AN INVESTIGATION OF STRUCTURE-PROPERTY RELATIONSHIPS IN SEVERAL CATEGORIES OF PROTON EXCHANGE MEMBRANES

by

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B.Sc. (Hons), St. Francis Xavier University, 2001

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

In the Department of Chemistry

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ABSTRACT

The chemical and structural features of proton exchange membranes (PEMs) are related to their fuel cell relevant properties. The objective of this work is to understand structure-property relationships in PEMs through the fabrication and characterization of several classes of membranes.

Incorporation of linear and angled monomers into the main chain of a polyimide permitted investigation of the effect of kinked versus linear polymers on membrane properties. The conductivity of angled sulfonated polyimide membranes is greater than those prepared from linear polymers, but water uptakes are lower. These differences are attributed to increased entanglements of angled polymers, which limit the degree of swelling and lead to increased proton concentration.

Polyelectrolytes were incorporated into reinforcing materials to study the effect of incorporating and confining polyelectrolytes in the pores of reinforcing materials. The employment of reinforcing materials reduces conductivity, mobility, and permeance due to decreased ionomer content and connectivity of the ionomer. However, membranes are stronger and thinner, which compensates for these losses in terms of lower resistance and increased dimensional stability.

Incorporating zirconium hydrogen phosphate (ZrP) and silicon dioxide (SiO₂) into Nafion® membranes permitted investigation of their effect on membrane properties. Data for Nafion®/ZrP membranes support the theory that ZrP disrupts cohesive forces in Nafion®, causing it to absorb more water. The increased water content of the membranes does not result in increased conductivity because there is a concurrent decrease in proton concentration and mobility due to poorly conducting ZrP disrupting the conduction pathway and increased water content diluting protons and separating proton conduction sites. The decreasing density of the Nafion®/SiO₂ composite membranes with
increasing SiO₂ content and the increased dimensional stability of the membranes increasing compared to unmodified Nafion® support the theory that a rigid scaffolding forms. Due to formation of void space that increases with increasing SiO₂ content, water content increases, thus diluting the protons in the membrane, leading to lower conductivity.

These structure-property relationships may be relevant to other membrane systems and should be considered when designing alternative systems for proton exchange membranes.
DEDICATION

To my family, who encouraged me and supported me throughout my studies.
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>APS1</td>
<td>4,4'-sulfonyldianiline</td>
</tr>
<tr>
<td>APS2</td>
<td>3,3'-sulfonyldianiline</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>attenuated total reflectance-Fourier transform infrared</td>
</tr>
<tr>
<td>BPSH-x</td>
<td>biphenol poly(arylene ether sulfone)</td>
</tr>
<tr>
<td>CG</td>
<td>Celgard®</td>
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<tr>
<td>DMAc</td>
<td>dimethylacetimide</td>
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<td>DMF</td>
<td>dimethylformamide</td>
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<tr>
<td>DMFC</td>
<td>direct methanol fuel cell</td>
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<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
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<tr>
<td>EDX</td>
<td>energy dispersive x-ray</td>
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<tr>
<td>ETFE</td>
<td>ethylene tetrafluoroethylene</td>
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<tr>
<td>FEP</td>
<td>fluorinated ethylene propylene</td>
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<tr>
<td>FRA</td>
<td>frequency response analyzer</td>
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<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>HPA</td>
<td>heteropolyacid</td>
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<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
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<tr>
<td>IEC</td>
<td>ion exchange capacity</td>
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<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
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<tr>
<td>Nafion®</td>
<td>perfluorosulfonic acid polymers from DuPont</td>
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<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<td>PAEK</td>
<td>poly(arylene ether ketone)</td>
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<td>poly(arylene ether sulfone)</td>
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<td>PFSA</td>
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<td>PPO</td>
<td>poly(phenylene oxide)</td>
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<td>relative humidity</td>
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<tr>
<td>S</td>
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<td>SAS</td>
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<td>sulfonated poly(ether sulfone)</td>
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<td>angled sulfonated polyimide</td>
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<td>sulfonated poly(phenylene oxide)</td>
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<td>x-ray diffractometry</td>
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<tr>
<td>ZrP</td>
<td>zirconium hydrogen phosphate</td>
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<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E )</td>
<td>activation energy of conduction</td>
</tr>
<tr>
<td>A</td>
<td>area of a cross-section of the membrane</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>an area of the membrane</td>
</tr>
<tr>
<td>[NaOH]</td>
<td>concentration of NaOH</td>
</tr>
<tr>
<td>( \rho_{\text{ionomer}} )</td>
<td>density of the ionomer</td>
</tr>
<tr>
<td>( d_{\text{wet}} )</td>
<td>dimension of the membrane under study (thickness, length, or width) in the wet state, mm</td>
</tr>
<tr>
<td>( d_{\text{dry}} )</td>
<td>dimension of the membrane under study (thickness, length, or width) in the dry state, mm</td>
</tr>
<tr>
<td>( \mu_{\text{eff}, \text{H}^+} )</td>
<td>effective proton mobility</td>
</tr>
<tr>
<td>( \mu_{\text{eff}, \text{H}^+, \text{ionomer}} )</td>
<td>effective proton mobility of the ionomer in the membrane</td>
</tr>
<tr>
<td>t</td>
<td>efflux time of the dilute polymer solution</td>
</tr>
<tr>
<td>( t_s )</td>
<td>efflux time of the pure solvent</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant (96485 C mol(^{-1}))</td>
</tr>
<tr>
<td>R</td>
<td>gas constant (8.31451 J K(^{-1}) mol(^{-1}))</td>
</tr>
<tr>
<td>IEC</td>
<td>ion exchange capacity</td>
</tr>
<tr>
<td>( \text{IEC}_{\text{ionomer}} )</td>
<td>ion exchange capacity of the ionomer</td>
</tr>
<tr>
<td>( \text{IEC}_{\text{Nafion}} )</td>
<td>ion exchange capacity of Nafion(^\text{®})</td>
</tr>
<tr>
<td>( \text{IEC}_{\text{norm}} )</td>
<td>ion exchange capacity normalized for ZrP content, assuming ZrP does not contribute to ion exchange capacity</td>
</tr>
<tr>
<td>Calculated IEC( \text{composite} )</td>
<td>ion exchange capacity of the composite membrane normalized for ZrP content, assuming ZrP contributes two protons</td>
</tr>
<tr>
<td>IECZrP</td>
<td>ion exchange capacity of ZrP, assuming ZrP contributes two protons</td>
</tr>
<tr>
<td>[( n )]</td>
<td>intrinsic viscosity</td>
</tr>
<tr>
<td>L</td>
<td>length between two Pt foil electrodes</td>
</tr>
<tr>
<td>M</td>
<td>mass change in WVT studies</td>
</tr>
<tr>
<td>( M_{\text{dry}} )</td>
<td>mass of the dry membrane</td>
</tr>
<tr>
<td>( M_{\text{dry}, \text{ionomer}} )</td>
<td>mass of the dry ionomer in the membrane</td>
</tr>
<tr>
<td>( M_{\text{ionomer}} )</td>
<td>mass of the ionomer in the membrane</td>
</tr>
<tr>
<td>( M_{\text{after}} )</td>
<td>mass of the membrane after treatment</td>
</tr>
<tr>
<td>( M_{\text{before}} )</td>
<td>mass of the membrane before treatment</td>
</tr>
<tr>
<td>( M_{\text{wet}} )</td>
<td>mass of the wet membrane</td>
</tr>
<tr>
<td>( M_{\text{H2O}} )</td>
<td>mass of water in the membrane</td>
</tr>
<tr>
<td>( X_A )</td>
<td>mole fraction of monomer A</td>
</tr>
<tr>
<td>( M_A )</td>
<td>molecular weight of segment A</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>wt%Nafion</td>
<td>Nafion® content in the membrane</td>
</tr>
<tr>
<td>N_sulfonated</td>
<td>number of sulfonated groups per sulfonated segment</td>
</tr>
<tr>
<td>λ</td>
<td>number of water molecules per sulfonated group</td>
</tr>
<tr>
<td>n_H2O</td>
<td>number of moles of water</td>
</tr>
<tr>
<td>n_SO3r</td>
<td>number of moles of sulfonic acid</td>
</tr>
<tr>
<td>%d</td>
<td>percent change in dimension of the membrane with swelling</td>
</tr>
<tr>
<td>[H+]</td>
<td>proton concentration</td>
</tr>
<tr>
<td>[H+]_ionomer</td>
<td>proton concentration of the ionomer in the membrane</td>
</tr>
<tr>
<td>σ</td>
<td>proton conductivity</td>
</tr>
<tr>
<td>σ_{ionomer}</td>
<td>proton conductivity of the ionomer in the membrane</td>
</tr>
<tr>
<td>η_i</td>
<td>relative viscosity increment</td>
</tr>
<tr>
<td>R_m</td>
<td>resistance of the membrane</td>
</tr>
<tr>
<td>S</td>
<td>saturated water vapour pressure</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>L_2</td>
<td>thickness of the membrane</td>
</tr>
<tr>
<td>R_{1-R_2}</td>
<td>vapour pressure difference in WVT studies</td>
</tr>
<tr>
<td>M_v</td>
<td>viscosity average molecular weight</td>
</tr>
<tr>
<td>η</td>
<td>viscosity of the dilute polymer solution</td>
</tr>
<tr>
<td>η_s</td>
<td>viscosity of the pure solvent</td>
</tr>
<tr>
<td>V_{NaOH}</td>
<td>volume of NaOH</td>
</tr>
<tr>
<td>V_{ionomer}</td>
<td>volume of the ionomer</td>
</tr>
<tr>
<td>V_{membrane}</td>
<td>volume of the membrane</td>
</tr>
<tr>
<td>V_{wet_ionomer}</td>
<td>volume of the wet ionomer in the membrane</td>
</tr>
<tr>
<td>V_{wet}</td>
<td>volume of the wet membrane</td>
</tr>
<tr>
<td>V_{wet%ionomer}</td>
<td>volume percent of ionomer in the membrane</td>
</tr>
<tr>
<td>wt%ZrP</td>
<td>ZrP content in the membrane</td>
</tr>
</tbody>
</table>
CHAPTER 1: PROTON EXCHANGE MEMBRANES

1.1 Fuel Cell Technology

Fuel cells are electrochemical devices that convert the energy of a fuel directly into electrical energy and have advantages over other energy conversion devices such as savings in fossil fuels, high efficiency of energy conversion, low pollution production, low noise, and low maintenance costs.\[1-4\] Fuel cells operate much like continuous batteries when supplied with fuel to the anode and oxidant to the cathode. In a fuel cells the molecules of a fuel and oxidizer are chemically combined without burning, eliminating the inefficiencies and pollution of traditional combustion.

**Figure 1.1** illustrates the operation of a proton exchange membrane fuel cell (PEMFC) using hydrogen as a fuel source. Proton exchange membranes (PEMs), which serve as both electrolyte and fuel separator, play a vital role in PEMFCs. They permit the flow of ions but not electrons or reactants between the anode and the cathode. The PEM is sandwiched between two catalyst layers composed of carbon supported platinum and ionomer. This catalytic electrode/membrane configuration is referred to as a membrane electrode assembly (MEA). The electrochemical reactions occur at the interface between the PEMs and catalyst layers.\[1-4\] Hydrogen fuel is fed to the anode of the fuel cell and reacts with a catalyst, thereby dissociating into protons, which are then
free to migrate through the electrolyte toward the cathode, and electrons, which can pass through the external load:

\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

Oxygen enters the fuel cell at the cathode. The oxygen molecules dissociate into atoms, which combine with electrons and the migrating \( H^+ \) ions to form water:

\[ 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \]

An electric potential appears between the electrodes because of the excess of electrons at the anode (where they are generated) compared with the cathode (where they are consumed).\[^{[1-4]}\] It is this potential difference that drives current through the external load, making the fuel cell a source of power. Overall, through the electrochemical reaction of hydrogen and oxygen, electrical energy and water are produced:

\[ 2H_2 + O_2 \rightarrow 2H_2O + \text{energy} \]
PEMFCs gained prominence after an ion-exchange resin was used as an electrolyte for space applications by General Electric in 1959. Hydrogen/Oxygen (H₂/O₂) fuel cells and direct methanol fuel cells (DMFCs) are the two types of fuel cells that use polymer electrolytes. DMFCs have higher energy density, favoured for portable applications, but have shortcomings such as slower oxidation kinetics than H₂/O₂ fuel cells below 100 °C and significant permeation of fuel from anode to cathode, resulting in a drop of efficiency of fuel utilization by up to 50%.

When using hydrogen as a fuel, water is the only product of the electrochemical reaction. However, if too much water is generated at the cathode, the water may condense and block the oxygen flow channels and the cathode may flood. Another source of excess water at the cathode occurs due to electro-osmotic drag, where water is transported from anode to cathode with
hydrated protons. Electro-osmotic drag can therefore dehydrate the anode side of the membrane. For the reasons stated above, proton conduction and water management within the membrane are two critical issues for PEMs. \(^1\)

### 1.2 PEMFC Membranes

#### 1.2.1 PEM Requirements

The membrane is the core component in PEMFCs where it acts as both a separator and electrolyte. PEMs are generally ion-containing polymers (ionomers) comprised of a hydrophobic polymer backbone and proton exchange sites (usually sulfonic acid groups). The ion exchange sites, such as \(-\text{SO}_3\text{H}\), have been observed to aggregate and form hydrophilic, ionic clusters. These hydrated ionic clusters are essential for the transport of protons. The hydrophobic backbone provides the mechanical properties necessary to prevent the membrane from excessive swelling. Membranes should have: high proton conductivity ($\geq 10^{-2}$ S cm\(^{-1}\)) to support high currents with minimal resistive losses; zero electronic conductivity; adequate mechanical strength and stability; chemical and electrochemical stability under operating conditions; moisture control; low fuel and oxygen crossover to maximize coulombic efficiency; and production costs that are compatible with the intended applications. \(^4\) The PEM must be thin, but also must be hydrogen impermeable and easily fabricated into high performance MEAs. \(^6\)

Nearly all membrane materials for PEMFC rely on absorbed water and its interaction with acid groups to facilitate proton conductivity. Due to the large
fraction of absorbed water in the membrane, both mechanical properties and water transport become key issues. Careful control of water uptake is critical for reducing the adverse effects of swelling and degradation of mechanical properties of the membrane in humid environments. Both proton conductivity and water uptake rely on ion content, where ion content is characterized by the molar equivalents of ion conductor per mass of dry membrane and is expressed as ion exchange capacity (IEC) with units of milliequivalent of protons per gram of polymer. Increasing the ion content leads to increased conductivity and increased water content while the mechanical integrity and durability of the membrane are diminished. \[2\] Designing systems that can conduct protons with little or no water thus represents a significant challenge.

The markets and applications for PEMFCs today and for the foreseeable future are in three areas: automotive, stationery, and portable. Each of these areas has different operating requirements, which leads to different membrane requirements. Although the exact conditions and membrane requirements are still evolving, the trends are clear. Automotive applications require higher temperatures and drier operating conditions because of the available radiator technology used to transport excess heat away from the stack. \[7\] To maintain the current size of automotive radiators in PEMFC vehicles, temperatures greater than 100 °C are needed to increase the heat transfer efficiency of the radiator. System size and weight constraints associated with water management are driving low humidity conditions as well. Stationary systems, on the other hand, require durability, power output, high efficiencies, and long life under relatively
constant operating conditions. High temperature conditions will use waste heat more efficiently and be less sensitive to fuel impurities. Drier operating conditions are not necessary for stationary fuel cell systems since fuel humidification is possible. These systems require 40 000 – 60 000 h life to reduce the cost of power generated. The requirements for portable fuel cell applications are the least well defined, but include no external humidification as well as the potential for frequent on/off cycling. DMFCs are favoured for portable applications because they have high energy density and portability.

High temperatures affect ionomers used in fuel cell membranes in many ways. The proposed temperatures of 100 – 200 °C may be above the glass transition temperature \( T_g \) of current membrane materials and are approaching the melting temperature \( T_m \) of others. Mechanical properties such as tensile strength, compression strength, and puncture resistance all decrease at higher temperatures.\[2,9\]

1.2.2 Fuel Cell Relevant Properties

Protons readily form multinuclear species with water molecules (e.g., \( H_3O^+ \), \( H_5O_2^+ \), \( H_9O_4^+ \)) within the ionic phase of the membrane and are transported predominately by proton hopping (the Grotthuss mechanism) and vehicular diffusion.\[10, 11\] In the vehicle mechanism, the proton diffuses together with a vehicle (e.g., as \( H_3O^+ \)). In the Grotthuss mechanism, protons are transferred within hydrogen bonds from one vehicle to another. An uninterrupted pathway for proton migration develops with reorganization of the proton environment. This reorganization is frequently established by the reorientation of solvent dipoles.
Proton concentration and effective proton mobility in a membrane have an important influence on proton conductivity. High values of both result in high proton conductivity. Proton concentration, \([H^+]\) is affected by both acid and water contents. The value of \([H^+]\) is determined experimentally by titration and represents the overall concentration of protons in the membrane without distinguishing between those protons that are mostly associated with the sulfonic acid groups and those that are fully dissociated and thus mainly present in the bulk water.

Mobility is defined as the rate of transport of a species under an applied electric field. \(^{[12]}\) Conductivity, \(\sigma_e\), is a function of the quantity of charge carriers in a given volume, \(v\), the mobility of those charge carriers, \(\mu_e\), and their charge, \(e\) (equation 1.1).

\[
\sigma_e = ve\mu_e
\]

This relationship is extended to ionic systems where the transference number of an ion is equal to one (equation 1.2), and \(\sigma\) is the specific conductivity of the ion, \(F\) is Faraday’s constant (96 485 C mol\(^{-1}\)), \(a_i\) is the activity of the ion, and \(Z_i\) is the charge on the ion.

\[
\sigma = Fa_i|Z_i|\mu
\]

The activity, \(a_i\), is obtained using equation 1.3 where \(f_i\) is the degree of dissociation of the ion and \(C_i\) is the analytical concentration of the ion. \(f_i\) depends on both the \(pK_a\) of the acid group and the water content of the PEM.
The proton mobility in PEMs can be estimated from the proton conductivity (equation 1.4) because the negatively charged $\text{SO}_3^-$ counter-ions are tethered to the backbone, which results in a transference number of one for the positively charged protons.

$$\sigma_{\text{H}^+} = F[H^+]\mu_{\text{H}^+}. \quad 1.4$$

To account for the effect of ionic strength, a more correct version of equation 1.4 replaces $[\text{H}^+]$ with the activity value for $\text{H}^+$. However, it is not possible to determine because the activity value requires an accurate knowledge of the activity coefficient of $\text{H}^+$, which is concentration dependent and therefore unattainable in these systems. Proton mobility in the aqueous phase of a PEM does not fall into the classical view of mobility of free ions in solution. For example, strong binding of a proton to the tethered anions as it passes through the membrane impedes its mobility. Therefore, the calculated proton mobility is an effective mobility that includes the uncertainties of the activity coefficient(s) for $\text{H}^+$. However, the titration measurement measures the concentration of $\text{SO}_3\text{H}$ groups in the membrane rather than an actual free proton concentration, thus combining both bound and unbound protons (equation 1.5):

$$\text{-SO}_3\text{H} \rightleftharpoons \text{H}^+ + \text{-SO}_3^- \quad 1.5$$

Calculation of proton mobility, therefore, allows a normalized proton conductivity to be determined; i.e., acid concentration effects are removed. By doing this, it is
possible to view the relative contributions of both proton mobility and acid concentration to the experimentally measured proton conductivity.\textsuperscript{[12]}

In addition to the effect dissociated and tethered anionic groups have on mobility, there are further effects on proton mobility in PEMs. One of these relates to the connectivity and effective mean-free path for protons. This is schematically illustrated in Figure 1.2 in which A has a more tortuous conduction pathway, with a series of dead ends, compared to the conduction pathway in B which is more linear. The supposition, therefore, is that proton mobility will be effectively greater in B relative to A. In fact, Kreuer has previously used these concepts of smaller conduction channels and dead ends to explain the lower proton mobility in SPEEK compared to Nafion\textsuperscript{®}.\textsuperscript{[13]}

Figure 1.2: Connectivity of aqueous domains in PEMs (black = aqueous domains) where the degree of tortuosity of the proton conduction pathway is greater in A than in B.

The distance between acid groups may also play a role in the mobility of protons. Pores having different distances between acidic groups are shown schematically in Figure 1.3. As the proton-bearing, positively charged species (e.g., H\textsubscript{3}O\textsuperscript{+}, H\textsubscript{2}O\textsubscript{5}\textsuperscript{+} and/or H\textsubscript{4}O\textsubscript{9}\textsuperscript{+} ions)\textsuperscript{[14]} are transported between the negatively
charged, tethered \(-\text{SO}_3^-\) groups, it is expected that it will be more difficult for a proton to be transported over the larger distances between \(-\text{SO}_3^-\) in \textbf{A} in comparison to the shorter distances between \(-\text{SO}_3^-\) groups in \textbf{B}. This would lead to a lower proton mobility in \textbf{A} compared to \textbf{B}. \cite{11,13,15}

![Spatial proximity of neighbouring acid groups within an aqueous channel](image)

In summary, the \textit{effective} proton mobility, \(\mu_{\text{eff,H}^+}\), as derived from the proton conductivity data using equation \ref{eq:1.4}, depends on acid dissociation, tortuosity, and spatial proximity of neighbouring acid groups. \cite{12}

\subsection*{1.2.3 History of PEMs}

The evolution of membranes for fuel cell applications began in 1959 when General Electric prepared membranes by polymerization of phenol-sulfonic acid with formaldehyde. These membranes displayed low mechanical strength, short lifetimes of 300 – 1000 h, and low power densities of 0.05 – 0.1 kW m\(^{-2}\). \cite{16} From 1962 – 1965, General Electric attempted to improve the power density by
developing partially sulfonated polystyrene membranes. These membranes had better water uptake and improved power density of 0.4 – 0.6 kW m\(^{-2}\), which enabled their use in NASA’s Gemini flights. However, these membranes were brittle in the dry state. In the late 1960s General Electric prepared cross-linked polystyrene-divinylbenzene sulfonic acid membranes in an inert matrix. The lifetime of these membranes ranged from 1000 – 10 000 h and power density ranged from 0.75 – 0.8 kW m\(^{-2}\).\[^{[17]}\] The main problem with these membranes was low conductivity.

In 1966, DuPont developed a perfluorosulfonic acid (PFSA) membrane called Nafion\(^\circledR\) that showed double the conductivity and a lifetime of \(10^4 – 10^5\) h. This is the current standard membrane used in PEMFCs.

1.2.4 Development of PEMs

A variety of polymers have been investigated as possible PEMs for fuel cell use. Several reviews \[^{[3, 14, 18, 19]}\] on the subject are available. This section briefly summarizes the classification of several PEMs in terms of their chemical structures and fabrication techniques.

1.2.4.1 Statistical Copolymers

1.2.4.1.1 Perfluorinated Ionomers

Currently, the most commonly used PEM is Nafion\(^\circledR\), whose PFSA structure imparts exceptional oxidative and chemical stability. These membranes exhibit excellent performance in fuel cells when operating at moderate temperatures (< 90 °C) and elevated relative humidity, with lifetimes greater than 60 000 h. Nafion\(^\circledR\) is a copolymer with a crystallizable, hydrophobic,
tetrafluoroethylene backbone sequence that has pendant side chains of perfluorinated vinyl ethers terminated by perfluorosulfonic acid groups. The reported chemical structure of Nafion® for PEM membranes is shown in Figure 1.4. [2]

Figure 1.4: Chemical structure of Nafion®. x and y represent molar compositions and do not imply a sequence length.

\[
\begin{align*}
\text{OCF}_2\text{CFO(CF}_2\text{)}_2\text{SO}_3\text{H} \\
\text{CF}_3
\end{align*}
\]

In theory, the ion content of Nafion® can be varied by changing the ratio of the two components (x and y in Figure 1.4). Commercial Nafion® is widely available with an IEC of 0.91 meq g⁻¹. This IEC provides high proton conductivity and moderate swelling in water, which suits most current applications. At this composition, a semi-crystalline morphology provides mechanical strength to the membrane. Fine dispersions of Nafion® in alcohol/water can be dried to form films, which are called “recast” Nafion®. The morphology and physical behaviour of recast Nafion® are much different from those of the extruded, more crystalline form, which results in recast Nafion® having inferior mechanical properties and increased solubility. [2]

PFSA polymers combine the extreme hydrophobicity of the perfluorinated backbone with the extreme hydrophilicity of the sulfonic acid functional groups. Especially in the presence of water, this gives rise to hydrophobic/hydrophilic nano-separation. The hydrophobic domain provides the polymer with
morphological stability and prevents the polymer from dissolving in water. The sulfonic acid functional groups aggregate to form a well-connected hydrophilic domain, which is responsible for the transport of protons and water. \cite{13} The presence of ion cluster morphology can be observed by small angle scattering (SAS \cite{20}), which includes small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS); electron microscopy, which includes scanning electron microscopy (SEM), and transmission electron microscopy (TEM); and atomic force microscopy (AFM). Geometric details of the microstructure can be obtained from SEM, TEM, and AFM images, while the wave length of periodicity can be acquired by SAS methods.

Many models describing the morphology of Nafion\textsuperscript{®} have been proposed to explain the properties of hydrated Nafion\textsuperscript{®} membranes since Eisenberg \cite{21} suggested the concept of cluster formation for ionomers, which was extended by Mauritz and Hopfinger \cite{22} in an attempt to represent the structural incorporation of water and ions by introducing configurational dipole-dipole interactions. In this model, the authors suggested structural organization of the Nafion\textsuperscript{®} membrane under different physiochemical conditions. \cite{22} One widely accepted empirical model for hydrated Nafion\textsuperscript{®} is the cluster-network model proposed by Hsu and Gierke (Figure 1.5a) \cite{23, 24} on the basis of SAXS experiments. In this model, spherical hydrophilic clusters (~ 4 nm diameter) of water are surrounded by sulfonate groups connected through cylindrical channels with ~ 1 nm diameter. One of the main problems with this model is that the three dimensional spatial distribution is based on a cubic array, which does not seem very realistic and
does not favour a percolation threshold at low water content. Litt et al. proposed a lamellar structure of Nafion® after consideration of the morphological and dimensional changes that had been observed in SAXS analysis of Nafion® during swelling and deswelling experiments (Figure 1.5b). [25] In this model, the ionic domains are defined as hydrophilic micelle layers separated by thin, lamellar PTFE-like crystallites. However, SAXS data were not analyzed in terms of this model and the extension of the lamellae and the domains on which they are oriented were not discussed. [25] A model based on ribbon-like particles has been proposed by Gebel and Diat that consists of elongated polymeric aggregates (cylindrical or ribbon-like) surrounded with ionic groups that are packed with an orientational ordering of bundles that are randomly ordered in space (Figure 1.5c). [26] Additional investigations need to be performed on Nafion® with this model in mind to fully investigate the interlamellar dimensions.

Figure 1.5: Schematic representation of A. cluster-network model for the morphology of hydrated Nafion®, B. lamellar model for the morphology of Nafion®, C. Nafion® with ribbon-like structures (reproduced with permission from [26]).

A.

Hydrophilic region Hydrophobic region
Other perfluorosulfonate PEMs with similar structures have been developed by the Asahi Chemical Company (Aciplex) and the Asahi Glass Company (Flemion). The Dow Chemical Company also developed a material with a shorter side-chain and higher ratio of SO$_3$H to CF$_2$ groups than the other perfluorosulfonates.$^{[27]}$

All of these PFSA membranes are expensive and suffer from the same shortcomings as Nafion®, namely low conductivity at low water contents, relatively low mechanical strength at higher temperature, and moderate glass transition temperatures.$^{[13]}$ Alternative PEMs could provide advantages in terms of system performance, cost, and operational flexibility that PFSA membranes cannot.
1.2.4.1.2 Partially Fluorinated Ionomers

One approach for new membranes involves the use of partially fluorinated polymers. These polymers consist of a fluorocarbon base with a hydrocarbon or aromatic side chain grafted onto the membrane. Along these lines poly-α,β,β-trifluorostyrene sulfonic acid was prepared (Figure 1.6). This polymer has been found to be resistant to oxidative modes of degradation, which cause drastic oxidative depolymerization of the polystyrene and polystyrene-divinylbenzenesulphonic acids. This degradation resistance is attributed to the substitution of fluorine in place of the benzene-hydrogen atom of polystyrene leading to the added C-F bond strength required to resist the oxidation environments. Thus, it was claimed that the high stability of the fluorine atoms attached to the alkyl carbon atoms impacts oxidative and thermal stability superior to that exhibited by conventional ion exchange polymers such as sulfonated polystyrene. [2] Their limited use in fuel cells may be attributed to their limited mechanical properties and/or chemical resistance in real fuel cell conditions. Lifetimes up to 3000 hours at low current densities and temperatures of 50 °C were achieved. [4]

Figure 1.6: Structure of sulfonated poly-α,β,β-trifluorostyrene. [4]
1.2.4.1.3 Hydrocarbon PEMs

Non-fluorinated hydrocarbons, such as polystyrene, are commercially available polymers whose structure permits the introduction of polar sites as pendant groups to increase water uptake. The structure of a sulfonated polystyrene (SPS) is shown in Figure 1.7. These membranes have high mechanical strength, but poor chemical and thermal stability, as well as low conductivity and low durability due to high swelling in water. Although these systems are not suitable for use in fuel cells, they serve as model systems for studying structure-property relationships. [4]

Figure 1.7: Structure of SPS [4]
and many different chemical structures are possible. Examples of several aromatic ionomers are shown in Figure 1.8.

Figure 1.8: Structures of sulfonated poly(arylene) membranes. A. SPEEK\textsuperscript{[28]}, B. BPSH\textsuperscript{[29]}, C. SPI\textsuperscript{[30]}, D. SPPO\textsuperscript{[28]}, E. SPBI\textsuperscript{[31]}, F. SDAPP\textsuperscript{[32]}

A.

\[
\begin{array}{c}
\text{H}_3\text{S} \text{O} \\
\text{HO}_3\text{S} \\
\text{O} \\
\text{O} \\
\end{array}
\]

B.

\[
\begin{array}{c}
\text{O} \text{Ar} \text{O} \\
\text{O} \text{Ar} \text{O} \\
\text{O} \text{Ar} \text{O} \\
\text{O} \text{Ar} \text{O} \\
\end{array}
\]

C.

\[
\begin{array}{c}
\text{N} \text{O} \text{SO}_3\text{H} \\
\text{O} \text{H}_3\text{S} \text{O} \\
\text{O} \text{H}_3\text{S} \text{O} \\
\text{O} \text{H}_3\text{S} \text{O} \\
\end{array}
\]

D.

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\end{array}
\]

E.

\[
\begin{array}{c}
\text{SO}_3\text{H} \\
\text{SO}_3\text{H} \\
\text{SO}_3\text{H} \\
\text{SO}_3\text{H} \\
\end{array}
\]
Introduction of proton exchange sites in aromatic polymers is accomplished by both polymer post modification and direct copolymerization of sulfonated monomers. Post sulfonation can lead to side reactions and may be hard to control. Synthesis of sulfonated macromolecules for use in PEMs by the direct reaction of sulfonated comonomers is a method of controlling structure, acid content, and molecular weight. [2]

Sulfonated poly(arylene ether)s have good water absorption and high proton conductivity, although they suffer from hydroxyl radical initiated degradation. [2, 4] Sulfonated poly(ether ether ketone) (SPEEK, Figure 1.8A) is a common example from this group because the base polymer poly(ether ether ketone) (PEEK) is commercially available and sulfonation is a straightforward procedure using sulfuric acid. [28] The proton conductivity of SPEEK is comparable to or higher than that of Nafion® at sufficient levels of sulfonation. However, these materials display less phase separation and have narrower
conductivity channels than Nafion®[14] and long-term testing of these materials in a fuel cell at 80 °C and 100% RH has shown that they are unstable and lose mechanical strength due to high water uptakes. [33]

SPAES are another class of sulfonated poly(arylene ether)s that have been extensively studied. Sulfonic acid groups in SPAES based PEMs have been introduced through copolymerization of sulfonated monomers. Increasing the degree of sulfonation in biphenol poly(arylene ether sulfone) copolymers (BPSH-x, where x represents the percentage of disulfonated diphenylsulfone groups in the polymer compared to unsulfonated diphenylsulfone groups) (Figure 1.8B), which is an example of a SPAES, leads to higher levels of conductivity as well as water uptake. [34] Evidence of microphase separation in BPSH has been observed by atomic force microscopy, especially for BPSH-50 and BPSH-60. [35]

Sulfonated aromatic polyimides (SPIs) (Figure 1.8C) are a sub-class of polyaromatics that have attracted attention as proton exchange membranes because of their good proton conductivity and relatively small geometrical changes upon swelling-deswelling. [36] SPIs are also reported to possess good thermal stability and mechanical durability, good oxidation resistance, and low methanol permeability. [37-39] Like SPAES, the sulfonated groups in SPIs are introduced through copolymerization of sulfonated monomers and thus the synthetic methods for preparing SPIs allows for careful control of the chemical structure, rigidity/flexibility of the backbone, ionic content, and distribution of ionic groups.

20
Other sulfonated poly(aromatic) systems that have been developed include sulphonated poly(phenylene oxide) (SPPO) (Figure 1.8D) \([34, 40]\) and sulfonated polybenzimidazoles (SPBI), (Figure 1.8E). \([31, 41]\) However, in common with the other sulfonated poly(aromatic) membranes mentioned above, these systems generally display lower degrees of microphase separation than Nafion® as well as a loss of mechanical stability at high degrees of sulfonation. Hydrolytic instability and desulfonation are also potential concerns for these systems.

All of the previously mentioned examples of polyarylenes have contained groups (e.g. sulfone, ketone, ether) other than aryl rings. Recently, in the interest of improving thermochemical stability, a purely aromatic PEM has been reported. Compared to SPAES and SPI membranes with similar IECs, sulfonated Diels-Alder Poly(phenylene) (SDAPP) membranes (Figure 1.8F) show slightly lower conductivity values, possibly due to the nature of the polymer backbone, the concentration density of ionic groups within the polymer, and the fact that water is bound within its microstructure. However, these membranes were physically sturdy and had high thermal stability. \([32]\)

### 1.2.4.2 Block and graft copolymers

Block and graft copolymers contain sequences of different monomer units. Block copolymers are composed of blocks of different polymerized monomer sequences, which are assembled linearly. For graft copolymers, side chains are structurally distinct from the main chain and blocks are grown from or attached to the backbone of another block as branches. When block and graft copolymers
are used to prepare PEMs, the blocks may have considerably different chemical units or units that are chemically identical except that one block is sulfonated and one is not. A microphase separation beyond that which occurs due to the hydrophilic and hydrophobic sites in Nafion® is induced in the membranes when the blocks within the copolymer are immiscible. Research on block and graft copolymers can provide basic comprehension about the influence of morphology upon proton conduction and other PEM properties. [42, 43]

1.2.4.2.1 Block copolymers

One of the first examples of a PEM fabricated from a block copolymer is sulfonated polystyrene-\(b\)-poly(ethylene-\(r\)-butylene)-\(b\)-polystyrene (S-SEBS) (Figure 1.9A). The water content for S-SEBS increased dramatically as the IEC increased from 1.13 to 1.71 meq g\(^{-1}\). However, the proton conductivities for S-SEBS are relatively independent of IEC, perhaps due to decreased proton concentration. [44] Investigation of the morphology of these membranes, obtained from SAXS and TEM, revealed that the morphology changes from lamellar to cylindrical depending on the IEC and the casting solvent, due to differences in the affinities of the blocks for different solvents. [45-47] Analogous dependence of morphology on casting solvent and IEC has been observed in a similar triblock copolymer, sulfonated poly(styrene-\(b\)-isobutylene-\(b\)-styrene), S-SIBS, which affects the proton conductivity of these membranes. [48]
Figure 1.9: Block copolymers, A. S-SEBS, B. Sulfonated-fluorinated poly(arylene ether) multiblocks, C. SPS-b-PVDF, D. P(VDF-co-HFP)-SPS

A.

\[
\begin{align*}
\text{CH}_2\text{CH}_m \left(\text{CH}_2\text{CH}_x\right)^n \text{CH}_2\text{CH} \left(\text{CH}_2\text{CH}_m\right) \\
\text{SO}_3\text{H} \quad \text{SO}_3\text{H}
\end{align*}
\]

B.

\[
\begin{align*}
\text{Ar} = 4,4'\text{-biphenyl}; \text{Ar}' = 4,4'\text{-perfluorobiphenyl}
\end{align*}
\]

C.

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

D.

Interest in the incorporation of fluoro-containing segments in block copolymers is based on the greater thermal and oxidative stability and
hydrophobicity they impart upon a polymer. Towards this end, McGrath et al. have investigated the influence of fluorinated blocks on BPSH-like systems. The structure is shown in Figure 1.9B. AFM morphological studies of the membrane surfaces reveal a well-defined phase separation with a distinctly different morphology than its random BPSH analogue, which can explain the higher conductivity of the former at similar IEC. [49] Morphological studies using TEM have shown that the aggregate size in another fluoro-block containing copolymer, sulfonated polysulfone-\textit{b}-polyvinylidene fluoride (SPS-\textit{b}-PVDF) (Figure 1.9C) decreases with increasing acid content. At IEC = 0.78 meq g\(^{-1}\), there are large regions of aggregation, possibly due to large-scale phase separation of the ionic and nonionic domains. [50, 51] TEM morphological studies of poly(vinylidene difluoride-co-hexafluoropropylene)-\textit{b}-sulfonatedpolystyrene (P(VDF-co-HFP)-\textit{b}-SPS) (Figure 1.9D) have shown that at low degrees of sulfonation, no well-defined domain formation was observed. However, as the ion content increases (20 - 40 mol\%), distinct domain formation can be seen, in the form of ordered, connected ionic channels (8-15 nm in width) with 20 - 40 nm spacings between domains. At higher than 50 mol\% sulfonation, there is a disruption in the ordered domains so that in the fully sulfonated polymer, the interfacial region between the hydrophilic and hydrophobic domains is less defined and the ionic aggregates tend to be disordered. [52, 53]
1.2.4.2.2 Graft copolymers

PEMs based on graft copolymers are usually prepared by irradiation grafting a suitable monomer in and onto a base substrate, followed by sulfonation of reactive units. Using graft copolymers allows use of commercially-available films as the base substrate and provides a material in which the base substrate can be chosen based on its mechanical properties and the grafted chains based on their proton conduction ability.

In most radiation-grafted PEMs, the proton conducting component is polystyrenesulfonic acid (PSSA), \(^\text{[42, 43, 54-56]}\) although \(\alpha\)-methyl styrene, glycidyl methacrylate, and substituted trifluorostyrene have also been used. When fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), and poly(vinylidene difluoride) (PVDF) were used as base substrates (Figure 1.10A - C), and PSSA as the monomer, the PEMs demonstrated performances comparable to Nafion\(^\text{®}\) under fully-humidified, 60 °C operation conditions. \(^\text{[43, 54-57]}\) From these studies, it was concluded that the grafting conditions and overall sulfonic acid content rather than the composition of the base substrate are significant for fuel cell performance.
Figure 1.10: Graft copolymers, A. FEP-g-PSSA, B. PVDF-g-PSSA, C. ETFE-g-PSSA, D. PS-g-macPSSNa, E. Fluorinated polyaromatic-based comb-shaped copolymers.
PEMs based on graft copolymers, such as polystyrene-g-poly(styrene sulfonate macroinitiator (PS-g-macPSSNA) (Figure 1.10D), have also been synthesized through radical polymerization. Analysis of the morphology of these membranes using TEM revealed ionic domains (5 – 10 nm) that are visibly connected, which results in a continuous network that extends with increasing IEC. Morphology of these membranes is affected by the length of the ionic graft. TEM morphological studies demonstrated that membranes containing longer ionic side chains microphase separate to a greater extent than those with shorter side chains for a set ionic content. At a low ionic content, only isolated domains are observed, but a continuous ionic network develops with increasing ionic content.

A macroinitiator route has also been used to synthesize partially fluorinated polyarylenes with grafted polystyrene sidechains (Figure 1.10E). TEM and SAXS morphological studies revealed that as the number of side chains increased, the morphology changed from wormlike to possessing cylindrical
domains. Proton conductivity and $T_g$ both increased with increasing number of side chains. [61]

1.2.4.3 Polymer Blends

A distinctly different approach to PEMs is based on the blending of two or more polymers to tune the properties to those desirable for fuel cell applications. These blends can be proton conducting polymers with non-ionic polymers, low IEC polymers, or base-containing polymers.

Due to its chemical and thermal stability, as well as its semi-crystalline nature, PVDF is an attractive non-ionic polymer to blend with Nafion®. [62-64] However, the conductivity of these blends are often significantly lower (two orders of magnitude) than unmodified Nafion®, [65, 66] likely due to the hydrophobicity of PVDF resulting in lower water uptake of the blended membrane. [67] When PVDF is treated by dehydrofluorination and doping with sulphuric acid prior to blending, the resulting Nafion®/PVDF blended polymer shows comparable conductivity and fuel cell performance to that of unmodified Nafion®. [68] Other non-ionic polymers that have been blended with Nafion® include PPO [69] and polypyrrole. [70]

Ionic polymers other than Nafion®, such as sulfonated poly(ether sulfone) (SPES), SPEEK, [71] and polystyrene-b-sulfonated polystyrene (PS-b-SPS), [72] have been blended with poly(ether sulfone) (PES), PVDF, and poly(phenylene oxide) (PPO). [72] When PVDF has been used as a blending material with SPEEK, the strength of the PEM was increased over unmodified SPEEK, but the conductivity decreased with increasing PVDF content. [73]
Blends of SPES (IEC = 2.5 meq g⁻¹) and sulfonated PPO (SPPO) (IEC = 2.6 meq g⁻¹) have been investigated to improve component compatibility. The blend exhibited higher conductivity and higher methanol permeability than either of the separate components, as well as DMFC performance comparable to Nafion®. SEM images of sulfonated PAES blended with Nafion® revealed a phase separated morphology that was controlled by both the blend ratio and the degree of sulfonation of the sulfonated PAES component. Conductivity and methanol permeability of this blended PEM were lower than Nafion®.

In blends of acidic and basic polymers, weakly basic polymers act as hydrogen bond acceptors for the protons on the acidic polymer; for more basic polymers, proton transfer from the acidic component produce an ionically crosslinked membrane. For example, SPEEK and SPES have been used in blends with polybenzimidazole (PBI), as well as with less basic components, such as polyetherimine, poly(4-vinylpyridine), and PES. In SPES/PBI blends, the ionic interaction increases the T_g compared to that of either of the components by 15 to > 50 °C. This increase in T_g is related to the proportion of sulfonated versus basic polymer and the strength of the base in the latter. TEM images of blends with low ionic crosslinking density (weakly basic and few sulfonic acid sites) show the membranes are microphase separated. Swelling in water and brittleness of the blended membranes in the dry state are both lower than the corresponding nonblended sulfonated polymer membrane. These advantages are lost at higher temperature because the degree of ionic crosslinking is reduced above 110 °C for sulfonated polymer/PBI. In a DMFC, a
MEA of SPEEK/PBI achieved a current density of 300 mA cm\(^{-2}\) at 500 mV and exhibited decreased methanol crossover at 110 °C. Increased power densities (0.25 W cm\(^{-2}\)) are attained by other blended systems (SPEEK/PBI), but methanol crossover is also higher. \[^{78}\]

The PBI component of blend membranes can also be acid doped. Acid doping increases the concentration of proton charge carriers. The conductivities of phosphoric acid doped PBI and SPES/PBI membranes (doping level 500 mol\%) are basically equal in a dry atmosphere at 175 °C (0.02 S cm\(^{-1}\)). \[^{79}\]

1.2.4.4 Reinforced Membranes

It is difficult to prepare thin membranes due to their reduced mechanical strength. However, thin membranes have advantages, such as lower internal resistance (resistance is proportional to thickness) and improved water management. \[^{80}\] Using reinforcing materials makes the fabrication of thin membranes possible without losing mechanical strength. In these materials, the ionomeric polymer is micro-reinforced with a thin, porous, and strong material (e.g. PTFE), making membranes stronger and more durable. The introduction of reinforced perfluorinated sulfonic acid based polymers has increased the durability and lifetimes of perfluorinated sulfonic acid membranes. Reinforced PEMs as thin as 5 μm, with good conductivity and mechanical properties, have been fabricated. \[^{81-85}\] Reinforced membranes offer the capability to use a wide variety of ionomeric polymers with the advantages of decreased resistance and increased performance and durability over thicker, non-reinforced membranes. Generally, Nafion® has been the ionomer used in these membranes although
SPES [86] and SPEEK [87] have also been used. Reinforcing materials include porous PTFE sheets, [88] expanded PTFE, [89] PTFE fibres, [90] porous polypropylene, [81, 91] polycarbonate, [92] polysulfone, [93] and glass microfiber fleece. [93]

1.2.4.4.1 Porous Sheet Reinforcement

The major challenge in fabricating ionomer membranes reinforced with porous sheets is to impregnate the ionomer uniformly into the porous material without forming cavities. Several methods have been proposed to make the reinforced membranes, such as vacuum impregnation. [94] The properties of reinforced PEMs depend not only on the nature of the reinforcing material and its thickness, but also upon the manner in which they are prepared. For example, Ramya et al. [95] found that solvents for which the solubility parameter was more compatible with acid containing side chains of Nafion® led to PEMs with improved conductivity, and Huang et al. found that using 1 - 3 wt% surfactant in the ionomer solution led to improved conductivity in PEMs compared to when no surfactant was used. [96]

A reinforced membrane comprised of an expanded PTFE porous sheet and a PFSA was developed by W.L. Gore & Associates in the 1990s and has been commercialized as Gore-select®. [97] Gore-select® is 20 - 40 μm thick, has excellent mechanical and electrochemical properties, and has been widely used in PEMFC systems. To prepare these membranes, a perfluorinated ionomer/surfactant solution is brushed on both sides of the porous PTFE sheet
having a thickness of less than 25 μm. Gore-select® shows higher tensile strength and smaller dimensional change in comparison with Nafion 117®.\[98]\]

Although Gore-select is the most well-known reinforced membrane, several others have also been fabricated. Using polycarbonate as a support material for a PFSA produced membranes with conductivities of 0.06 S cm\(^{-1}\),\[99]\] while PTFE and Celgard (polypropylene) reinforced Nafion® membranes showed conductivities of 0.10 and 0.021 S cm\(^{-1}\) at 65 °C and thicknesses of 25 and 28 μm, respectively.\[81]\] Water uptake and dimensional changes with swelling of PTFE reinforced Nafion® membranes are lower than that of pure Nafion®.\[95]\]

Using alternative ionomers in reinforced membranes found that SPEEK/PTFE membranes possessed larger resistance than the parent SPEEEK membranes, but improved dimensional stability and mechanical strength.\[86]\] SPS/PTFE membranes displayed comparable or higher conductivity than Nafion 117® membranes.\[87]\]

Fuel cell results reveal that these reinforced membranes have advantages over thicker, pure ionomer membranes in terms of fuel cell performance. For example, Lin et al. found the DMFC performance of 20 μm thick Nafion®/PTFE reinforced membranes were superior to that of Nafion 117® and 112® at 70 °C and with 2 M feed methanol, which has been attributed to low proton resistance of the reinforced membranes.\[100]\]
1.2.4.4.2 Fibril Reinforcement

The key concept in fibril reinforcement is to disperse small amounts of fibres, such as PTFE fibres, into the polymer matrix with higher IEC. Asahi Glass developed reinforced membranes in which small amounts of PTFE fibrils are dispersed in a perfluorosulfonic polymer. The proton resistance, water uptake, and hydrogen permeability values of these membranes are shown to be similar to that of non-reinforced membranes. However, improvements in these fibril-reinforced membranes are shown in increased mechanical strength. [90, 101]

1.2.4.5 Composite Membranes

Ionomeric membranes may be modified by incorporating inorganic compounds, such as silicon dioxide (SiO₂) [102] and zirconium hydrogen phosphate [103] into the hydrophilic domains of polyelectrolyte membranes to form nano-composite materials and to improve their mechanical strength, thermal stability, and water retention at elevated temperatures. This can be completed either by direct addition of particles to an ionomer solution, followed by casting, or by impregnation of membranes with solutions of inorganic precursors, such as tetraethylorthosilicate (TEOS) followed by in situ sol-gel reactions to produce a metal oxide.

1.2.4.5.1 Hydroscopic Oxides

The oxides SiO₂, ZrO₂, TiO₂, and Al₂O₃ have all been used as additives in composite membranes. These oxides are not proton conductive, but are hydroscopic and are added to increase water retention under high temperature and low relative humidity conditions. These oxides are generally available as
colloidal solutions or are formed through in situ, sol-gel chemistry from an appropriate alkoxide. [104]

For membranes cast from preformed silica particles (5 nm), the silica absorbs considerable amounts of water, but does not have a significant interaction with hydronium ions at low pH and therefore does not inhibit proton conduction. [105] Incorporation of SiO₂ particles increases the crystallinity of Nafion® and decreases the methanol permeability. [106]

Silica is formed inside pre-cast Nafion® through hydrolysis of TEOS. The nanophase separated morphology of Nafion® acts as a template for the silica phase. [102] When proton conductivity was studied as a function of silica loading at room temperature, water uptake increases and methanol permeability decreases as silica loading increases. Proton conductivity of the membrane also increases when the silica loading is greater than 10 wt%. [107]

Silica has also been incorporated into other polyelectrolytes such as sulfonated poly(fluorinated aromatic ethers), sulfonated styrene-(ethylene-butylene)-sulfonated styrene, and SPEEEK. When silica is incorporated into SPEEEK at 100% RH, the conductivity is unchanged at 0.065 S cm⁻¹ from 80 to 130°C. [108-113]

The hydroscopic oxides may be sulfonated to produce acidic materials with much higher proton conductivities. [114] By sulfonating the phenyl group of phenyltrialkoxysilane followed by hydrolysis, bifunctional silica that contains both –OH and –SO₃H functional groups is formed. When this bifunctional silica is incorporated into a polyelectrolyte membrane, there is an improvement in proton
conductivity compared to the membrane containing non-sulfonated silica, but it is still too low to be practical (0.02 S cm\(^{-1}\) at 80°C and 100% RH).\[^{115}\]

1.2.4.5.2 Clays

Clays are hydrous nanoparticles with a sheet structure where the sheets are bound by cations that lie between them, such as naturally occurring montmorillonite \(((\text{Mg}_{0.33}\text{Al}_{1.67})\text{Si}_{4}\text{O}_{10}(\text{OH})_{2})\text{Na}_{0.33}\) and synthetic laponite \((\text{Na}^{0.7+}[\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{0.2}(\text{OH})_4]^{0.7-}\). Composite membranes have been fabricated using clays with Nafion\(^\circledR\) as well as with SPEEK ionomers.\[^{116}\] Clays act as a barrier for methanol permeation and enhance or, at least, do not interfere with proton conductivity.\[^{117,118}\]

1.2.4.5.3 Zeolites

Zeolites are aluminosilicates with a framework structure enclosing cavities that may be occupied by large ions or water molecules. Zeolites that have been used as fuel cell membranes include chabazite and mordenite. Chabazite is stable in aqueous solution in the pH range 3-12 and is size selective to water over methanol. Mordenite is stable to 800 °C and is available in a protonated form. When zeolites are incorporated into Nafion\(^\circledR\) membranes, the membranes show decreased conductivity compared to unmodified Nafion\(^\circledR\).\[^{119,120}\]

1.2.4.5.4 Heteropolyacids

Heteropolyacids (HPAs) consist of clusters of tungsten, molybdenum, vanadium, and uranium oxides, which have a central heteroatom surrounded by tungsten or molybdenum oxygen octahedra. To prepare composite membranes,
HPAs are preferentially absorbed from aqueous solution into membranes. HPAs have high proton conductivity at room temperature (> 0.15 S cm\(^{-1}\)) where they are usually hydrated with about 20 water molecules per anion. However, at high temperatures, the conductivity decreases.\(^{121,122}\)

HPAs are generally water soluble, but can be immobilized in the membrane by formation of insoluble salts, by imbedding in a silicate matrix, or covalently linking an organic group to a coordination site. HPAs have been incorporated into Nafion\textsuperscript{®} membranes as well as SPAES and sulfonated (arylene ether nitrile ketone.\(^{121-125}\)

Fuel cell results show that using HPA composite membranes can lead to improvements in fuel cell performance. For example, when Nafion\textsuperscript{®} was imbibed with phosphotungstic acid in acetic acid at 80 °C for 24 h, the membrane had improved performance compared to unmodified Nafion\textsuperscript{®} at 110 °C.\(^{126}\) At 100 °C and 100% RH, the HPA-doped membranes exhibit improved conductivity compared to unmodified Nafion\textsuperscript{®}.

**1.2.4.5.5 Metal Phosphates**

Metal phosphates, such as zirconium phosphate (ZrP), tin phosphate, boron phosphate, and calcium hydrogen phosphate with Nafion\textsuperscript{®} and ZrP with SPEEEK have been used in fuel cells and show improved performance at high temperatures.\(^{103}\) For example, a series of Nafion 115\textsuperscript{®} and recast Nafion\textsuperscript{®} loaded with ZrP by exchange of Zr(IV) for protons followed by treatment of membrane with phosphoric acid have been fabricated and investigated. The proton conductivity of these membranes at 100% RH is lower than that of pure
Nafion® (0.13 vs 0.15 S cm⁻¹ at 100 °C). The fuel cell performance of these membranes at 130 °C is equivalent to that of Nafion 115® at 80 °C. [103]

A combination of reinforced and composite membranes have also been prepared with encouraging results. When ZrP/Nafion® membranes are supported by Teflon®, a decrease in resistance is achieved compared to that of the parent Nafion® (at 120 °C and 31%RH resistance is 0.25 Ω cm² for reinforced composite membrane vs 0.8 Ω cm² for unmodified Nafion®). [4]

1.3 Objectives

The focus of this thesis is on PEMs. An in-depth understanding of structure-property relationships in several categories of PEMs can be gained through the careful manipulation of a number of structural parameters. By examining many promising categories of PEMs, an overall picture can develop as to how to design PEMs for a variety of applications by controlling several structural features of PEMs to adjust their properties. In this thesis, a sulfonated polyimide was used as an example of a sulfonated aromatic hydrocarbon to investigate variations in the main chain structure. Adjusting the ionomer, reinforcing material composition, and reinforcing material pore size aided in the investigation of which features are important in reinforced membranes. Through the incorporation of two types of inorganic nanoparticles with a range of inorganic contents, it was possible to discern how the effect these nanoparticles have on the nanostructure of the membrane affects the composite membrane properties. Although all of these categories of PEMs have been well studied, there is still
fundamental knowledge of structure-property relationships missing. Comprehension of structure-property relationships in several categories of PEMs is the only way to competently design PEMs for a variety of applications. The understanding gained in this thesis is critical for the development of new PEM materials in the future.

In Chapter 2, the effect of incorporating a non-linear structure into the main chain of a sulfonated rigid rod polymer using the polyimide class of polymers is demonstrated. Two sulfonated polyimides are synthesized where the only difference is that one contains an angled structure. The angled structure of one of the sulfonated polyimides is expected to affect the macroscopic and physical properties of membranes prepared therefrom. The aim of this study is to investigate the role of angled versus linear polymer structures on membrane properties such as water uptake and proton conductivity.

The objective in Chapter 3 is to examine the effect of incorporating and confining polyelectrolytes inside the pores of reinforcing materials. In this investigation, thin, strong, reinforced polyelectrolyte membranes were fabricated and characterized. The effect of the reinforcing material on membrane properties such as proton conductivity, water vapour transmission, water uptake, and proton mobility are investigated. Also, by using a porous material of different pore sizes, the effect of pore size on the membrane properties is examined. By normalizing membrane properties for the ionomer content in the membranes, the effect of the reinforcing material on the ionomer inside the pores of the membrane is explored. These data are compared against those obtained from commercial
Nafion® membranes of different thickness, and against recast Nafion® and SPEEK.

In Chapter 4, the goal is to gain additional understanding of the effect of the inorganic components on membrane properties. Nafion® membranes are modified by the addition of variable amounts of ZrP or SiO₂. A systematic study of the effect of inorganic content on membrane properties is performed that includes confirming the structure of the inorganic component, changes in the morphology of the membranes, water sorption properties, water vapour transmission, proton conductivity, and proton mobility. The results are evaluated on the current theories for why inorganic nanoparticles improve fuel cell performance under certain conditions.

Chapter 5 is a summary of this work and a discussion of future work that may emerge from understanding structure-property relationships in several categories of PEM. This knowledge may aid in the development of PEMs that better suit the current requirements of low humidity, high temperature operating conditions.

1.4 References


CHAPTER 2: SULFONATED POLYIMIDES

2.1 Introduction

2.1.1 Condensation polymerization

Condensation polymers are obtained by the random encounter of two molecules. In condensation polymerization, monomers, oligomers, or higher molecular weight intermediates with complementary functional end units react to release a small molecule such as water. \[^{[1,2]}\]

Most condensation polymers are produced by step growth. Step reactions are those in which the chain growth occurs in a slow, stepwise manner. Two monomer molecules react to form a dimer. The dimer can then react with another monomer to form a trimer or with another dimer to form a tetramer. Thus, the average molecular weight of the system increases slowly over a period of time. In step polymerization, any two molecules in the system can react with each other, resulting in the disappearance of the monomer at an early stage in the polymerization and a broad molecular weight distribution in the later stages of the reaction. \[^{[3,4]}\]

High molecular weight condensation polymers are obtained when the starting materials are pure and the functional groups are present in exactly equal amounts. This requirement indicates that nearly an exact stoichiometric equivalence of monomers is required to obtain high conversion in A-A/B-B polycondensations. \[^{[1-4]}\]
In condensation reactions, the non-polymeric reaction products must be removed from the polymerization mixture. This is necessary to the growth of the polymer because at high temperatures most of the reactions are reversible and an equilibrium exists between the polymer species and the other condensation products. Heat, stirring, and reduced pressures all assist in the removal of volatile byproducts and increase the conversion to polymers with high molecular weights. \[^1,2\]

2.1.2 Polyimides

Polyimides are condensation polymers derived from bifunctional carboxylic acids or anhydrides and primary diamines. They contain the imide structure $-\text{CO-NR-CO-}$ as a linear or heterocyclic unit along the main chain of the polymer backbone, as shown in Figure 2.1. \[^1,2\]

![Figure 2.1: Polymers containing the imide structure.](image)

Selection of the specific monomers used in the synthesis of a polyimide depends on the desired polymer structure, the method of preparation to be employed, and the application in which the final polymer is used. \[^3,4\] The most general method for preparing polyimides involves the condensation of aromatic or aliphatic tetracarboxylic acids or anhydrides with primary aliphatic or aromatic
diamines. The water liberated in this reaction is removed by azeotropic distillation with an organic solvent. This method of preparation can be used for almost all aromatic diamines and dianhydrides. The reaction fails for diamines possessing bulky ortho substituents or orthophenylene diamines, which form benzimidazoles with anhydrides.\textsuperscript{[1, 2]}

Polyimides tend to share certain mechanical, physical, and electrical properties. They are generally tough with good impact strength. They are stiff and have a high flexural modulus below their glass transition temperature ($T_g$). Their tensile, flexural, and compressive strengths are excellent. The mechanical properties of polyimides can be improved by inert fillers such as glass, carbon powder, and minerals, which all serve to increase the stiffness. They tend to be good insulators and burn but are self-extinguishing.\textsuperscript{[1, 4]}

2.1.3 Sulfonated Polyimides

Over the last two decades, several new classes of proton-conducting polymer electrolytes have been formed into membranes and their properties investigated. These include membranes based on partially fluorinated polymers, composites, and aromatic polymers. The latter are particularly promising because they can be prepared in a wide variety of chemical structures and can be chemically modified at potentially low cost. The major approach to preparation of aromatic polyelectrolytes has been the attachment of sulfonic acid groups onto highly stable aromatic polymers such as poly(ether ether ketones) (PEEK)\textsuperscript{[5]}, polysulfones\textsuperscript{[6]}, and poly(phenylene sulfides).\textsuperscript{[7]} The introduction of sulfonic acid groups is achieved either by direct sulfonation of the parent
polymers or by polymerization of sulfonated monomers. Several classes possess good proton conductivities at elevated temperature and/or low humidity and show promising thermal and chemical stability. [8]

Sulfonated aromatic polyimides are a sub-class of polyaromatics that have attracted attention as PEMs because of their good proton conductivity and relatively small geometrical changes upon swelling-deswelling. [9] They are also reported to possess good thermal stability and mechanical durability, good oxidation resistance, and low methanol permeability. [10-12] It is found that rigid rod aromatic polyimides bearing sulfonic acid groups display high proton conductivity, comparable to, or greater than, that of Nafion®. At elevated temperatures, the conductivity of the sulfonated polyimides are reported to be even higher than Nafion® - up to 0.8 S cm⁻¹ at 100% relative humidity (RH) and 75 °C (c.f 0.08 S cm⁻¹ for Nafion® under similar conditions). [13] The synthetic methods for preparing sulfonated polyimides allow for careful control of the chemical structure, rigidity/flexibility of the backbone, ionic content, and distribution of ionic groups.

Previous studies on sulfonated polyimides have included investigating the effect of the distribution of ionic groups along the polymer backbone and variations in polymer structure on the membrane’s properties; [13-20] swelling in aqueous solution and gas transport mechanisms; [12, 21] proton conductivity, hydrolytic stability; and their use in gas diffusion electrodes in membrane electrode assemblies. [22-24] Generally, conductivity increases upon swelling in water; however, for block copolymers of polyimides, the conductivity decreases
as the ionic block length increases, even though swelling increases. Membranes based on random copolyimides possess lower conductivity than sequenced (block) structures but have better hydrolytic and oxidative stability than corresponding sequenced ones. [17] Further studies on structure-property relationships in polyimides find that hydrolytic stability of membranes is increased by introducing flexibility into the backbone, [21] and it has also been reported that the higher the basicity of the diamine group constituting the backbone, the greater the hydrolytic stability. [21, 24] Few studies have reported the effect of incorporating angled units in the polymer chain on the membrane properties. Furthermore, reported studies of a series of sulfonated polyimides involve changes in several structural parameters so that the effect of varying a single parameter is difficult to determine. [25]

2.1.4 Objectives

In this chapter, the effect of incorporating a non-linear structure into the main chain of a sulfonated rigid rod polymer using the polyimide class of polymers is demonstrated. The synthesis of random naphthalenic sulfonated polyimides by condensation polymerization of a sulfonated diamine, a non-sulfonated diamine, and a dianhydride is reported. The sulfonated diamine, 4,4’diamino-2,2’biphenyl disulfonic acid, A (Figure 2.2), provided sulfonic acid sites necessary for proton conductivity, and the naphthalenic dianhydride was incorporated because it is reported that membranes prepared from these substituents exhibit superior stability and higher conductivity than those prepared using phthalic dianhydrides. [26] The incorporation of thermostable diamines
containing sulfone groups was used as a diluting moiety to control the IEC of the final copolymer. The two non-sulfonated diamines, 4,4'-sulfonyldianiline (APS1) and 3,3'-sulfonyldianiline (APS2), differ only in the position of linking of the phenyl groups (see Figure 2.2): APS1 and APS2 are linked via the 1,4- and 1,3-positions, respectively. The angled structure of APS2 is expected to affect the macroscopic and physical properties of membranes prepared therefrom. The aim of this study is to investigate the role of angled versus linear polymer structures on membrane properties such as water uptake and proton conductivity.

2.2 Experimental Section

2.2.1 Materials

Concentrated hydrochloric acid (HCl) was purchased from Anachemia. Concentrated sodium hydroxide (NaOH) was purchased from Fisher Scientific. These were both diluted using MilliQ water (Millipore). The monomers used in this work, 4,4' diamino-2,2' biphenyl disulfonic acid (A), APS1, 1,4,5,8-Naphthalenetetracarboxylic dianhydride (B), and APS2, were purchased from Aldrich. A was dissolved in 1 M NaOH and recrystallized from 1 M HCl. APS1 and APS2 were recrystallized from ethanol. B was dried in a vacuum oven at 110 °C prior to use. Triethylamine, m-cresol, ethanol, dimethylformamide (DMF), isopropanol, sodium chloride, lithium chloride, and benzoic acid were purchased from Aldrich and were used as received.
2.2.2 Synthesis of Polyimides

The monomers were added to a 50 mL 3-necked flask equipped with a mechanical stirring device and a Dean-Stark trap attached to a condenser under nitrogen. The mole ratio of sulfonated and unsulfonated diamine was varied to achieve a range of ion exchange capacities (IEC). Sufficient dianhydride monomer was added to completely react with the diamine monomers. The polymers made from APS1 are named SPI1, and the polymers made from APS2, SPI2. The membranes of each type will be described by their IEC or by the ratio of sulfonated to unsulfonated monomer used. To prepare 50/50 SPI1, 0.379 g (1.10 mmol) A, 0.273 g (1.10 mmol) APS1, and 0.590 g (2.20 mmol) B were dissolved in 8 mL of m-cresol and 0.5 mL triethylamine. Then 0.25 g of benzoic acid and 20 mL of chlorobenzene were added and the mixture heated to 180 °C for 24 h. After cooling, the solutions were poured into isopropanol to precipitate the polymer. A fiberlike precipitate was filtered, washed with isopropanol, and dried in a vacuum oven at 80 °C. The remainder of the solvent was extracted from the polymer by Soxhlet extraction using methanol. This synthesis is outlined in Figure 2.2.
2.2.3 Viscosity Measurements

The relative and intrinsic viscosities of the polyimides were determined using an Ostwald viscometer tube equipped with an integrated temperature jacket and a digital timer.

The relative viscosity increment, $\eta_r$, defined in equation 2.1, was obtained from the efflux time.
\[ \eta_i = \frac{\eta - \eta_s}{\eta_s} = \frac{t - t_s}{t_s} \quad 2.1 \]

Where \( \eta \), \( \eta_s \), \( t \), and \( t_s \) are the viscosities and efflux times of the dilute polymer solution and pure solvent, respectively. As indicated by equation 2.2, intrinsic viscosity, \([\eta]\), is obtained from the intercept of a plot of reduced viscosity \((\eta/c)\) versus concentration, \( c \).

\[ \frac{\eta_i}{c} = [\eta] + k_H[\eta]^2c \quad 2.2 \]

Where \( k_H \) is a constant. Intrinsic viscosity is related to molecular weight by the Mark-Houwink-Sakurada equation, 2.3.

\[ [\eta] = K M^a_v \quad 2.3 \]

Where \( M_v \) is the viscosity average molecular weight. Both \( K \) and \( a \) are empirical constants that are specific for a given polymer, solvent and temperature.

The intrinsic viscosities of copolymer solutions at various concentrations in 14:1 DMF:water and 1% LiCl were determined at 30 °C. The molecular weights are not listed because \( K \) and \( a \) are unknown.

2.2.4 NMR Measurements

\(^1\)H NMR spectra were obtained by Dr. Yunsong Yang on a Varian Unity Spectrometer 500 MHz. The copolyimides in triethylammonium salt form were dissolved in DMSO-d6 at a concentration of ~10 mg mL\(^{-1}\).
2.2.5 Membrane Preparation

To prepare membranes, the copolyimides (in triethylammonium salt form) were dissolved in DMF and the solution was cast onto glass or Teflon plates. The films were fully protonated by soaking in 0.1 M HCl for 48 h, washing with deionized water, and drying under vacuum for 20 h.

2.2.6 Ion Exchange Capacity

Ion exchange capacity is defined as the millimolar equivalents of reactive $-\text{SO}_3\text{H}$ sites per gram of polymer and has units of meq g$^{-1}$. The ion exchange capacities, IEC, of the polyimides were experimentally verified. Acidified sulfonated polymer membranes were dried overnight at ~80 °C under vacuum before being weighed. The films were soaked in 2 M NaCl solution for ~2 h to extract all the protons from the membrane. The electrolyte solution was then neutralized using a dilute NaOH solution of known concentration. The end-point was detected using phenolphthalein as an indicator. The IEC values were calculated from the moles of NaOH used divided by the mass of the dry sample, $M_{\text{dry}}$, as given by equation 2.4. The reported experimentally-determined ion exchange capacities are the average of at least three separate titrated samples.

$$\text{IEC}_{\text{Experimental}} = \frac{V_{\text{NaOH}}[\text{NaOH}]}{M_{\text{dry}}}$$  \hspace{1cm} 2.4

Where $V_{\text{NaOH}}$ is the volume of NaOH that was titrated and $[\text{NaOH}]$ is the concentration of NaOH that was titrated.

The experimental values can be compared to the calculated IEC, which is based on the moles of sulfonated monomer added to the reaction flask was

56
determined using equation 2.5.

\[ \text{IEC}_{\text{Calculated}} = \frac{X_A N_{\text{sulfonated}}}{X_A M_A + X_B M_B} \]  

Where \( X_A \) and \( X_B \) are the mole fractions of monomers A and B, respectively, added to the reaction flask; \( M_A \) and \( M_B \) are the molecular weights of the sulfonated and unsulfonated segments, respectively; and \( N_{\text{sulfonated}} \) is the number of sulfonated groups per sulfonated segment.

### 2.2.7 Thermal Properties

Thermogravimetric analysis (TGA) of the copolymers in their acid form were measured on a Shimadzu instrument TGA-50. The copolymers were evaluated from room temperature to 700 °C in air at a heating rate of 10 °C per minute. Prior to measurement, the samples were dried at 150 °C for 30 minutes in the instrument chamber to remove excess water.

### 2.2.8 Water Sorption Properties

Water uptake was measured gravimetrically by determining the difference in mass of the swollen and dry membranes. The membrane was first dried under vacuum at 80 °C for at least 10 h and then weighed. The membranes were then soaked for several hours in water. The samples were wiped dry and weighed at room temperature. Water uptake is defined as the amount of water per gram of dry membrane and can be calculated using equation 2.6.

\[ \text{Water Uptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100 \]  

2.6

57
Where $M_{\text{wet}}$ is the mass of the saturated membrane and $M_{\text{dry}}$ is the mass of the dry membrane. Error bars were determined from the standard deviation of the measurements, where at least three measurements were made for each sample.

Water content is defined as the percent of water that is contained in the membrane. It may be calculated using equation 2.7, using the same symbols as those used in equation 2.6.

$$\text{Water Content} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{wet}}} \times 100$$

Water uptakes cannot be meaningfully compared to each other due to the difference in density among different polymer series. Therefore, water uptake is expressed as the number of water molecules per ionic group, $\lambda$, defined below in equation 2.8.

$$\lambda = \frac{n_{\text{H}_2\text{O}}}{n_{\text{SO}_3^-}} = \frac{\text{Water Uptake} \times 10}{18 \cdot \text{IEC}}$$

Where $n_{\text{H}_2\text{O}}$ is the number of moles of H$_2$O, $n_{\text{SO}_3^-}$ is the number of moles of SO$_3^-$, and 18 corresponds to the molecular weight of water.

The change in dimensions of the membranes was calculated by measuring the dimensions of the swollen and dry membranes along the x, y, z directions (equation 2.9). Membranes were first dried under vacuum for at least four hours and measured using a digital micrometer (Mitutoyo) and digital calliper (Mitutoyo) and then soaked for several hours in water and measured again.
2.2.9 Proton Conductivity

A Hewlett 8753A Network Analyzer was used to measure impedance spectra in the frequency range of 300 KHz to 1 GHz using a two-point probe, as shown in Figure 2.3. The relative humidity was controlled with an ESPEC Temp and Humid Chamber SH240 and by immersing the membrane in water. Proton conductivity was calculated using equation 2.10.

\[
\sigma = \frac{L}{R_m \times A}
\]

Where \(L\) is the distance between two Pt foil electrodes, \(R_m\) is the membrane resistance determined from AC impedance spectra, and \(A\) is the cross section area of the membrane. The thickness of the membranes was measured using a digital micrometer (Mitutoyo) and the width and length was measured using a digital calliper (Mitutoyo). The resistivities of the membranes were calculated using Zplot 2.8 for windows (Scribner Associates, Inc.).

\[
\%_d = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{wet}}} \times 100\%
\]

2.9

Figure 2.3: Schematic drawing of the proton conductivity probe.
The system used in this work can be represented as an equivalent circuit (Figure 2.4) \( C_M \) (bulk capacitance) and \( R_M \) (membrane resistance) are the main components. The relationship between the applied potential and the current flow is known as the impedance, which is the ac analog to the resistance-current-potential relationship of a dc circuit. The impedance (Z) has a magnitude \( (\Delta E/\Delta i) \) and phase (\( \phi \)) and is thus a vector quantity. Figure 2.4 shows a typical result obtained for our system. The important feature is the diameter of the semi-circle. The larger it is, the higher is the resistance. At low frequency, (the right side of the semi-circle) where it intersects the Z axis, the system is considered as pure resistance. When the frequency increases, the membrane capacitance dominates the impedance. The combination of the capacitance and resistance leads to the semi-circle. Due to the complexity of the results, software (Zplot 2.8) is needed to extract the membrane resistance (\( R_M \)).

Figure 2.4: A typical impedance plot from which conductivity data is calculated
Proton conductivity was measured at 95% RH with increasing temperature, and the temperature dependence of the conductivity and the activation energy determined using the slope of a plot of \( \ln(\text{conductivity}) \) vs \( \frac{1000}{T} \) (see equations 2.11 and 2.12).

\[
\sigma = \sigma_0 e^{\frac{\Delta E}{RT}} \tag{2.11}
\]

\[
\ln(\sigma) = \ln(\sigma_0) - \frac{\Delta E}{RT} \tag{2.12}
\]

Where \( \Delta E \) is the activation energy, \( R \) is the gas constant (8.31451 J K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the temperature.

### 2.2.10 Proton Concentration and Effective Proton Mobility

The ionic concentration of each membrane, \([H^+]\), was calculated using equation 2.13.

\[
[H^+] = \frac{\text{IEC} \times M_{\text{dry}}}{V_{\text{wet}}} \tag{2.13}
\]

Where \( \text{IEC} \) is the experimental IEC, \( M_{\text{dry}} \) is the mass of the dry membrane, and \( V_{\text{wet}} \) is the volume of the wet membrane.

The effective proton mobility, \( \mu_{\text{eff, H}^+} \), can be then be estimated from the experimental results for the proton conductivity and proton concentration (equation 2.14).
2.3 Results

2.3.1 Synthesis

Polymers were prepared by condensation polymerization as described in the experimental section. In this procedure the dianhydride and diamines are polymerized in *m*-cresol at 180 °C using benzoic acid as catalyst and chlorobenzene as an azoetrope. Under these conditions, chain growth and imidization occur spontaneously. The sulfonated diamine mole number is denoted *X* and the non-sulfonated diamine, *Y*. The ion-exchange capacity of the final sulfonated copolyimide was adjusted by adjusting the molar ratio of the two diamines.

2.3.2 NMR Measurements

Figure 2.5 shows representative $^1$H NMR spectra of SPI1 and SPI2 membranes with *x*=*y*=5. Peaks at 1.1, 3.05, and 3.15 ppm are assigned to the methyl and ethyl protons in triethyl ammonium and water protons, respectively. The peaks at 8.8 ppm are assigned to the protons on the naphthalene structure in both polyimides. The peaks at 8.0, 7.8, and 7.35 ppm are assigned to the protons ortho, para, and meta to the sulfonic acid, respectively in both SPI1 and SPI2. In SPI1, the peaks at 7.85 and 8.3 ppm are assigned to the protons meta and ortho to the sulfonyl group, respectively. In SPI2, the peaks at 7.9, 8.31, and 8.13 ppm are assigned to the protons para, meta, and ortho to the sulfonyl group,
respectively, while the peak at 8.29 is assigned to the peak ortho to both the sulfonyl group and the imide. The assignment of these peaks was determined based on that described by Mercier et al. \cite{10} on a similar polymer, as well as through the comparison of the spectra with that determined from Chemdraw Ultra™.

Figure 2.5: NMR spectra; A. SPI1, x=y=5; B. SPI2, x=y=5; and labelled structure C. SPI1; D. SPI2 of sulfonated copolyimide membranes.
2.3.3 Viscosity Measurements

Since the viscosity of a polymer solution is related to the molecular weight of the polymer, this method was used to give an indication of polymer molecular weight by comparing the results with those in the literature. [1,3] Because these polymers are ionomers, they behave differently from non-ionic polymers in solution. [27] The reduced and inherent viscosity of strong polyelectrolytes increases rapidly with dilution, instead of increasing linearly with concentration as is the case for neutral polymers. This phenomenon, the "polyelectrolyte effect", is well documented, and is due to intramolecular and/or intermolecular ionic interactions. As the solutions are diluted, the concentration of the counter ions decreases, forcing ionomer chains to extend (repulsion of anions). This results in an increase of reduced and inherent viscosity.

To avoid the polyelectrolyte effect 1 wt% LiCl was added to the DMF solution. Viscosity data for polymer solutions are presented in Table 2.1 and a representative plot for the determination of the intrinsic viscosity for SPI1 and SPI2 where x/y = 60/40 is presented in Figure 2.6. Viscosities range from 0.012 to 0.233 L g⁻¹, and are similar to those reported by other groups. For example,
Gunduz and McGrath report intrinsic viscosities of polymers prepared from phthalic dianhydrides possessing bulky groups that ranged from 0.021 - 0.123 L g\(^{-1}\), and which corresponded to molecular weights of 22.3-43.4 kg mol\(^{-1}\), as estimated by GPC. \(^{[9, 11]}\) Others report similar viscosity data for phthalic and naphthalenic dianhydride - based polyimides. \(^{[13, 25]}\) Based on this data, it is deduced that SPI1 and SPI2 are high molecular weight polymers. Furthermore, casting of solutions of SPI1 and SPI2 produced strong, flexible films, which also indicates a significant molecular weight.

Figure 2.6: Representative viscosity plots of SPI1 and SPI2 where x/y = 60/40.
Table 2.1: Physical properties of SPI1 and SPI2 membranes possessing varied IEC.

<table>
<thead>
<tr>
<th>X/Y</th>
<th>$\eta$ g/cm$^3$ dl$^{-1}$</th>
<th>Theoretical IEC$^a$ meq g$^{-1}$</th>
<th>Experimental IEC$^b$ meq g$^{-1}$</th>
<th>$\lambda$</th>
<th>$E_a$ KJ mol$^{-1}$</th>
<th>$%_1$</th>
<th>$%_2$</th>
<th>$[H^+]$ M</th>
<th>$\mu_{gfr,H^+}$ cm$^2$ V$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPI1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/80</td>
<td>0.79</td>
<td>0.81 (0.03)</td>
<td>24</td>
<td>6</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30/70</td>
<td>1.14</td>
<td>1.09 (0.08)</td>
<td>25</td>
<td>6</td>
<td>12</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40/60</td>
<td>0.56</td>
<td>1.51</td>
<td>1.45 (0.07)</td>
<td>23</td>
<td>10.3</td>
<td>7</td>
<td>11</td>
<td>1.1</td>
<td>$4.0 \times 10^4$</td>
</tr>
<tr>
<td>50/50</td>
<td>2.33</td>
<td>2.83</td>
<td>1.77 (0.07)</td>
<td>21</td>
<td>11.6</td>
<td>32</td>
<td>8</td>
<td>1.6</td>
<td>$4.3 \times 10^4$</td>
</tr>
<tr>
<td>60/40</td>
<td>0.88</td>
<td>2.15</td>
<td>1.95 (0.09)</td>
<td>21</td>
<td>11.8</td>
<td>33</td>
<td>11</td>
<td>1.5</td>
<td>$4.3 \times 10^4$</td>
</tr>
<tr>
<td>70/30</td>
<td>2.46</td>
<td>2.40 (0.07)</td>
<td>25</td>
<td>15.3</td>
<td>101</td>
<td>13</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80/20</td>
<td>0.56</td>
<td>2.75</td>
<td>2.70 (0.09)</td>
<td>32</td>
<td>12.9</td>
<td>143</td>
<td>13</td>
<td>0.96</td>
<td>$8.9 \times 10^4$</td>
</tr>
<tr>
<td>SPI2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/80</td>
<td>0.79</td>
<td>0.77 (0.07)</td>
<td>25</td>
<td>16.8</td>
<td>7</td>
<td>7</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30/70</td>
<td>1.14</td>
<td>1.11 (0.08)</td>
<td>18</td>
<td>10.5</td>
<td>10</td>
<td>6.8</td>
<td>1.4</td>
<td>$4.3 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>40/60</td>
<td>1.13</td>
<td>1.83</td>
<td>1.80 (0.03)</td>
<td>18</td>
<td>9.2</td>
<td>7</td>
<td>7</td>
<td>1.5</td>
<td>$4.3 \times 10^4$</td>
</tr>
<tr>
<td>50/50</td>
<td>1.16</td>
<td>2.15</td>
<td>2.10 (0.08)</td>
<td>17</td>
<td>12.6</td>
<td>22</td>
<td>11</td>
<td>1.7</td>
<td>$5.6 \times 10^4$</td>
</tr>
<tr>
<td>60/40</td>
<td>0.98</td>
<td>2.75</td>
<td>2.68 (0.09)</td>
<td>19</td>
<td>9.9</td>
<td>64</td>
<td>13</td>
<td>1.4</td>
<td>$8.5 \times 10^4$</td>
</tr>
<tr>
<td>70/30</td>
<td>2.46</td>
<td>2.43 (0.08)</td>
<td>20</td>
<td>12.8</td>
<td>86</td>
<td>18</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80/20</td>
<td>0.56</td>
<td>2.75</td>
<td>2.68 (0.09)</td>
<td>19</td>
<td>9.9</td>
<td>64</td>
<td>13</td>
<td>1.4</td>
<td>$8.5 \times 10^4$</td>
</tr>
</tbody>
</table>


2.3.4 Ion Exchange Capacity

The ion exchange capacity is a measure of the number of ionic groups (sulfonic acid) per gram of polymer. Ion exchange capacity has a direct influence on membrane properties such as water uptake, swelling, and proton conductivity. The IEC of the membranes was determined by titration and the values compared to theoretical values. These comparisons are reported in Table 2.1 and show
good agreement (+/-10%) even for membranes possessing low IEC. This indicates that water is accessible to all sulfonic acid groups and that all protons should contribute to proton conduction, i.e. there are no buried acidic sites, which implies a contiguous phase separated network of ionic domains.

2.3.5 Water Sorption and Proton Conductivity

As anticipated, the room temperature conductivity of both SPI1 and SPI2 membranes increases with increasing IEC, as shown in Figure 2.7. The room temperature conductivity values of SPI1 and SPI2 membranes are high, ranging from 0.031 ± 0.003 to 0.071 ± 0.006 and 0.019 ± 0.003 to 0.095 ± 0.006 S cm⁻¹, respectively. The conductivity of the SPI2 membrane is generally higher than that of the SPI1 membrane by 0.01 to 0.02 S cm⁻¹. Water uptake data for the membranes are plotted in Figure 2.8 to visualize the trend. For SPI1, water uptake increases from 37 ± 3 to 158 ± 30 wt% as IEC increases from 0.81 to 2.70 meq g⁻¹. For SPI2, the increase is 34 ± 3 to 89 ± 5 wt% for an increase in IEC from 0.77 to 2.68 meq g⁻¹. That is, the linear polymer, SPI1, swells to a greater extent. The corresponding lambda values (water molecules per ionic group) are calculated to range from 21 ± 2 to 33 ± 2 for SPI1 and 16 ± 2 to 25 ± 2 for SPI2 (Table 2.1): consistent which the observation that SPI1 absorbs more water than SPI2. The absorption of water necessitates an increase in volume of the membrane. Changes in the length and thickness of the membranes were measured and data listed in Table 2.1. The percentage increase in length upon absorption of water from the dry state ranges between 7 ± 0.7 and 18 ± 2%, showing no clear trends with IEC because of the inherent inaccuracy of the
technique. The thickness, however, increases significantly especially for high IEC membranes. The percentage increase in thickness is 143 ± 0.4 and 64 ± 0.3% for high IEC SPI1 and SPI2 membranes, respectively, which is consistent with the larger uptake of water by SPI1. Having knowledge of the volume of the water-swollen membranes and the IEC, the average proton concentration in the membrane was calculated (Table 2.1). Both series show a trend wherein [H+] increases with increasing IEC for low IEC membranes, is maximum for intermediate IEC, and decreases with increasing IEC in the high IEC regime. The proton concentrations of SPI1 membranes were lower than that of the SPI2 membranes. Using the proton concentration and proton conductivity, the effective proton mobility was calculated (Table 2.1). Both SPI1 and SPI2 membranes show increasing effective proton mobility with increasing IEC. For similar IEC values, the effective proton mobilities of the membranes are similar to each other.

Figure 2.7: Proton conductivity of SPI1 and SPI2 as a function of IEC. 95% RH, 30 °C.
The conductivity of several polyimide membranes was determined under 95% RH at various temperatures; these data are plotted in Figure 2.9. Generally, it is found that conductivity increases with increasing temperature but levels off at ~60°C. The apparent activation energy of conduction for these polymers has been determined from the slope of the Arrhenius plot shown in Figure 2.10. For SPI1, they range from $10 \pm 0.8$ to $15 \pm 0.7$ kJ mol$^{-1}$; for SPI2, $9 \pm 0.7$ to $15 \pm 0.7$ kJ mol$^{-1}$.
2.3.6 Thermal Properties

A three-step degradation profile is observed for the polymers using TGA (Figure 2.11). The first significant weight loss (below 200 °C) is due to loss of water. Desulfonation of the polyimides starts at ~ 300 °C. A third weight loss at
550 °C is attributed to the degradation of the polymer backbone. These values are similar in both SPI1 and SPI2 and similar in nature to those reported in the literature for similar structures.

Figure 2.11: TGA profiles of SPI1 and SPI2.

2.4 Discussion

In this work, it was found that the conductivity of SPI2 is higher than SPI1 while water uptake is lower. The lower degree of swelling in SPI2 may be due to the angled structures, which promote entanglement of individual chains and restrict the remobilization of chains required for swelling. In SPI1 membranes, the chains are linear, rigid rods in nature, and thereby less entangled than SPI2. This results in lower λ values, lower anisotropic swelling, higher [H+] and increased proton conductivity for SPI2 membranes. Furthermore, the fact that swelling increases significantly in the direction parallel with the film implies the polymers have a preferential alignment parallel to the surface and the observation that swelling in this direction is even larger in SPI1 implies that these
membranes have a higher degree of ordering parallel to the surface than SPI2; this is illustrated schematically in Figure 2.12. Despite λ values being lower in SPI2 than SPI1 for a given IEC and despite the indication that these polymers are less likely to form stacked rigid rods, SPI2 exhibits a higher conductivity, as shown in Table 2.1; this is most likely due to a higher proton concentration.

A.

B.

\[
\text{H}_2\text{O}
\]

Having postulated that angled polymer chains reduced swelling and possess higher conductivity, SPI1 and SPI2 are compared with literature data to determine if this is a representative trend. A comparison of membrane properties prepared from a variety of sulfonated polyimides reported in the literature is shown in Table 2.2 and the related polymer structures are shown in Figure 2.13. Polymers 1 [14], 3 [16], 4Ai, 4Aii, and 4B [13] are relatively flexible by virtue of the presence of ether groups. In 2 [18], 3 [16], 4Biv [13] the chains are flexible and contain “angled” motifs because of the introduction of phenyl groups linked via the 1,3 position (2, 3iii) and 9,9-bis(4-aminophenyl)fluorene (3, 4iv).
Figure 2.13: Examples of related sulfonated polyimides reported in the literature.

1 \([6, 18]\)

2 \([21]\)

3 \([11]\)

4 \([6]\)

5 \([8]\)
Table 2.2: Physical properties for selected polyimides.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>X</th>
<th>X/Y</th>
<th>IEC (meq g(^{-1}))</th>
<th>S (%)</th>
<th>λ (S cm(^{-1}))</th>
<th>Δt/Δl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[4,15]</td>
<td>1</td>
<td>30/70</td>
<td>1.26</td>
<td>39.3</td>
<td>0.010</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>30/70</td>
<td>1.26</td>
<td>40.6</td>
<td>18</td>
<td>0.018</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>30/70</td>
<td>1.26</td>
<td>44.3</td>
<td>20</td>
<td>0.012</td>
<td>31</td>
</tr>
<tr>
<td>9</td>
<td>30/70</td>
<td>1.26</td>
<td>69.3</td>
<td>30</td>
<td>0.004</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>40/60</td>
<td>1.63</td>
<td>56.5</td>
<td>19</td>
<td>0.014</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>50/50</td>
<td>1.98</td>
<td>67.8</td>
<td>19</td>
<td>0.037</td>
<td>59</td>
</tr>
<tr>
<td>2[16]</td>
<td>5</td>
<td>30/70</td>
<td>0.96</td>
<td>19.0</td>
<td>0.0013</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>40/60</td>
<td>1.30</td>
<td>27.0</td>
<td>12.0</td>
<td>0.0065</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50/50</td>
<td>1.64</td>
<td>42.0</td>
<td>15.0</td>
<td>0.0059</td>
<td></td>
</tr>
<tr>
<td>Statistical</td>
<td>1</td>
<td>30/70</td>
<td>0.96</td>
<td>11.0</td>
<td>7.0</td>
<td>0.00091</td>
</tr>
<tr>
<td>Statistical</td>
<td>1</td>
<td>50/50</td>
<td>1.64</td>
<td>31.0</td>
<td>11.0</td>
<td>0.0041</td>
</tr>
<tr>
<td>3[13] Homo</td>
<td>4/1</td>
<td>2.36</td>
<td>122</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i, statistical</td>
<td>2/1</td>
<td>2.09</td>
<td>76</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i, statistical</td>
<td>1/1</td>
<td>1.71</td>
<td>57</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii, statistical</td>
<td>4/3</td>
<td>1.68</td>
<td>56</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ii, statistical</td>
<td>2/1</td>
<td>1.87</td>
<td>69</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i, sequenced</td>
<td>2/1</td>
<td>2.09</td>
<td>102</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii, sequenced</td>
<td>2/1</td>
<td>1.87</td>
<td>77</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i, statistical</td>
<td>1/1</td>
<td>1.98</td>
<td>79</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4[2] B</td>
<td>3.37</td>
<td>3.37</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aiv</td>
<td>1/1</td>
<td>1.73</td>
<td>63</td>
<td>0.096</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5[2]</td>
<td>18/2</td>
<td>3.26</td>
<td>9</td>
<td>9.22^b</td>
<td>0.0001</td>
<td></td>
</tr>
</tbody>
</table>

a: reference given in parentheses, b: at 100% RH

In this study, the conductivity of the polymers is high, ranging from 0.019 to 0.095 S cm\(^{-1}\). These are comparable to those of sulfonated polyimides that are reported in the literature. For example, the conductivity of 4Aiv\(^{[13]}\) is 0.096 S cm\(^{-1}\) possessing an IEC of 1.73 meq g\(^{-1}\); the conductivity of 1\(^{[15]}\) having an IEC of 1.26 meq g\(^{-1}\) is 0.018 S cm\(^{-1}\). For comparison, the conductivity of Nafion® is 0.08 S cm\(^{-1}\). The conductivity values of the polymers described in the current study are much higher than several sulfonated polyimides described in the literature. For example, the conductivity of 2\(^{[18]}\) ranges from 0.00091 to 0.0065 S cm\(^{-1}\). In contrast, some other examples sulfonated polyimides report much higher...
conductivity values than SPI1 and SPI2. For example, the conductivity of 3\cite{16} ranges from 0.10 to 0.30 S cm\(^{-1}\).

The conductivity values and water content of SPI1 and SPI2 increase with IEC. This behaviour is similar to that reported for sulfonated polyimide membranes in the literature. For example, for polymer 1, as the IEC increases from 1.26 to 1.98 meq g\(^{-1}\), the water uptake increases from 44.3 to 67.8\%, and proton conductivity increases from 0.012 to 0.037 S cm\(^{-1}\).\cite{15} The conductivities of SPI1 and SPI2 membranes generally increase with increasing temperature and level off at \(-60\) °C, which is most likely due to loss of water. For membranes based on polymer 3, the conductivities also level off at \(-60\) °C.\cite{16} Proton conductivity of Nafion\textsuperscript{®} also maximises in this region.\cite{28}

The conductivity of SPI2 is greater than SPI1 while the water swelling is lower. Previous studies on related polymers report conflicting results. Polymers 1 and 2 differ mainly in the fact that 1 is angled. Compared to membranes based on polymer 1\cite{15}, 2\cite{18} has fewer water molecules per sulfonate group and a lower conductivity, e.g. for 2, \(\lambda=15.0\) and \(\sigma=0.0059\) S cm\(^{-1}\) for an IEC of 1.64 meq g\(^{-1}\); for 1, \(\lambda=19.0\) and \(\sigma=0.014\) S cm\(^{-1}\) for an IEC of 1.63 meq g\(^{-1}\). However, other studies report that introducing angled species into polymers can increase the conductivity with little effect on the water uptake. For example, the conductivity of 5\cite{11}, which is prepared from linear polymers, is 0.003 S cm\(^{-1}\) with \(\lambda=4\) for (IEC of 3.26 meq g\(^{-1}\)) at 50% RH. This is much less than that of angled polymer 4Aiv\cite{13}, \(\sigma=0.01\) S cm\(^{-1}\), \(\lambda=5\) (IEC of 3.37 meq g\(^{-1}\)) under the same conditions.

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The calculated activation energies of proton conduction for SPI1 and SPI2 range from 9 to 15 kJ mol\(^{-1}\). These values are higher than the reported values for Nafion\(^\oplus\) \([29]\) (~4 kJ mol\(^{-1}\)) and slightly lower than other polyimide membranes, such as 4iv \([13]\) (21 kJ mol\(^{-1}\)). Both vehicular transport of hydronium ions and the structural diffusion may potentially be applicable for the proton conduction in hydrated polymer membranes. \([29]\) The high values for \(E_a\) in SPI1 and SPI2 imply that vehicular transport is dominant.

Studies of changes in dimension with swelling reveal that SPI1 and SPI2 membranes do not significantly increase in length, but increase considerably in thickness, especially for membranes with high IEC. These results are similar to the dimensional changes that are reported for polymer 1: as the IEC increases from 1.26 to 1.98 meq g\(^{-1}\), its thickness increases from 31 to 59%; but its length increases by only 5%. \([15]\) The anisotropy of SPI membranes has been studied by other groups. \([30]\) Through small angle x-ray scattering and TEM studies, it is observed that there are not ionic domains in the polymer matrix, but disk-like hydrophobic domains spaced by a continuous hydrophilic phase.

### 2.5 Conclusion

A comparison of linear and angled sulfonated polyimides reveals that the membranes formed from the angled polymers, SPI2, exhibit lower water uptake, higher proton concentration, and higher conductivity than the membranes prepared from the linear polymers, SPI1. These differences are attributed to increased entanglements of the non-linear polymers. These structure-property relationships may be relevant to other rigid sulfonated polymer systems and
should be taken into consideration when fine-tuning the physical and transport properties of alternative polymer systems for proton exchange membranes.

2.6 References


CHAPTER 3: REINFORCED MEMBRANES

3.1 Introduction

3.1.1 Reinforced Ionomer Membranes

Reinforced membranes are obtained by filling a non-proton conducting polymeric matrix with ionomer. In reinforced membranes only ionomers of high proton conductivity are used. Furthermore, in order to make the membrane proton conductive, the ionomers must be situated along continuous pathways. The proton conductivity of these membranes depends on the degree of porosity, and on the size and distribution (or tortuosity) of the preformed pores, as well as on the nature of the filler and the degree of pore filling.

There is increasing interest in thin membranes for PEMFCs because they can lead to improved water management of the membrane and lower internal resistance during fuel cell operation. [1-6] During fuel cell operation, water is carried into the cell by humidified fuel and oxidant and also produced electrolytically at the cathode. Water is transported from anode to cathode by electro-osmotic drag, and is opposed by back diffusion due to a water activity gradient and hydraulic pressures in the cell. Thinner membranes are preferred for low humidification or non-humidification operating conditions because back diffusion of water is enhanced, thereby reducing dehydration at the anode and/or flooding at the cathode. A challenge in the development of thinner membranes is their reduced mechanical strength, especially when fully hydrated. The use of
reinforcing materials in conjunction with ionomers allows fabrication of thin membranes with improved mechanical strength. This has been demonstrated through the fabrication of PFSA membranes reinforced with a porous PTFE sheet. [7] Nafion®-impregnation into porous polypropylene, [4,8] polycarbonate, [9] expanded PTFE, [5] polysulfone, and microglass fiber fleece [10] has also been demonstrated. Other solid polymer electrolytes have been used to prepare reinforced membranes, including sulfonated polystyrene [11] and sulfonated poly(ether ether ketone). [6]

By means of reinforcement, the thickness of PFSA membranes can be reduced to as low as 5 μm with satisfactory conducting and mechanical properties: [4, 12-15] Lee et al. used polycarbonate as a support material for PFSA to fabricate membranes with conductivities of 0.06 S cm⁻¹ and thicknesses of 42.3 μm. [16] Nouel and Fedkiw used PTFE and Celgard® (polypropylene) as supporting materials with PFSA to fabricate membranes with conductivities of 0.10 and 0.021 S cm⁻¹ at 65 °C and thicknesses of 25 and 28 μm, respectively. [4] Dhathathreyan et al. [17] fabricated PTFE-based membranes with thicknesses of 35 μm, and found that the conductivity of the membrane is dependent on the solubility parameter of the solvent: solvents having a solubility parameter closer to that of the ionic side chains improve the conductivity due to a reduction in bonding between Nafion® and PTFE, allowing the ionic groups to remain unbound, freeing protons for migration. Huang et al. prepared reinforced membranes by impregnation of porous PTFE membranes with Nafion® solutions containing various contents of surfactant. Experimental results reveal that mixing
1 - 3 wt% surfactant into the Nafion® solution facilitates penetration of Nafion® into PTFE pores, leading to improved ionic conductivity compared to when surfactant is absent. [18]

When examining the swelling behaviour of the reinforced membranes, Oh et al. [5] impregnated Nafion® solution into porous expanded PTFE and discovered that water uptake and the water flux of the reinforced membrane increased as the Nafion® loading amount increased and the rate of water uptake with temperature for the composite membrane was determined to be larger than Nafion 112®. Dhathathreyan et al. [17] also studied water uptake of a porous PTFE + Nafion® reinforced membrane and found that the water uptake of the reinforced membrane was about half the value of Nafion 1135®. The dimensional changes with swelling for these membranes were also less than Nafion®.

There have been promising fuel cell performances observed using reinforced membranes. [6,18-20] Lin et al. [18] used 20μm thick PTFE + Nafion® membranes for operation in a direct methanol fuel cell. At 70 °C and with 2 M feed methanol, the performance of the reinforced membranes was 390 mA cm⁻² at 0.2 V. This is superior to that of Nafion 117® and Nafion 112®, which had performances of 310 and 275 mA cm⁻², respectively. At 70 °C, the proton resistances of the reinforced membrane, Nafion 112® and Nafion 117® are 0.192, 0.162, and 0.552 Ω, respectively. The reinforced membrane had lower methanol crossover than Nafion 117® and Nafion 112®. The improved fuel cell performance of the reinforced membranes compared to Nafion 112® and Nafion 117® is
attributed to low proton resistance of the reinforced membranes compared to Nafion 117® and/or low methanol crossover.

Zhang et al. [3] found that the porosity and thickness of porous PTFE affected membrane properties. In H2/O2 fuel cells at 80 °C and with a gas pressure of 0.2 MPa, the current densities of fuel cells at 0.6 V using reinforced Nafion® with PTFE having pore sizes of 0.3 - 0.5μm were 500 - 850 mA cm−2, respectively. At 80 °C and with gas pressures of 0.2 MPa, the current densities at 0.6 V were 800, 800, and 950 mA cm−2 for Nafion 115® and Nafion® incorporated into PTFE having thicknesses of 45μm and 25μm, respectively.

These fuel cell testing results show that increasing the pore size and decreasing the thickness of the reinforcing materials leads to improved current densities. Their dimensional stability in the presence of water, mechanical strength, and the areal proton resistance were also improved compared to thicker bulk Nafion® membrane. Water content increased with increasing thickness of the reinforcing material, although it is still lower than Nafion®.

Reinforced membranes have also been fabricated using SPEEK and sulfonated polystyrene. [6,11] Membranes based on SPEEK incorporated into PTFE were found to possess a larger resistance than the bulk SPEEK membrane, but these disadvantages were compensated by the much thinner membrane, obtained by virtue of the improved dimensional stability and mechanical strength. Lifetime analysis indicated that the cell performance could be maintained for > 150 hours. [6] PTFE + SPS membranes showed comparable
or higher conductivity and lower methanol permeability than Nafion 117\textsuperscript{®} membranes.\textsuperscript{[11]}

3.1.2 Reinforcing Materials

3.1.2.1 Polypropylene

Polypropylene is a light-weight plastic with a moderately high melting temperature (200 °C) that finds use in the manufacture of materials such as pipes, sheets, and textile fibres.\textsuperscript{[21]}

Polypropylene changes from a glassy to a rubbery or flexible thermoplastic state (glass transition) above -10 to -18 °C. The methyl groups in polypropylene are susceptible to thermooxidative degradation when heated. Above 300 °C the rate of polymer propagation and depopagation are equal and the polymer begins to degrade.\textsuperscript{[21]}

A common use for polypropylene membranes is in the filtration of solid particles such as dust, salts, and bacteria from liquids or airstreams. To prepare microporous membranes, a semicrystalline polypropylene film is stretched in the solid state. Stretching forces a separation of crystalline lamella and results in the creation of slitlike pores.\textsuperscript{[21]}

3.1.2.2 Ultrahigh molecular weight polyethylene

One class of polyethylene, which has molecular weight in the range of one to five million, has exceptional impact and tensile strength, tear and puncture resistance, high abrasion resistance, low coefficient of friction, and chemical inertness. Applications for this ultrahigh molecular weight polyethylene
(UHMWPE) include orthopaedic implants, battery separators, and as additives for improving the sliding and wear behaviour of other thermoplastics. [21]

UHMWPE is a type of polyolefin and, despite relatively weak Van der Waals bonds between its molecules, derives strength from the length of each individual molecule. It is made up of extremely long chains of polyethylene, which all align in the same direction. Each chain is bonded to the others with so many Van der Waals bonds that the whole can support great tensile loads. [22] When formed to fibers, the polymer chains can attain a parallel orientation greater than 95% and a level of crystallinity of up to 85%.

The weak bonding between ethylene molecules in UHMWPE allows local thermal excitations to disrupt the crystalline order of a given chain piece-by-piece, giving it much poorer heat resistance than other high-strength fibers. Its melting point is around 144 to 152 °C, and it should not be used at temperatures exceeding 80 to 100 °C for long periods of time. It becomes brittle at temperatures below -150 °C. [22]

The simple structure of the molecule also gives rise to surface and chemical properties that are rare in high-performance polymers. Aromatic polymers are often susceptible to aromatic solvents due to aromatic stacking interactions, an effect aliphatic polymers like UHMWPE (and polypropylene) are immune to. Since UHMWPE does not contain chemically reactive groups (such as esters, amides, or hydroxylic groups) that are susceptible to attack from aggressive agents, it is very resistant to water, moisture, most chemicals, UV
radiation, and micro-organisms. Because there are no polar groups, UHMWPE does not absorb water readily, but it also does not get wet easily, which makes bonding it to other polymers difficult. It is possible to increase the hydrophilicity of UHMWPE by incorporation of hydrophilic molecules such as silicon dioxide. [22]

3.1.2.3 Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer, which finds numerous applications. PTFE's most well known trademark in the industry is the DuPont brand name Teflon®, as DuPont initially discovered PTFE. PTFE has an extremely low coefficient of friction, is very non-reactive, and has excellent dielectric properties. This makes PTFE suitable for use as a non-stick coating for pans and other cookware, in containers and pipework for reactive and corrosive chemicals, and as an insulator in cables and connector assemblies. [21]

PTFE is a white solid at room temperature, and has a density of about 2.2 g cm\(^{-3}\). Its melting point is 327 °C, but its properties degrade above 260 °C. [21]

PTFE is either synthesized by the emulsion polymerization of tetrafluoroethylene monomers under pressure, using free-radical initiators, or it may be produced by the direct substitution of hydrogen atoms on polyethylene with fluorine, using polyethylene and fluorine gas at 20 °C. [21]

Rapidly stretching PTFE under the right conditions creates a very strong, microporous material. The result, known as GORE™ expanded PTFE (ePTFE), exhibits an amazing array of properties including strength (high strength-to-
weight ratio), high thermal resistance, low flammability, low water adsorption, and good weathering properties.\textsuperscript{[21]}

3.1.3 Sulfonated Poly(ether etherketone)

Currently PFSA membranes, such as Nafion\textsuperscript{®}, are the most widely used membranes in fuel cell studies. Although there are many positive attributes of Nafion\textsuperscript{®}, their conductivity at low relative humidity due to dehydration is a cause for concern.\textsuperscript{[1]} In the development of alternative polymer electrolyte membranes, aromatic polymers containing ether links have been widely investigated, e.g., polyetheretherketone (PEEK, Victrex\textsuperscript{®}). Being aromatic, the base polymer has excellent thermal and oxidative stability and a higher glass transition temperature of 143 °C.

Proton conductivity can be bestowed on the polymer by sulfonation. Sulfonation of PEEK is a second order reaction, which takes place at the aromatic ring flanked by two ether links, due to higher electron density of that ring because the other rings have low electron density due to the carbonyl bond, resulting in only one sulfonic acid group per repeat unit. The sulfonation rate of PEEK in sulphuric acid can be controlled by adjusting the reaction time, temperature, and acid concentration resulting in sulfonation degrees of 30 – 100\textsuperscript{%}.\textsuperscript{[23]} The degrees of sulfonation required for sufficient conductivity results in excessive swelling in water and poor mechanical properties, especially at higher operating temperature.\textsuperscript{[24]} These materials exhibit less phase separation than Nafion\textsuperscript{®} and have narrower proton conduction channels, resulting in an increased dependence on water for proton conduction. Long-term testing of these materials
under typical fuel cell operating conditions (e.g. 80 °C, 100% RH) has shown that they are unstable, generally losing mechanical strength due to excessive swelling. The chemical structure of SPEEK is shown in Figure 3.1. [24]

Figure 3.1: Chemical structure of SPEEK

3.1.4 Objectives

Although there has been much emphasis on evaluating bulk properties of proton resistance and fuel cell performance of reinforced membranes, by comparison, there has been little effort towards understanding how the properties of the ionomer inside the membrane are affected, i.e., what are the effects of confining polyelectrolytes in porous media and how does this relate to the bulk properties of the membrane? Despite the perceived advantages of employing thinner, reinforced membranes in regards to increased back diffusion of water during fuel cell operation, there is little work in the published literature on the transport of water through reinforced membranes. The objective of this work is to examine water vapour transport through reinforced membranes and to study the effect of incorporating and confining polyelectrolytes in the pores of reinforcing materials. In this investigation, thin, strong, reinforced polyelectrolyte membranes are fabricated and characterized. They include Nafion® and SPEEK in Celgard® (polypropylene), Daramic® (ultra-high molecular weight polyethylene), and PTFE membranes. The effect of the reinforcing material on membrane properties such
as proton conductivity, water vapour transmission, water uptake, and proton mobility are investigated. Also, by using a porous material of different pore sizes, the effect of pore size on the membrane properties is examined. By normalizing membrane properties for the ionomer content in the membranes, the effect of the reinforcing material on the ionomer inside the pores of the membrane is explored. These data are compared against those obtained for commercial Nafion® membranes of different thickness, and against recast Nafion® and SPEEK.

3.2 Experimental Section

3.2.1 Materials

Dimethylformamide (DMF), dimethylacetamide (DMAc), sulfuric acid (H₂SO₄), and 5 wt% Nafion® solution in water/alcohol were purchased from Alfa Aesar and used as received. Hydrogen peroxide (H₂O₂), sodium hydroxide (NaOH), and sodium chloride (NaCl, 99%, reagent grade) were purchased from Sigma Aldrich and used as received. PEEK was supplied by Victrex USA Inc. MilliQ water (Millipore) was used in washing and swelling membranes and for making solutions. Celgard® (CG) with different pore sizes and Daramic® (WDM) were supplied by Celgard. Polytetrafluoroethylene (PTFE) with different pore sizes and thicknesses was purchased from Millipore® Corporation. The porosity and pore size are taken from their respective product specification sheets.

Extruded membranes, Nafion 112® and 115®, were purchased from Sigma Aldrich and dispersion cast NRE 211® was purchased from DuPont. These
membranes have thicknesses of 51, 127, and 25 μm, respectively. The IEC of the extruded membranes is 0.91 meq g⁻¹, while the IEC of NRE 211 is 0.92 meq g⁻¹.

3.2.2 Membrane Fabrication

200 g of 5 wt% Nafion® solution in water/alcohol (IEC=0.9 meq g⁻¹) was added to a beaker to prepare 20-25 wt% Nafion®/DMF solution. The solution was heated and stirred at 80 °C until the volume reduced by half. 45 g of DMF was added and the solution heated and stirred until 50-60 g solution remained.

PEEK was dried in a vacuum oven at 100 °C overnight. Ten g of PEEK were dissolved in 500 mL c.Η₂SO₄ and stirred at room temperature for 90 h. The polymer solution was gradually precipitated over 1 hour into a stirred, large excess of ice water. Yellow polymer spheres were filtered and washed several times with water until neutral pH was achieved. SPEEK was dried for 8-10 hours at 100 °C.

Reinforced membranes containing Nafion® were prepared in the following manner: The porous reinforcing material was submerged into 20-25 wt% Nafion®/DMF solution at 60 °C and the pressure was reduced to 0.086 bar twice. The membrane was dried for four hours at 0.32 bar at 60 °C, and further dried under vacuum at 80 °C for four hours. The membrane was re-immersed in the Nafion® solution a third time and the pressure reduction and drying process repeated. Reinforced membranes containing SPEEK were prepared using a similar method. The only differences are that a solution of 10 wt% SPEEK/DMAC solution was used and on the third immersion of the membrane into the solution
a vacuum is not applied. The nomenclature used to describe the membranes is **reinforcing material + ionomer**, e.g., a membrane prepared from Nafion® and Celgard 3501, is denoted by **CG3501 + Nafion®**.

Cast, bulk polyelectrolyte membranes were obtained under similar conditions used for reinforced membranes, i.e., cast from a 20-25 wt% DMF (Nafion®) or 10 wt% DMAC (SPEEK) solution and dried in an oven at 80 °C under vacuum overnight.

Membranes were pretreated at 80 °C in 5 wt% hydrogen peroxide, water, sulphuric acid, and finally water, for one hour each.

### 3.2.3 Ionomer Loading

To determine the volume percent of the ionomer in the membranes (Vol%_{ionomer}), the mass of the ionomer (M_{ionomer}) was divided by the density of the ionomer (ρ_{ionomer}) and the volume of the membrane (V_{membrane}), as shown in equation 3.1. The mass of the dry ionomer was determined from the difference between the dry reinforced membrane and dry reinforcing material. A rectangular punch was used to ensure that the membranes and reinforcement materials had the same dimensions.

\[
\text{Vol}\%_{\text{ionomer}} = \frac{M_{\text{ionomer}}}{\rho_{\text{ionomer}} \cdot V_{\text{membrane}}} \tag{3.1}
\]

The density of the ionomer was obtained using the mass and volume of recast Nafion®, as shown in equation 3.2.

\[
\rho_{\text{ionomer}} = \frac{M_{\text{ionomer}}}{V_{\text{ionomer}}} \tag{3.2}
\]
3.2.4 Water Sorption

The water content was obtained using the mass of the wet and dry membrane ($M_{wet}$ and $M_{dry}$), as shown in equation 2.7, and described in Section 2.2.8. The water content of the ionomer in the membrane, Water Contentionomer, was determined using equation 3.3.

$$\text{Water Content}_{\text{ionomer}} \times \frac{\text{Water Contentionomer}}{\text{Vol} \%_{\text{ionomer}}} \quad 3.3$$

The percentage change in dimensions of the membranes with swelling in water, $\%d$, was obtained using equation 2.9, as described in Section 2.2.8.

3.2.5 Water Vapour Transmission

Water vapour transmission (WVT) is a measure of the rate of water vapour transmitted through a membrane of specific area with a specific vapour pressure differential. The experimental set up used is based on ASTM E96/E96M-05, standard test methods for water vapour transmission through materials. The membranes were sandwiched between two Teflon® disks with openings of known area and placed above liquid water in a vial with a hole in the top of known area and positioned in an ESPEC Temp and Humid Chamber SH-240 to control the temperature and relative humidity, as shown in Figure 3.2. The chamber was maintained at 80 °C and 40% RH. The mass of the vial containing water and the membrane was monitored over time to determine the mass of water lost from the vial by transportation through the membrane. WVT was determined using equation 3.4, where $M$ is the overall mass change, $A$ is the area of the opening in the top of the vial, and $t$ is time.
From this value, water vapour permeance was obtained using equation 3.5, where $S$ is the saturated water vapour pressure ($47342.8 \text{ Pa at } 80^\circ\text{C}$) and $R_1 - R_2$ is the vapour pressure difference, which is 0.6 in this case.

$$\text{Water Vapour Permeance} = \frac{WVT}{S(R_1 - R_2)}$$  \hspace{1cm} 3.5
calculated using equation 2.10, as described in Section 2.2.9. The conductivity was normalized for ionomer content using the value obtained in equation 3.1 using equation 3.6.

$$\sigma_{\text{ionomer}} = \frac{\sigma}{\text{Vol\%}_{\text{ionomer}}}$$  \hspace{1cm} 3.6

The areal resistance value of the membranes was calculated using equation 3.7, where $A_2$ is an area of the membrane, and $L_2$ is the thickness of the membrane.

$$\text{Resistance} = \frac{L_2}{A_2 \sigma}$$ \hspace{1cm} 3.7

3.2.7 $[H^+]$ and $\mu_{\text{eff},H^+}$

The analytical concentration of protons in the membrane, $[H^+]$, was calculated using equation 2.13, as described in Section 2.2.10.

The concentration of protons in the ionomer of the membrane, $[H^+]_{\text{ionomer}}$, was obtained using equation 3.8. Here, the $\text{IEC}_{\text{ionomer}}$ is IEC of the membrane divided by the $%_{\text{ionomer}}$ and $V_{\text{wet ionomer}}$ was obtained by dividing the wet mass of the ionomer in the membrane by the wet density of the ionomer.

$$[H^+]_{\text{ionomer}} = \frac{\text{IEC}_{\text{ionomer}} \times M_{\text{dry ionomer}}}{V_{\text{wet ionomer}}}$$ \hspace{1cm} 3.8

The effective mobility of the protons in the membrane, $\mu_{\text{eff},H^+}$, was determined using equation 2.14, as described in Section 2.2.10. The effective mobility of the protons in the ionomer, $\mu_{\text{eff},H^+\text{ionomer}}$, was calculated using equation 3.9.

$$\mu_{\text{eff},H^+\text{ionomer}} = \frac{\sigma_{\text{ionomer}}}{F \cdot [H^+]_{\text{ionomer}}}$$ \hspace{1cm} 3.9
3.2.8 Physical Characterization

Reinforced membranes were investigated using scanning electron microscopy (SEM) following coating the membranes with gold/palladium. A SEM-S-4700 and SEM-S-3500N from Hitachi with energy dispersive x-ray (EDX) was used to confirm that the ionomer permeated through the pores. The cross-sections of membranes were examined using EDX and mapped for sulphur and fluorine content (for the PTFE-reinforced membranes) and sulphur and carbon content (for the Daramic- and Celgard-reinforced membranes).

Leakage of membrane to gases due to pores was estimated by measuring the amount of helium able to pass through the membrane at a given pressure. The gas pressure was controlled using mass-flow meters (Alicat Scientific).

The mechanical strength of membranes was determined using an Instron Mechanical analyzer at a strain rate of 100 mm/min on three 1 cm wide by 5 cm long samples at room temperature. Membranes were soaked in deionized water for at least four hours before measurement.

3.3 Results and Discussion

Reinforced membranes were fabricated from Celgard (polypropylene), Daramic (ultra high molecular weight polyethylene), and PTFE porous films using Nafion® or SPEEK as solid polymer electrolytes. The composition, thickness, pore size, and porosity of each reinforcing material are listed in Table 3.1, together with their notation. Pore sizes of the films range from 0.08 μm for
CG3401 to 10 μm for PTFE MP 10. The porosities of the materials range from 37% for CG3401 to 80% for PTFE MP. The thicknesses of the reinforcing materials range from 18 μm for PTFE MP 0.1 to 70 μm for PTFE MP 10. In all cases the reinforcing materials were treated in some way to render them hydrophilic. The PTFE reinforcing materials are woven while the Celgard® and Daramic® materials are stretched with slit-like pores.

<table>
<thead>
<tr>
<th>Name</th>
<th>Notation in Composition</th>
<th>Pore</th>
<th>Porosity</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celgard</td>
<td>CG3401</td>
<td>0.08</td>
<td>37</td>
<td>25</td>
</tr>
<tr>
<td>Celgard</td>
<td>CG3501</td>
<td>0.13</td>
<td>55</td>
<td>25</td>
</tr>
<tr>
<td>Daramic</td>
<td>WDM</td>
<td>0.1</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>PTFE Millipore</td>
<td>PTFE MP 0.1</td>
<td>0.1</td>
<td>80</td>
<td>18</td>
</tr>
<tr>
<td>PTFE Millipore</td>
<td>PTFE MP 1</td>
<td>1</td>
<td>80</td>
<td>30</td>
</tr>
<tr>
<td>PTFE Millipore</td>
<td>PTFE MP 10</td>
<td>10</td>
<td>80</td>
<td>70</td>
</tr>
</tbody>
</table>

*As described in the product specifications

### 3.3.1 Physical Characterization

The volumes of helium that can pass through Nafion 115®, Nafion 112®, and Nafion NRE 211® in 10 minutes at 0.069 bar are experimentally determined to be 0.063, 0.067, and 0.13 mL, respectively. The thicknesses of Nafion 115®, Nafion 112®, and Nafion NRE 211® membranes are 132, 53, and 28 μm, respectively. If the reinforced membranes displace an amount of He that is equal to or less than that displaced by commercial Nafion® membrane of similar thickness, it indicates that the pores of the reinforcement material have been
sufficiently filled and that there will not be significant gas crossover in the fuel cell. A leak test performed on each reinforced polyelectrolyte membrane indicated that the amount of helium that diffused at 0.069 bar in 10 minutes was less than that for commercial Nafion® membrane of similar thickness (ranging from 0 to 0.05 mL) and that the pores of the membranes are sufficiently filled so as to limit gas transport through open pores.

SEM images of cross-sections of membranes were examined to confirm that the ionomer permeated through the pores of the reinforcing material. While similar results were obtained for other membranes, representative images of cross-sections of unfilled reinforcing material PTFE MP 1 and PTFE MP 1 + Nafion® are displayed in Figure 3.3. In the unfilled reinforcing material (Figure 3.3A), the unfilled pores are clearly visible, while in the reinforced membrane, (Figure 3.3B) it is evident that most of the pores of the reinforcing material are filled by Nafion®.

Figure 3.3: SEM images of the cross-section of unfilled reinforcing material PTFE MP 1 (A) and PTFE MP 1 + Nafion® (B).
The homogeneity of pore-filling was also investigated using backscattered electron imaging and EDX mapping of cross-sections of membranes. EDX spectra and images of cross-sections and the corresponding dot mapping profile of fluorine or carbon and sulphur atoms for the porous substrates before and after filling with polyelectrolytes are shown in Figure 3.4. If the ionomer solution has been completely infused into the reinforcing material, there should be sulphur, carbon, and fluorine (when Nafion® is the ionomer) content along the cross-section of the membrane. If the ionomer solution has not been infused into the reinforcing material, there will still be carbon and fluorine (for the membranes fabricated using PTFE) along the cross-section of the membrane due to the reinforcing material, but there will not be any sulphur in the membrane. EDX spectra of ionomer impregnated membranes reveal the presence of a small peak at 2.15 keV due to sulfur (Figure 3.4B, D, F, H, I, K, M, N (iv)), but this peak is absent in the original, unfilled porous films (Figure 3.4A, C, E, G, J, L (iv)). EDX dot mapping illustrates the distribution of a chosen element across the image. This is carried out in conjunction with a backscattered electron image, where each pixel of the image has an exact and corresponding pixel on each of the element maps, which are collected at the same time and at the same resolution. The EDX sulphur mapping of unfilled membranes (Figure 3.4A, C, E, G, J, L (ii)) shows no signal due to sulphur indicating that sulphur is not present in these materials. However, when the reinforcing materials contain ionomer, the homogeneous dispersion of dots in the EDX mapping of sulphur shows that there is sulphur present throughout the thickness of the membrane (Figure 3.4B, D, F,
This indicates that the fabrication process permitted the ionomer to permeate throughout the membrane, creating membranes that are homogeneous in ionomer content.

Figure 3.4: Cross sections of reinforced membranes and reinforcing materials. A. PTFE MP 0.1, B. PTFE MP 0.1 + Nafion®, C. PTFE MP 1, D. PTFE MP 1 + Nafion®, E. PTFE MP 10, F. PTFE MP 10 + Nafion®, G. CG3501, H. CG3501 + Nafion®, I. CG3501 + SPEEK, J. CG3401, K. CG3401 + Nafion®, L. WDM, M. WDM + Nafion®, N. WDM + SPEEK: (i) EDX image, (ii) EDX mapping of sulphur, (iii) EDX mapping of fluorine/carbon, (iv) EDX spectra; Dashed lines represent the upper and lower edges of the cross-sections.
Ionomer content, thickness, and changes in dimensions with swelling of the reinforced membranes are listed in Table 3.2. The properties of Nafion®-based reinforced membranes are plotted in Figure 3.5 and those based on SPEEK are plotted in Figure 3.6. Data for various cast and commercial Nafion® membranes are included in Figure 3.5 and Table 3.2 for reference.
Table 3.2: Ionomer content, thickness, and change in dimension with swelling of reinforced membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Ionomer Content (^a)</th>
<th>Thickness (^b) (\mu m)</th>
<th>Change in Dimensions (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>thickness</td>
<td>length</td>
</tr>
<tr>
<td>Nafton 115(^\circ)</td>
<td>100</td>
<td>132 (0.9)</td>
<td>14 (2)</td>
</tr>
<tr>
<td>Nafton 112(^\circ)</td>
<td>100</td>
<td>53 (0.1)</td>
<td>11 (2)</td>
</tr>
<tr>
<td>NRE 211(^\circ)</td>
<td>100</td>
<td>28 (0.1)</td>
<td>7.7 (1)</td>
</tr>
<tr>
<td>Cast Nafton(^\circ)</td>
<td>100</td>
<td>89 (5)</td>
<td>33 (2)</td>
</tr>
<tr>
<td>WDM + Nafton(^\circ)</td>
<td>58 (2)</td>
<td>44 (0.7)</td>
<td>16 (2)</td>
</tr>
<tr>
<td>CG 3501 + Nafton(^\circ)</td>
<td>35 (4)</td>
<td>41 (7)</td>
<td>26 (4)</td>
</tr>
<tr>
<td>CG 3401 + Nafton(^\circ)</td>
<td>40 (6)</td>
<td>54 (0.7)</td>
<td>24 (1)</td>
</tr>
<tr>
<td>PTFE MP 0.1 + Nafton(^\circ)</td>
<td>55 (5)</td>
<td>47 (3)</td>
<td>8.6 (1)</td>
</tr>
<tr>
<td>PTFE MP 1 + Nafton(^\circ)</td>
<td>70 (3)</td>
<td>50 (3)</td>
<td>7.9 (2)</td>
</tr>
<tr>
<td>PTFE MP 10 + Nafton(^\circ)</td>
<td>62 (2)</td>
<td>67 (5)</td>
<td>12 (2)</td>
</tr>
<tr>
<td>SPEEK</td>
<td>100</td>
<td>33 (3)</td>
<td>16 (1)</td>
</tr>
<tr>
<td>WDM + SPEEK</td>
<td>21 (2)</td>
<td>22 (0.4)</td>
<td>6.9 (1)</td>
</tr>
<tr>
<td>CG3501 + SPEEK</td>
<td>28 (5)</td>
<td>40 (5)</td>
<td>28 (3)</td>
</tr>
</tbody>
</table>

Error (±) is shown in brackets after the value, \(^a\)Using equation 3.1, \(^b\)Dry membrane, \(^c\)Using equation 2.9

Figure 3.5: Data for reinforced membranes containing Nafton\(^\circ\). A. Water content (wet, room temperature), B. \(\lambda\) (wet, room temperature), C. Proton Conductivity (wet, room temperature), D. Areal Proton Resistance (wet, room temperature), E. Proton concentration (wet, room temperature), F. Effective Proton Mobility (wet, room temperature), G. Water Vapour Permeance (40% RH, 80 °C).
Figure 3.6: Data for reinforced membranes containing SPEEK. A. Water Content (wet, room temperature), B. $\lambda$ (wet, room temperature), C. Proton Conductivity (wet, room temperature), D. Areal Proton Resistance (wet, room temperature), E. Proton Concentration (wet, room temperature), F. Effective Proton Mobility (wet, room temperature), G. Water Vapour Permeance (40% RH, 80 °C).
The percent of ionomer in the membranes ranges from 21 vol% for WDM + SPEEEK to 70 wt% for PTFE MP 0.1 + Nafion®, with the smallest amounts belonging to SPEEEK-based membranes (Table 3.2). The thicknesses of the reinforced membranes, as shown in Table 3.2, vary from 22 µm for WDM + SPEEEK to 67 µm for PTFE MP 10 + Nafion®, depending on the thickness of the original porous film and the final ionomer content. The thicknesses of the reinforced membranes are 8% for PTFE MP 10 + Nafion® to 67% for CG3401 + Nafion®, larger than the parent film. Increased thickness of the reinforced membranes compared to the original porous material is likely due to a coating of the ionomer on the surface of the porous film. Selecting hydrophilic reinforcing materials and using ionomer solutions at 60 °C to decrease the solution viscosity, as well as applying a vacuum, facilitate ingress of the solution. Similar increase in thickness has been reported in literature. Dhathathreyan et al. [17] impregnated Nafion® into PTFE, and observed the thickness to increase from 25 to 35 µm; Nouel and Fedkiw impregnated Celgard and PTFE with Nafion® and the thicknesses increased from 15 and 25 µm to 25 and 28 µm, respectively. [4]
Data from mechanical analyses are shown in Table 3.3. The Young's modulus of recast Nafion® is 189 MPa, while the Young's modulus of reinforced membranes containing Nafion® ranges from 249 MPa for PTFE MP 0.1 + Nafion® to 2323 MPa for CG3501 + Nafion®. The Young's modulus of SPEEK is 1185 MPa, while the values for SPEEK-reinforced membranes are 1470 MPa for WDM + SPEEK and 1321 MPa for CG3501 + SPEEK. Using reinforcement materials greatly increases the Young's modulus compared to the bulk ionomer membranes. Similar results are observed in literature where the Young's modulus values for PTFE + Nafion® membranes are reportedly higher than Nafion 112®. [3] It is also reported that the Young's modulus for PTFE + SPEEK membranes are higher than pure SPEEK or Nafion 112®. [6] The mechanical properties of reinforced membranes, such as Young's modulus, are dominated by the mechanical properties of the reinforcing material.
Table 3.3: Young’s Modulus of wet reinforced membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Young’s Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
</tr>
<tr>
<td>WDM</td>
<td>963 (95)</td>
</tr>
<tr>
<td>CG3401</td>
<td>1255 (102)</td>
</tr>
<tr>
<td>CG3501</td>
<td>2894 (145)</td>
</tr>
<tr>
<td>PTFE MP 0.1</td>
<td>240 (59)</td>
</tr>
<tr>
<td>PTFE MP 1</td>
<td>308 (59)</td>
</tr>
<tr>
<td>PTFE MP 10</td>
<td>467 (31)</td>
</tr>
<tr>
<td>WDM + Nafion®</td>
<td>950 (87)</td>
</tr>
<tr>
<td>CG3401 + Nafion®</td>
<td>403 (30)</td>
</tr>
<tr>
<td>CG3501 + Nafion®</td>
<td>2323 (105)</td>
</tr>
<tr>
<td>PTFE MP 0.1 + Nafion®</td>
<td>249 (20)</td>
</tr>
<tr>
<td>PTFE MP 1 + Nafion®</td>
<td>266 (30)</td>
</tr>
<tr>
<td>PTFE MP 10 + Nafion®</td>
<td>331 (30)</td>
</tr>
<tr>
<td>Cast Nafion®</td>
<td>189 (15)</td>
</tr>
<tr>
<td>Nafion 211®</td>
<td>285 (20)</td>
</tr>
<tr>
<td>Nafion 112®</td>
<td>236 (28)</td>
</tr>
<tr>
<td>Nafion 115®</td>
<td>200 (8)</td>
</tr>
<tr>
<td>SPEEK</td>
<td>1185 (102)</td>
</tr>
<tr>
<td>WDM + SPEEK</td>
<td>1470 (120)</td>
</tr>
<tr>
<td>CG3501 + SPEEK</td>
<td>1321 (120)</td>
</tr>
</tbody>
</table>

Error (±) is shown in brackets after the value.

3.3.2 Reinforced Membranes Using Reinforcing Materials with Pore Sizes \( \sim 0.1 \mu m \)

In this section all of the reinforcing materials used in the membranes have pore sizes around 0.1 \( \mu m \) (0.08-0.13 \( \mu m \)). This means the main difference among the membranes is the substance the reinforcing material is composed of, allowing the membranes to be meaningfully compared.

3.3.2.1 Water Sorption

The amount of water present in a membrane is an important parameter for fuel cell operation. Generally, conductivity increases with water content, but too much water can lead to decreased mechanical stability of the membrane and a decrease in conductivity. Water contents of the reinforced membranes containing
Nafion® range from 10 ± 1 wt% for WDM + Nafion® to 27 ± 1 wt% for CG3401 + Nafion®, as shown in Figure 3.5A. The number of water molecules per sulfonated group in the membranes containing Nafion, λ, as shown in Figure 3.5B, ranges from 10 ± 3 for WDM + Nafion® to 29 ± 4 for CG3501 + Nafion®. The water content of recast Nafion® (IEC= 0.9 meq g⁻¹) is 20 ± 1 wt% and λ is 27 ± 1. Some of the water contents of the reinforced membranes containing Nafion® are lower at 10 ± 1 wt% for WDM + Nafion® and 12 ± 2 wt% for PTFE MP 0.1 + Nafion®. However, the water content of CG3401 + Nafion® (21 ± 1 wt%) and CG3501 + Nafion® (27 ± 1 wt%) are larger than that of bulk Nafion®. The water contents and λ of WDM + SPEEK and CG3501 + SPEEK are shown in Figure 3.6A and Figure 3.6B, respectively. Although the water content and λ of WDM + SPEEK (20 ± 1 wt% and 16.8 ± 2, respectively) is lower than that of SPEEK (28 ± 2 wt% and 20.0 ± 1, respectively), the water content and λ of CG3501 + SPEEK (34 ± 3 wt% and 21.6 ± 4) is higher. In general, except for the Celgard membranes, the water contents and λ of reinforced membranes are less than that of their parent ionomer. The water contents of the Celgard reinforced membranes are higher than that of their parent ionomer. As reported in the literature, reinforced membranes generally possess lower water content than their parent ionomer: Fuqiang et al. found that PTFE + Nafion® membranes fabricated using reinforcing materials with 0.3 μm pores and 25 and 45 μm thicknesses had water contents of 7 and 9 wt%, respectively; lower than the water content found for Nafion 115® (16 wt%). [6] Zhang et al. found that PTFE + SPEEK membranes fabricated using PTFE films with 0.3–0.5 μm pores and 15-
20 μm had water contents of 24 wt%. This is lower than the water content they obtained for SPEEK (29 wt%). Examination of the water content of the ionomer inside the membranes could lead to greater insight into the effect of encapsulating the ionomer inside the membrane. The water content of Nafion® inside the membranes containing Nafion® ranged from 15.2 ± 1 wt% for WDM + Nafion® to 46.6 ± 1 wt% for CG3501 + Nafion®, while the water content of recast Nafion® is 18.4 ± 2 wt%. The water content of SPEEK inside the WDM + SPEEK and CG3501 + SPEEK are 97.0 ± 1 and 55.5 ± 2 wt%, while the water content of SPEEK is 28.1 ± 1 wt%. For all the reinforced membranes except for WDM + Nafion®, the water content of the ionomer in the membrane was higher than that of the bulk parent ionomer. This is surprising, especially considering that the water content of the bulk reinforced membranes are lower and is likely a result of assuming that all the water in the membrane can be attributed to the ionomer in equation 3.3. In fact, all the reinforcing materials have been hydrophilically treated, so could contribute to the water content as well.

The percentage changes in dimensions of the membranes with water swelling are shown in Table 3.2. The percentage increase in thickness of recast Nafion® is 33 ± 2%, and that for membranes fabricated from WDM and PTFE MP are < 20 ± 2%. The percentage increase in thickness of membranes fabricated from Celgard is ~25 ± 4%, which is also smaller than recast Nafion®. Cast SPEEK increases in thickness by 16 ± 1% upon absorbing water, while for the membranes fabricated from Celgard the increase value is larger (28 ± 3%), but for WDM + SPEEK it is smaller (6.9 ± 1%). The percent change in length and
width decreases from 13 ± 2% for bulk Nafion® to 3-8 ± 2% for all the Nafion®-containing membranes compared to bulk Nafion®. The percent change in length and width is smaller for WDM + SPEEK (3.9 ± 1% increase) compared to bulk SPEEK (12 ± 2% increase). However the percentage increase in length and width with swelling in water for CG3501 + SPEEK (12 ± 3%) is similar to that of bulk SPEEK. In summary, the reinforced membranes are more dimensionally stable to water swelling than cast ionomer membranes. Although recast Nafion®, cast SPEEK and the Celgard-reinforced membranes show anisotropy with respect to dimensional changes (swelling is higher in the thickness direction), the other reinforced membranes are more isotropic. Thus the nature of porous film used has an effect on the dimensional stability of the hydrated reinforced membranes, although all reinforcing materials impart increased dimensional stability compared to the bulk ionomer. Similar results for dimensional stability of reinforced membranes have been reported in the literature. [3,6,17] For example, Dhathathreyan et al. [21] observed dimensional changes of 16, 4.5, and 4.8% with respect to thickness, length, and width respectively, for PTFE + Nafion® membrane. These are lower than values they obtained for Nafion 1135®, which are 25, 11.9, and 6.2% for thickness, length and width, respectively.

3.3.2.2 Proton Conductivity

The proton conductivity of Nafion®-based membranes are plotted in Figure 3.5C. Of the reinforced membranes, the highest conductivities are found for CG3501 + Nafion® (0.034 ± 0.003 S cm⁻¹) and WDM + Nafion® (0.027 ± 0.003 S cm⁻¹). CG3401 + Nafion® possesses the lowest conductivity value
(0.016 ± 0.0001 S cm⁻¹). These values are all significantly lower than recast Nafion® (0.076 ± 0.003 S cm⁻¹). A similar trend is observed with SPEEK-containing membranes, shown in Figure 3.6C. The proton conductivity of SPEEK is 0.037 ± 0.001 S cm⁻¹ while the proton conductivity values of WDM + SPEEK and CG3501 + SPEEK are much lower at 0.0064 ± 0.0003 and 0.0088 ± 0.0004 S cm⁻¹, respectively. Incorporating the ionomer in porous materials lowers the conductivity compared to the parent ionomer. This is expected because the non-conducting polymer takes up an appreciable fraction of the membrane. By examining the conductivity values of the ionomer in the membrane (the conductivity divided by the Vol%ionomer, equation 3.7), with respect to the parent ionomer, more insight can be obtained on the effects of confinement and connectivity. The conductivity of recast Nafion® is 0.076 ± 0.003 S cm⁻¹. Conductivity (Figure 3.7B) values for the ionomer in Nafion® reinforced membranes, with pore sizes ~ 0.1 μm, range from 0.032 ± 0.005 S cm⁻¹ for CG3401 + Nafion® to 0.063 ± 0.009 S cm⁻¹ for CG3501 + Nafion®. The highest value observed is still much less than recast Nafion®. Normalized conductivity values for the SPEEK reinforced membranes (Figure 3.8B) range from 0.017 ± 0.005 S cm⁻¹ for CG3501 + SPEEK to 0.029 ± 0.005 S cm⁻¹ for WDM + SPEEK. Again, these are lower than the value of SPEEK alone. Proton conductivity of the ionomer, even when normalized for ionomer content, is observed to be lower in reinforced membranes.
Figure 3.7: Properties of Nafion® inside the reinforced membrane. A. Water content, B. Proton conductivity, C. Proton concentration, D. Effective proton mobility (wet, room temperature).

Figure 3.8: Properties of SPEEK inside the reinforced membrane. A. Water content, B. Proton conductivity, C. Proton concentration, D. Effective proton mobility (wet, room temperature).
Upon examination of areal proton resistance of the membranes, i.e. the membrane thickness divided by the proton conductivity, as shown in Figure 3.5D and Figure 3.6D, the advantages of employing thinner membranes is realized: CG3501 + Nafion® has the lowest areal resistance (0.14 ± 0.02 Ω cm², 57 μm), which is lower than recast Nafion® (0.34 ± 0.04 Ω cm², 89 μm) and commercial Nafion 115® (0.17 ± 0.03 Ω cm², 132 μm). However, the areal resistance of CG3401 + Nafion® is higher (0.39 ± 0.001 Ω cm², 54 μm). Although the areal resistances of the other reinforced membranes are lower than the 89 μm thick recast Nafion®, they are higher than both the thinner commercial membranes, NRE 211® (0.045 ± 0.002 Ω cm²) and Nafion 112® (0.069 ± 0.0001 Ω cm²), which are 28 and 54 μm thick, respectively. The areal resistance values of the reinforced membranes containing SPEEK (Figure 3.6D) are much higher at 1.1 ± 0.1 and 0.36 ± 0.1 Ω cm² for CG3501 + SPEEK and WDM + SPEEK, respectively. These data illustrate that decreasing the thickness of reinforced membranes does not always necessarily compensate for the loss in proton conductivity that occurs when ionomer is incorporated into porous membranes.
These results are similar to results reported in the literature: Nouel and Fedkiw\textsuperscript{[4]} immersed Nafion\textsuperscript{®} into Celgard 2400 and 2500 to obtain an ionomer uptake of \(\sim 45\) wt\%. The wetted membranes were 28 \(\mu\)m thick, but not thin enough to compensate for the low conductivity of the reinforced membrane. The areal resistance values of Celgard 2400 + Nafion\textsuperscript{®} and Celgard 2500 + Nafion\textsuperscript{®} are reported as being 3.9 and 3.1 times larger than that of Nafion 112\textsuperscript{®} (0.036 \(\Omega\) cm\(^2\)), respectively. In addition they prepared 70 wt\% Nafion\textsuperscript{®} in PTFE to obtain hydrated membranes 31 \(\mu\)m thick. The areal resistance of this membrane (0.031 \(\Omega\) cm\(^2\)) was lower than Nafion 112\textsuperscript{®}.

### 3.3.2.3 Proton Concentration and Effective Proton Mobility

Proton mobility is the rate of transport of protons under an applied electric field. By removing the effect of acid concentration (equation 2.14), it is possible to view the relative contributions of both proton mobility and acid concentration to the experimentally determined proton conductivity. Acid concentration consists of contributions from both acid and water contents. Proton mobility depends on the degree of dissociation of the proton, the tortuosity of the proton conducting pathway (shorter effective mean-free paths for protons result in higher proton mobility), and the distance between acid groups (shorter distances between acid groups result in higher proton mobility).\textsuperscript{[25]}

Proton concentration and effective proton mobility in a membrane have an important influence on proton conductivity. High values of both result in high proton conductivity. The proton concentrations of Nafion\textsuperscript{®}-based reinforced membranes are shown in Figure 3.5E. The proton concentration of hydrated
recast Nafion® is 1.0 ± 0.1 M. [H+] for Nafion®-reinforced membranes range from 0.38 ± 0.04 M for CG3501 + Nafion® to 0.63 ± 0.1 M for PTFE MP 0.1 + Nafion®. [H+] values for SPEEK membranes are shown in Figure 3.6E. [H+] for SPEEK, CG3501 + SPEEK, and WDM + SPEEK are 1.7 ± 0.1, 0.41 ± 0.06, and 0.82 ± 0.1 M, respectively. The reinforced membranes possess lower proton concentrations than their parent ionomer. The proton concentrations in the majority of reinforced membranes are lower than that of their parent ionomer simply because the ionomer is diluted by the reinforcing material. Using equation 3.8, it is possible to evaluate the proton concentration in the ionomer itself (as opposed to the membrane as a whole). The normalized proton concentrations in the ionomer as shown in Figure 3.7C, range from 1.0 ± 0.1 M for CG3401 + Nafion® to 1.2 ± 0.05 M for WDM + Nafion®. All the reinforced membranes containing Nafion® possess a similar ionomer proton concentration to Nafion® (1.0 ± 0.2 M). The proton concentration in bulk SPEEK is 1.7 ± 0.1 M (Figure 3.8E). The proton concentrations in the ionomer in CG3501 + SPEEK and WDM + SPEEK are slightly higher than that of bulk SPEEK at 1.7 ± 0.06 and 2.1 ± 0.1 M, respectively. In most cases, by impregnating the ionomer inside the pores of the reinforcing material a similar proton concentration of the ionomer is achieved.

Effective proton mobility values for the various membranes are plotted in Figure 3.5F and 3.6F. $\mu_{\text{eff}, \text{H}^+}$ for recast Nafion® is $7.6 \times 10^{-4} \pm 0.5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, and range from $3.2 \times 10^{-4} \pm 0.2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for CG3401 + Nafion® to $6.4 \times 10^{-4} \pm 0.4 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for CG3501 + Nafion®. Effective proton mobility values of SPEEK membranes are $2.5 \times 10^{-4} \pm 0.4 \times 10^{-4}$, $8.1 \times 10^{-5} \pm 0.1 \times 10^{-5}$,
and $1.8 \times 10^{-4} \pm 0.4 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for SPEEK, WDM + SPEEK, and CG3501 + SPEEK, respectively (Figure 3.6F). The effective proton mobility values of reinforced membranes are lower than that of their parent ionomer. Using equation 3.9, it is possible to normalize for ionomer content and calculate the mobility of the protons inside the ionomer. The normalized effective proton mobility values of the ionomer inside the porous materials, shown in Figure 3.7C, range from $3.6 \times 10^{-4} \pm 0.1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for CG3401 + Nafion® to $6.8 \times 10^{-4} \pm 0.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for CG3501 + Nafion®. The $\mu_{\text{eff, H}^+}$ of recast Nafion® is $7.6 \times 10^{-4} \pm 0.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The $\mu_{\text{eff, H}^+}$ values of the ionomer in reinforced membranes containing SPEEK, shown in Figure 3.8D, are $2.0 \times 10^{-4} \pm 0.3 \times 10^{-4}$ and $1.5 \times 10^{-4} \pm 0.5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for CG3501 + SPEEK and WDM + SPEEK, respectively. The $\mu_{\text{eff, H}^+}$ of SPEEK is $2.5 \times 10^{-4} \pm 0.5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The effective proton mobility of the ionomer inside the porous material is thus lower than the effective proton mobility of the bulk parent ionomer. The decrease in effective proton mobility of the ionomer in the membranes compared to their bulk parent ionomer is most likely due to a lack of connectivity of the ionomer inside the membranes, which results in increased tortuosity for proton transport.

3.3.2.4 Water Vapour Transmission

Water transport through proton exchange membranes is important for fuel cell operation and the water vapour permeance can give an indication of how facile water transport is through the membrane. A high water vapour permeance signifies higher diffusion of the water through the membrane during fuel cell operation, which can lead to a more uniform distribution of water during fuel cell
operation. It was anticipated that water vapour permeance would increase with decreasing membrane thickness. This is indeed observed for the Nafion® membranes (Figure 3.5G): as the thickness increases from 54 to 132 μm (Table 3.2), the water vapour permeance decreases from 0.068 ± 0.002 to 0.056 ± 0.005 g Pa⁻¹ h⁻¹ m⁻². The lowest value of water vapour permeance for reinforced Nafion® membranes is observed for WDM + Nafion® (0.036 ± 0.002 g Pa⁻¹ h⁻¹ m⁻²) while CG3401 + Nafion® gives the highest value (0.050 ± 0.0002 g Pa⁻¹ h⁻¹ m⁻²). Thus, the water vapour permeability values of reinforced Nafion® membranes generally are lower than recast Nafion® (0.056 ± 0.001 g Pa⁻¹ h⁻¹ m⁻²). A similar result for in situ water transport studies was reported by Shim et al., who found that 30 μm PTFE + Nafion® reinforced membranes with a Nafion® loading of 82 wt% had higher water flux (0.14 H₂O/H⁺) than 25 μm PTFE + Nafion® with a Nafion® loading of 78 wt% (0.10 H₂O/H⁺). [5] This trend is not observed for reinforced SPEEK membranes (Figure 3.6G). Here, the water vapour permeance is higher for the reinforced membranes, e.g., for WDM + SPEEK, the value is 0.067 g Pa⁻¹ h⁻¹ m⁻², whereas SPEEK has a water vapour permeance of 0.059 g Pa⁻¹ h⁻¹ m⁻².

3.3.3 Nafion® Membranes Fabricated Using PTFE MP with Different Pore Sizes

Studies were carried out on Nafion® + PTFE MP membranes possessing different pore sizes (0.1, 1 and 10 μm) to investigate the effect of pore size on membrane properties. The results for these studies are presented in Table 3.2 and Figure 3.9A-F.
Figure 3.9: The effect of reinforcing material pore size on membrane properties for PTFE MP + Nafion® membranes. A. Water content (wet, room temperature), B. A (wet, room temperature), C. Proton conductivity (wet, room temperature), D. Areal proton resistance (wet, room temperature), E. Proton concentration (wet, room temperature), F. Effective proton mobility (wet, room temperature), G. Water vapour permeance (40% RH, 80 °C).
The water contents of PTFE MP + Nafion® membranes, shown in Figure 3.9A, increase from 12 ± 2 to 25 ± 2 wt% with increasing pore size. The λ of PTFE MP + Nafion® membranes, shown in Figure 3.9B, increase from 13 ± 2 to 29 ± 2 with increasing pore size. The highest water content and λ, found for PTFE MP 10 + Nafion®, are slightly higher than the values for recast Nafion® (18 ± 2 wt% and 27 ± 2, respectively). Increasing the pore size of the reinforcing material results in water sorption that is similar or higher than Nafion®. The water contents of the ionomer in the PTFE MP + Nafion® membranes increase from 23 ± 1 to 41 ± 2 wt% as the pore size increases from 0.1 to 10 μm. These values are higher than the water content of recast Nafion®, which is likely a result of the reinforcing material contributing to the water content as well. The proton conductivity values of PTFE MP + Nafion® membranes, shown in Figure 3.9C, increase from 0.022 ± 0.001 to 0.041 ± 0.006 S cm⁻¹ with increasing pore size. The highest proton conductivity value, found for PTFE MP 10 + Nafion®, is only ~ ½ the value of recast Nafion®, which is 0.076 ± 0.003 S cm⁻¹. Increasing the pore size of the reinforcing material increases proton conductivity values,
although these values are still lower than that of Nafion®. The conductivity of the ionomer inside the membrane, Figure 3.10B, increases from 0.038 ± 0.0001 to 0.067 ± 0.001 S cm⁻¹ when the pore size of the reinforcing material increases from 0.1 to 10 μm. The highest value is approaching the conductivity of recast Nafion® (0.076 ± 0.001 S cm⁻¹) and indicates that increasing the pore size, and therefore the connectivity of the Nafion® in the membrane, leads to more pure Nafion-like behaviour. The areal proton resistance values, shown in Figure 3.9D, which are proportional to the thicknesses of the membranes, have little dependence on the increasing pore size of the reinforcing material and range from 0.16 ± 0.02 to 0.17 ± 0.05 Ω cm² for pore sizes of PTFE MP of 0.1 to 10 μm. All of these values are lower than the areal proton resistance value of 89 μm recast Nafion® (0.35 ± 0.02 Ω cm²), but are higher than values for thin, commercial Nafion® membranes, Nafion 112® and NRE211® (0.069 ± 0.005 and 0.045 ± 0.005 Ω cm², respectively). Increasing the pore size of the reinforcing material is offset by the increased thickness that occurs with increasing pore size, resulting in little change in areal proton resistance with changing pore size of the reinforcing material. However, although these areal proton resistance values are lower than thick recast Nafion®, they are higher than the extruded membranes of comparable thickness.
The proton concentrations of the PTFE MP + Nafion® reinforced membranes are shown in Figure 3.9D. [H+] for PTFE MP + Nafion® membranes increases from 0.60 ± 0.01 to 0.68 ± 0.005 M with increasing pore size. This is due to the increased quantity of Nafion® contained within the membrane as pore size increases. The proton concentration of the ionomer inside the membrane, however, remains relatively constant (Figure 3.10B), and similar to that for bulk Nafion®. The $\mu_{\text{eff, } H^+}$ (Figure 3.9E) increase from $4.1 \times 10^{-4} \pm 0.01 \times 10^{-4}$ to $5.6 \times$
10^{-4} \pm 0.05 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ with increasing pore size. The effective proton mobility of bulk Nafion™ is } 7.6 \times 10^{-4} \pm 0.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}. \text{ Increasing the pore size of the reinforcing material thus increases the effective proton mobility in the membrane although it is still lower than in bulk Nafion™. As the pore size of the reinforcing material increases from 0.1 to 10 \mu m, the effective proton mobility values of the ionomer inside PTFE MP + Nafion™ increases from 4.5 \times 10^{-4} \pm 0.5 
\times 10^{-4} \text{ to } 6.2 \times 10^{-4} \pm 0.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} (\text{Figure 3.10C}). \text{ As the pore size of the reinforcing material increases, the effective proton mobility of the ionomer inside the reinforced membrane increases to near the value of that of recast Nafion™. Increasing pore size of the reinforcing material leads to increased connectivity of the ionomer in the reinforced membrane and decreased tortuosity of the proton conducting pathway.}

\text{Water vapour transmission plots for these PTFE MP + Nafion™ membranes are shown in Figures 3.9F. The water vapour permeance for PTFE MP 10 + Nafion is the highest (0.064 \pm 0.006 \text{ g Pa}^{-1} \text{ h}^{-1} \text{ m}^{-2}) \text{ and for PTFE MP 0.1 it is the lowest (0.046 \pm 0.004 \text{ g Pa}^{-1} \text{ h}^{-1} \text{ m}^{-2}). The water vapour permeance of PTFE MP 10 + Nafion™ is slightly larger than for Nafion™ (0.056 \pm 0.005 \text{ g Pa}^{-1} \text{ h}^{-1} \text{ m}^{-2}). This indicates that increasing the pore size and therefore the connectivity of the ionomer in the membrane, leads to membrane properties that are similar to that of bulk Nafion™.}

\text{3.4 Summary and Conclusions}

\text{From a technological perspective, the properties of CG + Nafion™ membranes possess higher water content, water vapour permeance, and}
permeability, but lower dimensional stability to swelling than the membranes fabricated from the other reinforcing materials. The PTFE MP + Nafion® membranes tend to have lower water content, but higher proton concentration and greater dimensional stability in water. The WDM + Nafion® membranes exhibit the lowest water vapour permeance and water content. The proton conductivity and effective proton mobility of all the reinforced membranes containing Nafion® were similar. The proton conductivity, effective proton mobility, and water vapour transmission of all the reinforced membranes were inferior to that of bulk Nafion®. The areal proton resistance and the dimensional stability in water of the thin, reinforced membranes were improved compared to 89 μm recast Nafion®.

CG3501 + SPEEK membranes possessed higher areal proton resistance and water vapour permeance than SPEEK. WDM + SPEEK membranes had lower areal proton resistance, but higher water vapour permeance than SPEEK. The proton conductivity, proton concentration, and effective proton mobility of the reinforced membranes are inferior to SPEEK, while the water vapour permeance and dimensional stability in water of both reinforced membranes is improved compared to SPEEK.

The water content, proton conductivity, proton concentration, effective proton mobility, and water vapour permeance of the PTFE MP + Nafion® membranes increased with increasing pore size of the reinforcing material, while the areal proton resistance and dimensional stability decreased.
From a more scientific viewpoint, it is interesting to examine the change in effective properties of the ionomer when the ionomer is constrained within the pores of the reinforcing material, which can be achieved by normalizing the data for ionomer content. With the normalized data, the water contents and proton concentrations of Nafion® inside the reinforced membranes are higher than that of bulk Nafion®, while the proton conductivity and effective proton mobility are still lower. For the SPEEK reinforced membranes, the normalized proton concentrations of the SPEEK in the membrane are higher, but the normalized proton conductivity and effective proton mobility are still lower. That these values are not equal to the values of their parent ionomers is an effect of encapsulating the ionomer inside the pores of the reinforcing material, and is attributed to a lack of connectivity of the ionomer in the reinforced membrane. Increasing the pore size of the reinforcing material, which is expected to increase the connectivity of the ionomer inside the membrane, increases proton conductivity, lowers areal resistance, increases effective proton mobility, and increases water vapour permeance of the ionomer inside the membranes, and leads to properties that approach recast Nafion®.

The employment of reinforcing materials in membranes is found to deleteriously affect properties such as proton conductivity, effective proton mobility, and water vapour permeance due to decreased ionomer content in the membrane and less connectivity of the ionomer. However, the membranes are stronger and can be prepared thinner, which can compensate for these losses. Thin membranes may have advantages such as lower areal resistance, lower
dimensional changes with swelling, and higher water vapour permeance. To fully take advantage of reinforced membranes, there is benefit to using reinforcing materials that are thin and possess large pores.

3.5 References


CHAPTER 4: COMPOSITE MEMBRANES

4.1 Introduction

4.1.1 Sol-Gel Reactions

Sol-gel materials are a wide range of inorganic and organic/inorganic materials that share a preparation strategy. In sol-gel processing, colloidal suspensions (sols) are converted to viscous gels and then solid materials. A sol is a dispersion of colloidal particles suspended within a fluid matrix. Colloids are suspensions of particles of dimensions between 1 nm – 1 μm. The sol-gel process allows the fabrication of materials with a large variety of properties: ultrafine powders, monolithic ceramics and glasses, ceramic fibers, inorganic membranes, thin film coatings and aerogels. Sol-gel chemistry is a remarkably versatile approach for fabricating materials. Scientists have used it to produce the world’s lightest materials and some of its toughest ceramics. [1]

The sol is made of solid particles of a diameter of few hundred nm, usually inorganic metal salts, suspended in a liquid phase. The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkoxides are the alkoxyssilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates are also commonly
used in the sol-gel process, often mixed with TEOS. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, then the particles condense in a new phase, the gel, in which a solid macromolecule is immersed in a solvent. The steps in sol-gel synthesis, using alkoxysilanes, as examples are outlined in Figure 4.1. [{1}]

**Figure 4.1: Stages in sol-gel reactions, using silicon alkoxides as an example**

1. **Hydrolysis:** $\text{Si(OR)}_4 + n\text{H}_2\text{O} \rightarrow \text{Si(OR)}_{4-n}(\text{OH})_n + n\text{ROH}$

2. **Condensation:** $\text{R}_3\text{SiOH} + \text{HOSiR'}_3 \rightarrow \text{R}_3\text{Si-O-SiR'}_3 + \text{H}_2\text{O}$ or $\text{R}_3\text{SiOR''} + \text{HOSiR'}_3 \rightarrow \text{R}_3\text{Si-O-SiR'}_3 + \text{R''OH}$

3. **Gelation:** Formation of a "spanning cluster" across the vessel, giving a network which entraps the remaining solution with high viscosity.

4. **Ageing:** Formation of further crosslinks, shrinkage of the gel as covalent links replace non-bonded contacts. Structural evolution with changes in pore sizes and pore wall strengths.

5. **Drying:** The loss of water, alcohol and other volatile components, first as expulsion of the liquid as the gel shrinks, then as evaporation of liquid within the pore structure with associated developments of capillary stress, which often leads to cracking.

6. **Densification:** Thermal treatment leading to collapse of the open structure and formation of a dense ceramic.

The hydrolysis reaction (Stage 1 in Figure 4.1), replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions (Stage 2)
involving the silanol groups (Si-OH) produce siloxane bonds (Si-O-Si) plus the by-products water or alcohol. Under most conditions, condensation commences before hydrolysis is complete. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. When the sol particles aggregate, or inter-knit into a network, a gel is formed (Stage 3). Upon drying, trapped volatiles (water, alcohol, etc.) are driven off and the network shrinks as further condensation can occur (Stage 4). The addition of solvents and certain reaction conditions promote esterification and depolymerization reactions according to the reverse of reactions in Stages 1 and 2.\textsuperscript{[2]}

Many factors affect the reaction rate in the hydrolysis and condensation stages of sol-gel reactions (Stage 1 in Figure 4.1), such as pH, catalyst nature and concentration, \textit{H}_2\textit{O}/Si molar ratio, and temperature. For example, silica has no net charge at pH 2.2, and the reaction rate is slowest at this point and rapidly increases in conditions that are more acidic or basic than this\textsuperscript{[2, 3]}. Sol-gel derived silicon oxide networks, under acid-catalyzed conditions, yield primarily linear or randomly branched polymers, which entangle and form additional branches resulting in gelation. On the other hand, silicon oxide networks derived under base-catalyzed conditions yield more highly branched clusters, which do not interpenetrate prior to gelation and thus behave as discrete clusters. For complete hydrolysis, the ratio of \textit{H}_2\textit{O}/Si is 4. If the amount of water becomes small, the hydrolysis rate slows down due to reduced reactant concentration, but a large amount of water dilutes the alkoxide and increases reaction time. Generally, the bulk density of silicon dioxide prepared by sol-gel reactions ranges
from 1.39 to 1.65 g cm\(^{-3}\) and the skeletal density ranges from 1.88-2.3 g cm\(^{-3}\) as the ratio of H\(_2\)O/Si ranges from 4 to 24. The hydrophilicity of the silicon dioxide particles produced by sol-gel synthesis depends on the number of Si-OH groups: A large number of Si-OH groups results in increased hydrophilicity.\(^{[2]}\)

Sol-gel synthesis possesses several advantages that have led to increased interest in this method. The temperatures required for all stages except densification are low, frequently close to room temperature. The chemical conditions are mild. Hydrolysis and condensation are catalyzed by acids and bases, but extreme pH conditions are easily avoided. By controlling aging and drying conditions, pore size and mechanical strength of the final product can be controlled.\(^{[2]}\)

Silicon sol-gel processing has been the most extensively studied, therefore best understood system. Furthermore, the sol-gel synthesis of non-silica, both inorganic precursors in an aqueous solution and metal organic precursors in a variety of mixed solvents have a wide range of uses. Generally, these systems are distinguished from silica by greater chemical reactivity resulting from the lower electronegativity of the metal and its ability to exhibit several coordination states.\(^{[1]}\)

When dissolved in pure water, metal cations, M\(^{z+}\), often introduced as salts, are solvated by water molecules. Because of the high electropositive character of the metal atoms, the rate of nucleophilic attack on the central atom of metal hydroxides is fast and hydrated metal ions have an increasing tendency
towards acid dissociation as the electropositive character of the metal increases, as shown in Figure 4.2; this equilibria is defined as hydrolysis.\textsuperscript{[1, 2]}

Figure 4.2: Hydrolysis equilibria of metal alkoxides.

\[
[M\cdots\text{OH}]^{2+} \rightleftharpoons [M\cdots\text{OH}]^{(x-1)+} + \text{H}^+ \rightleftharpoons [M=\text{O}]^{(x-2)+} + 2\text{H}^+ 
\]

In general, hydrolysis is facilitated by increases in the charge density on the metal, the number of metal ions bridged by a hydroxo- or oxo- ligand, and the number of hydrogens contained in the ligand. Hydrolysis is inhibited as the number of hydroxo ligands coordinating M increases.\textsuperscript{[1]}

Condensation can proceed by either of two nucleophilic mechanisms depending on the coordination number of the metal. When the preferred coordination is satisfied, condensation occurs by nucleophilic substitution (Figure 4.3A); when the preferred coordination number has not been satisfied, condensation can occur by nucleophilic addition (Figure 4.3B). Olation is a condensation process in which a hydroxyl bridge is formed between two metal centres. For coordinatively saturated hydroxo-aquo precursors, olation occurs by nucleophilic substitution where the hydroxyl group is the nucleophile and H\textsubscript{2}O is the leaving group. Oxolation is a condensation reaction in which an oxo bridge (\textmd{O\textemdash\textmd{O}}) is formed between two metal centres. When the metal is co-ordinately unsaturated, oxolation occurs by nucleophilic addition; for coordinatively saturated metals, oxolation proceeds by a two-step nucleophilic substitution reaction between oxyhydroxy precursors followed by water elimination to form an M\textmd{O\textemdashM} bond.\textsuperscript{[1, 2]}
Near the isoelectric point (the pH at which a molecule carries no net charge), neutral precursors are able to condense indefinitely via olation and/or oxolation reactions to form metal hydroxide or oxyhydroxide products. Whether precipitation or gelation occurs depends not only on processing factors (such as pH gradients, temperature, and speed of mixing), but also on the condensation kinetics. ⁠¹,²⁷⁴

4.1.2 Composite Membranes

For most PEMs, proton conductance depends on the existence of water in the membranes. Several technical approaches have been considered in the prevention of loss of water from the ionic regions of the membrane in order to maintain ionic conductivity at temperatures near and above the normal boiling point of water (90 - 160 °C). The effectiveness of hydrophilic additives has been demonstrated in the case of heteropolyacids in Nafion®.⁴ Water molecules are strongly attracted to the inorganic material via a dipole interaction with ions; the acidic nature of the inorganic component may also contribute to proton conductivity by increasing the internal proton concentration. However, if the heteropolyacid is partially water soluble, it may leach from the membrane over time. This may be overcome by using insoluble materials, but this requires
additional processing steps. In some examples, the ionomer solution is mixed with the inorganic components \cite{5} while in others, the inorganic component may be impregnated inside the preformed membrane. \cite{6} In the former, special care is required to avoid particle agglomeration, and undesirable non-homogeneous dispersions of micro-sized particles are obtained even when ultrasonic mixing is used. \cite{7} In the case of impregnation, composite membranes are obtained by growing the inorganic component within the hydrophilic domains of preformed proton exchange membrane. It is possible to make use of the quasiordered nanophase-separated morphology of the membrane to serve as a reaction template to direct the growth of the inorganic phase; that is, within the nano-sized ionic aggregates. The most extensively studied systems are silicon dioxide (SiO$_2$) \cite{8} and zirconium phosphate (ZrP) \cite{9} with Nafion® membranes.

### 4.1.3 Nafion® + Zirconium Phosphate Membranes

In zirconium phosphate, in its crystalline state of zirconium bis (monohydrogenphosphate) monohydrated ($\alpha$-Zr(HPO$_4$)$_2$·H$_2$O), hereafter denoted ZrP, each zirconium shares six oxygens with six different O$_2$P-OH groups. There is one monolayer of metal atoms, bridged by monohydrogen phosphate groups. Van der Waals forces hold the layers together and the intercalated water molecules form hydrogen bondings with the P-OH groups belonging to only one side of the layers. ZrP fabrication yields discrete nanoparticles rather than network structures. \cite{11} ZrP is a desirable additive to Nafion®-based membranes because it has many advantageous attributes: it has moderate proton conductivity of $\sim 10^{-3}$ S cm$^{-1}$ when humidified; \cite{10} it has two exchangeable
hydrogen ions, which may contribute to proton conduction; \cite{11} it is thermally stable up to 180 °C; and is hygroscopic and hydrophilic. It is also easily synthesized in a manner that is compatible within the chemical and physical processing limits of many organic polymer membranes. However, the amorphous phase and other crystalline phases of zirconium phosphate are not so conductive, and thus as-prepared zirconium phosphate exhibits a proton conductivity of $10^{-7}$ to $10^{-3}$ S cm$^{-1}$ depending on the phase composition, structure, and hydration state. \cite{10}

The majority of investigations of Nafion$^\text{®}$/ZrP composite membranes have focused largely on fuel cell performance, especially at temperatures > 100 °C, \cite{13, 14, 15} although a few studies have also examined the effect of incorporating ZrP on the proton conductivity, water uptake, mechanical properties, and methanol crossover of membranes. \cite{13-15} Bauer and Porada studied several properties of Nafion$^\text{®}$ membranes with increasing ZrP content from 0 to 35.1 wt% and found that the number of water molecules per sulfonate group (λ) barely changed from 19.6 for pure Nafion 117$^\text{®}$ to 20.0 for Nafion 117$^\text{®}$ that contained 24.4 wt% ZrP. ZrP was found to serve as diffusion barrier for the methanol transport. A strong influence of ZrP content on the mechanical loss, glass transition, and crystallinity of the polymer backbone indicates major structural changes within the perfluorinated polymer when the inorganic component is incorporated \cite{14}. Benziger et al. fabricated Nafion 115$^\text{®}$ that contained 25 wt% ZrP and reported a lower liquid water uptake at 25 °C than Nafion$^\text{®}$ (33 vs 41 wt%), but higher water vapour uptake under saturated conditions at 80 °C than Nafion$^\text{®}$ (25 vs 18 wt%).
However, Nafion® with 25 wt% ZrP exhibited a lower proton conductivity than unmodified Nafion® for all temperatures (80 to 140 °C) and humidity conditions. In a second study, Bauer and Porada determined water sorption isotherms and related them to changes in mechanical and electrical properties. Proton conductivity of Nafion 117® and Nafion® + 21 wt% ZrP increased from 0.01 to 0.07 S cm⁻¹ and 0 to 0.02 S cm⁻¹, respectively, as λ increased (via increasing RH) from 2.5 to 10. The elastic modulus of Nafion 117® and Nafion® + 21 wt% ZrP decreased from 300 to 100 MPa and from 1100 to 100 MPa, respectively, as λ increased from 0 to 10. When a characteristic water content, λ, of 2 to 3.5 water molecules per sulfonic acid group was exceeded, the conductivity increased linearly with the amount of water in the polymer.

It has been demonstrated that direct methanol fuel cells using Nafion® + 23 wt% ZrP membranes achieved excellent performance up to 140 °C without humidification at the cathode. At 140 °C and under dry conditions, the current density obtained at 0.6 V for Nafion 115® was 41 mA cm⁻², and for Nafion® + 23 wt% ZrP, 270 mA cm⁻². Improvement in H₂/O₂ fuel cell performance for Nafion® + 25 wt% ZrP membranes compared to Nafion® was observed in conditions where the water activity is less than 1. At 80 °C the current density obtained at 0.6 V is 1000 mA cm⁻² for Nafion 115® and 700 mA cm⁻² for Nafion® + 25 wt% ZrP. At 130 °C the current density obtained at 0.6 V is 150 mA cm⁻² for Nafion 115®, and 550 mA cm⁻² for Nafion® + 25 wt% ZrP. Thus Nafion®/ZrP systems exhibit reportedly encouraging performance in fuel cell operation up to 150 °C and at reduced humidification.
4.1.4 Nafion® + Silicon Dioxide Membranes

Initially, SiO₂ was added to Nafion® membranes because it was well-known for its hygroscopic properties. It was believed that SiO₂ would aid in water retention of Nafion® in dehydrating conditions. Until now, many investigations of Nafion®/SiO₂ membranes fabricated through in situ sol-gel reactions have focused on fuel cell performance, [9, 11, 13] especially at temperatures above 100 °C. Other studies have focused on mechanical properties, [6, 8, 14, 15] confirmation of the SiO₂ structure inside the membrane, [6, 8, 17-21] thermal behaviour, [8, 19, 22] optimization of SiO₂ distribution through the membrane, [17, 20, 23, 24] methanol uptake and permeability, [19, 20, 25] water content, [20, 26] and proton conductivity. [19, 20]

In 1989, Mauritz et al. [6] reported the in situ growth of silicon oxide microclusters or interpenetrating networks in Nafion® membranes using the sol-gel reaction of TEOS. In that and subsequent studies, characterization of these nano-composites by Fourier transform infra red (FTIR) spectroscopy, [6] dielectric relaxation, [27] thermal analysis [28], and small angle X-ray scattering (SAXS) [28] suggests that the nano-phase separated morphology of Nafion® acts as a template for the growth of the silica phase. More specifically, the SAXS peak characteristic of quasi-ordered clusters in unfilled Nafion® persists in the SiO₂-Nafion®. Relationships between tensile properties and solids uptake indicate an initial strengthening, followed by a ductile-brittle transition suggesting a silicon oxide phase percolation threshold. [6] FTIR spectroscopy [6] and ²⁹Si solid state NMR analyses [6] portray microstructural evolution and an inorganic network that
is not as highly crosslinked as that of sol-gel derived free silica and which becomes less coordinated and connected with increasing solids uptake.

Savinell et al. [25] investigated Nafion®/SiO₂ membranes as potential polymer electrolytes for DMFC applications. Methanol uptake and methanol permeability were measured as a function of temperature, methanol vapour activity, and silica content. Decreased methanol uptake from liquid methanol was observed in the hybrid membranes for silica contents of 10 and 21 wt%. Methanol uptake from the vapour phase by the composite membranes appears similar to that of unmodified Nafion®. Savinell et al. also investigated Nafion®/SiO₂ membranes as potential polymer electrolytes for fuel cell applications. [26] Membrane proton conductivity and water content were measured as a function of temperature, water vapour activity, and silica content. The composite membranes have higher water content at 25 and 120 °C, but not at 150 and 170 °C. Despite the higher water content, the proton conductivities in the composite membranes are lower than, or equal to that of unmodified Nafion® membranes under all conditions investigated. The proton conductivity of the composite membranes decreased with increasing silica content under all conditions. At room temperature, Hong et al. [20] found that the water content and conductivity of Nafion®/SiO₂ composite membranes increased with increasing SiO₂ content up to 10 wt% SiO₂ and then decreased with increasing SiO₂ content up to 45 wt% SiO₂. Through NMR studies, Goward et al. [20, 24] investigated the proton dynamics of Nafion® and Nafion®/SiO₂ composites and demonstrated the
role of high surface area SiO$_2$ particles in trapping water and building a pathway for structural proton diffusion.

Bocarsly et al. studied Nafion$^\text{®}$ + 6 wt% SiO$_2$ for operation in proton exchange membrane fuel cells from 80 to 140°C. At 80°C and 1 atm pressure the current densities at 0.6 V for Nafion 115$^\text{®}$ + 6 wt% SiO$_2$ and Nafion 115$^\text{®}$ are 200 and 600 mA cm$^{-2}$, respectively. At 130°C and 3 atm pressure, the current densities at 0.6 V for Nafion 115$^\text{®}$ + 6 wt% SiO$_2$ and Nafion 115$^\text{®}$ are 400 and 75 mA cm$^{-2}$, respectively. The Nafion 115$^\text{®}$ membrane's performance decreased rapidly with time and within an hour no current was observed, while after 50 h of continuous operation at 0.65 V, the current output of the composite membrane remained unchanged. The improved fuel cell performance for the composite membrane was attributed to improved water management of the membrane at high temperatures. [29] Dehydration of unmodified Nafion$^\text{®}$ at elevated temperatures leads to the destruction of the pore structure as detected by a decrease in proton conductivity. The presence of the silicon dioxide within the membranes apparently prevented these temperature-related structural changes, and conductivity is maintained even after thermal cycling to above 130°C. [30]

Kim et al. prepared Nafion$^\text{®}$/SiO$_2$ composite membranes with various silicon dioxide contents. The rate of methanol crossover was reduced by impregnation of silicon dioxide into the Nafion$^\text{®}$ membrane. The highest performance of the single cell was evaluated at a cell temperature of 125°C using Nafion 115$^\text{®}$ membranes containing 6.4 to 21.2 wt% SiO$_2$. At higher silicon oxide content (>12.4 wt%), the performance in DMFCs was reduced due to the
decrease of proton conductivity of the membrane. The highest current density using the composite membrane with 12.4 wt% silicon dioxide at a cell voltage of 0.6 was 350 mA cm\(^{-2}\) at 120 °C. Improved performance for the composite membrane compared to pure Nafion\(^\circledR\) at high temperature was attributed to enhanced water uptake and reduced methanol crossover.\(^{[19]}\)

### 4.1.5 Objectives

A common observation with Nafion\(^\circledR\) composite membranes is that while fuel cell performances are improved at elevated temperature, \textit{ex situ} proton conductivity measurements are not. For example, Nafion\(^\circledR\) + 25 wt\% ZrP, in comparison to unaltered Nafion\(^\circledR\), exhibits lower proton conductivity for all temperature from 80 to 140 °C and all relative humidity conditions between 0 to 100\%. However, the composite membrane relative to Nafion 115\(^\circledR\) exhibits a better fuel cell performance at 140 °C.\(^{[10]}\) Improved fuel cell performance in these cases has been ascribed to enhanced water retention induced by the inorganic component, for which three explanations have been proposed:

1) Replacement of unassociated bulk water with hydrophilic inorganic nanoparticles

2) Capillary condensation effects due to the smaller dimensions of the inorganic filled pores. Theoretically, the average pores of Nafion\(^\circledR\) membranes themselves should be small enough (2 - 3 nm) to induce a significant depression of the vapor pressure due to capillarity. However, the pore size distribution in Nafion\(^\circledR\) membranes is very broad, and a small fraction of pores is larger than 10 nm.
Capillary depression of the water vapor pressure is not appreciable in pores larger than 10 nm, and thus at high temperatures the largest pores dehydrate first, interrupting the continuity of proton conduction paths through the membrane. The presence of zirconium phosphate is likely to reduce the free space in the larger nanopores, promoting capillary condensation and thus water retention and proton conductivity.

3) Improved mechanical properties. The inorganic nanoparticle is formed when the membrane is fully hydrated. When the membrane is dehydrated, the Nafion® contracts, but the inorganic group cannot. The inorganic group may act as a scaffold that limits membrane contraction upon dehydration. In a fuel cell, the MEA is compressed between the bipolar plates. The applied pressure on the MEA limits the swelling of the membrane. Adsorbed water swells the membrane creating a “swelling pressure” that must overcome the applied sealing pressure of the fuel cell. In the fuel cell environment, that water content of the membrane is probably much less than that expected based on ex situ measurements because the sealing pressure squeezes water from the membrane. The inorganic group in the composite membrane may form rigid internal scaffolding, which would resist compression of the sealing pressure. At reduced water activity, the composite membrane can take up water and swell without having to overcome the applied sealing pressure. This would lead to improved water retention at high temperatures and, therefore, improved fuel cell performance.

However, despite numerous fuel cell studies on Nafion®/inorganic membranes, it is not fully understood why fuel cell performance improves upon
incorporation of the inorganic component. This stems from an incomplete knowledge of the inherent properties of composite membrane. In this study, the goal is to gain additional understanding of the effect of the inorganic component on inherent, *ex situ* measured, membrane properties. Nafion® membranes are modified by the addition of variable amounts of ZrP or SiO₂. A systematic study of the effect of inorganic content on membrane properties is performed that includes confirming the structure of the inorganic component using scanning electron microscopy energy dispersive X-ray analysis (SEM/EDX), X-ray diffractometry (XRD), ²⁹Si-NMR, and FTIR-ATR; changes in the morphology of the membranes as revealed by transmission electron microscopy (TEM); water sorption properties, water vapour transmission, proton conductivity, and proton mobility. Transport data are obtained on membranes equilibrated at 80 °C and 40% RH as well as at room temperature for fully hydrated membranes. The results are evaluated on the basis of current theories for why inorganic nanoparticles improve fuel cell performance under certain conditions.

### 4.2 Nafion® + Zirconium Phosphate Membranes

#### 4.2.1 Experimental

##### 4.2.1.1 Materials

Nafion 115® was purchased from Alfa Aesar. Zirconyl chloride (ZrOCl₂), sulfuric acid (H₂SO₄) and sodium chloride (NaCl) (99%, reagent grade) were purchased from Alfa Aesar and used as received. Hydrogen peroxide (H₂O₂), phosphoric acid (H₃PO₄) and sodium hydroxide (NaOH) were purchased from
Sigma Aldrich and used as received. MilliQ water (Millipore) was used in washing and hydrating membranes and for making solutions.

4.2.1.2 Membrane Fabrication and Treatment

Nafion 115® was pretreated at 80 °C in: 3 wt% hydrogen peroxide, water, 10 wt% sulfuric acid, and finally water for an hour each.

ZrP was incorporated into pretreated Nafion® using a similar procedure to that first described by Grot and Rajendran. [31] Membranes were swollen in MeOH/H₂O 1:1 (v/v) solution overnight and at 80 °C for the last hour. The membranes were then immersed in a stirring 1 M ZrOCl₂ solution at 80 °C for 3 h to 71 h, controlling the ZrP content. The ZrOCl₂ solution diffuses into the membrane and the excess of Zr⁴⁺ ions within the membrane leads to an exchange with sulphonic acid protons in the membrane. After that, the membranes were rinsed in cold water to remove the zirconyl chloride solution from the surface and placed in 1 M H₃PO₄ at 80 °C and stirred for 5 to 60 h. The phosphoric acid reacts with the Zr⁴⁺ ions to form insoluble ZrP in situ, and the acidic solution can reprotoante the sulphonate anions to regenerate the acidity of the membrane. The membranes were rinsed in cold water again and were then dried in a vacuum oven at 80 °C for 4 h. The membranes were rinsed in water and dried several times until the mass of the membrane became constant.

To determine the inorganic content (Wt% ZrP) of the composite membranes, the mass of the dry membrane before and after the reaction (M_{before} and M_{after}) was used, as seen in equation 4.1.
4.2.1.3 Ion Exchange Capacity

The ion exchange capacities, IEC, of the membranes were experimentally verified through titration, as described in Section 2.2.6, and calculated from equation 2.4. To find the normalized IEC for the Nafion 115®/ZrP composite membranes, equation 4.2 was used.

\[
\text{IEC}_{\text{Norm}} = \frac{\text{IEC}_{\text{Nafion}} \times \text{Wt}\%_{\text{Nafion}}}{100}
\]

Where IEC_{Nafion} is 0.906 meq g^{-1}, the IEC determined experimentally for Nafion®, and Wt\%_{Nafion} is (100 - Wt\%_{ZrP}). To find the calculated IEC for the composite membranes, equation 4.3 was used.

\[
\text{Calculated IEC}_{\text{Composite}} = \text{Wt}\%_{\text{Nafion}} \times \text{IEC}_{\text{Nafion}} + \text{Wt}\%_{\text{inorg}} \times \text{IEC}_{\text{ZrP}}
\]

Where IEC_{ZrP} is 6.64 meq g^{-1}, assuming two protons in ZrP.

4.2.1.4 Water Sorption

The water content, water uptake, \( \lambda \) and \( \rho \) were determined as described in Section 2.2.8 and seen equations 2.7, 2.6, 2.8, and 2.9 respectively.

To calculate the dry density of the membranes, \( \rho \), the mass of the dry membrane was divided by the dry volume of the membrane, obtained by measurement, as shown in equation 4.4.
4.2.1.5 Water Vapour Transmission

Water vapour transmission was measured using an ESPEC Temperature and Humidity Chamber SH240 to control the temperature and relative humidity. The set up was based on ASTM E96/E96M-05, standard test methods for water vapor transmission of materials. Further details on this procedure are in Section 3.2.5 and equations 3.4 and 3.5 were used to determine the WVT and water vapour permeance, respectively.

4.2.1.6 Proton Conductivity

The proton conductivity of ionomer membranes was measured by EIS, as described in Section 2.2.9, using equation 2.10.

4.2.1.7 Proton Concentration and Effective Proton Mobility

$[H^+]$ was calculated using equation 4.5.

$$[H^+] = \frac{\text{IEC} \cdot M_{\text{dry}}}{V_{\text{dry}} + M_{\text{H}_2\text{O}}}$$  

Where $M_{\text{H}_2\text{O}}$ is the mass of water in the hydrated membrane. This procedure is altered from the one described in Section 2.2.10 because when the membrane is not fully hydrated, as is the case at 40% RH and 80 °C, the wet volume of the membrane will not account for the possibility that hydrophilic regions of the membrane are not completely filled with water.

$\mu_{\text{eff},H^+}$ was calculated using equation 2.14, as described in Section 2.2.10.
4.2.1.8 Physical Characterization of Membranes

XRD analysis was carried out on Nafion®/ZrP membranes using a Bruker AXS diffractometer with a Cu Ka radiation source. Membranes were exposed to ambient conditions for several days prior to testing. Samples were mounted in an in-house made sample holder to ensure a smooth sample surface during testing. The measurements were carried out under ambient conditions. XRD can help determine the phase of ZrP present in the membrane.

TGA of the composite membranes was measured on a TA Instruments 2950 TGA HR instrument. The polymers were evaluated from 100 °C to 550 °C under nitrogen at a heating rate of 10 °C per minute. Prior to measurement, the samples were dried at 150°C for 30 minutes in the instrument chamber to remove excess water.

The mechanical strength of wet membranes was determined as described in Section 3.2.8.

The Nafion®/ZrP membrane cross-sections were studied with a Hitachi SEM-S-3500 system equipped with an energy dispersive X-ray (EDX) spectrometer. Both backscattered and EDX analyses were used to examine the homogeneity of ZrP in the membranes.

To prepare samples for TEM, selected polymer samples were stained by soaking in a concentrated lead acetate solution overnight, if the samples required staining. After drying in a vacuum oven for four hours at 80 °C, the polymers were embedded in Spurr's epoxy and cured overnight in an oven at 60 °C. The samples were then cut using a Leica UC6 Ultramicrotome to slices with
thicknesses of 75-90 nm, placed on copper grids, and examined using a Hitachi H7600 TEM.

4.2.2 Results and Discussion

4.2.2.1 Physical Characterization

Composite membranes composed of Nafion 115® and 7.8 to 25.0 wt% zirconium phosphate were fabricated by controlling the immersion time of swollen Nafion® in ZrOCl₂ and phosphoric acid solutions as indicated in Table 4.1. Incorporation of ZrP increased the thickness of the Nafion 115® membranes from 0.75% for the 7.8 wt% ZrP membrane to 25% for the 25.0 wt% ZrP membrane. The formation of ZrP in the membranes was confirmed by SEM/EDX and XRD, typical results are shown in Figures 4.4 and 4.5 for samples containing 0-25 wt% ZrP. EDX spectra for each membrane indicate elemental peaks for elements carbon, oxygen, fluorine, and sulfur. A strong EDX signal for zirconium is also observed for Nafion®/ZrP composite membranes. The backscattered electron image, EDX spectra, and EDX dot mapping images of cross-sections of the entire thickness of Nafion 115® (A) and Nafion 115® + 11-25 wt% ZrP (B-D) membranes are shown in Figure 4.4 (A-D). The EDX dot mapping images illustrates the distribution of a chosen element across the image. As expected, fluorine is present in all the membranes (Figure 4.4A-D(ii)). EDX dot mapping images of the composite membranes illustrate a homogeneous distribution of Zr throughout the entire cross section of membrane. Note that the apparent increase in concentration of Zr beyond the edges of the cross-section is because
the cross section is slightly tilted so that the top of the membrane can also be observed.

Table 4.1: Membrane properties including ZrP content, dimensional stability, IEC, and thickness for Nafion 115\(^\text{\textregistered}\)/ZrP membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Inorganic Content (wt %)</th>
<th>(\Delta t^a) (%)</th>
<th>(\Delta l^b) (%)</th>
<th>(\Delta w^c) (%)</th>
<th>IEC(^d) (meq g(^{-1}))</th>
<th>IEC(_{\text{Nom}}^e) (meq g(^{-1}))</th>
<th>Calc. IEC(_{\text{comp}}) (meq g(^{-1}))</th>
<th>Thickness(^g) ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 115(^\text{\textregistered})</td>
<td>0</td>
<td>14</td>
<td>11</td>
<td>11</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
<td>132 (0.9)</td>
</tr>
<tr>
<td>Nafion 115(^\text{\textregistered})/ZrP</td>
<td>7.8 (0.8)</td>
<td>22</td>
<td>25</td>
<td>11</td>
<td>0.89</td>
<td>0.84</td>
<td>1.35</td>
<td>138 (0.3)</td>
</tr>
<tr>
<td></td>
<td>10.9 (0.2)</td>
<td>8.9</td>
<td>16</td>
<td>19</td>
<td>0.85</td>
<td>0.81</td>
<td>1.53</td>
<td>158 (3)</td>
</tr>
<tr>
<td></td>
<td>11.4 (0.4)</td>
<td>12</td>
<td>25</td>
<td>23</td>
<td>1.10</td>
<td>0.80</td>
<td>1.56</td>
<td>157 (3)</td>
</tr>
<tr>
<td></td>
<td>16.0 (0.7)</td>
<td>16</td>
<td>18</td>
<td>18</td>
<td>0.89</td>
<td>0.76</td>
<td>1.82</td>
<td>144 (6)</td>
</tr>
<tr>
<td></td>
<td>19.4 (0.4)</td>
<td>17</td>
<td>19</td>
<td>22</td>
<td>0.93</td>
<td>0.73</td>
<td>2.02</td>
<td>155 (5)</td>
</tr>
<tr>
<td></td>
<td>22.0 (0.7)</td>
<td>15</td>
<td>27</td>
<td>27</td>
<td>0.76</td>
<td>0.71</td>
<td>2.17</td>
<td>148 (9)</td>
</tr>
<tr>
<td></td>
<td>22.9 (0.7)</td>
<td>15</td>
<td>20</td>
<td>8.6</td>
<td>0.75</td>
<td>0.70</td>
<td>2.22</td>
<td>150 (2)</td>
</tr>
<tr>
<td></td>
<td>25.0 (0.6)</td>
<td>5</td>
<td>21</td>
<td>20</td>
<td>0.74</td>
<td>0.68</td>
<td>2.34</td>
<td>177 (9)</td>
</tr>
</tbody>
</table>

Error (\(\pm\)) is shown in brackets after the value, \(^a\)Change in thickness with swelling in water; \(^b\)Change in length with swelling in water; \(^c\)Change in width with swelling in water; \(^d\)Ion exchange capacity, a measure of the degree of sulfonation of the polymer, measured by titration; \(^e\)IEC if the inorganic group has no contribution; \(^f\)As determined using the IEC of Nafion\(^\text{\textregistered}\) from titration (0.906 meq g\(^{-1}\)) and zirconium hydrogen phosphate assuming 2 exchangeable hydrogens (6.64 meq g\(^{-1}\)); \(^g\)Dry membrane.
Figure 4.4: i) EDX image, ii) EDX mapping fluorine, and iii) EDX mapping of Zr for A) Nafion 115®, B) Nafion® +11 wt.% ZrP, C) Nafion® +19 wt.% ZrP, D) Nafion® +25 wt.% ZrP.

A.
XRD patterns of Teflon®, Nafion 115®, Nafion 115® + 10.9 wt.% ZrP, Nafion 115® +16.0 wt.% ZrP, Nafion 115® + 19.4wt% ZrP, Nafion 115® + 22.0 wt % ZrP and Zr(HPO₄)₂•0.5H₂O are shown in Figure 4.5 A-F. A pattern is the list of peaks that can be considered as the signature of a given crystalline phase. It is a list of the d-spacings and relative intensity of a given peak. Reference patterns are stored in diffraction databases. When a pattern is obtained for a material, it is possible to search through the database and match the peaks. The peaks of the composite materials can be matched to patterns found for Teflon® and ZrP in the
International Centre for Diffraction Data (ICDD). The diffraction peaks at 5.1 and 2.4 Å observed for Nafion 115® (Figure 4.5B) are attributed to the Teflon®-like domains (Figure 4.5A) and appear for each of the composite membranes. Peaks at 4.6, 3.7, 2.7, and 1.7 Å in the diffraction patterns for the composite membranes in Figures 4.5C-E match up with typical peaks found for α-zirconium phosphate hemihydrate (Zr(HPO$_4$)$_2$$\cdot$0.5H$_2$O) (Figure 4.5 F). The pattern in Figure 4.5D is less noisy than the others and this is likely due to this membrane being more even (which is an effect of ensuring the membrane is flat as it is dried). The XRD patterns of the membranes are not very sharp and this may be due to water uptake which influences the crystalline packing of polymer chains as well as the structure of the ZrP phases. [9]
Figure 4.5: X-ray diffraction of A) Teflon®, B) Nafion 115®, C) Nafion® + 11 wt% ZrP, D) Nafion® + 16 wt% ZrP, E) Nafion® + 22 wt% ZrP, F) Zr(HPO₄)₂·0.5H₂O, from ICDD.
TEM images of Pb\(^{2+}\) stained and unstained Nafion 115\(^{®}\)/ZrP membranes are presented in Figure 4.6(A-J). No features can be observed from the unmodified Nafion\(^{®}\) membrane that has not been stained (Figure 4.6B) so that the dark features observed for unstained images of Nafion 115\(^{®}\)/ZrP composite membranes are due to ZrP. In contrast, stained images accentuate, as dark areas, hydrophilic ionic regions of Nafion\(^{®}\) as well as ZrP. For stained Nafion\(^{®}\) (Figure 4.6A), the fine phase separation of hydrophilic sections are visible in the form of small dark circles (5-10 nm) that are < 5 nm apart, embedded in a pale background of fluorous polymer. For composite membranes, phase separation becomes less fine as the ZrP component is increased. For Nafion\(^{®}\) + 8 wt% ZrP (Figure 4.6C), the dark domains have increased to 5-25 nm in size, but are still in close proximity. For Nafion\(^{®}\) + 11 wt% ZrP (Figure 4.6E) the features have increased to 5-50 nm, and for Nafion\(^{®}\) + 23 wt% ZrP (Figure 4.6I), the same features are 100 nm in size. The darker, stained features are believed to be ZrP because in the lighter areas, the less dark features arising from ionic aggregates of Nafion\(^{®}\) in the form of circles with a 5 nm diameter are still visible. The large dark features in the stained samples are often long and narrow rather than circular. In the unstained images, the dark regions representing ZrP become larger and denser as the ZrP content is increased. For unstained images of Nafion\(^{®}\) + 8 wt% ZrP (Figure 4.6D), the ZrP particles are of similar size to the hydrophilic pores of Nafion\(^{®}\) (5-10 nm diameter), which are visible in Figure 4.6B (5-25 nm diameter), and they are distributed rather evenly, like the hydrophilic domains of Nafion\(^{®}\). An even distribution of zirconium phosphate is obtained as
expected because the zirconium ion exchanges with protons contained within the hydrophilic domains of Nafion®. The size and distribution of ZrP particles suggests that ZrP is formed inside the ionic regions of Nafion® for low contents of ZrP. As the ZrP content of the membranes is increased from 8-23 wt%, the size of ZrP particles increases from 5 nm to as large as 135 nm, and consequently, the morphology of the Nafion® membrane is disrupted. The ZrP particles are an order of magnitude larger in size than the hydrophilic pores in Nafion® and have no regular orientation. However, not all ionic aggregates are affected, so for the 23 wt% ZrP membrane, both ZrP domains and ionic aggregates of Nafion® co-exist (Figure 4.6I), which could have a significant effect on water and proton transport properties. Similar results were obtained by Gebel et al., who determined the shape and size of Nafion® + 14.5 wt% ZrP using wide angle x-ray scattering, small angle x-ray scattering, and SEM - field emission gun [32] and related their findings to the ribbon-like polymer particle model for Nafion®. [33] They found the ZrP particles appeared as 56 nm wide platelets with a thickness of 7 nm and suggested that the large dimensions imply that the synthesis does not occur within the ionic domains, but in the inter-bundle areas where the spatial arrangement of the perfluorinated ribbons should be less compact. In this study, lower ZrP contents were harder to investigate because their particle size were similar to the size of the ionic aggregates in Nafion®.
Figure 4.6: TEM images of Nafion 115\textsuperscript{®}/ZrP. A. stained Nafion 115\textsuperscript{®}, B. non-stained Nafion 115\textsuperscript{®}, C. stained Nafion 115\textsuperscript{®} + 8 wt\% ZrP, D. non-stained Nafion 115\textsuperscript{®} + 8 wt\% ZrP, E. stained Nafion 115\textsuperscript{®} + 11 wt\% ZrP, F. non-stained Nafion 115\textsuperscript{®} + 11 wt\% ZrP, G. stained Nafion 115\textsuperscript{®} + 16 wt\% ZrP, H. non-stained Nafion 115\textsuperscript{®} + 16 wt\% ZrP, I. stained Nafion 115\textsuperscript{®} + 23 wt\% ZrP, J. non-stained Nafion 115\textsuperscript{®} + 23 wt\% ZrP.
In Table 4.2 it is shown that the Young's modulus of hydrated Nafion 115® is 238 MPa, while that for ZrP composite membranes ranges from 35.5 ± to 193 MPa when the ZrP content ranges from 7.8 to 25.0 wt%; i.e., addition of ZrP decreases the stiffness of Nafion 115®.

Table 4.2. Mechanical Strength Data for Nafion®/ZrP composite membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 115®</td>
<td>238 (8)</td>
</tr>
<tr>
<td>Nafion 115®/7.8 wt % ZrP</td>
<td>35.5 (3)</td>
</tr>
<tr>
<td>Nafion 115®/10.9 wt % ZrP</td>
<td>193 (34)</td>
</tr>
<tr>
<td>Nafion 115®/25.0 wt % ZrP</td>
<td>154 (17)</td>
</tr>
</tbody>
</table>

Error (±) is shown in brackets after the value.
The IEC is a measure of the exchangeable protons in the membrane. The IEC of the Nafion 115®/ZrP composite membranes, determined by titration, are shown in Table 4.1. The IEC of Nafion 115® is 0.91 ± 0.001 meq g⁻¹ and the IEC of the composite membranes range from 0.74 ± 0.02 to 1.10 ± 0.0005 meq g⁻¹, i.e., both higher and lower than that of Nafion 115® and no clear trend is evident. The IEC of Nafion® measured by titration can be normalized to account for the inorganic content, according to equation 4.2. The results from this calculation are shown in Table 4.1. In all cases, the measured IEC is higher than the normalized IEC, providing supporting evidence that ZrP contributes protons to the IEC of the membrane. The number of exchangeable protons depends on the chemical form of the zirconium phosphate. The IEC of α-Zr(HPO₄)₂·H₂O is 6.640 meq g⁻¹, based on two exchangeable protons. However, this is the phase of ZrP that possesses the highest IEC; other forms of ZrP have lower IECs. For example, although there are two acid –OH groups in γ-ZrPO₄(H₂PO₄)·H₂O, due to the difference in their acidities, only one proton is exchangeable, giving an IEC of 3.320 meq g⁻¹. Assuming for the moment that the α- is the only form present, the IEC can be divided into contributions from the Nafion® and from the zirconium phosphate, as in equation 4.3. The results from this calculation are shown in Table 4.1. The measured IEC of the Nafion®/ZrP composite membranes ranges from 0.738 to 1.10 meq g⁻¹ and the calculated IEC values for the Nafion®/ZrP composite membranes based on α-Zr(HPO₄)₂·H₂O range from 1.35 to 2.34 meq g⁻¹. Thus, each ZrP does not contribute two hydrogens, which could be because α-Zr(HPO₄)₂·H₂O is not the only form of ZrP present in the composite membrane,
but rather a mixture of different phases, with some having lower IEC values or because the protons in ZrP have much lower acidities than the ones in Nafion® so they are not as easily exchanged. These results agree with those obtained by Benziger et al. [10] who found that the IEC of a Nafion® + 25 wt% ZrP membrane was 1.46 meq g⁻¹. The predicted value based on Zr(HPO₄)₂·H₂O is 2.67 meq g⁻¹.

The density of each membrane was found using the dry mass and volume, as in equation 4.4. The density of zirconium phosphate is 2.1 g cm⁻³ [10] and the dry density of Nafion 115® is 1.8 ± 0.001 g cm⁻³. The density of the membranes is plotted against inorganic content in Figure 4.7. The density values of the Nafion®/ZrP membranes range from 1.8 ± 0.01 to 2.1 ± 0.02 g cm⁻³, thus the ZrP content has little effect on the density of the composite membrane. This finding is contrary to that reported by Benziger et al., [10] who found that addition of 25 wt% ZrP caused the density of the Nafion® membrane to drop from 2.0 to 1.6 g cm⁻³, and attributed it to the formation of a rigid internal scaffolding which creates void space within the membrane and lowers its density.

Figure 4.7: Dry density of Nafion 115®/ZrP membranes as a function of inorganic content.
4.2.2.2 Thermal Behaviour

The TGA curves are plotted in Figure 4.8. A three-step degradation profile is observed for the polymers using TGA. The first significant weight loss (below 200 °C) is due to loss of water. Desulfonation of the polymers begins at ~300 °C. A third weight loss that starts between 400 and 500 °C is attributed to degradation of the polymer backbone. The addition of ZrP to Nafion 115® does not significantly effect the thermal degradation of the membranes.

Figure 4.8: TGA profiles of Nafion 115® and Nafion 115®/ZrP composite membranes.

4.2.2.3 Water Sorption Behaviour

The percentage changes in dimensions that occur with swelling in water, as determined by measurement and calculated using equation 2.9, are shown in Table 4.1. The percent change in thickness, length, and width for Nafion 115® are 14 ± 1%, 11± 2%, and 11 ± 2%, respectively. The percentage change in thickness with swelling in water for the composite membranes ranges from 8.9 ± 0.7 – 22 ± 0.2%. The percentage changes in length and width for the composite
membranes range from $14 \pm 0.3 - 27 \pm 3\%$. The composite membranes thus exhibit a greater change in dimension with swelling than the pure Nafion 115®. This result also disputes the rigid scaffolding explanation in the composite membranes prepared for this study, because such scaffolding would resist dimensional changes.

The water contents of the composite membranes, which were determined from the mass of the wet and dry membranes according to equation 2.7, are plotted in Figures 4.9A and B. The water content of wet Nafion 115®/ZrP composite membranes at room temperature increases from $23 \pm 1 \text{ wt}\%$ to $35 \pm 0.1 \text{ wt}\%$ as the inorganic content increases from 0 to 19.4 wt%. Then, as the inorganic content increases from 19.4 to 25.0 wt%, the water content decreases from $35 \pm 0.1$ to $27 \pm 2 \text{ wt}\%$. The water content of Nafion 115® under conditions of 80 °C and 40% RH is $1.3 \pm 0.1 \text{ wt}\%$, while for Nafion 115®/ZrP composite membranes it ranges from $0.52 \pm 0.1$ to $4.3 \pm 0.01 \text{ wt}\%$ and decreases as ZrP content increases.

From the water uptake and the IEC values it is possible to determine the “effective” number of water molecules per sulfonated group ($\lambda$) for the membranes. These are plotted in Figures 4.9C and D. The $\lambda$ value of wet Nafion 115®/ZrP composite membranes at room temperature increases from $19 \pm 0.1$ to $48 \pm 0.1$ as the inorganic content increases from 0 to 19.4 wt%. As the inorganic content increases from 19.4 to 25.0 wt%, $\lambda$ decreases slightly from $48 \pm 0.1$ to 40 $\pm 7$. The $\lambda$ value of Nafion 115® at 80 °C, 40% RH is $1.1 \pm 0.1$, while $\lambda$ for the composite membranes ranges from $0.58 \pm 0.05$ to $4.3 \pm 0.02$. At room
temperature, the water contents and λ of the saturated composite membranes are higher than that of Nafion® and reach a peak at 19.4 wt% ZrP. At 80 °C and 40% RH, the water content and λ are higher than Nafion® at low Wt%ZrP and lower than Nafion® when ZrP is 25 wt% and reach a peak at ~11-16 wt% ZrP. In a similar study, Bauer et al. immersed membranes in water at room temperature and observed that increasing the amount of ZrP leads to increasing λ values: for ZrP contents in Nafion 117® of 0, 10.4, 14.9, 20.9, and 35.1, the λ values are 15.7, 17.1, 19.9, 22.7, and 21.4, respectively, [16] indicating that ZrP contributes to the uptake of water. Even though ZrP contains exchangeable protons, they likely do not contribute to the water content as much as the protons associated with the sulfonate groups in Nafion®. It has been reported that ZrP itself has a water content of 5 wt%, [20] which is equivalent to one water molecule per ZrP molecule, i.e., much lower than λ for Nafion®, which is ~ 19 in the fully hydrated state. At low inorganic contents (< 20 wt%) ZrP increases the water content of the membranes, possibly due to disruption of the cohesive forces in Nafion®, but as more ZrP is incorporated (> 20 wt.%), and the ZrP particles grow in size, the water content of the membrane decreases as ZrP begins to form between the bundles in the region where the spatial arrangement of the perfluorinated ribbon should be less compact. In these regions, the ZrP no longer contributes to increasing the water uptake of the membrane.
Figure 4.9: (A, B) water content and (C, D) $\lambda$ as a function of inorganic content for Nafion 115°/ZrP membranes in wet, RT (A, C) and 80 °C, 40% RH (B,D) conditions.

4.2.2.4 Proton Conductivity

The results of proton conductivity measurements, as calculated using equation 2.10, are shown in Table 4.3 and Figure 4.10. Proton conductivity of fully hydrated Nafion®/ZrP composite membranes at room temperature decreases from 0.076 ± 0.007 to 0.038 ± 0.007 S cm$^{-1}$ as the inorganic content is increased from 0 to 25.0 wt%. At 80 °C and 40% RH, proton conductivity values
of the composite membranes decreases from 0.0078 ± 0.0008 to 0.0037 ± 0.0001 S cm⁻¹ as the ZrP content increases from 0 to 25.0 wt%. At 120 °C and 45% RH, the proton conductivity of the Nafion®/ZrP composite membranes are 0.0053 ± 0.0009 and 0.0011 ± 0.0009 S cm⁻¹ for Nafion® + 7.8 and 16.0 wt% ZrP, respectively, which is lower than that of Nafion in these conditions (0.0062 ± 0.0008 S cm⁻¹). For ZrP contents > ~ 10 wt%, the proton conductivity of the composite membranes decreases with additional ZrP content in all temperature and humidity conditions. This is surprising in wet, room temperature conditions given that the water content for the composite membranes is similar to or higher and proton conductivity usually increases with water content. [34] Either the additional water simply hydrates the ZrP and is unavailable for proton conduction, or if it is available for improving the mobility of protons, the ZrP actually gives rise to a more tortuous path by blocking hydrophilic pores within the membrane. Bauer and Porada [16] found similar results for the conductivity of their fully hydrated, composite membranes.
Figure 4.10: Conductivity as a function of inorganic content of Nafion 115®/ZrP in (A) fully hydrated, room temperature (RT) and (B) 80 °C, 40% RH conditions.

![Conductivity as a function of inorganic content of Nafion 115®/ZrP](image)

Table 4.3: Conductivity results under different temperature and humidity conditions for Nafion 115®/ZrP membranes.

<table>
<thead>
<tr>
<th>Conductivity (S cm⁻¹)</th>
<th>Wet, RT¹</th>
<th>80 °C, 40% RH</th>
<th>120 °C, 45% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 115®</td>
<td>0.076 (0.007)</td>
<td>0.0078 (0.0007)</td>
<td>0.0062 (0.0008)</td>
</tr>
<tr>
<td>Nafion 115®/7.8 wt% ZrP</td>
<td>0.058 (0.002)</td>
<td>0.0084 (0.0009)</td>
<td>0.0053 (0.0009)</td>
</tr>
<tr>
<td>Nafion 115®/11.4 wt% ZrP</td>
<td>0.060 (0.005)</td>
<td>0.0049 (0.0008)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/16.0 wt% ZrP</td>
<td>0.057 (0.003)</td>
<td>0.0052 (0.0002)</td>
<td>0.0011 (0.0009)</td>
</tr>
<tr>
<td>Nafion 115®/19.4 wt% ZrP</td>
<td>0.052 (0.002)</td>
<td>0.0028 (0.0005)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/22.0 wt% ZrP</td>
<td>0.041 (0.006)</td>
<td>0.0011 (0.0007)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/23.0 wt% ZrP</td>
<td>0.038 (0.001)</td>
<td>0.0023 (0.0005)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/25.0 wt% ZrP</td>
<td>0.049 (0.003)</td>
<td>0.0016 (0.0002)</td>
<td></td>
</tr>
</tbody>
</table>

Error (±) is shown in brackets after the value, °RT is 20 °C

### 4.2.2.4 Proton Concentration and Effective Proton Mobility

Proton conductivity depends on the concentration and effective mobility of the protons in the membrane. The analytical [H⁺], which has contributions from Nafion® and ZrP, is plotted in Figure 4.11A as a function of ZrP content. [H⁺] of hydrated Nafion 115®/ZrP membranes at room temperature, calculated using the IEC obtained from titration, mass, and volume of the membranes, as in equation 2.4, decreases from 0.91 ± 0.08 to 0.60 ± 0.001 M as ZrP content is increased from 0 to 25.0 wt.%.. When equilibrated at 80 °C and 40% RH, [H⁺] of the composite membranes decreases from 1.3 ± 0.08 to 1.0 ± 0.001 M as the ZrP
content is similarly increased. \([H^+]\) is higher at 80 °C and 40% RH than in hydrated membranes because of their lower water content. For both conditions, \([H^+]\) marginally decreases with incorporation of ZrP into Nafion®.

The effective proton mobility, calculated using equation 2.14 and plotted in Figure 4.11B, for the hydrated Nafion 115®/ZrP composite membranes at room temperature decreases from \(6.5 \times 10^{-4} \pm 0.5 \times 10^{-4}\) to \(4.3 \times 10^{-4} \pm 0.5 \times 10^{-4}\) cm² s⁻¹ V⁻¹ as the ZrP content increases from 0 to 25.0 wt%. When the membranes are equilibrated at 80 °C and 40% RH (Figure 4.11C), the effective proton mobility of the composite membranes is decreased from \(4.6 \times 10^{-5} \pm 0.5 \times 10^{-5}\) to \(1.6 \times 10^{-5} \pm 0.1 \times 10^{-5}\) cm² V⁻¹ s⁻¹ as the ZrP content is increased from 0 to 25.0 wt%. The effective proton mobility in hydrated membranes at room temperature is ~10x higher than in membranes equilibrated at 80 °C and 40% RH due to higher water content in these hydrated conditions, but generally decreases with ZrP content under both conditions. One reason for the observed lower effective proton mobility of composite membranes compared to Nafion® is that ZrP is not a strong acid, unlike Nafion®. Thus not all phosphoric acid sites dissociate, especially under low humidity conditions. Alternatively, the tortuosity of the protonic conducting path could be substantially higher when ZrP is incorporated.
Figure 4.11: Proton concentration (A) and effective proton mobility (B,C) as a function of inorganic content for Nafion 115®/ZrP at 80 °C, 40% RH (A,C) and room temperature (RT), wet (A,B) conditions

A.

B.

C.

4.2.2.5 Water Vapour Transmission

The water management of the membrane is a key issue for continued operation of a fuel cell. Since water introduced into and exiting from a fuel cell is often in the form of vapor, especially at higher temperatures, the water vapor permeance may give an indication of the ability of water to transport through the membrane. For example, a high water vapor permeance could signify higher back diffusion of the water through the membrane during fuel cell operation, and
could lead to a more uniform distribution of the water and hence higher current density during fuel cell operation. The water vapour permeance takes into account the vapour pressure difference on either side of the membrane. Figure 4.12 shows the water vapour permeance of the composite membranes with different ZrP contents. The water vapour permeance of Nafion 115® is 0.056 ± 0.005 g Pa⁻¹ m⁻² h⁻¹. The water vapour permeance of the composite membranes ranges from 0.057 ± 0.005 to 0.060 ± 0.005 g Pa⁻¹ h⁻¹ m⁻². The water vapour permeance of the Nafion 115®/ZrP composite membranes is similar to or slightly higher than that of Nafion 115® and does not depend on ZrP content.

Figure 4.12: Water vapour permeance as a function of inorganic content for Nafion 115®/ZrP membranes at 80 °C, 40% RH.

4.2.3 Summary and Conclusions

Nafion®/ZrP membranes were fabricated with ZrP contents ranging from 7.8 - 25.0 wt%. The XRD data indicate that α-Zr(HPO₄)₂·0.5H₂O is formed in the membrane. IEC data suggests that the exchangeable protons on ZrP contribute to the IEC, but not enough so that each ZrP provides two protons, indicating that either phases of ZrP are formed that have less exchangeable protons or that
both protons on $\alpha\text{-Zr(HPO}_4\text{)}_2\cdot0.5\text{H}_2\text{O}$ are not exchangeable due to low acidity. The density of composite membranes lies between those of Nafion® and ZrP. Incorporation of ZrP into Nafion® membranes results in larger dimensional changes in the presence of water. Water content and $\lambda$ values indicate that ZrP increases water content of the membrane at low ZrP contents (<20 wt%), but decreases it at higher ZrP contents (> 20 wt%). Any increased water content, however, does not translate into increased proton conductivity or mobility. Both proton conductivity and effective proton mobility decrease with increasing inorganic content. Despite increased water content, incorporation of ZrP into Nafion® membranes does not affect the transmission of water vapour through the membranes. Water vapour transmission values of composite membranes are similar to values for Nafion® and are independent of ZrP content, within the range studied.

For the samples prepared for this study, the changes in dimension upon hydration and dry membrane density data do not support the concept of ZrP forming an internal rigid scaffold, as has previously been presented. Since ZrP does not retain as much water as Nafion®, the increase in water content of the composite membranes cannot be due to the hydrophilicity of ZrP. Most likely, hygroscopic ZrP disrupts cohesive forces in Nafion®, causing it to take up more water, and thus resulting in the observed decreased dimensional stability upon swelling. A schematic illustration of ZrP in the Nafion® membrane is presented in Figure 4.13A using the ribbon-like structural model at different contents of ZrP. Initially, as ZrP enters the hydrophilic pores of Nafion® there is an increase in
water content due to a reduction in pore size and thus an increase in capillary condensation. As the ZrP grows in size, it disrupts the cohesive forces in the hydrophilic regions of Nafion®, resulting in increased water uptake (Figure 4.13B). When the ZrP content increases past ~20 wt%, the ZrP no longer fits inside the hydrophilic pores, and instead may exist in inter-bundle regions of a ribbon-like Nafion® structure, so it gives no benefit in terms of increased water content (Figure 4.13C). This assertion is supported by the TEM images (Figure 4.6), which shows that initially (up to ~20 wt%) ZrP particles fit into the hydrophilic pores, but when the ZrP content increases past ~20 wt%, ZrP are much bigger than the hydrophilic pores, but the original dimensions of the hydrophilic/hydrophobic phase separation still exists.

Although ZrP possesses titrateable protons, these protons do not appear to participate in proton conduction. These protons contribute to water uptake in the membrane, but much less than Nafion®. The increase in water content of the composite membranes does not contribute to the conductivity because poorly conducting ZrP disrupts the proton conducting pathway through the membranes. This also explains the lower mobility of the protons in the composite membranes.
4.3 Nafion® + Silicon Dioxide Membranes

4.3.1 Experimental

4.3.1.1 Materials

Nafion 115® was purchased from Alfa Aesar. Sulfuric acid (H₂SO₄) and sodium chloride (NaCl, 99%, reagent grade) were purchased from Alfa Aesar and used as received. Hydrogen peroxide (H₂O₂), TEOS, methanol, and sodium hydroxide (NaOH) were purchased from Sigma Aldrich and used as received. MilliQ water (Millipore) was used in washing and hydrating membranes and for making solutions.

4.3.1.2 Membrane Fabrication and Treatment

Nafion 115® was pretreated at 80 °C in 3 wt% hydrogen peroxide, water, sulfuric acid, and water, each for an hour. The procedure for preparing Nafion/SiO₂ membranes was based on that described by Deng et al. Dried Nafion® membranes were swollen in stirred solutions of 2:1 (v/v) methanol:water.
at room temperature for 16 h in covered glass jars. The methanol serves to swell the membranes, facilitating the permeation of water and, subsequently, TEOS, and acts as a good solvent for both these species. Swollen membranes were added to a solution of 14.5 g TEOS, 14.5 g methanol, and 5 mL water, and stirred for 2 - 10 minutes to obtain different SiO₂ contents. The membranes were dipped in methanol to stop the sol-gel reaction. The composite membranes were dried in a vacuum oven at 80 °C for 24 h. The membranes were rinsed with water and dried several times until the mass of the membrane remained constant.

The inorganic content (Wt%SiO₂) of the composite membranes was determined using the dry mass of the membrane before and after the reaction (M<sub>before</sub> and M<sub>after</sub>), as seen in equation 4.5.

\[
Wt\%_{SiO₂} = \frac{M_{after} - M_{before}}{M_{after}}
\]

4.3.1.3 Thermal Behaviour

Thermogravimetric analysis of the composite membranes were measured as described in Section 4.2.1.8.

4.3.1.4 Water Sorption Behaviour

Water content, water uptake, λ, and ρ were determined as described in Sections 2.2.8 and 4.2.1.4, using equations 2.7, 2.6, 2.8, 4.4, respectively.
4.3.1.5 Water Vapour Transmission

Water vapour transmission was measured as described in Section 3.2.5, using equations 3.4 and 3.5 to find the WVT and water vapour permeability, respectively.

4.3.1.6 Proton Conductivity

The proton conductivity of ionomer membranes was measured by EIS as described in Section 3.2.6, using equation 2.10.

4.3.1.7 Proton Concentration and Effective Proton Mobility

\([H^+]\) and \(\mu_{\text{eff, } H^+}\) were calculated as described in Sections 2.2.10 and 4.2.1.7, using equations 4.5 and 2.14, respectively.

4.3.1.8 Physical Characterization

Due to the high infrared absorbance of the films, composite membranes with \(\text{SiO}_2\) samples were studied by reflectance. These spectra were considered to be representative of the bulk sample. \(^{[18]}\) FTIR-ATR subtraction spectra (hybrid - dry sulfonic acid form) were obtained for Nafion 115\(^{®}\)/\(\text{SiO}_2\) using a KRS-5ATR plate. The solid-state \(^{29}\)Si NMR spectrum for the Nafion 115\(^{®}\)/\(\text{SiO}_2\) composite membrane was obtained on a Bruker Avance DSX 400 spectrometer using a Bruker 4mm MAS probe to acquire spectra. The sample spinning rate was 5 kHz. Spectra were acquired using high power decoupling during acquisition only. The spectral width was 484 ppm and a dwell time of 12.975 \(\mu\)s was used. 1280 scans were accumulated using a 4 \(\mu\)s pulse and 180 s delay between scans. Chemical shift scale was referenced using cubic octameric silicate (Q8M8) as an external...
standard (highest field peak set to -109.71 ppm). Peak deconvolution was performed using two mixed Gaussian/Lorentzian peaks at -101 and -112 ppm in DMFit. [35]

The mechanical strength of membranes was determined as described in Section 3.2.8.

Nafion/SiO$_2$ composite membranes were investigated using scanning electron microscopy (SEM) following coating the membranes with gold/palladium. A SEM-S-3500N from Hitachi with energy dispersive x-ray (EDX) was used to determine the concentration profile of SiO$_2$. The cross-sections of membranes were examined using EDX and mapped for silicon and fluorine content.

4.3.2 Results and Discussion

Composite membranes composed of Nafion 115$^\text{®}$ with varying quantities of silicon dioxide were fabricated. By controlling the reaction time, it is possible to control the amount of SiO$_2$ incorporated into the membrane. Using equation 4.15, it was calculated that 5.9 - 33.3 wt% SiO$_2$ was incorporated into Nafion 115$^\text{®}$. These results along with the thickness and dimensional changes with swelling of the membrane are shown in Table 4.4. After incorporation of SiO$_2$, the thickness of the membranes was seen to increase by up to 26%.
Table 4.4: Properties of Nafion®/SiO₂ composite membranes including inorganic content, dimensional stability, and thickness.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Inorganic Content&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Δl&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Δl&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Δl&lt;sup&gt;d&lt;/sup&gt; (%)</th>
<th>Thickness&lt;sup&gt;e&lt;/sup&gt; (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 115®</td>
<td>0</td>
<td>14 (2)</td>
<td>11 (2)</td>
<td>11 (2)</td>
<td>132 (0.9)</td>
</tr>
<tr>
<td>Nafion 115®/SiO₂</td>
<td>5.9 (0.4)</td>
<td>5.1 (1)</td>
<td>9.1 (2)</td>
<td>14 (2)</td>
<td>126 (2)</td>
</tr>
<tr>
<td></td>
<td>7.2 (0.5)</td>
<td>6.5 (0.6)</td>
<td>8.6 (0.9)</td>
<td>13 (1)</td>
<td>157 (7)</td>
</tr>
<tr>
<td></td>
<td>9.9 (0.9)</td>
<td>10 (0.9)</td>
<td>6.0 (0.5)</td>
<td>7.2 (2)</td>
<td>134 (1)</td>
</tr>
<tr>
<td></td>
<td>10.1 (0.6)</td>
<td>12 (3)</td>
<td>16 (1)</td>
<td>15 (0.7)</td>
<td>150 (2)</td>
</tr>
<tr>
<td></td>
<td>11.8 (0.1)</td>
<td>9.3 (3)</td>
<td>15 (1)</td>
<td>12 (0.3)</td>
<td>160 (2)</td>
</tr>
<tr>
<td></td>
<td>13.0 (0.1)</td>
<td>7.9 (0.4)</td>
<td>11 (0.5)</td>
<td>10 (0.5)</td>
<td>168 (7)</td>
</tr>
<tr>
<td></td>
<td>14.2 (0.1)</td>
<td>8.4 (0.4)</td>
<td>13 (0.7)</td>
<td>16 (1)</td>
<td>158 (1)</td>
</tr>
<tr>
<td></td>
<td>15.2 (0.1)</td>
<td>7.2 (0.7)</td>
<td>14 (2)</td>
<td>11 (0.8)</td>
<td>178 (2)</td>
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<td>16.0 (0.08)</td>
<td>8.9 (3)</td>
<td>13 (0.1)</td>
<td>20 (0.6)</td>
<td>142 (9)</td>
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<tr>
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<td>16.2 (0.2)</td>
<td>8.1 (0.9)</td>
<td>3.8 (1)</td>
<td>5.2 (1)</td>
<td>153 (1)</td>
</tr>
<tr>
<td></td>
<td>16.5 (0.09)</td>
<td>7.8 (0.8)</td>
<td>13 (1)</td>
<td>13 (2)</td>
<td>160 (5)</td>
</tr>
<tr>
<td></td>
<td>18.2 (0.6)</td>
<td>14 (2)</td>
<td>11 (2)</td>
<td>14 (2)</td>
<td>134 (5)</td>
</tr>
<tr>
<td></td>
<td>19.9 (0.2)</td>
<td>8.9 (0.6)</td>
<td>16 (0.3)</td>
<td>17 (3)</td>
<td>139 (0.2)</td>
</tr>
<tr>
<td></td>
<td>33.3 (0.1)</td>
<td>8.0 (3)</td>
<td>11 (0.5)</td>
<td>10 (0.9)</td>
<td>171 (4)</td>
</tr>
</tbody>
</table>

Errors (±) are in brackets after the value, <sup>a</sup>using Equation 1, <sup>b</sup>change in thickness of the membrane upon exposure to water, <sup>c</sup>change in length of the membrane upon exposure to water, <sup>d</sup>change in width of the membrane upon exposure to water, <sup>e</sup>thickness of the dry membrane

4.3.2.1 Physical Characterization

The structure of the SiO₂ from the sol-gel reaction in the Nafion® membrane was confirmed by FTIR-ATR and ²⁹Si-NMR spectroscopy. FTIR-ATR data for Nafion®/SiO₂ indicate that the sol-gel reaction proceeded as desired (Figure 4.14). The asymmetric stretching vibration of Si-O-Si groups between 1000 to 1100 cm⁻¹ is a signature of bridging oxygens and an indication of the extent of the in situ condensation reaction. [18, 37] This vibration often consists of two components corresponding to Si-O-Si groups in cyclic (~1180 cm⁻¹) and linear (~1050 cm⁻¹) configurations. The linear/cyclic component intensity ratio
measures the degree of molecular connectivity within the silicon oxide. For example, a large $A_{\text{cyclic}}/A_{\text{linear}}$ ratio reflects considerable silicon oxide cross-linking. It appears that there is a higher degree of cross-linking in the Nafion$^\circledR$ + 33 wt% SiO$_2$ and Nafion$^\circledR$ + 20 wt% SiO$_2$ membranes than in the Nafion$^\circledR$ + 10 wt% SiO$_2$ and Nafion$^\circledR$ + 5.9 wt% SiO$_2$ membranes. Also important is the absorbance associated with the Si-OH stretching vibration (~950 cm$^{-1}$), which is a measure of uncondensed SiOH groups. Unfortunately, the Si-OH stretch is often not useful in these systems as a diagnostic peak in which obscuring absorbances associated with OH groups in residual alcohol or water molecules are present.

Figure 4.14: FTIR-ATR spectra of Nafion$^\circledR$/SiO$_2$ composite membranes.

The structure of the SiO$_2$ in the membranes was also elucidated by $^{29}$Si NMR. A representative spectrum is shown in Figure 4.15. In a pure silicate, SiO$_2$
tetrahedra can exist in five states of coordination, each state designated by the symbol $Q^n$, $n$ being the degree of Si atom substitution. The approximate chemical shift ranges (ppm, relative to Si-(Me)$_4$) of these states are listed in Table 4.5[36]. The resonance at -101 ppm corresponds most closely to $(\text{SiO})_3\text{SiOH}$ and the -112 ppm peak to $(\text{SiO})_4\text{Si}$. The presence of only two peaks indicate that only two states are formed in the membrane, which indicates the near completion of the sol-gel reaction. The peak assigned to $Q3$ was 43.6% of the total intensity, and the remaining 56.4% of the intensity was in the $Q4$ peak.

Figure 4.15: $^{29}\text{Si}$ NMR of Nafion 115°/19.1 wt% SiO$_2$. 
Table 4.5: Chemical Shift (ppm) Ranges for Qⁿ Species

<table>
<thead>
<tr>
<th>Si substitution</th>
<th>Chemical Shift ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q⁰</td>
<td>-60 to -82</td>
</tr>
<tr>
<td>Q¹</td>
<td>-68 to -83</td>
</tr>
<tr>
<td>Q²</td>
<td>-74 to -93</td>
</tr>
<tr>
<td>Q³</td>
<td>-91 to -101</td>
</tr>
<tr>
<td>Q⁴</td>
<td>-106 to -120</td>
</tr>
</tbody>
</table>

The formation of SiO₂ in the membranes was also confirmed by SEM/EDX, shown in Figure 4.16. The backscattered electron image, and EDX dot mapping images, shown in Figure 4.17A - D, are cross-sections of Nafion 115⁰ (A) and Nafion 115⁰ + 10.0 - 33.3 wt% SiO₂ (B - D). These images show the entire thickness of the membrane. The EDX spectra allow determination of which elements are present in the membranes. For the membranes under study, it is expected that fluorine will be present in all the membranes, but silicon should only be present in the composite membranes. EDX spectra (Figure 3 iv) for each membrane indicate elemental peaks for elements carbon, oxygen, fluorine, and sulphur. A strong EDX signal for silicon is also observed for Nafion/SiO₂ composite membranes. EDX dot mapping illustrates the distribution of a chosen element across the image. EDX dot mapping was performed on each membrane for silicon and fluorine atoms (Figure 4.16A - D(ii and iii)). Pure Nafion 115⁰ membrane is silicon-free and the weak signal observed in Figure 4.17A(iii) is due to background noise. As expected, fluorine is observed in all the membranes (Figure 4.17A - D(ii)). Silicon appears to be homogeneously distributed...
throughout the cross-section of the composite membranes (Figures 4.17B - D(iii)).

Figure 4.16: SEM/EDX analysis of cross sections of Nafion 115®/SiO₂ composite membranes. A. Nafion 115®, B. Nafion 115®/10 wt% SiO₂, C. Nafion 115®/19 wt% SiO₂, D. Nafion 115®/33 wt% SiO₂: i. backscattered electron image, ii. EDX mapping of fluorine, iii. EDX mapping of silicon, iv. EDX spectra.
The Young's modulus of wet Nafion 115® is 200 MPa (Table 4.6) and for the composite membranes range from 143 to 186 MPa. The Young's modulus of wet Nafion 115®, and therefore the stiffness, is thus slightly decreased with the addition of SiO₂. Similarly, Mauritz et al. [6] also found that the Young's modulus of Nafion + 10 wt% SiO₂ was similar to that of unmodified Nafion.

Table 4.6: Mechanical strength data of Nafion 115®/SiO₂ composite membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 115®</td>
<td>200 (9)</td>
</tr>
<tr>
<td>Nafion 115®/5.9 wt% SiO₂</td>
<td>186 (13)</td>
</tr>
<tr>
<td>Nafion 115®/7.2 wt% SiO₂</td>
<td>181 (13)</td>
</tr>
<tr>
<td>Nafion 115®/9.9 wt% SiO₂</td>
<td>169 (23)</td>
</tr>
<tr>
<td>Nafion 115®/16.5 wt% SiO₂</td>
<td>143 (15)</td>
</tr>
<tr>
<td>Nafion 115®/33.3 wt% SiO₂</td>
<td>153 (32)</td>
</tr>
</tbody>
</table>

Error (±) is shown in brackets after the value

4.3.2.2 Thermal Behaviour

The TGA curves for the Nafion 115®/SiO₂ membranes are plotted in Figures 4.17. A three-step degradation profile is observed for the polymers using
TGA. The first significant weight loss (below 200 °C) is due to loss of water. Desulfonation of the polymers begins at ~300 °C. A third weight loss that starts between 400 and 500 °C is attributed to degradation of the polymer backbone. The addition of SiO₂ to Nafion 115® does not significantly affect the thermal degradation of the membranes. Mauritz et al. [8] also observed three significant mass loss steps in the TGA degradation profile of Nafion®/SiO₂ membranes.

Figure 4.17: TGA profiles of Nafion 115® and Nafion 115®/SiO₂ composite membranes

4.3.2.3 Water Sorption Behaviour

The percentage change in dimensions of the membranes upon exposure to water are shown in Table 4.4. The percentage change in thickness of unmodified Nafion 115® is 14 ± 2%, while that of the composite membranes ranges from 2.7 ± 1 to 10 ± 0.9%. The change in length and width of unmodified Nafion 115® is 11 ± 2%, while that of the Nafion 115®/SiO₂ membranes ranges from 3.8 ± 1 to 17 ± 3%. In most cases, the change in dimensions with swelling of the Nafion®/SiO₂ membranes is smaller than that of unmodified Nafion 115®. This supports Yang's assertion that inorganic nanoparticles form a rigid scaffold
inside the membrane. This scaffolding prevents the membrane from contracting upon dehydration, resulting in smaller dimensional changes with swelling of these membranes. This result can also be correlated well with the observation by Mauritz et al. that Nafion®/SiO₂ membranes have a ductile to brittle transition as the SiO₂ content increases. Because SiO₂ is a network structure, the SiO₂ can grow and percolate through the hydrophilic regions of Nafion, forming a rigid scaffolding and increasing the brittleness of the Nafion membrane.

The effect of the SiO₂ on the water content and number of water molecules per sulfonated group, λ, of the hydrated membranes is shown in Figure 4.18. The water content of wet Nafion 115® at room temperature (Figure 4.18A) is 23 ± 1 wt%, and the water content for Nafion 115®/SiO₂ composite membranes varies between 25 ± 0.5 to 33 ± 3 wt%. The water content of Nafion 115® at 80 °C and 40% relative humidity (Figure 4.18B) is 1.3 ± 0.1 wt%, but for the composite membranes ranges from 2.0 ± 0.1 to 4.2 ± 0.2 wt%, i.e. higher than that of unmodified Nafion®. The λ value of wet Nafion 115® at room temperature (Figure 4.18C) is 19 ± 1 and for the Nafion 115®/SiO₂ composite membranes, the λ value ranges from 19 ± 1 to 33 ± 2. The λ value of Nafion 115® at 80 °C and 40% relative humidity (Figure 4.18D) is 0.82 ± 0.06, but for the composite membranes ranges from 1.3 ± 0.1 to 3.4 ± 0.7. Commensurate with the higher water content, λ for the hydrated composite membranes is generally higher than that of unmodified Nafion 115® and increases with increasing inorganic content. These results are consistent with results found in literature.
Figure 4.18: Water sorption properties of Nafion 115®/SiO₂ composite membranes in different temperature and relative humidity conditions. A) Water content (wet, room temperature), B) Water content (80 °C, 40% RH), C) λ (wet, room temperature), D) λ (80 °C, 40% RH).

The dry density of Nafion 115®/SiO₂ composite membranes, shown in Figure 4.19, range from 1.9 ± 0.1 to 1.5 ± 0.1 g cm⁻³. The density of Nafion® is 2.0 ± 0.1 g cm⁻³ and the structural density of silicon dioxide is ~2 g cm⁻³. The fact that the density of the composite membranes decreases with increasing inorganic component indicates that void space is being created. This also
supports the contention that SiO₂ forms a rigid, internal scaffolding inside the membrane, which prevents the membrane from contracting upon dehydration [10].

Figure 4.19: Density of dry Nafion 115°/SiO₂ composite membrane.

4.3.2.4 Proton Conductivity

The results from proton conductivity measurements are shown in Table 4.7 and Figure 4.20. The proton conductivity of wet Nafion 115° at room temperature (Figure 4.20A) is 0.076 ± 0.007 S cm⁻¹, while the proton conductivity values for the composite membranes range from 0.034 ± 0.002 to 0.064 ± 0.0005 S cm⁻¹, and generally decrease with increasing inorganic content. The proton conductivity of Nafion 115° at 80 °C and 40% RH (Figure 4.20B) is 0.0078 ± 0.002 S cm⁻¹, and for the composite membranes it ranges from 0.0029 ± 0.0003 to 0.0064 ± 0.0004 S cm⁻¹. The proton conductivity of Nafion 115° at 120 °C, 40% RH is 0.0021 ± 0.0008 S cm⁻¹, while for the composite membranes it ranges from 0.00097 ± 0.0001 to 0.0015 ± 0.0002 S cm⁻¹. Thus the proton conductivity of the composite membranes is found to be lower than that of Nafion 115° for all temperature and humidity conditions studied; furthermore, it decreases with
increasing inorganic content, despite having higher water content and λ values in these conditions. These results are in agreement with results determined by Savinell et al. [26] and Kim et al. [19], whom evaluated membranes with SiO$_2$ contents ranging from 0 - 21 wt.%.

**Figure 4.20:** Proton conductivity of Nafion 115®/SiO$_2$ composite membranes A) Wet, room temperature, B) 40% RH, 80 °C.
Table 4.7: Conductivity of Nafion 115®/SiO₂ composite membranes in different temperature and relative humidity conditions.

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Conductivity / S cm⁻¹</th>
<th>Wet, RT</th>
<th>80 °C, 40% RH</th>
<th>120 °C, 45% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 115®</td>
<td>0.074 (0.007)</td>
<td>0.0078 (0.002)</td>
<td>0.0021 (0.0008)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/5.9 wt% SiO₂</td>
<td>0.064 (0.0005)</td>
<td>0.0043 (0.0003)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/7.2 wt% SiO₂</td>
<td>0.058 (0.004)</td>
<td>0.0064 (0.0004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/9.9 wt% SiO₂</td>
<td>0.063 (0.0005)</td>
<td>0.0062 (0.00005)</td>
<td>0.0010 (0.0002)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/10.1 wt% SiO₂</td>
<td>0.040 (0.002)</td>
<td>0.0030 (0.0004)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/11.8 wt% SiO₂</td>
<td>0.051 (0.002)</td>
<td>0.0058 (0.001)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/13.0 wt% SiO₂</td>
<td>0.046 (0.002)</td>
<td>0.0052 (0.0007)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/14.2 wt% SiO₂</td>
<td>0.046 (0.002)</td>
<td>0.0028 (0.0002)</td>
<td>0.00097 (0.0001)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/15.2 wt% SiO₂</td>
<td>0.034 (0.002)</td>
<td>0.0063 (0.0007)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/16.0 wt% SiO₂</td>
<td>0.036 (0.006)</td>
<td>0.0074 (0.00008)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/16.2 wt% SiO₂</td>
<td>0.045 (0.0008)</td>
<td>0.0038 (0.001)</td>
<td>0.0015 (0.0002)</td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/16.5 wt% SiO₂</td>
<td>0.044 (0.002)</td>
<td>0.0042 (0.0002)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/19.9 wt% SiO₂</td>
<td>0.042 (0.0002)</td>
<td>0.0041 (0.0008)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 115®/33.3 wt% SiO₂</td>
<td>0.036 (0.003)</td>
<td>0.0029 (0.0003)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Error (±) shown in brackets after the value

4.3.2.5 Proton Concentration and Effective Proton Mobility

Proton conductivity depends on the proton concentration and the effective proton mobility in the membrane. Figure 4.21 shows plots of calculated proton concentration (Figure 4.21A) and effective proton mobility (Figure 4.21B and C) as a function of inorganic content. The proton concentrations of the wet membranes at room temperature are lower than the proton concentrations of the membranes at 80 °C and 40% relative humidity, as shown in Figure 4.21A,
because the composite membranes in room temperature and wet conditions take in more water for the same amount of acid present and hence dilution of the protons. The analytical proton concentration of wet Nafion 115® at room temperature is $1.3 \pm 0.1$ M, and for the composite membranes range from $0.62 \pm 0.2$ to $1.0 \pm 0.1$ M. The proton concentration of Nafion 115® at $80 \ ^\circ C$ and 40% relative humidity is $1.8 \pm 0.1$ M. The proton concentrations of Nafion 115®/SiO$_2$ composite membranes at $80 \ ^\circ C$ and 40% relative humidity range from $0.85 \pm 0.2$ to $1.6 \pm 0.1$ M. As the inorganic contents of the Nafion 115® membranes increase from 0 to 33.3 wt%, the proton concentration decreases. The decrease in proton concentration with increasing inorganic content is a result of the increased water content in these membranes diluting the protons and contributes to the decrease in proton conductivity with increasing SiO$_2$ content.

Figure 4.21: Proton concentration (A) and effective proton mobility (B, C) in wet, room temperature (A, B) and 40% RH, $80 \ ^\circ C$ (A, C) conditions.
The effective proton mobilities of the wet membranes at room temperature (Figure 4.21A), calculated using equation 4.24 are about ten times higher than the effective proton mobilities of the membranes at 40% RH and 80 °C (Figure 4.21B). The effective proton mobility of wet Nafion 115 at room temperature is $6.9 \times 10^{-4} \pm 0.1 \times 10^{-4}$ cm V$^{-1}$ s$^{-1}$. The effective proton mobility values of wet Nafion 115/SiO$_2$ composite membranes at room temperature range from $4.1 \times 10^{-4} \pm 0.1 \times 10^{-4}$ to $6.8 \times 10^{-4} \pm 0.7 \times 10^{-4}$ cm V$^{-1}$ s$^{-1}$. The effective proton mobility of Nafion 115 at 80 °C and 40% relative humidity is $6.5 \times 10^{-5} \pm 0.1 \times 10^{-5}$ cm V$^{-1}$ s$^{-1}$. The effective proton mobilities of Nafion 115/SiO$_2$ composite membranes at 80 °C and 40% relative humidity range from $2.8 \times 10^{-5} \pm 0.1 \times 10^{-5}$ to $6.0 \times 10^{-5} \pm 0.1 \times 10^{-5}$ cm V$^{-1}$ s$^{-1}$. The effective proton mobilities of saturated Nafion 115/SiO$_2$ composite membranes are less than that of unmodified Nafion and generally decrease with increasing inorganic content. The decrease in effective proton mobilities with increasing SiO$_2$ content is likely a result of increased tortuosity of the proton-conducting pathway caused by the incorporated SiO$_2$ nanoparticles.
and is a contributing factor in the observed decreasing conductivity with increasing inorganic content.

4.3.2.6 Water Vapour Transmission

Figure 4.24 shows the water vapour permeance of the Nafion 115®/SiO₂ composite membranes as a function of inorganic content. The water vapour permeance of Nafion 115® is 0.056 ± 0.005 g Pa⁻¹ m⁻² h⁻¹, and for composite membranes ranges from 0.052 ± 0.002 to 0.072 ± 0.004 g Pa⁻¹ m⁻² h⁻¹. It appears that inorganic content has little effect on water vapour transport. This indicates that the SiO₂ nanoparticles do not increase the tortuosity of the water vapour pathway through the membrane. This is a surprising result given that proton conduction and mobility are reduced by the addition of SiO₂. It may speak to the observation that the membrane is generally expanded upon incorporation of SiO₂ and although the proton conductive pathways are restricted because they necessitate a continuous pathway of polyelectrolyte, water may transport through water-filled voids created in the membrane.

Figure 4.23: Water vapour permeance of Nafion 115®/SiO₂ composite membranes.
4.3.3 Summary and Conclusions

Based on the observations that the density of the membranes decreased with increasing SiO₂ content and the dimensional changes with swelling of the composite membranes were less than that of unmodified Nafion 115®, it supports the assumption that a rigid SiO₂ scaffolding is formed inside the membrane. As a consequence, water contents increase with increasing SiO₂ content. This additional water content dilutes the protons in the membrane leading to lower proton concentration and contributes to lower proton conductivity. Furthermore, a decrease in effective proton mobility with increasing SiO₂ content is also observed, and appears due to constriction in the proton-conducting pathway. However, in contrast, water vapour permeance studies indicate that the water vapour transmission pathways are not constricted.

4.4 References


CHAPTER 5: SUMMARY AND FUTURE WORK

Structure-property relationships of several classes of PEMs were studied through the synthesis, fabrication, and characterization of PEMs with careful control of structural parameters.

5.1 Sulfonated Polyimides

In Chapter 2, a comparison of linear and angled sulfonated polyimides revealed that the membranes formed from the angled polymers exhibit lower water uptake, higher proton concentration, and higher conductivity than the membranes prepared from the linear polymers. These differences have been attributed to increased entanglements of the non-linear polymers. Due to their hydrolytic instability, the sulfonated polyimides studied in this work are not a practical alternative fuel cell membrane. However, the structure-property relationships discovered may be relevant to other sulfonated aromatic polymer systems and should be considered when designing alternative polymer systems for proton exchange membranes. When synthesizing polymers for alternative membrane systems, using a twisted backbone structure is advantageous because it leads to higher proton conductivity and lower water uptake in the membrane.
5.2 Reinforced Membranes

Chapter 3 revealed that the employment of reinforcing materials in PEMs deleteriously affects properties such as proton conductivity, effective proton mobility, and water vapour permeability due to decreased ionomer content in the membrane and less connectivity of the ionomer. However, the membranes are stronger and can be prepared thinner, which can compensate for these losses. Thin membranes have advantages such as lower areal resistance, lower dimensional changes with swelling, and higher water vapour permeance. To fully take advantage of reinforced membranes, there is benefit to use reinforcing materials that are thin and possess large pores.

With reinforced membranes, it is important to study through-plane conductivity as well as in-plane conductivity because of the unavoidable anisotropy of these membranes caused by the fabrication technique. Through-plane conductivity of membranes is more relevant for fuel cell investigations because in a fuel cell the protons actually conduct through the plane. Because of the anisotropy in these membranes, it is not possible to determine ex situ whether they would perform well in a fuel cell without knowledge of the through-plane conductivity.

Another area that should be explored with reinforced membranes is the hydraulic and liquid water permeability to determine whether there is a benefit in terms of water balance to using thin, reinforced membranes. Understanding the permeability of water through these membranes is key in evaluating the advantages of using these membranes in fuel cells.
Obviously, there are some advantages to using reinforced membranes. However, for these membranes to be viable alternatives PEMs, it is important to optimize the ionomer, the reinforcing material, and the fabrication procedure to achieve the best possible reinforced membranes. In this work, by examining the properties of the ionomer in the membrane, it was discovered that some detrimental properties result due to a lack of connectivity of the ionomer in the membrane. By altering the fabrication method and the reinforcing materials, it is possible to increase the connectivity of the ionomer in the membrane and therefore improve the membrane properties. Because reinforcement materials provide membrane strength and dimensional stability, it should be possible to fabricate reinforced membranes using ionomers with higher IEC. This should lead to higher proton conductivity, lower areal resistance, and higher water vapour permeance.

5.3 Composite Membranes

TEM, water content, and proton mobility data for composite Nafion®/ZrP membranes in Chapter 4 support the theory that hygroscopic ZrP disrupts cohesive forces in Nafion®, causing it take up more water, thus resulting in the observed decreased dimensional stability upon swelling. As the ZrP content increases past ~ 20 wt%, the ZrP begins to fill the hydrophilic pores, so it gives no benefit in terms of increased water content. The increase in water content of the composite membranes does not contribute to the conductivity because there is a concurrent decrease in proton concentration and effective proton mobility due to poorly conducting ZrP disrupting the proton-conducting pathway through
the membranes and the increased water content diluting the protons and separating proton conducting sites.

Based on the observations that the density of the Nafion®/SiO<sub>2</sub> membranes in Chapter 4 decreases with increasing SiO<sub>2</sub> content and the dimensional changes with swelling of the composite membranes were less than that of unmodified Nafion 115®, it is believed that a rigid SiO<sub>2</sub> scaffolding is formed inside the membrane. As a consequence, water contents increase with increasing SiO<sub>2</sub> content. This additional water content dilutes the protons in the membrane leading to lower proton concentration and contributes to lower proton conductivity. Furthermore, a decrease in effective proton mobility with increasing SiO<sub>2</sub> content is also observed, and appears due to constriction in the proton conducting pathway as well as separation of proton conduction sites.

There would be benefit to additional understanding of the state of water in the Nafion®/ZrP and Nafion®/SiO<sub>2</sub> composite membranes over a range of inorganic contents through low temperature DSC and pulsed-field gradient NMR investigations and, in the future, this area should be explored further. Through low temperature DSC it is possible to determine the amount of tightly bound, loosely bound, and free water in the membrane. [1] The nature of water, as indicated by thermal transitions, can be directly connected to the resulting properties of the membrane. More loosely bound and free water induces higher conductivity, while more tightly bound water leads to lower conductivity. Pulsed-field gradient NMR can be used to measure the water diffusion coefficients in PEMs. [2] This measurement helps understand the overall behaviour of water.
over all its states within the membrane. This further understanding of the behaviour of water in the composite membranes would help paint a clearer picture of how the incorporation of the inorganic nanoparticles alters the membrane properties. Although neither of these composite membrane systems displayed any advantageous \textit{ex situ} behaviour (lower conductivity and higher water content are the opposite of what is desired), research shows that they did display superior behaviour in fuel cells at high temperatures.\cite{3-8} This means that to gain a complete understanding of the affect of incorporating inorganic nanoparticles, it is necessary to study them at high temperatures.

The fact that the \textit{ex situ} properties of the composite membranes were inferior to unmodified Nafion\textsuperscript{®} means that they do not appear to be realistic alternative fuel cell membranes. However, it is interesting to understand how these membranes are affected by the incorporation of the inorganic groups. Since the behaviour of the inorganic nanoparticles in these two systems is clearly not equivalent, the systematic procedure used in this work should also be used in studying other composite membrane systems that show more promising \textit{ex situ} behaviour, such as Nafion\textsuperscript{®}/HPA systems.\cite{9}

\textbf{5.4 Conclusion}

The knowledge about structure-property relationships gained from this thesis may aid in the development of PEMs that better suit the current requirements of low humidity, high temperature operating conditions. Information can be gleaned from each chapter that can aid in the design of an alternative membrane system. From chapter 2 it is shown that it is desirable to use angled
backbones in polymer synthesis. Chapter 3 indicates that using thin reinforcing materials with large pores are desirable. The use of reinforcing materials would also permit the use of membranes with higher IEC, which would lead to increased proton conductivity without excessive water content. Although incorporation of inorganic nanoparticles in chapter 4 did not result in any advantages for use in fuel cells, it is possible that these advantages could be seen at higher temperatures, or though the use of other inorganic groups, such as acidic nanoparticles.

5.5 References