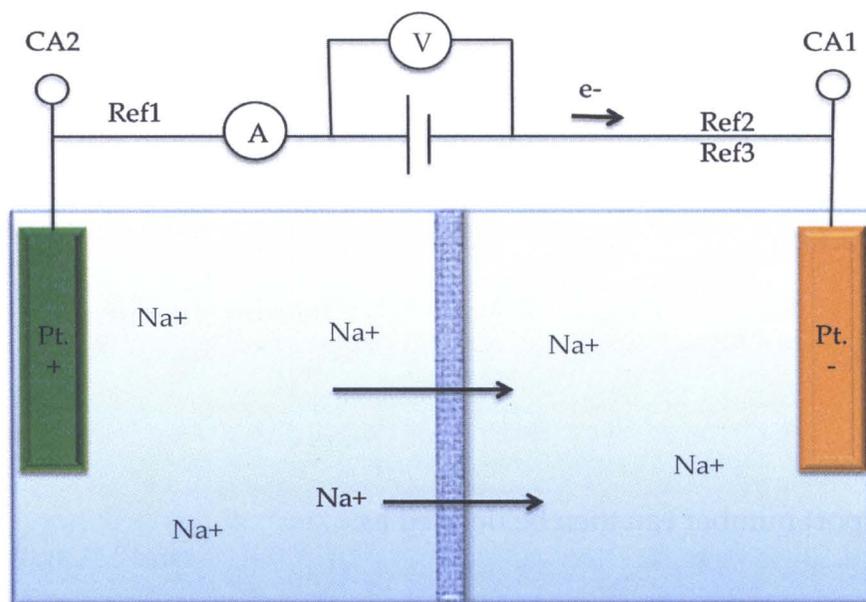
Figure 5.3: Two-compartment, two-electrode setup in the initial state for study of ion transport

One section was filled with 0.5 M NaCl and the other with 0.1 M NaCl to

produce a concentration gradient across the membrane. When a membrane

separates electrolyte solutions at different concentrations, an electrical

potential difference develops across the membrane[32]. The platinum reference

electrodes monitored this potential, which was plotted against time. The OCV

was measured where no potential or current is applied to the working

electrodes. The resting cell potential, E_M, was recorded when the system

reached steady state.

Equation 5.17:

$$\varepsilon_M = \frac{RT}{F}(2t_+ - 1)\ln\left(\frac{C_1}{C_2}\right)$$

Where ε_M is the cell potential (mV), R is the molar gas constant (8.31447 J mol⁻

¹ K⁻¹), T is the absolute temperature (K), F is the Faraday constant, t_+ is the

transport number of the cation under investigation, and C_1 and C_2 are the

concentrations of the electrolyte in the different chambers (C_1 = 0.5 M of NaCl,

C_2 = 0.1 M of NaCl).

Analysis of the sodium transport number describes the transport rate of Na^+

across a membrane. The transport number of an ionic species is dependent on

the mobilities of all the ions in the electrolytic solution, on the concentrations of the ions, and on the temperature of the solution[34,36]. The ion transport number gives an indication of an ion's electrical mobility. This provides information as to the rate of ion permeation through the membrane.

5.2.2.3 Cation Selectivity

To determine a membrane's capacity to preferentially transport certain cations based on valency, a novel method was developed to compare the concentration of several cations (K^+, Ca^{2+}, Cu^{2+}, Fe^{3+}) to the concentration of the reference monovalent ions, Na+, transported across the membrane under an applied current. The cell set-up is illustrated in Figure 5.3, which was equilibrated by first establishing steady state potential. Each membrane was tested for the transport of ions; Na^+, K^+, Ca^{2+}, Cu^{2+}, and Fe^{3+}. The following binary solutions were used for the initial state in the anode compartment.

- 0.5M KCl/0. 5 M NaCl;

- 0.5M $CaCl_2$/0. 5 M NaCl;

- 0.5M $CuCl_2$/0. 5 M NaCl;

- 0.5M $FeCl_3$/0. 5 M NaCl;

The initial cathode side was filled with a 0.1M NaCl solution. After the cell reached steady state, a maximum current of 60 mA was applied. In chronocoulometry mode, the total charge transferred (ΔQ) across the circuit was recorded as the electrochemical response to the applied potential.

Five samples of ~20μL were taken from the cathode compartment every hour. A Perkin-Elmer Optima 7000 DV ICP-OES spectrometer was used to measure the precise ion concentrations in these solution samples. The samples were first diluted several times with ~15mL aliquots of 2% nitric acid to achieve a mass dilution factor suitable for analysis within the ICP-OES calibration curve of 1-10ppm.

In this study, Na^+ is a common ionic species present in most wastewater solutions and can be used as the reference monovalent cation. Membrane selectivity, $\alpha_{Na^+/i^{n+}}$, is calculated using the following equation.

Equation 5.18:

$$\alpha_{Na^+/i^{n+}} = \frac{[Na^+]_c - [Na^+]_{c_0}}{[i^{n+}]_c - [i^{n+}]_{c_0}}$$

Where i^{n+} denotes the relevant cation, $[Na^+]$ and $[i^{n+}]$ refers to the concentrations of sodium and the comparative cation, respectively, and the

subscripts c and c_0 referring to the cathode side when the sample was taken and at the initial state, respectively. This measures the amount of sodium ions transferred across the membrane with respect to the amount of the other ion transferred from the binary solution.

5.3.   Results and Discussion

5.3.1   Conductivity

Membrane conductivity is a crucial parameter for cell performance. A Nyquist Plot was plotted for each sample tested, and the cell resistance determined at the x-axis intercept as $\omega \to 0$, as shown in Figure 5.4, where the resistive component is represented by the real impedence value. This is a typical Nyquist Admittance curve, where the resistance is taken directly from the low frequency intercept.
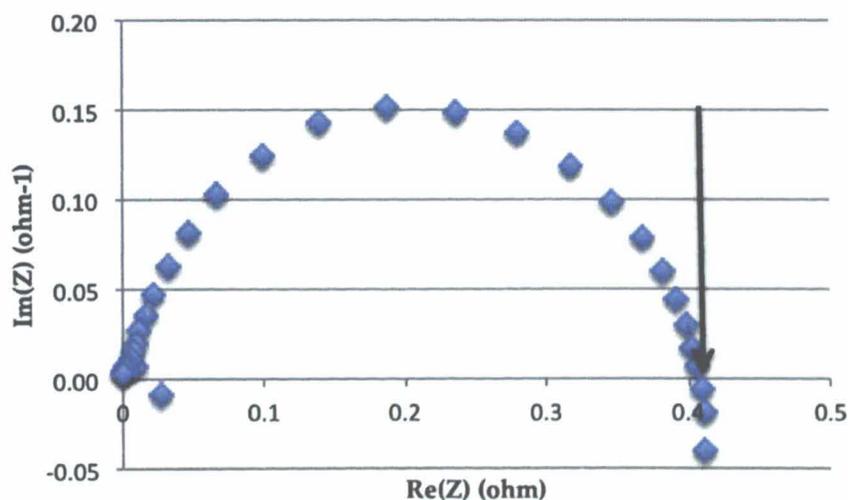
Figure 5.4: Example Nyquist Admittance Plot of SPEEK-SiO₂-NH₂(5%) membrane with arrow

indicating real impedence measured

Measurements were taken for several blank cells to determine the average blank cell's resistance. A Nyquist plot was recorded for at least three samples

of each SPEEK and SPEEK nanocomposite membrane. The average conductivity of each membrane is presented in Figure 5.5 with error bars of one standard deviation.

Sample membranes of Nafion® 117 and pure SPEEK were used as references in Figure 5.5. SPEEK-TiO$_2$-NH$_2$ was found to have extremely high conductivities compared to the references and to the other nanocomposites. Figure 5.6 presents the conductivity of the membranes with a smaller scale of the y-axis to visualize the remaining nanocomposite membrane conductivities.
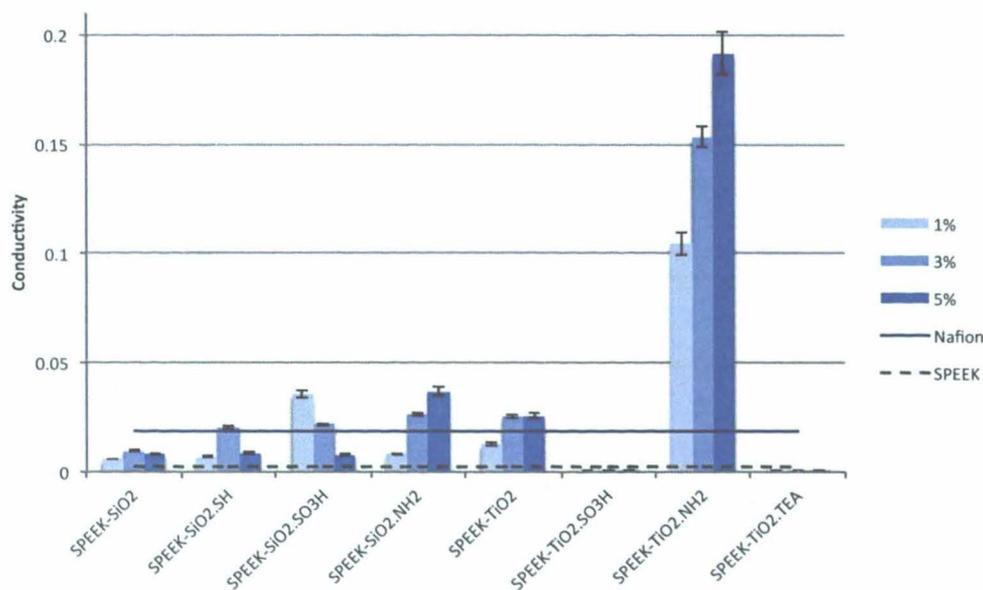
Figure 5.5: Conductivity of SPEEK nanocomposite membranes
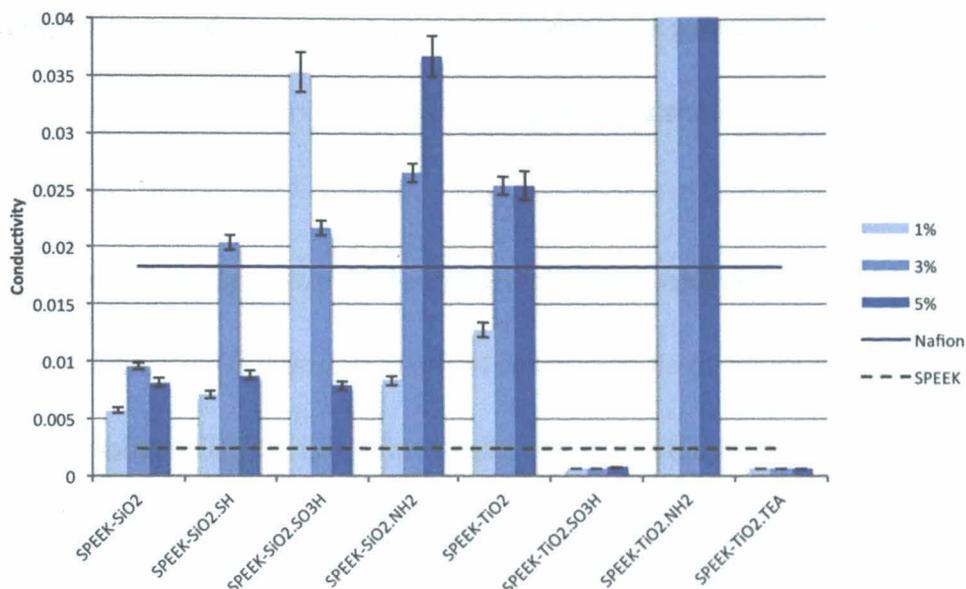
Figure 5.6: Conductivity of SPEEK nanocomposite membranes - rescaled y-axis

The conductivity of the Nafion® 117 membrane sample was measured as 0.0182 S/cm. The conductivity of pure SPEEK was found to be much lower at 0.0024 S/cm, which is consistent with previous studies[37-39]. This lower conductivity is still viable for commercial use as the material cost can be significantly reduced and other properties may compensate for other performance parameters.

Nearly all of the nanocomposite membranes had higher conductivities than the pure SPEEK membranes, except for SPEEK-TiO$_2$-SO$_3$H and SPEEK-TiO$_2$-TEA. In Chapter 4, the nanocomposite membranes were found to have significantly less water uptake than the pure SPEEK membrane. The higher

conductivities found here indicates that the nanoparticle fillers provides additional pathways for ion transport through the membrane other than the water mediated channels expected in pure polymer membranes.

The titania nanoparticles modified with –TEA were studied with SEM in Chapter 4 and found to sit on surface of the membrane. This morphology may restrict ions from penetrating the membrane skin. This would reduce the transport of ions through the bulk of the membrane, which explains the very low conductivity of the SPEEK-TiO_2-TEA membranes.

Both the silica and titania additives functionalized with –NH_2 were found to increase conductivity significantly with increased loading concentrations of nanoparticles in the SPEEK nanocomposite membranes. This surface functionalization increases pathways for ion transport. The hydrogen ions of the amine group are readily dissociated, facilitating proton movement through the membrane. H-bonding between functionalized nanoparticle surface and the sulfonic acid groups on the SPEEK polymer chains also contributes to increased regions for ion transfer while maintaining dimensional stability. In particular, SPEEK-TiO_2-NH_2 with loadings of 1-5%w/w were found to exhibit water uptake values of ~15%w/w while maintaining very high conductivities of 0.104-0.192 S/cm. The conductivity of the SPEEK membranes integrated with SiO_2-NH_2 and TiO_2-NH_2 was also

found to be proportional to the loading concentration of the nanoparticles. This indicates that within the 1-5%w/w range, nanoparticles are still sufficiently dispersed to ensure high surface to volume ratio of the nanoparticles. Interactions with the polymer chains and the nanospheres are not reduced by nanoparticle agglomeration at these concentrations.

In contrast, SPEEK-SiO_2-SO_3H resulted in lowered conductivity with increased sulfonated silica loading. At 1%w/w nanoparticle concentration, a higher conductivity of 0.035 S/cm was found. This SPEEK composite membrane showed better dispersion of the nanoparticles through the polymer matrix structure. Increased loading may result in increased agglomeration, causing most of the additional sulfonic acid groups to exist in the agglomerated bulk, rather than at the surface where they are able to interact with the polymer network. This was seen in previous studies using nanoparticle concentrations of 5 and 10%w/w where little conductivity difference was found between nanocomposite membranes loaded with unmodified and sulfonated silica[40]. Here, the SPEEK-SiO_2-SO_3H at 1% and 3%w/w loading resulted in conductivities higher than that of Nafion® 117. At 5%w/w, however, the conductivity is similar to that of the unfunctionalized SPEEK-SiO_2 membranes. The lower nanoparticle concentration allows for better dispersion where the mixed matrix structure improves ion transport.

The mechanism for conducting ions through functionalized ion exchange membranes can be attributed to both Grotthuss-type and vehicle-type mechanism[23,27]. Vehicle-type ion transport occurs in hydrophilic regions formed by the clustering of sulfonic acid groups, where hydrated protons are able to migrate. This is the predominant kinetic pathway for most polymer membranes. The unmodified SiO_2 and TiO_2 particles showing improved conductivity compared to pure SPEEK indicate that such additional hydrophilic domains have been introduced. Grotthuss-type mechanism can occur in regions where the functional groups interact with the sulfonic acid groups on the polymer chains by hydrogen bonding[41]. Free protons and other cations are able to diffuse through the composite network through the formation of covalent and hydrogen bonds with the fixed charged groups of the embedded nanoparticles. This hopping mechanism is shown in Figure 5.7 and phenomena may be most prevalent in the highly conductive SPEEK loaded with silica modified with –SH, –SO₃H and –NH₂, and in the titania modified with –NH₂.
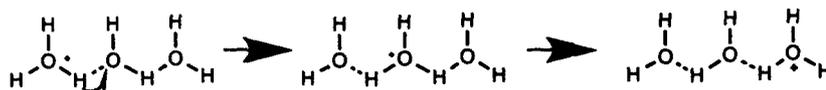

Figure 5.7: Grotthuss proton-hopping mechanism of ion transport

While interactions between the fillers and polymer matrix allows for improvements to the membrane's stability, as discussed in Chapter 4, the influence of the loading concentration and the functional groups must also be considered when designing IEMs with good electrochemical properties. Polymer conductivity depends on a several factors, including casting conditions, relative humidity, and the cell configuration for measuring film resistance. Incorporating the inorganic fillers of SiO_2, SiO_2-SH, SiO_2-SO₃H, SiO_2-NH₂, TiO_2, and TiO_2-NH₂ can dramatically enhance the ion conductivity of SPEEK membranes while maintaining suitable physicochemical structure.

5.3.2   Transport Number

The transport numbers of sodium for each membrane was calculated on the basis of the resting potential recorded from the OCV procedure and presented in Figure 5.8. Nafion® 117 was found to have a sodium transport number of 0.87, consistent with literature values of ~0.9, which shows a relatively high permselectivity for the cation counter ions over coions[24,28]. Pure SPEEK membranes were also shown to have high permselectivity with a sodium transport number of 0.80. The unmodified silica and titania nancomposite membranes were found to have comparatively low transport numbers, indicating that the transport rate of sodium across these membranes is low. The agglomeration of these unmodified nanoparticles may restrict the

mobilities of cations through the membrane. SPEEK-TiO$_2$-TEA also showed low transport rates of sodium. As previously discussed, the nanoparticles residing on the external membrane skin may limit the penetration of Na+ cations into the membrane, limiting their through-plane transport. The structure and thickness of this skin layer is known to affect transport properties[42].

All other modified nanocomposite membranes were found to have reasonably high sodium transport numbers above 0.8. These membranes show good ionic mobility where the monovalent cations are able to permeate freely through the membrane.
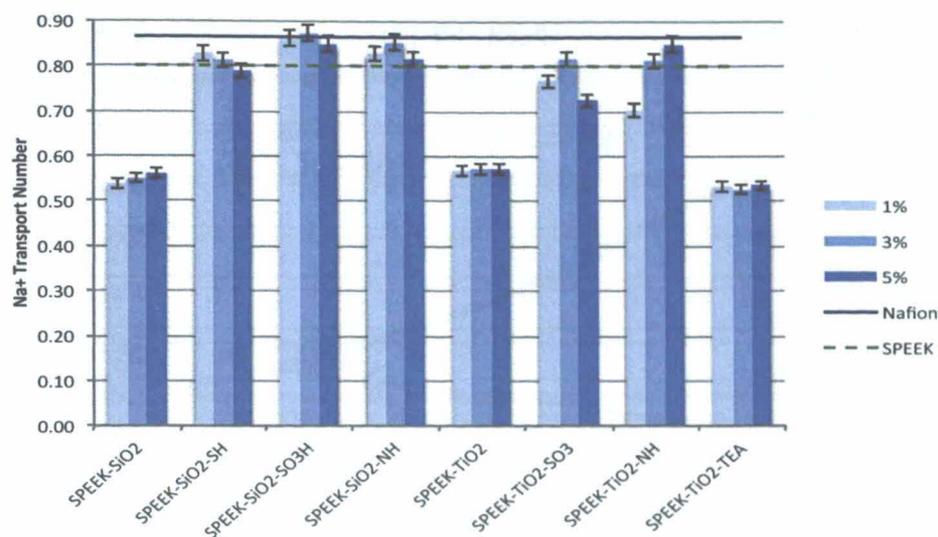
Figure 5.8: Na+ transport number for SPEEK nanocomposite membranes with 1, 3, and

5%w/w nanoparticle loadings

5.3.3 Cation Selectivity

It was found that at least three dilutions of 2%w/w nitric acid was necessary

to achieve concentrations within the range of 0-10 ppm, which allowed for

interpolation inside the ICP-OES calibration. Figure 5.9 exemplifies the

transport rate of K^+ ions through an unmodified SPEEK membrane sample.

As current is applied, the concentration of K^+ ions in the anode decreases as

they are transferred to the cathode side, which subsequently increases the K^+

concentration. The flux rates determined from fitted linear gradients were

similar in magnitude for the anode and cathode, indicating consistent molar

transfer in opposite directions.

SPEEK - ICP [K+]
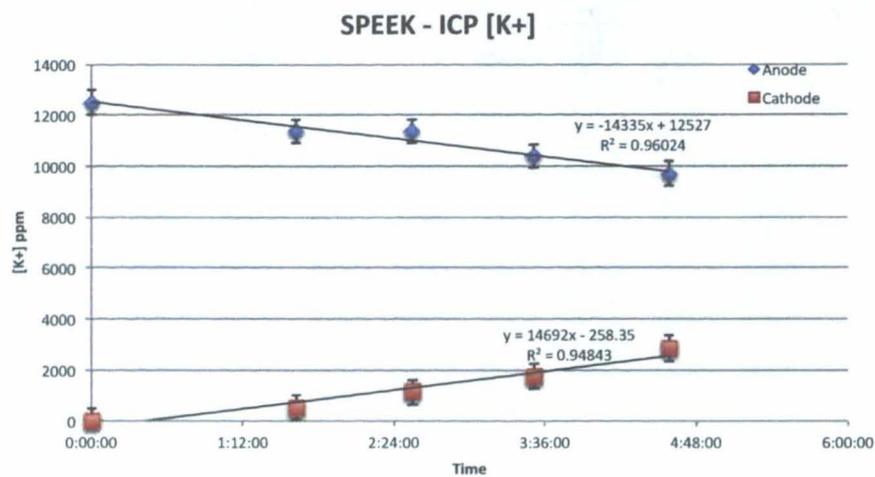
Figure 5.9: ICP-OES measured concentrations of anode and cathode samples as a function of

time

In chronocoulometry mode, the total charge transferred (ΔQ) was recorded as the electrochemical response to an applied potential. Figure 5.9 shows a typical example curve for the recorded plot of SPEEK-TiO$_2$-TEA.
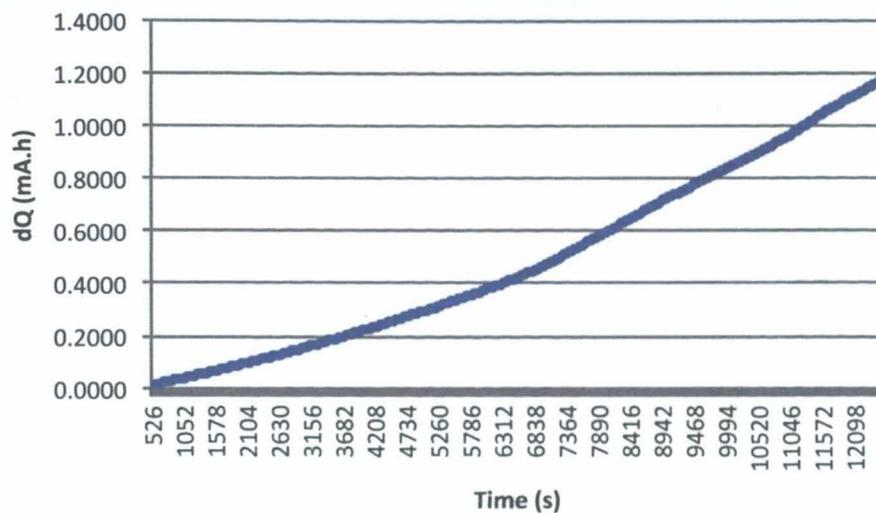
Figure 5.10 Accumulated charge vs. time of SPEEK-TiO$_2$-TEA membrane in 2-compartment

cell

Direct samples were taken every hour to provide several points for the average selectivity determined for each ion pair. Figure 5.11 presents the selectivity values for the SPEEK and SPEEK based nanocomposite membranes. Figure 5.12 shows this same graph plotted on a smaller y-axis for comparison of the membranes with lower ratios. Membranes with a selectivity values over 1 suggests a preference for sodium transport. A selectivity of 1 indicates that the cations are transferred at the same rate. Selectivity of less than one means that the other ion has a higher rate of transport than Na$^+$.
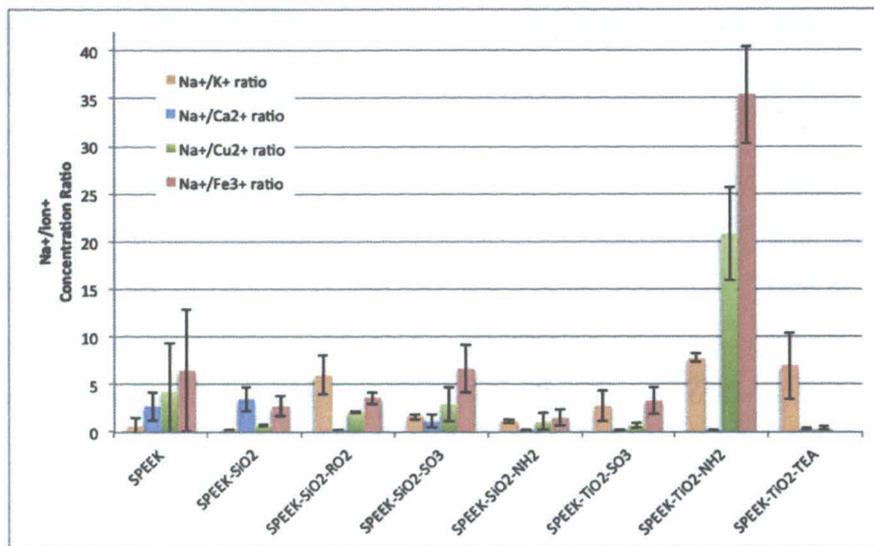
Figure 5.11: Selectivity of Na$^+$/(K$^+$, Ca^{2+}, Cu^{2+} and Fe^{3+}) for SPEEK and SPEEK nanocomposite
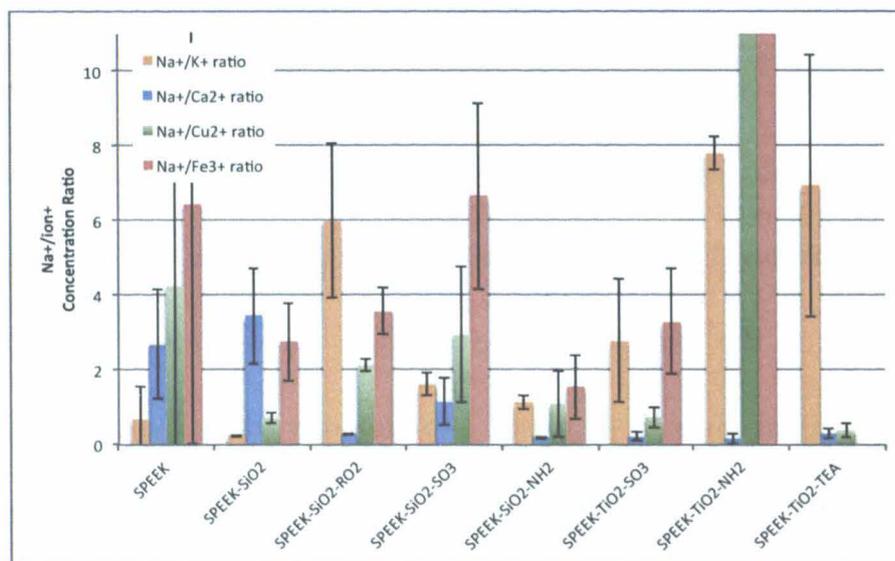
membranes

Figure 5.12: Selectivity of Na$^+$/(K$^+$, Ca^{2+}, Cu^{2+} and Fe^{3+}) for SPEEK and SPEEK nanocomposite

membranes on closer y-axis scale

SPEEK-TiO$_2$-NH$_2$ shows very high preference for the transport of Na$^+$ ions,

with 21 times the amount of Cu^{2+} and 35 times the amount of Fe^{3+} ions

transferred through the membrane. This membrane was also shown to have a low water uptake of 15%, showing good dimensional stability and indicating different pathways are used for ion transport other than water mediated channels. These membranes have also been shown to have good room temperature conductivity of 0.15 S/cm for membranes with loading concentrations of 3%w/w of TiO_2-NH_2 to SPEEK. Na^+ was also observed to transfer through the membrane at nearly 8 times the rate of K^+. Though both were monovalent cations, the potassium ions may be limited by their larger size by smaller conductive pathways in this membrane structure.

While the selectivity ratios of Na^+/K^+ were expected to be close to unity as both ions were monovalent, SPEEK-SiO_2-SH, SPEEK-TiO_2-SO_3, SPEEK-TiO_2-NH_2 and SPEEK-TiO_2-TEA showed unexpectedly high selectivity for Na^+ ions over K^+. Membrane rejection characteristics are not only based on charge, but are also influenced by ion size. In **Error! Reference source not found.**, the ionic radius and hydrated radius of the tested cations are summarized[43]. The ionic radius of Na^+ is smaller than K^+, however, K^+ ions have more electron shells insulating the positive nucleous, so K^+ ions attract fewer molecules of water for hydration, giving it smaller hydrated radius. Previous aqueous gel sieving chromatography studies showed that small monovalent ions (Na^+) flow through the matrix with water molecules attached, whereas large monovalent ions (K^+) are bound less strongly to the adjacent water molecules

and undergoes partial dehydration to permeate the membrane[44]. This may indicate why sodium was more readily transported through these membranes.

In aqueous solutions, non-covalent interactions define the arrangement of molecules and ions. These weak forces allow the relative positions of the ions and molecules to continually rearrange. The ionic potential indicates how strongly the electrostatic attraction or repulsion forces will affect like or opposite charges and is correlated to the ratio of the ionic charge to the ionic radius. Similarly, the hydration potential indicates how strongly an ion will interact with the surrounding water molecules[45]. Ions hydrated by this shell of dipolar water molecules must be considered as a complete mobile unit rather than just as the bare ion[46]. The effective diameter of the cation is a critical factor in determining the membrane's selective transport preferences[45].

The hydrated radius influences the ion's selective permeation through the membrane as well as the charge and ionic radius. Ion transport is hindered when the effective pore radius is smaller than the hydrated radius, as the ion has to first lose associated water molecules to enter the membrane channels. Ions with less strongly bound shells may actually detach from their hydration layer while passing through the membrane. Differences in the strength of the binding of these hydration shells may also influence the selective permeation

phenomena. Hydration energy affects the hydration tendency of ions, strength of hydration shells, and the number of water molecules that can be accommodated within the hydration shell. The strength of hydration shells also depend on the ionic characteristics of the solution such as ionic strength, pH and temperature. The hydration free energy for the cations sampled have been ordered as $K^+ < Na^+ < Ca^{2+} < Cu^{2+} < Fe^{3+}$, where a lower hydration free energy allows ions to easily detach water molecules in their hydration shells and permeate the membrane more readily[43,46]. Previous studies have shown that in free energy profiles for ion transport through selective channels, energy barriers depend on pore size, ion type, and membrane surface charge[47].

Ion selectivity of the membrane is governed by differences in relative free energies between solution and membrane phases, allowing some ions to permeate either by size exclusion or by the ability to rearrange the hydration waters under shear forces during transport. An unexpected trend was noted for the rate of Ca^{2+} transfer for $SPEEK-TiO_2-NH_2$ to be higher than Na^+. Similarly for $SPEEK-SiO_2-SH$, $SPEEK-SiO_2-NH_2$, $SPEEK-TiO_2-SO_3$, $SPEEK-TiO_2-NH_2$ and $SPEEK-SiO_2-TEA$, the Na^+/Ca^{2+} selectivity was found to be lower than 1, indicating higher rates of transport of Ca^{2+} compared to Na^+. As the hydrated radius and hydration free energy of Na^+ is lower than that of Ca^{2+}, a higher transport rate of sodium was expected. This phenomenon may

be explained by differences in the ion sizes. While the hydrated radius of sodium is smaller than that of calcium, the ionic radius of calcium is slightly smaller than that of sodium. There may also be differences in the strength of binding of their hydration shells that explain the higher rate of transport of Ca^{2+}. In an aqueous solution, calcium is a free ion with very few surrounding electron shells[47]. Hence, the Ca^{2+} ion attracts many water molecules. During transport through the membrane, shear stress created by transmembrane pressure may cause the ions with relatively weak hydration potential to rearrange their hydration shells[48]. Ca^{2+} ions, with weaker hydration shells, may detach from their hydration layer, allowing them to more readily pass through the membrane. For relatively larger ions with more dispersed charge, hydration shells are held by a weaker electric field in comparison to smaller ions with stronger electrical fields[46,49].

Table 5.2: Ionic radius, hydrated radius and hydration free energy of tested cations

Ion	Ionic Radius (nm)	Hydrated Radius (nm)
Na+	0.098 – 0.117	0.276 – 0.360
K+	0.133 – 0.152	0.201 – 0.331
Ca2+	0.100 – 0.123	0.412 – 0.420
Cu2+	0.072 – 0.077	0.419
Fe3+	0.064	0.480

Other promising candidate materials with selective properties for monovalent cation transfer include plain SPEEK, which shows high selectivity for Na^+ compared to Ca^{2+}, Cu^{2+} and particularly Fe^{3+}. SPEEK-SiO_2 showed the highest Na^+/Ca^{2+} selectivity ratio of 3.4 and a reasonable Na^+/Fe^{3+} selectivity of 2.7. However, the rate of transfer of Na^+ compared to Cu^{2+} was nearly identical as the ratio was near unity. SPEEK-SiO_2-SO_3 also showed good selectivity ratios of 2.9 for Cu^{2+} and 6.7 for Fe^{3+} and, with a low water uptake of 16%, wmay be promising for the separation of these cations.

SPEEK-SiO_2-NH_2, despite having a good conductivity of over 0.26 S/cm, had selectivity ratios of K^+, Cu^{2+} and Fe^{3+} to Na^+ of nearly all 1, indicating that all the cations were transferred through the membrane at the same rate regardless of valency. This may be useful to consider for other applications that require equal cation transport.

No concentration data for Fe^{3+} was available for membrane SPEEK-TiO_2-TEA. However, from the low Ca^{2+} and Cu^{2+} selectivity ratios, the selectivity ratio of Na^+/Fe^{3+} is not expected to have much potential. With poor morphology, poor conductivity and a low Na transport number, this membrane is not expected to be particularly useful for commercial applications.

5.3.4   SPEEK Nanocomposite Membrane Matrix Structure

The mobility of free ionic species through a thin film is highly dependent on the physicochemical structure of the membrane. The addition of nanoparticles has been seen to reduce water uptake, which demonstrates an influence on the dimensional stability of the polymer matrix. These fillers have also shown an effect on the conductivity and ion transport rates. It is evident that the inclusion of nanoparticles and their functionalization affects the charge channels through the membrane structure.

Unmodified nanoparticles were found to readily agglomerate in the membrane bulk section. The lack of uniform dispersion results in the formation of clusters, which reduces the surface area to volume ratio. Fewer potential interactions between the surface charges and polymer chains are available to stabilize the matrix.

The nanoparticle fillers influences the polymer chain folding by providing new hydrophobic and hydrophilic regions, which subsequently develops new ionic channels. These channels enhance proton conductivity while allowing for reduced water uptake. The membrane morphology influences the phase separation between these hydrophilic and hydrophobic domains. These hydrophilic domains allow for the membrane's water uptake. The polymer

backbone is hydrophobic and will fold into regions that provide mechanical integrity to the structure. Ion transport is also dependent on the connectivity between the domains.

The modified inorganic fillers integrate well with the SPEEK chains as surface modification generates repulsion between the nanoparticles, dispersing the particles with even spacing throughout the polymer matrix. Functionalized surfaces are able to bind covalently or through H-bonding to the polymer chains. Amine groups were found to most significantly influence dispersion through the membrane, and also resulted in membranes with low water uptake, high conductivity and high selectivity for Na+ transport.

A SPEEK polymer ion exchange membrane cross-section, as illustrated in Figure 5.13, consists of a bulk interior with denser membrane surface skins due to different rates of solvent evaporation. A matrix is formed by the SPEEK polymer backbone, where the sulfonic groups on the SPEEK chains cluster to form hydrophilic domains. These sulfonic groups readily dissociate and have a negative charge available for interaction with positively charged surface functionalization. Amine groups do not dissociate as readily and molecular folding creates a charged polarity across the $-NH_2$ structure. These allow many available sites for hydrogen and covalent bonding with the SPEEK sulfonic groups. This slight positive surface charge on the silica and

titania nanoparticles will typically create steric hindrance that restricts higher valency cations. This explains the benefits of amine functionalization to allow for selective permeation of sodium over specific multivalent ions of K^+, Cu^{2+} and Fe^{3+}. Calcium was found to permeate preferentially over sodium for this membrane and may be attributed to hydration influences. The transport of charged species through the membrane is influenced electrostatic forces but the hydration of the ions in the aqueous environment can also impact the selectivity between different cations. Membrane rejection characteristics are not only based on charge, but are also influenced by factors such as size exclusion or hydration potential of the free species.
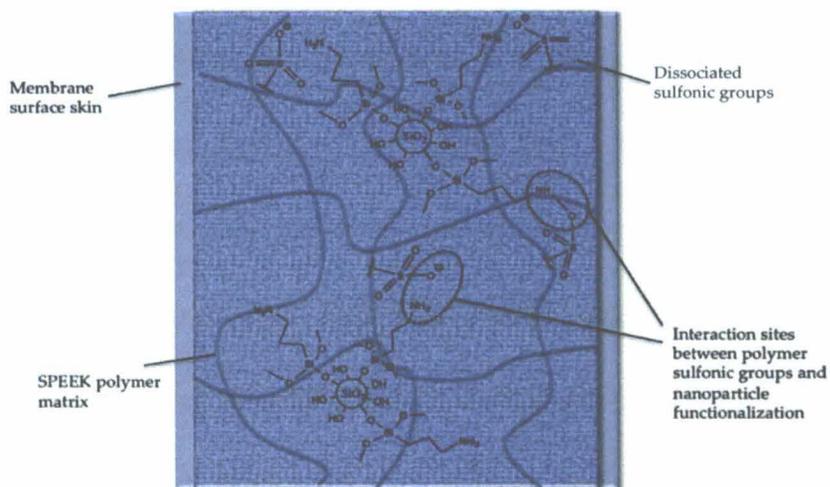
Figure 5.13: Schematic representation of the interactions between dissociated sulfonic groups on the polymer chains and the $-NH_2$ surface modification of the silica nanoparticles

The schematic structures of the other surface functionalization groups are illustrated in Figure 5.14. The dissociated sulfonic acid groups on the nanoparticle surface provides additional negative charges distributed through the membrane matrix similarly to the sulfonic groups attached to the SPEEK polymer chains. This surface charge ensures the nanoparticles are well dispersed but were not found to significantly affect membrane selectivity. The thiol groups would also dissociate, though with weaker charge polarity than the sulfonic groups having three oxygen atoms contributing to the polar charges. The structure of –TEA also provides readily dissociated sites at the – OH regions. However, the molecular folding allows this structure to interact with itself, allowing these charged sites to interact and bind back to the nanoparticle surface. The lack of embedded TiO_2-TEA in the membrane bulk may be attributed to this effective cancellation of charged sites.
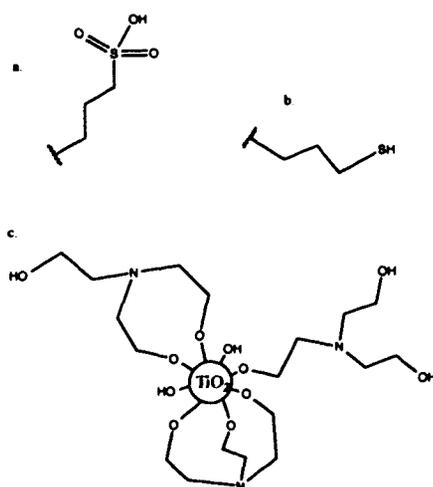

Figure 5.14: Surface functionalization groups; a. sulfonic, b. thiol, and c. triethanolamine

Introducing fillers into the polymer matrix was found to cause interesting structural changes as the porous nanoparticles have a high surface area to volume ratio and effects the distribution of the polymer chains. A schematic representation of the SPEEK membrane microstructure in Figure 5.15 shows how free ionic charges could be transported through the SPEEK membrane matrix. The embedded nanoparticles having amine functionalized surface charges create steric hindrance that restricts the permeation of large, multivalent cations. Monovalent cations are small enough to travel through these channels. The mobility of free ionic species through the charge channels has been proven to depend on the different functionalized groups on the nanoparticle surfaces. Certain surface charges and additive concentrations creates a preference for certain cations.
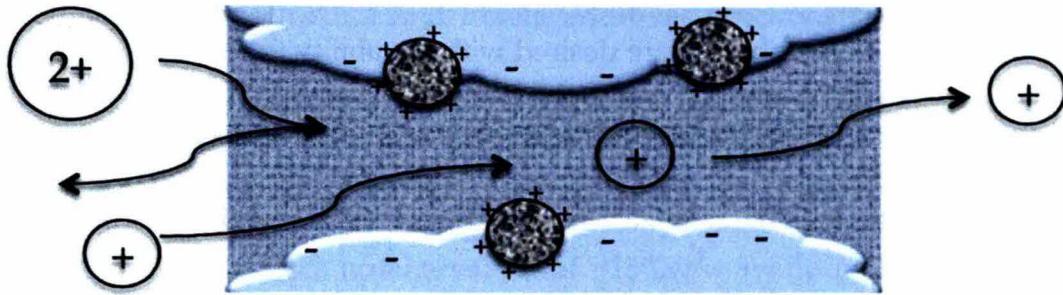
Figure 5.15 Schematic of ion transport channels where the polymer bulk is embedded with

nanoparticles (SiO_2-NH_2 or TiO_2-NH_2) with positive surface charges creating steric hindrance

for larger multivalent cations

5.4. Conclusions

Cation selective membranes are desired with the ability to separate cations of different valency. SPEEK nanocomposite membranes prepared in Chapter 4 were studied to characterize their electrochemical and ion transport performance. Several of the nanocomposite materials were determined to preferentially transport monovalent cations. This chapter provides a direct systematic comparison of several functional groups attached to silica and titania. SPEEK membranes were incorporated with silica modified with thiol, sulfonic and amine groups, and titania modified with sulfonic, amine and triethanolamine groups.

Membrane performance was investigated by electrochemical impedence techniques to determine the conductivities and transport numbers of the SPEEK based nanocomposite ion exchange membranes. Sample membranes of Nafion® 117 and pure SPEEK were used as references for comparison. The conductivity of Nafion® and pure SPEEK was found to be 0.0182 and 0.0024 S/cm, respectively, which is consistent with previous literature. Nearly all of the nanocomposite membranes had higher conductivities than the pure SPEEK membrane. SPEEK-TiO_2-TEA was an exception, which demonstrated morphologies that may inhibit ion permeation into the membrane bulk. SPEEK-TiO_2-NH_2 was found to have extremely high conductivities (0.10 – 0.19

S cm⁻¹) compared to the references and to the other nanocomposites. The conductivity of both silica and titania additives functionalized with $-NH_2$ were found to increase with increased loading concentrations of nanoparticles. In particular, SPEEK-TiO_2-NH_2 with loadings of 1-5%w/w were found to exhibit water uptake values of ~15%w/w while maintaining very high conductivities of 0.104-0.192 S/cm. This indicates that these nanoparticles were sufficiently dispersed to ensure high surface to volume ratio of the nanoparticles. A 1%w/w nanoparticle loading concentration of SPEEK-SiO_2-SO_3H also resulted in a high conductivity of 0.035 S/cm. However, conductivity decreased with increases in this nanoparticle loading. This indicates that increased loading resulted in increased agglomeration.

Sodium transport numbers calculated for the membranes gives an indication as to the rate of current transported by free sodium ions. Pure SPEEK membranes were found to have high permselectivity with a sodium transport number of 0.80. Unmodified silica and titania nancomposite membranes were found to have comparatively low transport numbers, indicating that the transport rate of sodium across these membranes is low. SPEEK-TiO_2-TEA also showed low transport rates of sodium. All other modified nanocomposite membranes were found to have reasonably high sodium transport numbers above 0.8, which demonstrates good ionic mobility with cations able to freely permeate through the membrane.

To determine the rate of ion transport through the membrane, aqueous solutions containing cation pairs of K^+, Ca^{2+}, Cu^{2+}, and Fe^{3+} were compared with Na^+ as the reference cation. Membrane selectivity was determined using the concentration change in the cathode compartment. Inorganic nanoparticles functionalized with amine groups, particularly SPEEK-TiO_2-NH_2, showed high selectivity preference for the transport of Na^+ ions over multivalent ions, except for Ca^{2+}, with 21 times the amount of Cu^{2+} and 35 times the amount of Fe^{3+} ions transferred through the membrane. This membrane was also shown to have a low water uptake of 15%, showing good dimensional stability and indicating different pathways are used for ion transport other than water mediated channels. These membranes have also been shown to have good room temperature conductivity of 0.15 S/cm for 3%w/w membrane. SPEEK-SiO_2-SO_3 is also a promising candidate material with selective preferences for monovalent cation transfer. This membrane demonstrated good selectivity ratios of 2.9 for Cu^{2+} and 6.7 for Fe^{3+} and, with a low water uptake of 16%, which indicates good dimensional stability. However, additive loadings higher than 3%w/w were found to reduce the nanocomposite's selectivity due to the agglomeration of nanoparticles. As such, 1%w/w of SPEEK loaded with SiO_2-SO_3 was found to have the most promising membrane characteristics suitable for bioelectrochemical systems.

This work also provides a detailed discussion of the structure of surface functionalization of the nanoparticles integrated into the SPEEK membranes. This provides a deep understanding of the influences on the polymer matrix structure and how certain functional group can have significant affects on the ion transport of SPEEK nanocomposite membranes. Cation transport through these nanocomposite membranes requires well-connected channels formed by ion clusters of hydrophilic sulfonic functional groups. The content and diameter of the connected channels have significant effects on the ionic transport rate. With the introduction of surface charged nanoparticles, interactions with the polymer network will influence the movement of ions through the membrane. The charge distribution of this functional group allows for strong interactions with the sulfonic groups on the polymer membrane, improving dimensional stability. $-NH_2$ does not dissociate as readily as $-SO_3H$, and the additional proton presence creates a slight steric hindrance. Dissociation of acidic groups on the surface of a particle will give rise to a negatively charged surface while a basic surface will take on a positive charge. Particularly large cations and multivalent cations would feel this charge hindrance most. Strong interactions may also allow for tighter and narrower ion channels that permeate smaller monovalent sodium but restricts the transport of larger multivalent cations. This explains the high conductivity and low water uptake capacity of nanocomposites with $-NH_2$ surface charges on the nanoparticles.

SPEEK-SiO$_2$-NH$_2$ and SPEEK-TiO$_2$-NH$_2$ are of particular interest for further study on conductive and selective membranes. The conductivity was noted to increase for the tested range of 1-5%w/w. Increased loadings above this range may see a limit in conductivity caused by agglomeration. SPEEK-SiO$_2$-SO$_3$H at 1% is also a promising candidate as a highly conductive membrane suitable for use in fuel cells and bioelectrochemical systems.

This comparison of the impact of various functional groups on nanoparticle additives in a SPEEK polymer base provides valuable insight for designing a cation selective ion exchange membrane. Previous studies on amine surface functionalization have found nanoparticle integration as a possible route to improve polymer membrane properties, however, this investigation shows the benefits directly compared to other functionalized additive options. Further investigation into the membranes selected for the most promising ionic characteristics (SPEEK-SiO$_2$-NH$_2$, SPEEK-TiO$_2$-NH$_2$, and SPEEK-SiO$_2$-SO$_3$) will be beneficial to optimize the performance of these membranes. In future studies, membranes can be tested directly in bioelectrochemical systems to determine their effectiveness in such applications. Investigation of the selectivity for additional free ion species, such as magnesium, would provide a comprehensive understanding of membrane selectivity. It would also be valuable to further study the hydration influences on the permeation

of various cations to understand the kinetics of ion transport through these

composite membranes.

5.5.   References

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CHAPTER 6

CONCLUSIONS

6.1.   Conclusions

Increasing environmental concerns in the past few decades around water usage has seen significant focus on developing efficient and sustainable water treatment systems. Ion exchange membranes (IEMs) are a promising technology that can be applied to many clean and sustainable separation processes. They can be utilized in many diverse processes such as electrodialysis and bioelectrochemical systems. However, membrane components are a significant cost contributor to developing these technologies commercially. Current perfluorinated membanes such as Nafion® are expensive and are also limited by fouling and other performance issues at temperatures above 80°C. This research project has developed several SPEEK based nanocomposite membranes that are promising candidates for use as selective cation exchange membranes in bioelectrochemical systems.

In Chapter 2, the history and fundamentals of ion exchange materials is described to provide background for this project. To gain greater insight into the economic challenges of membrane technology, several patented examples of commercial IEMs were presented as context for the many industrial applications of these membranes.

Aromatic polymers are a promising material to obtain a cost effective base to produce high performance polymer electrolytes. PEEK was functionalized with sulfuric acid to develop SPEEK membranes. A systematic study of SPEEK sulfonation and casting conditions was presented in Chapter 3. The influences of sulfonation time and temperature on sulfonation degree were investigated. Optimal preparation conditions were established for the production of reproducible SPEEK membranes with suitable IEC of 2.21 meq/g and good water uptake characteristics. Pure SPEEK membranes with excessively high degrees of sulfonation exhibited poor stability and deteriorated in an aqueous environment. This study was used to develop a high performing SPEEK material as a base for developing nanocomposite ion exchange membranes with improved ion transport performance.

Increased sulfonation temperatures and longer times were found to increase the sulfonation degree of SPEEK membranes. Sulfonation degree was limited by excessive sulfonation over 80%. At lower temperatures, over 48 hours was required to achieve reasonable membranes with sulfonation degrees. Appropriate sulfonation conditions were noted at 60°C and 6 hours to reliably reproduce high ion exchange capacity membranes of 2.21 meq/g with appropriate water uptake of 35.9%w/w. 15 – 25% concentrations of SPEEK to the casting solvent was used to produce homogenous and defect-free

membranes. These SPEEK ion exchange membranes were then used as a cost effective base for further membrane development.

To improve the electrochemical ion transport properties of SPEEK, several novel nanocomposite SPEEK based membranes were developed in Chapter 4. Silica nanoparticles were surface functionalized with thiol, sulfonic and amine groups. Titania nanoparticles were modified with sulfonic, amine and triethanolamine groups. Unmodified and surface functionalized silica and titania nanoparticles were embedded in SPEEK with 1-5%w/w nanoparticle loadings. The functionalization of the surface properties of these nanoparticle additives was confirmed by FTIR spectroscopy. The resulting nanocomposite membranes were characterized for water uptake, IEC, morphology, conductivity, ion transport properties and thermal stability. Inorganic fillers were found to modify the microstructure of the membrane with amine and sulfonic functional groups showing particular promise for improving the conductivity of the membrane. Chapter 4 and 5 provides a unique systematic comparison of the different functional groups attached to silica and titania nanoparticles. In Chapter 4, the physicochemical properties of SPEEK and SPEEK nancomposite membranes were evaluated. In Chapter 5, the structural influences on the electrochemical performance of the nanocomoposite membranes were investigated in detail.

SPEEK membrane cross-sections showed a bulk interior with dense, thin, surface skins. The functionalized nanoparticles were found to be better dispersion throughout the polymer matrix compared with the unmodified SPEEK-SiO$_2$ and SPEEK-TiO$_2$, which showed highly agglomerated inorganic regions. The improved morphology corresponded with reduced water uptake, indicating improved dimensional stability. In the presence of water, the folding of the functionalized polymer chains gives rise to nanoscale hydrophobic/hydrophilic regions. The presence of nanoparticles influences this regional morphology and subsequently alters the ionic transport potential of the membranes.

The exception of this phenomenon was noted for SPEEK-TiO$_2$-TEA, where the nanoparticles were found to sit on the membrane skin surface rather than being embedded in the bulk. The charge sites on the functional groups may fold into a structure that negates any interactive effects with the sulfonic acid groups on the SPEEK polymer chains. These nanoparticles would not interact well with the polymer network, which explains their location after drying. This material was found to have a low water uptake of ~15%, but also had particularly low conductivity and low transport rates of sodium. The presences of nanoparticles on the dense surface layers of the membrane may restrict the initial permeation of ions into the membrane, resulting in poor ionic transport properties of SPEEK-TiO$_2$-TEA.

Distinct differences in performance can be explained by the differences in the nanocomposite microstructure. Functionalized composite membranes were found to exhibit lower water uptake than pure SPEEK membranes. SPEEK-SiO_2-SO_3 and SPEEK-TiO_2-NH_2 were also found to have promising low water uptake of ~15%, showing similar structural integrity as Nafion® 117. Nanocomposite membranes were found to have good IEC values over 2.0 meq/g while maintaining this structural integrity. The membranes of SPEEK-SiO_2, SPEEK-SiO_2-SH, SPEEK-SiO_2-SO_3, SPEEK-SiO_2-NH_2, SPEEK-TiO_2-SO_3, and SPEEK-TiO_2-NH_2 are particularly promising for applications requiring good ion transport and dimensional stability.

The conductivity of pure SPEEK was found to be 0.0024 S/cm. Nearly all the produced nanocomposite membranes had higher conductivities than this, which demonstrated improved ion transport. The conductivity of both silica and titania additives functionalized with –NH_2 were found to increase with increased loading concentrations of nanoparticles. In particular, SPEEK-TiO_2-NH2 with loadings of 1-5%w/w were found to exhibit water uptake values of ~15%w/w while maintaining very high conductivities of 0.104-0.192 S/cm. A 1%w/w nanoparticle loading concentration of SPEEK-SiO_2-SO_3H also resulted in a high conductivity of 0.035 S/cm, but showed reduced dispersion at higher loadings.

In addition to separating cations and anions based on charge, membranes are desired to have the ability to separate cations of different valency. To determine the rate of ion transport through the membrane, aqueous solutions containing cation pairs of K^+, Ca^{2+}, Cu^{2+}, and Fe^{3+} were compared with Na^+ as the reference cation. Membrane selectivity was determined by the concentration change in the cathode compartment. Several of the nanocomposite materials were determined to preferentially transport monovalent cations. Inorganic nanoparticles functionalized with amine groups, particularly SPEEK-TiO_2-NH_2, showed high selectivity preference for the transport of Na^+ ions over multivalent ions, except for Ca^{2+}. These membranes have also been shown to have good room temperature conductivity of 0.15 S/cm for 3%w/w membrane. SPEEK-SiO_2-SO_3 is also a promising candidate material with selective preferences for monovalent cation transfer. This membrane demonstrated good selectivity ratios of 2.9 for Cu^{2+} and 6.7 for Fe^{3+} and, with a low water uptake of 16%, which indicates good dimensional stability. However, additive loadings higher than 3%w/w were found to reduce the nanocomposite's selectivity due to the agglomeration of nanoparticles. As such, 1%w/w of SPEEK loaded with SiO_2-SO_3 was found to have the most promising membrane characteristics suitable for bioelectrochemical systems.

Inorganic nanoparticles functionalized with amine groups, particularly SPEEK-TiO$_2$-NH2, showed very high selectivity preference for the transport of Na+ ions. This membrane was also shown to have a low water uptake of 15%, showing good dimensional stability and indicating different pathways are used for ion transport other than water mediated channels. These membranes had good room temperature conductivity of 0.15 S/cm for 3%w/w membrane. SPEEK-SiO$_2$-SO$_3$ is also a promising candidate material for industrial use with highly selective preferences for monovalent cation transfer. This membrane demonstrated good selectivity ratios for Cu2+ and Fe3+ and also demonstrated a low water uptake of 16%, which indicates good dimensional stability. However, additive loadings higher than 3%w/w were found to reduce the nanocomposite's selectivity due to significant agglomeration of nanoparticles. As such, 1%w/w of SPEEK loaded with SiO$_2$-SO$_3$ was found to have the most promising membrane characteristics suitable for use in separating cations based on valency.

This work provides a comprehensive understanding of the influences of membrane synthesis on the matrix structure and how this affects the ion transport performance of SPEEK nanocomposite membranes. The transport properties of the SPEEK nanocomposites have been discussed in terms of the distinct influences on the matrix microstructure influenced by certain functional groups. Previous studies have investigated amine functionalization

as a possible route to improve membrane properties, but this study directly compares these benefits directly to other functionalized additives. Amine-functionalized silica and titania SPEEK-based nanocomposites offer low ionic resistance, high sodium transport number, and high selectivity for monovalent cations, while also maintaining good thermal stability. SPEEK-SiO_2-SO_3 is also a membrane material with promising selective preferences for monovalent cation transfer.

These robust membranes have potential to be commercialized in bioelectrochemical separation processes that require monovalent cation selective membranes. The performance of these polymer nanocomposites should be investigated further directly in an active bioelectrochemical system, particularly to assess membrane performance in caustic environments. For large-scale applications, a cost analysis of these membrane materials would also beneficial for economic context. In future studies, the selectivity for additional free ion species, such as magnesium, would provide a more comprehensive understanding of membrane selectivity. This method for determining selectivity has potential to be further explored to assess the ion kinetics of combinations of ion species and the influences of membrane structure and composition on ion transport properties.

6.2.   Contribution to Knowledge

A cation exchange membrane has been developed using poly(ether ether ketone) (PEEK). This material is presented as an alternative to current commercial membranes. Membrane properties, including selectivity, are affected by the morphology and physicochemical structure of the material. These characteristics are controlled by precursors used in the synthesis of the material as well as by reaction and preparation conditions of the membrane. Understanding the relationships between these parameters and resulting membrane performance is essential in designing and developing a suitably robust and selective membrane. In addition to developing several membrane candidates appropriate for use in bioelectrochemical systems, this thesis provides a deeper understanding of state-of-the-art membrane design and the unique ionic transport phenomena within these novel structures.

The specific contributions to knowledge from this PhD candidature is listed as follows:

- Critical review of the current state of commercial polymer ion exchange membranes

- Optimal sulfonation conditions of 60 °C for 6 hours with a casting concentration of 10% w/w was established to produce SPEEK membranes with an IEC of 2.21 meq/g and water uptake of 36% w/w

- This thesis describes the novel manufacture of SPEEK membranes incorporated with silica modified with thiol, sulfonic and amine groups, and titania modified with sulfonic, amine and triethanolamine groups.

- Nanocomposites with loadings in the range of 1-5% w/w provided a series for direct comparison of the relative effects of surface functionalized nanoparticles on SPEEK nanocomposite membrane morphology and ion transport performance.

- The conductivities of the tested SPEEK based nanocomposites were found to be higher than pure SPEEK.

- A quantifiable and consistent technique to determine membrane cation selectivity based on comparative concentrations of transported ions in a two-compartment cell was established. To determine the rate of ion transport through the membrane, aqueous solutions containing cation pairs of K^+, Ca^{2+}, Cu^{2+}, and Fe^{3+} were compared with Na^+ as the reference cation.

- SPEEK-TiO$_2$-NH$_2$ was determined as a promising ion exchange membrane candidate having a preference for the transport of Na^+ ions over Cu^{2+} and Fe^{3+}. This membrane was also shown to have a water uptake of 15% and room temperature conductivity of 0.15 S/cm for a membrane with 3% w/w loading.

- SPEEK-SiO_2-SO_3 is also a promising ion exchange membrane material with selective preferences for monovalent cation transfer. This membrane demonstrated a water uptake of 16%. A 1% w/w nanoparticle loading concentration of SPEEK-SiO_2-SO_3H resulted in a high conductivity of 0.035 S/cm.

6.3. Recommendations For Future Work

SPEEK based composite membranes embedded with silica or titania nanoparticles surface functionalized with amine or sulfonic groups are promising candidates for cation selective membranes with good physicochemical and electrochemical performance. To determine if the surface functionalized nanoparticles with $-NH_2$ are limited by agglomeration, further investigation into the conductivity and selectivity of membrane materials with increased loadings of amine functionalized silica and titania are recommended.

Further understanding of fundamental material properties can be developed by investigating the effects of different particle shapes and sizes, such as nanorods or shells, on the morphology of additional series of SPEEK based nanocomposite membranes.

SPEEK-SiO_2-SO_3 at 1%w/w, SPEEK-SiO_2-NH_2 and SPEEK-TiO_2-NH_2 are recommended for further study in pilot or plant scale bioelectrochemical operations. The performance of these membranes should be evaluated with regard to the separation of multi-ion solutions from industrial effluent. These membranes are recommended as candidates for bioelectrochemical

wastewater treatment systems. Their performance and potential use in commercial microbial electrolysis cells for industrial wastewater treatment can be evaluated in pilot or trail systems to demonstrate their effectiveness and viability. With proven industrial performance, these SPEEK based nanocomposite membranes can provide economic and environmental benefit in the development of new membrane technologies for sustainable water management.

APPENDIX

Figure 7.1:(a)-(c) SEM Images for SPEEK

a. | 10/29/2014 10:36:10 AM | HV 5.00 kV | WD 5.0 mm | det ETD | mag ☐ 22 197 x | ⊢——— 3 µm ———⊣ MCEM Nova NanoSEM 450

b. | 8/11/2014 12:23:26 PM | HV 5.00 kV | WD 4.8 mm | det ETD | mag ☐ 10 889 x | ⊢—— 5 µm ——⊣ MCEM Nova NanoSEM 450

c.

Figure 7.2:(a)-(c) SEM Images for SPEEK-SiO$_2$

c.

| 10/29/2014 | HV | WD | det | mag □ | ⟵ 5 µm ⟶ |
| 11:20:08 AM | 5.00 kV | 5.2 mm | ETD | 8 772 x | MCEM Nova NanoSEM 450 |
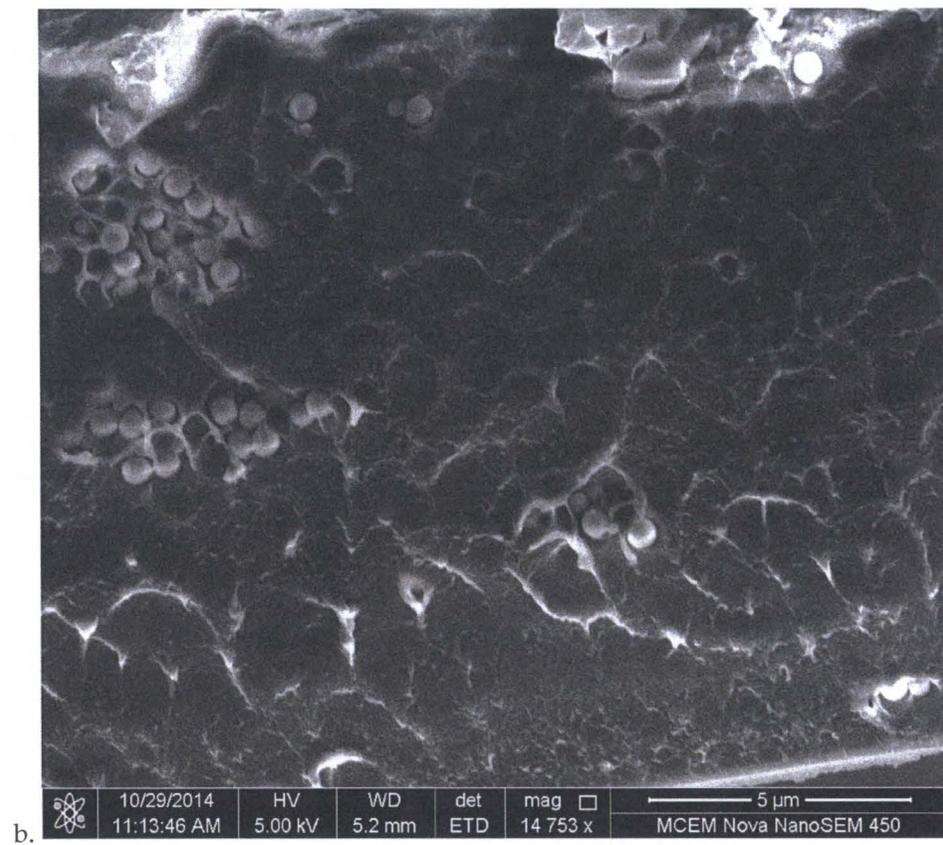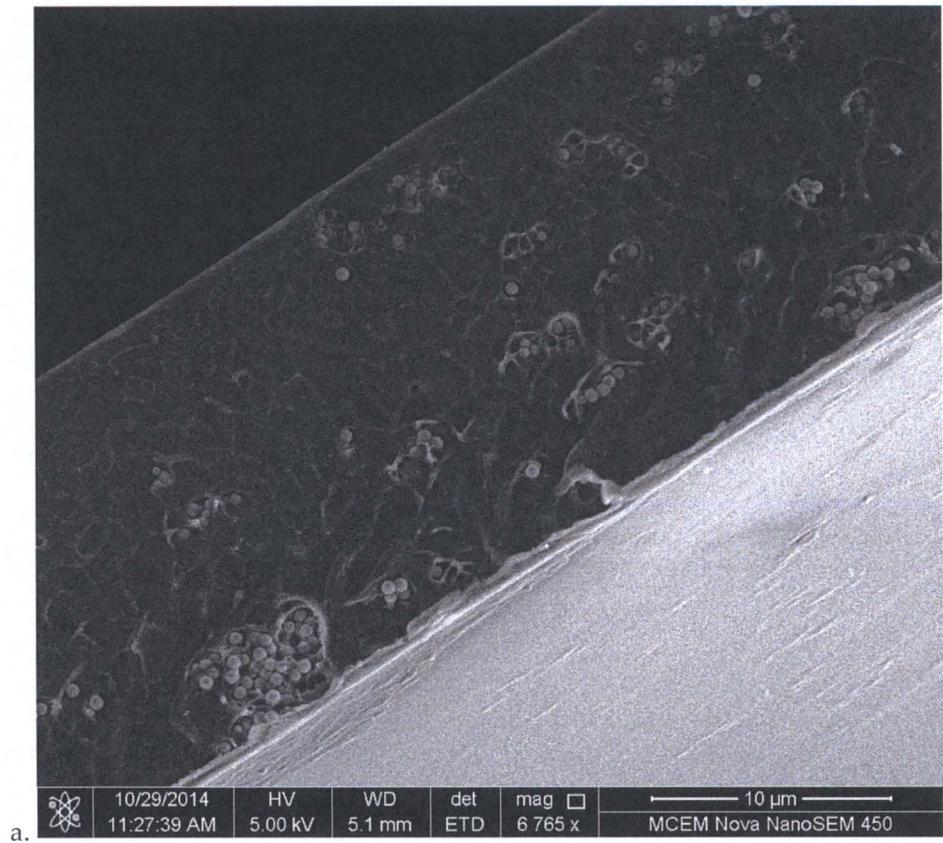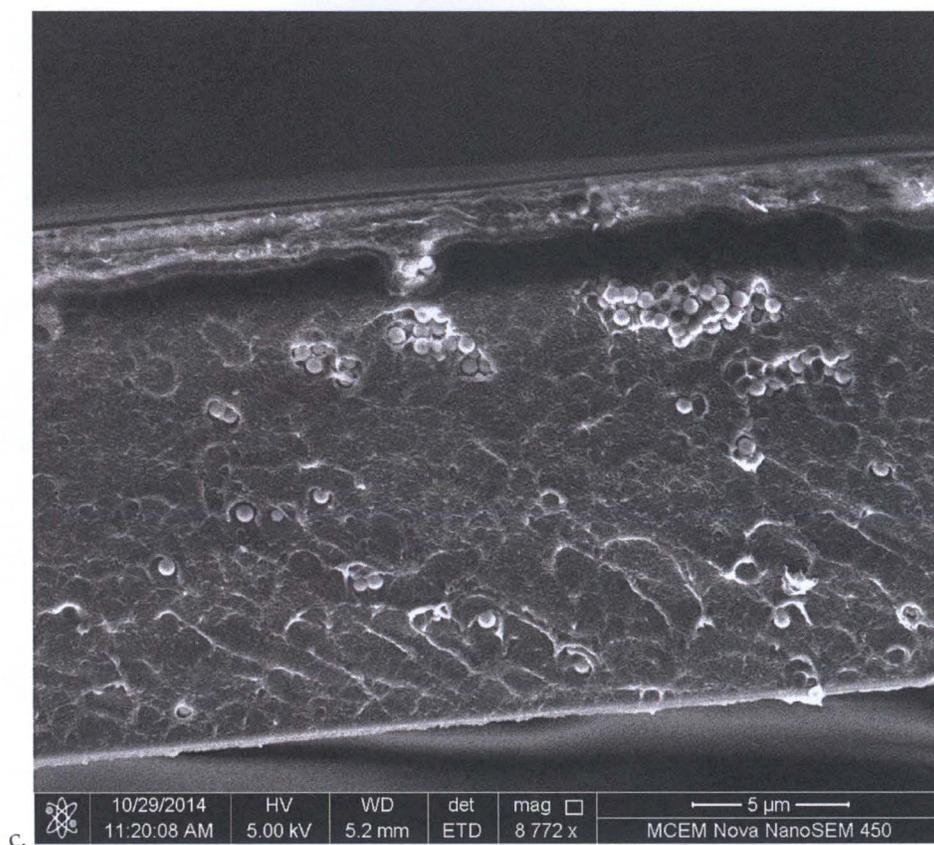
Figure 7.3:(a)-(c) SEM Images for SPEEK-SiO$_2$-SH

a.

| 10/29/2014 10:52:47 AM | HV 5.00 kV | WD 5.3 mm | det ETD | mag □ 13 198 x | ⊢————— 5 µm ————⊣ MCEM Nova NanoSEM 450 |

b.

| 10/29/2014 11:03:03 AM | HV 5.00 kV | WD 5.5 mm | det ETD | mag □ 5 272 x | ⊢———— 10 µm ————⊣ MCEM Nova NanoSEM 450 |

| 10/29/2014 | HV | WD | det | mag □ | ⊢————— 5 µm —————⊣ |
| 10:59:26 AM | 5.00 kV | 5.5 mm | ETD | 11 499 x | MCEM Nova NanoSEM 450 |

c.
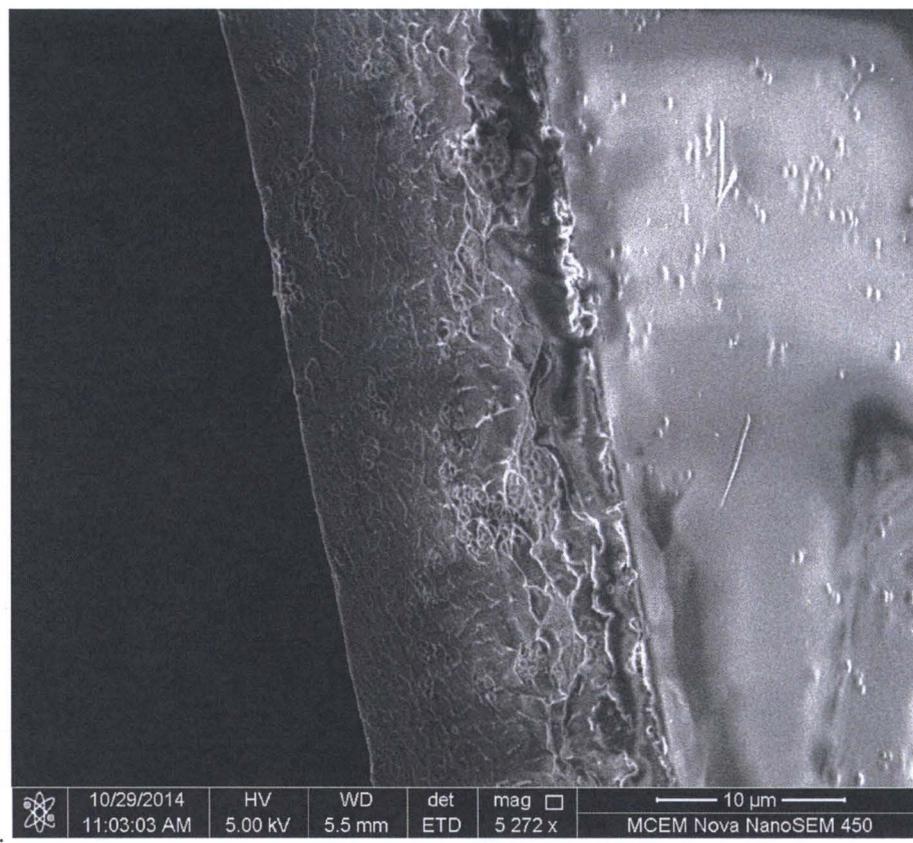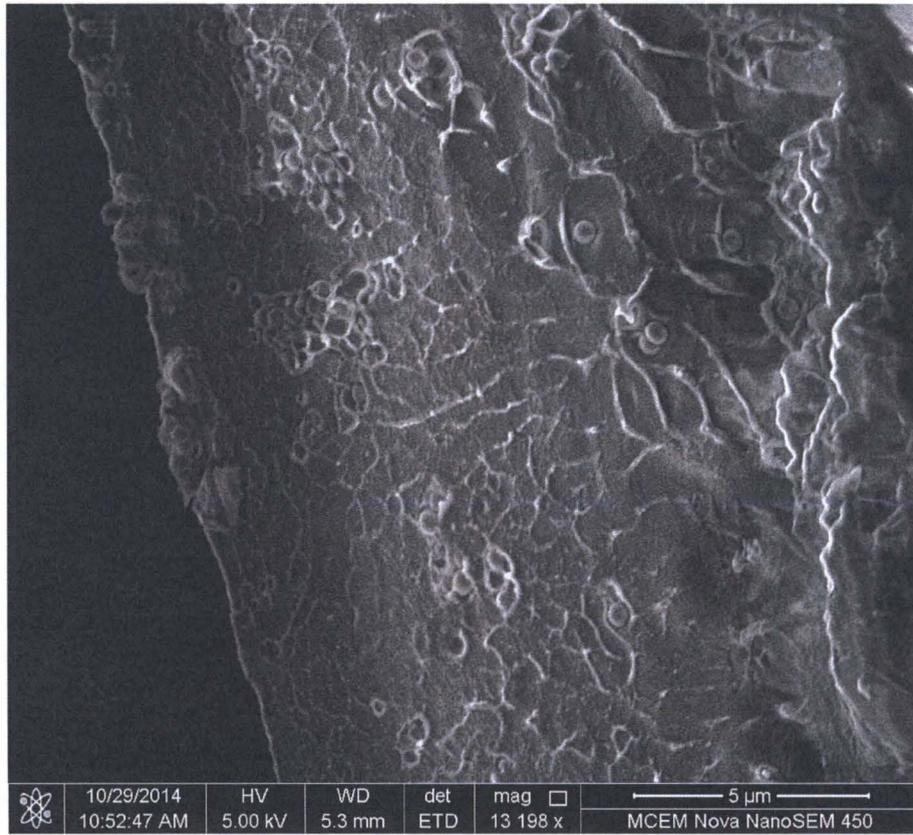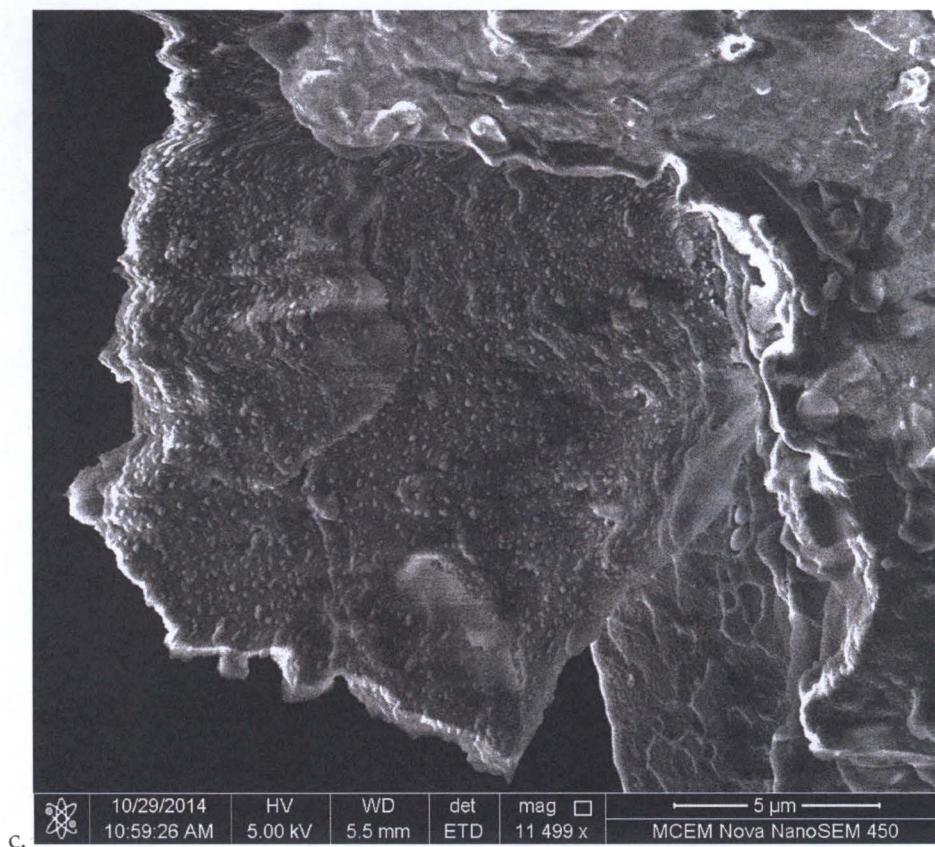
Figure 7.4:(a)-(c) SEM Images for SPEEK-SiO_2-SO_3

a. | 10/29/2014 11:33:38 AM | HV 5.00 kV | WD 6.1 mm | det ETD | mag □ 13 741 x | 5 µm MCEM Nova NanoSEM 450 |

b. | 10/29/2014 11:04:53 AM | HV 5.00 kV | WD 5.9 mm | det ETD | mag □ 9 629 x | 5 µm MCEM Nova NanoSEM 450 |
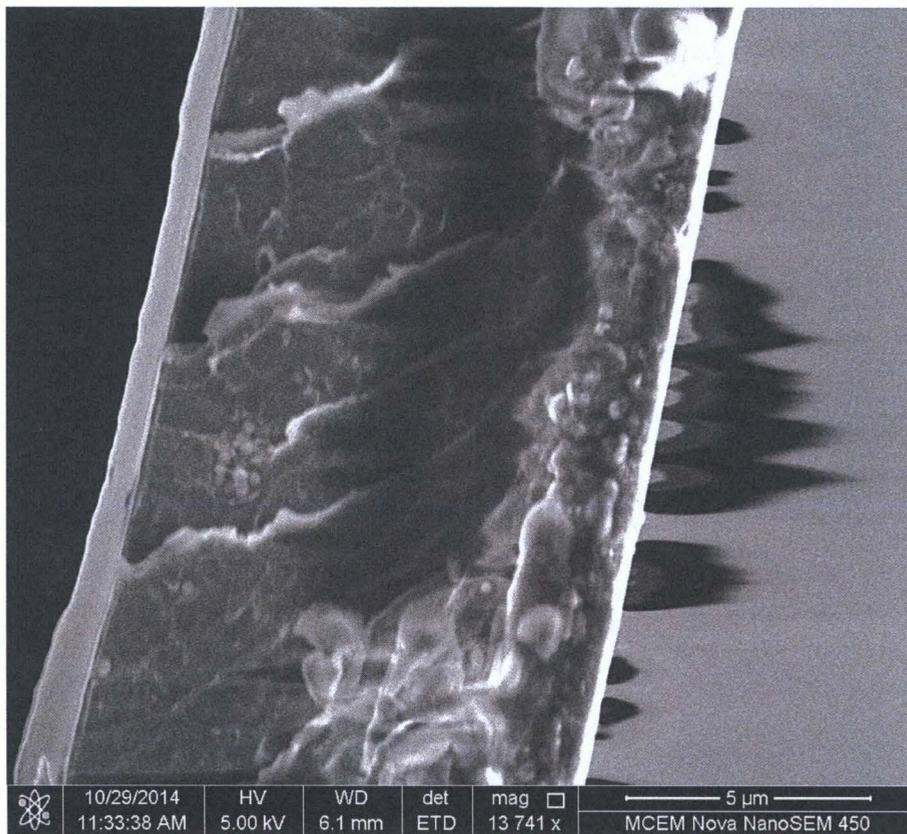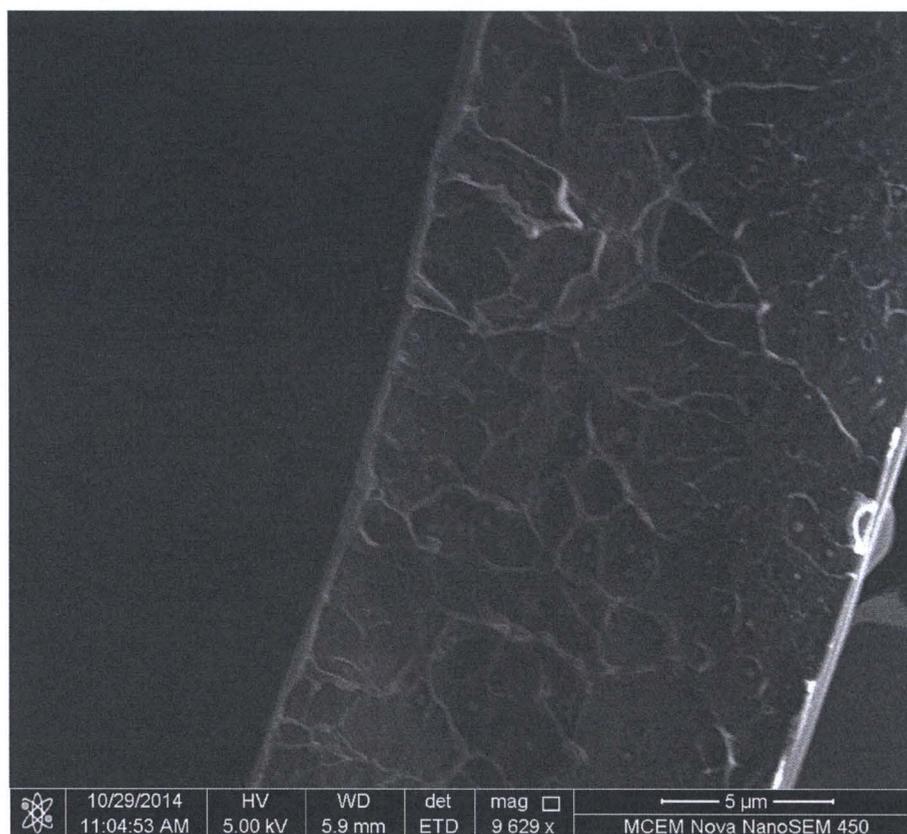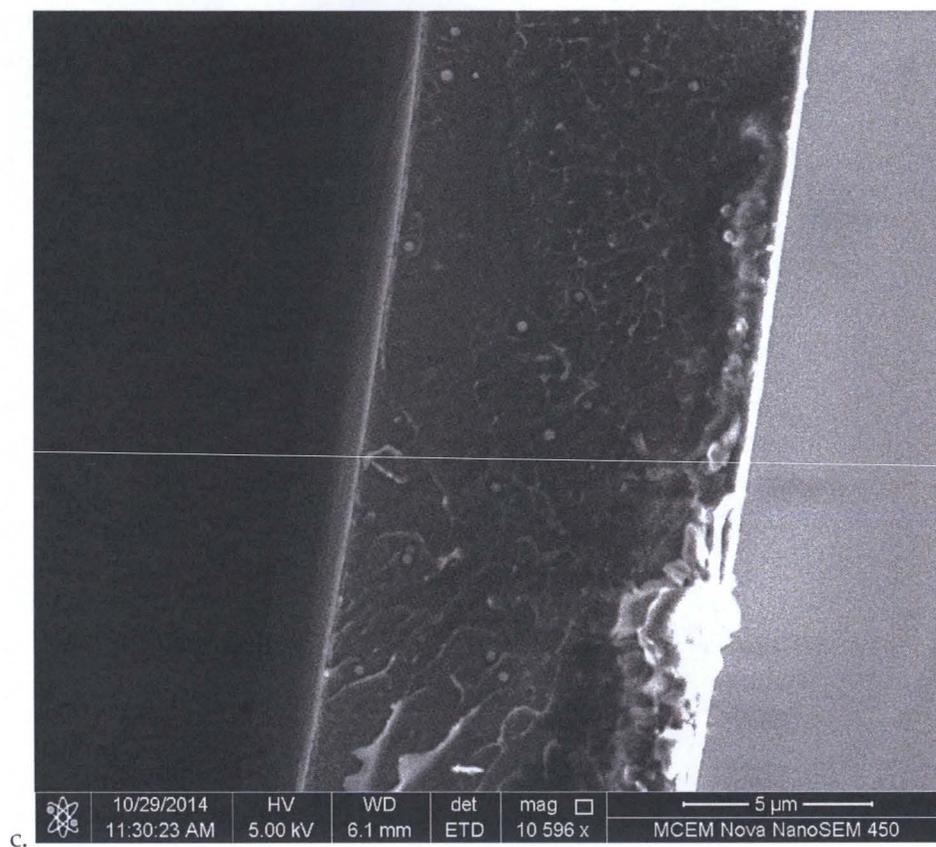
Figure 7.5:(a)-(c) SEM Images for SPEEK-SiO$_2$-NH$_2$
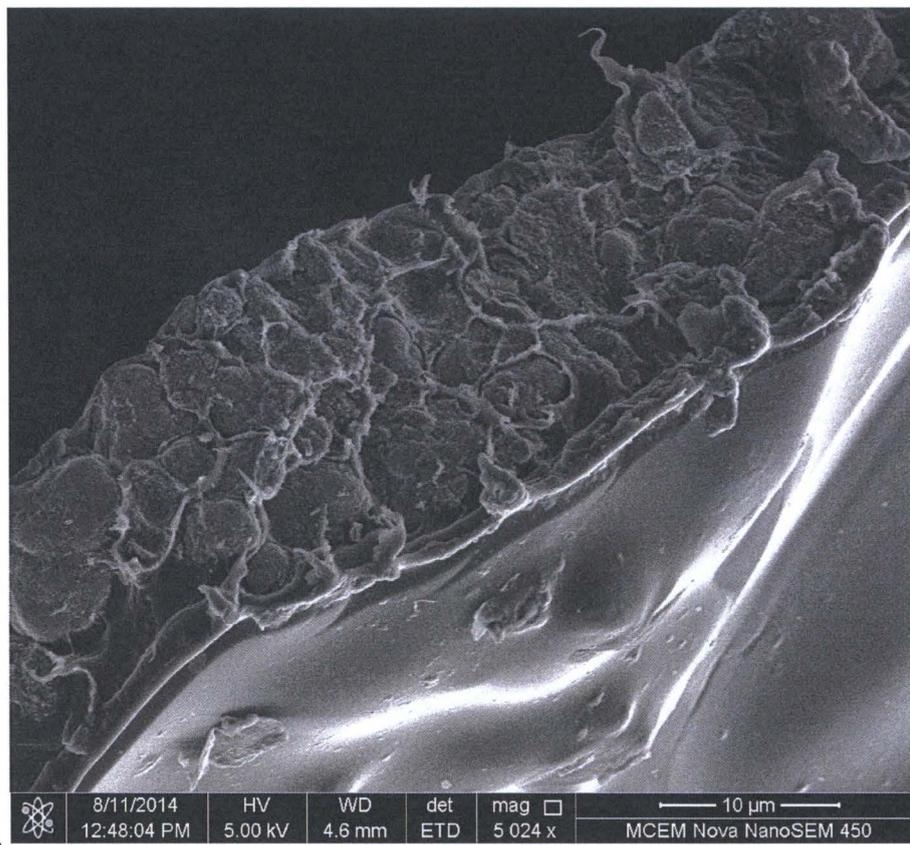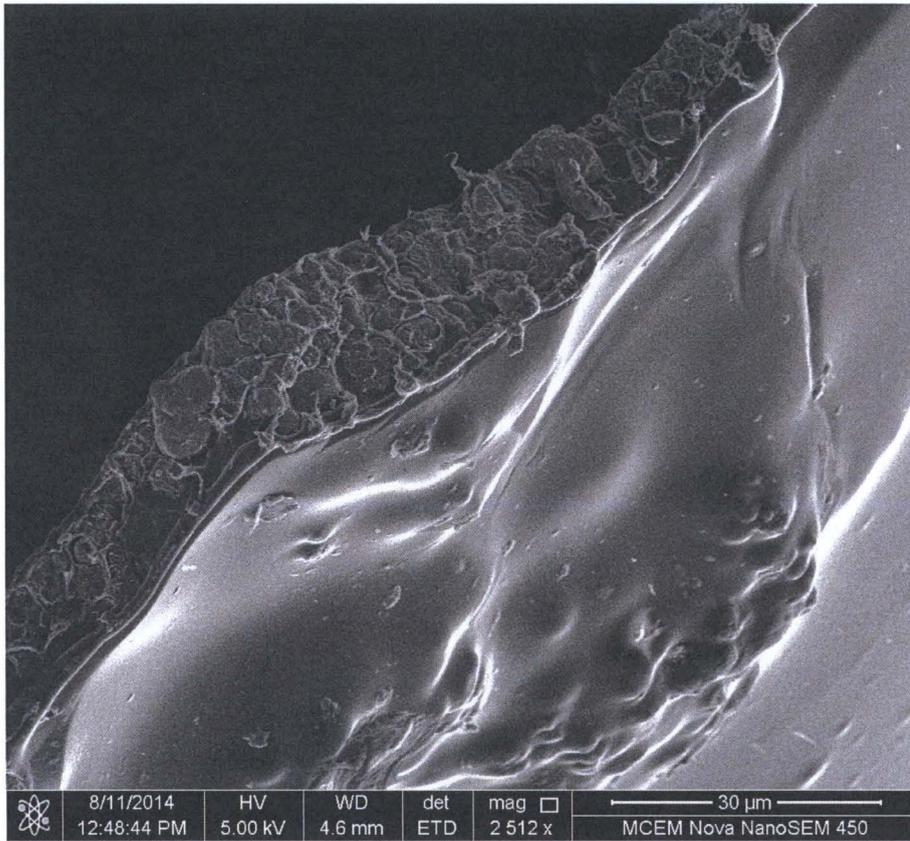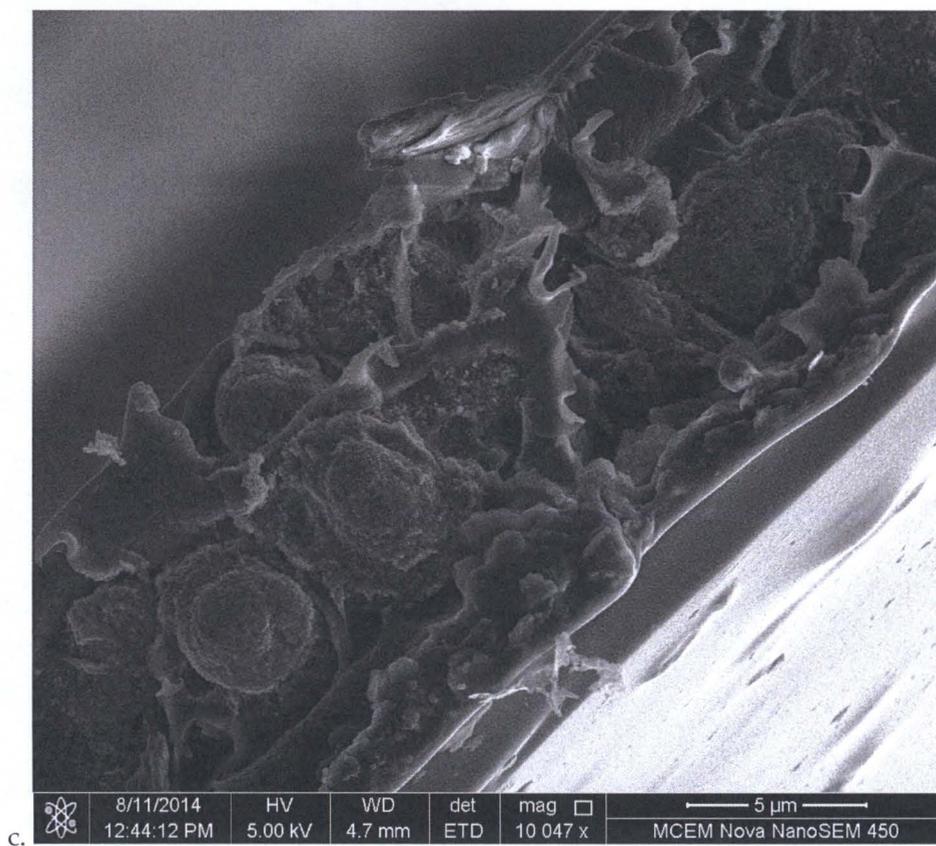
Figure 7.6:(a)-(c) SEM Images for SPEEK-TiO$_2$
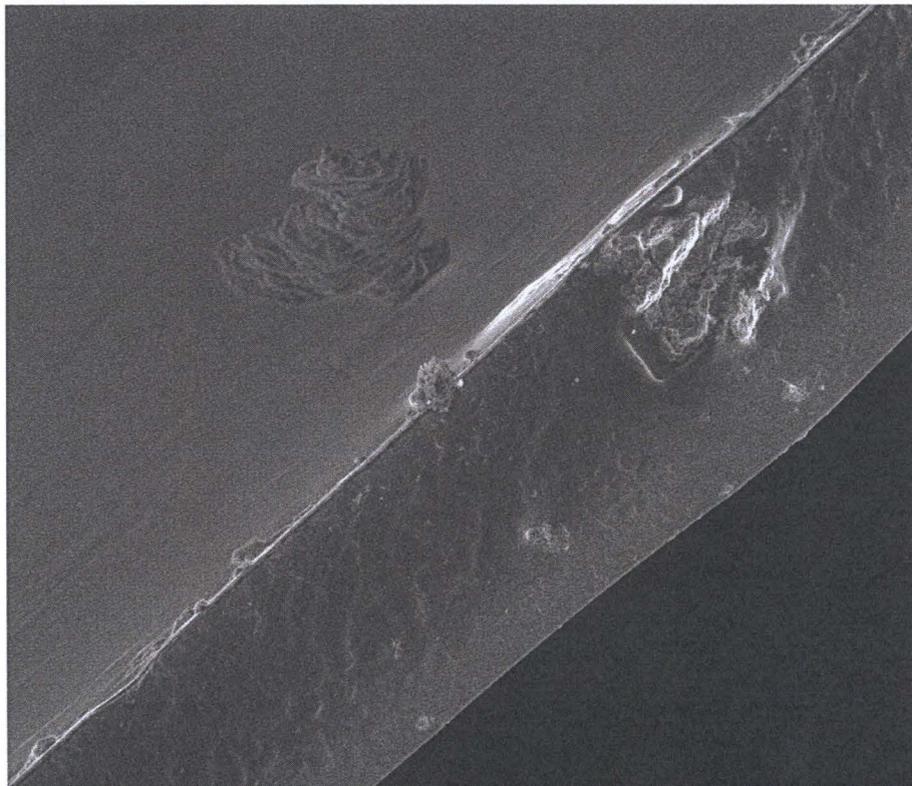
a.

| 11/10/2014 2:02:29 PM | HV 5.00 kV | WD 5.8 mm | det ETD | mag ☐ 3 257 x | 20 µm MCEM Nova NanoSEM 450 |
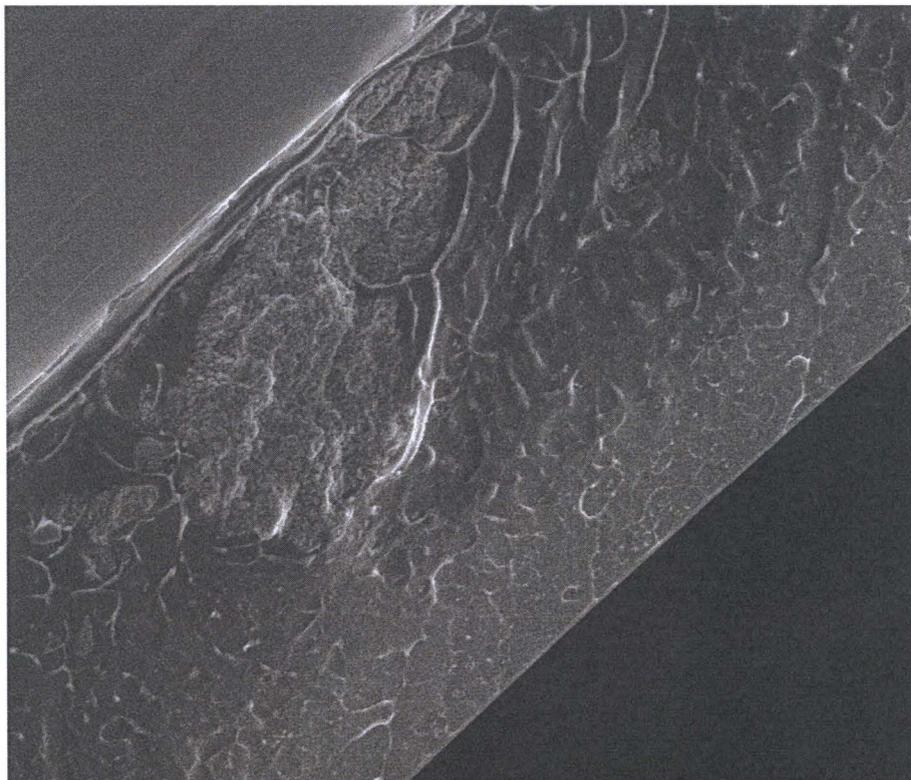
b.

| 11/10/2014 2:03:01 PM | HV 5.00 kV | WD 5.8 mm | det ETD | mag ☐ 7 377 x | 10 µm MCEM Nova NanoSEM 450 |
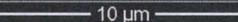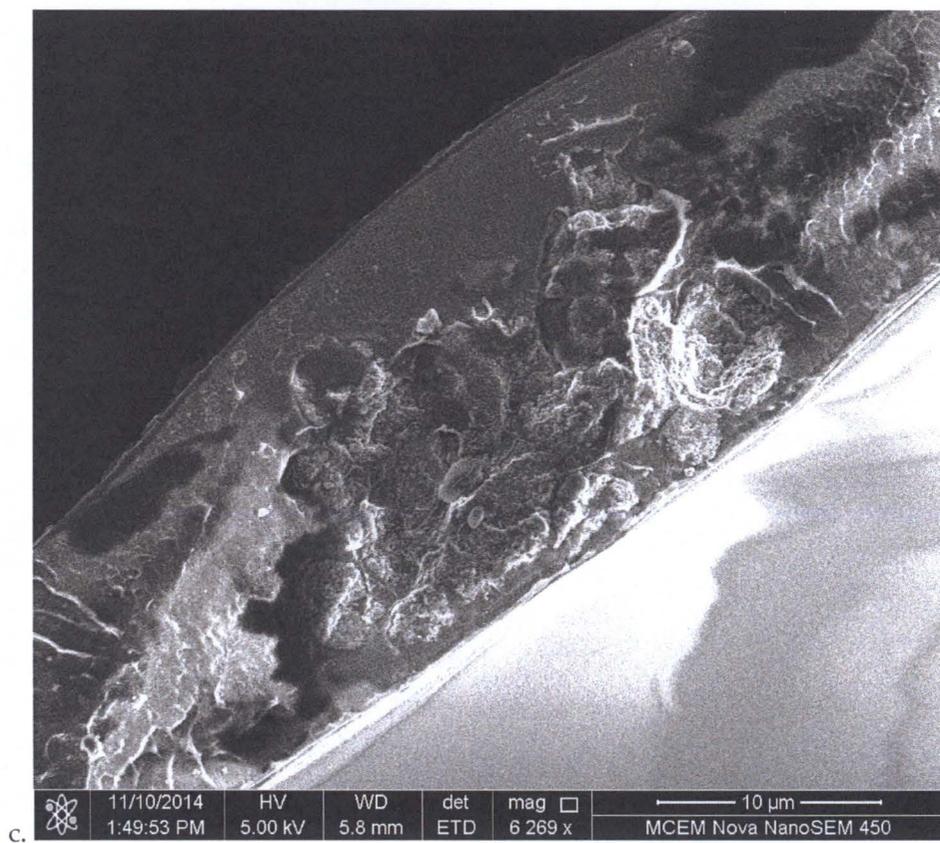
Figure 7.7:(a)-(c) SEM Images for SPEEK-TiO$_2$-NH$_2$

b.

| | 11/10/2014 | HV | WD | det | mag ☐ | 5 µm |
| | 2:26:25 PM | 5.00 kV | 5.5 mm | ETD | 11 519 x | MCEM Nova NanoSEM 450 |

c.

Figure 7.1:(a)-(c) SEM Images for SPEEK-TiO$_2$-TEA