TRANSPORT AND SURFACE PROPERTIES
OF ION-CONTAINING POLYMER MEMBRANES

A Dissertation in
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by
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ABSTRACT

Ion-containing polymer membranes have wide applications in desalination, electrochemical devices, and other technologies that require semipermeable membranes with specific transport selectivity properties. Therefore, a great deal of research has focused on the transport of ions and water in these materials and the correlation of these properties with polymer backbone chemical structure, the type of tethered ionic group to the polymer backbone, and polymer membrane morphology. The way that water is bound within the polymer membrane also attracts great interest because species like protons, methanol, and salt ions transport through the hydrophilic domain of the phase separated polymer membrane and thus are affected by the water dynamics. In addition to the bulk properties of these materials, surface properties are also important for practical applications and have been the focus of significant efforts in new membranes. Surface fouling presents severe problems in the applications of ionic polymer membranes, especially in water treatment. New tools to control fouling and understanding the fundamental interactions in these materials that contribute to fouling are important to improve material antifouling performance and guide future material design. It is the goal of this dissertation to investigate the water binding in ion-containing polymer membranes and make correlations to their transport properties, as well as study the use of layer-by-layer assembly as a surface antifouling modification for desalination membranes.

The uptake and dynamics of water in polymer membranes have been found to influence their transport properties. Using Fourier transform infrared spectroscopy (FTIR), the water-polymer interactions in sulfonated and aminated poly(phenylsulfone) membranes were investigated and compared. The OD stretch region in D_2O-doped water absorbed in the polymer membrane gives information on the water-water hydrogen bonding dynamics and the interaction of water with the ionic functional groups. The fingerprint region spectra representing water-
polymer backbone interactions were analyzed as well. It was found that anion exchange membranes with tethered quaternary ammonium functional groups exhibited more free water content and less water-polymer interactions than cation exchange membranes with tethered sulfonate groups. Measures of membrane water flux and rejection were correlated to these observations and it was found that membranes with quaternary ammonium functional groups displayed faster water and salt transport due to their greater free water content.

Highly selective proton conductive networks were prepared based on crosslinking of chain-end functionalized polymers with perfluorosulfonate side groups. A study was carried out regarding the water binding in these crosslinked membranes and the water binding results were tied to their superior electrochemical selectivity. It was found that for these membranes the content of bound water increased with increasing relative humidity or increasing IEC. The lack of bulk-like water explained their low methanol permeability and the presence of bound water still facilitated proton conductivity due to these polymers’ high water uptake.

Polystyrene-based homopolymers and block copolymers with quaternary ammonium or imidazolium functional groups were investigated to elucidate the influence of membrane morphology as well as ionic groups on water binding. Based on observations of the OD stretch vibration of water absorbed in the polymer membranes, it was found that homopolymers displayed more bulk-like water than copolymers due to their higher degree of functionalization. From the OD stretch peak, water interacted more strongly with the imidazolium group than with the quaternary ammonium group and imidazolium functionalized polymers exhibited higher bound water content than quaternary ammonium functionalized polymers.

Membrane surface charge has a significant influence on membrane retention and fouling performance. As a key parameter describing the surface charge properties of membranes used in aqueous applications, zeta potential measurements on membranes of various types have been used as a standard evaluation method to assess the possible fouling of the material’s surface. In
electrokinetic streaming measurements, it was found that the measured streaming current unexpectedly varied with the thickness of the sample and decreased with increasing ion exchange capacity of ion-conductive sulfonated poly(phenylsulfone) membranes. It was determined that membrane bulk conductance influenced the streaming current in the microfluidic channel and produced unanticipated results given the materials’ composition. Extrapolating the measured streaming current to a membrane thickness of zero has proven to be a feasible method for eliminating the error and obtaining correct surface charge information for ion conductive polymer membranes. A linear resistance model relating measured streaming current to membrane bulk conductance is proposed based on the hypothesis that ion conductive membranes reduced the observed streaming current by allowing ions to flow back through the membrane bulk.

To better control the surface properties and improve the antifouling performance of polymer surfaces, layer by layer (LBL) assembly of anionic and cationic PEO-based polyurethanes were used to modify surfaces. Surface charge and dynamic protein and polysaccharide adsorption behaviors were measured and correlated to the chemical composition of the assemblies. The PEO-based polyurethanes LBL helped reduce protein fouling on sulfonated and aminated poly(phenylsulfone) membrane surfaces due to the hydrophilicity of PEO. After salt annealing, intermixing between LBL assembly layers was promoted. Salt ions were absorbed into the assembly and increased the hydration of the layers by breaking some of the electrostatic crosslinks between anionic and cationic PEO-poly(urethane)s. By comparing the surface charge as well as protein and polysaccharide adsorption behavior of the LBL assembly surfaces before and after salt annealing, it was discovered that bovine serum albumin adsorption was governed by surface charge while sodium alginate adsorption was influenced by electrostatic interaction with the surface besides surface distribution of charged groups.
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Chapter 1

Transport and Surface Properties of Ion-Containing Polymer Membranes

1.1 Transport properties and water binding in ion-containing polymer membranes

For polymer electrolyte membranes employed in fuel cells or other electrochemical technologies such as flow batteries, transport properties such as proton conductivity, water permeability and methanol permeability play critical roles in the performance of the device. In membrane-facilitated desalination, water and salt permeability are also key features of the polymer membrane. The water content and its dynamic motion in an ion-containing, hydrophilic polymer matrix are affected by attached ion type, polymer chemical properties and morphology of the polymer membrane. Relative humidity and temperature affect the absorbed water in the membrane and have been found to have significant influence on transport properties of the membrane.\textsuperscript{1–4} Techniques such as differential scanning calorimetry (DSC),\textsuperscript{5,6} pulsed field gradient nuclear magnetic resonance (PFG-NMR),\textsuperscript{7,8} Fourier transform infrared spectroscopy (FTIR)\textsuperscript{9–11} and positron annihilation lifetime spectroscopy (PALS)\textsuperscript{12,13} have all been employed to characterize how water is bound within the polymer membrane and how the water behavior is correlated to the properties of the hydrated membrane.

In this work the water-polymer interactions in quaternary ammonium functionalized poly(phenylsulfone) anion exchange membranes (AEM) and sulfonated poly(phenylsulfone) cation exchange membranes (CEM), Figure 1-1, were investigated using FTIR and direct connections between the water-polymer associations and the water permeability and salt rejection of the ion-containing polymers were made. In AEMs, the OD stretch of HOD-doped H$_2$O absorbed in the membrane from 2515 to 2509 cm$^{-1}$ showed that water had weak interactions with
the quaternary ammonium groups. The OD stretch for CEMs occurred between the wavenumber 2553 to 2549 cm$^{-1}$, indicating that water was more strongly associated to the sulfonate groups in CEMs than in AEMs. AEMs displayed higher water flux and lower salt rejection than CEMs, which correlated to the FTIR data from the main OD stretch region. Shifts in the diaryl sulfone backbone vibrations at 1152 cm$^{-1}$ with increasing hydration of the AEM demonstrated that water-polymer backbone interactions increased with hydration, which was not observed for CEMs. This difference in water-polymer backbone interactions may be due to the different morphologies of each type of membrane.

![Repeat unit](image)

**Figure 1-1.** Repeat unit of the poly(phenylsulfone)-based CEMs and AEMs where R is either sulfonic acid, trimethylbenzyl quaternary ammonium hydroxide functional groups or H.

Amino terminated copolymer of vinylidene fluoride (VDF) and perfluoro(4-methyl-3,6-dioxane-7-ene) sulfonyl fluoride (PFSVE) underwent chain-end crosslinking. The resulting crosslinked fluoropolymers network was developed for direct methanol fuel cell and displayed superior electrochemical selectivity and reasonably high proton conductivity compared to Nafion$^{14,15}$ Employing FTIR, investigation about the water-binding in the membranes has found that water-polymer interactions were much stronger in the P(VDF-PFSVE) crosslinked network
and it contained a smaller portion of bulk like water than Nafion®. The greatly reduced methanol permeability could be attributed to the lack of bulk-like water while the large portion of bound water could still take part in proton transport thus maintaining high proton conductivity.

To study the influence of membrane phase separation and different ionic functional groups on water binding, FTIR was employed to characterize polystyrene-based homopolymers and copolymers with quaternary ammonium or imidazolium groups. It was found that homopolymers displayed a higher fraction of bulk-like water than copolymers due to their higher degree of functionalization and no hydrophobic regions. Water interacted more strongly with imidazolium groups than with quaternary ammonium groups as evidenced by the OD stretch vibration frequency which contributes to the fact that imidazolium functionalized polymers exhibited higher content of bound water than quaternary ammonium functionalized polymers.

1.2 Surface charge of ion-containing polymer membranes and antifouling surface modification using layer-by-layer assembly

Fouling, the adsorption and accumulation of contaminants such as colloidal particles and dissolved organics at a surface, is a problematic issue in membrane facilitated desalination, marine applications and medical applications. Specifically for filtration membranes, fouling decreases efficiency and increases operation cost by causing the membrane to have lower hydraulic permeability due to the fouling layer.\textsuperscript{16,17} To conquer fouling problems, the mechanisms of fouling need to be better understood and new methodologies need to be developed to improve the surface antifouling properties of polymers.

Fouling processes are strongly influenced by the surface charge properties of the membrane and the type of foulant in the surrounding environment. Zeta potential, which provides useful information about the surface charge properties of the membrane in solution, is an
important parameter in fouling studies.\textsuperscript{18,19} Streaming potential or streaming current measurements, the most suitable method for measuring flat membrane surface zeta potential, is traditionally only applicable to nonconductive membranes.\textsuperscript{20} Using sulfonated poly(phenylsulfone) as a model membrane system, detailed analysis of the measured streaming current in a microfluidic channel with sulfonated membrane walls and subsequent calculation of zeta potential for materials with different ion contents were carried out. It was found that the measured streaming current varied with the thickness of the sample, which was not predicted by the classical Smoluchowski equation. Moreover, for higher conductivity membranes with an increased concentration of sulfonate groups, the zeta potential tended towards zero. It was determined that the influence of membrane bulk conductance on the measured streaming current must be taken into account in order to correctly interpret the streaming current data for ion-conductive polymers. Extrapolating the measured streaming current to a membrane thickness of zero has proven to be a feasible method of eliminating the error associated with measuring the zeta potential of ion-conductive polymer membranes. A linear resistance model was proposed to account for the observed streaming currents where the electrolyte channel is in parallel with the ion-conductive membranes, Figure 1-2.
In order to improve the surface antifouling properties of solid surfaces and membranes, layer-by-layer (LBL) modification was employed to effectively incorporate hydrophilic PEO onto a surface using the electrostatic attraction of ionic PEO-based poly(urethane)s, Figure 1-3. Sequential addition of layers was shown to cease after 6 layers (3 bilayers) due to a decrease in surface overcharging caused by interlayer mixing of the polymer chain, which was confirmed by zeta potential measurements. Bovine serum albumin (BSA) adsorption were shown to reduce on the LBL assembly surface compared to ionic poly(phenylsulfone) surfaces.

Figure 1-3. Chemical structure of quaternary ammonium functionalized PEO-based poly(urethane) (QA-PEO) (left) and sulfonated PEO-based poly(urethane) (Sulf-PEO) (right).
Salt annealing was found to promote the mixing between layers, leading to a more neutrally charged surface and higher hydration level of the LBL assembly. These effects had a minor influence on the fouling properties of the surface and the amount of protein adsorbed seemed correlated directly to the zeta potential. Sodium alginate adsorption was influenced by electrostatic interaction with the surface as characterized by the zeta potential as well as the possible surface distribution of charged groups.

The goal of this thesis is to demonstrate some key concepts and insights that motivate the use of ion-containing polymers in membrane transport applications. Both bulk transport properties and surface properties are addressed with the objective of tying to gather key themes of hydration state and transport properties in these types of materials. Chapter 2 reviews the state-of-the-art literature in the fields addressed in this work, and Chapters 3-7 contain the bulk of the technical data and scientific insights. The thesis is closed with concluding remarks and future work in Chapter 8. Detailed spectra deconvolution information and some preliminary studies on finite element modeling of streaming channels are given in the appendices.
Chapter 2

Literature Review

2.1 Introduction

Ionic polymer membranes have wide applications in batteries, fuel cells as well as membrane-facilitated desalination and water treatment. The transport properties of ions and small molecules are the key features of these types of materials and determine a membrane’s success in a given application. Water binding in ionic polymer membranes has been shown to affect membrane transport properties such as methanol permeability and proton conductivity. In this section, previous work on water dynamics and membrane transport properties will be reviewed as well as different techniques employed for characterizing water absorbed in polymer membranes.

Membrane-facilitated desalination, especially reverse osmosis, is the most widespread process for producing fresh water from seawater or brackish water. As fresh water resources grow increasingly scarce, reverse osmosis has become more and more important for producing water for human consumption. In this section, the theory of reverse osmosis and important properties of desalination membranes will be introduced. Additionally, materials currently employed in reverse osmosis will be discussed and their shortcomings evaluated. New materials to overcome these disadvantages have been studied such as sulfonated polysulfone, which will be the focus of our research on water binding and membrane desalination properties.

The surface charge of polymer membranes has a significant influence on fouling, which is a severe problem for membrane desalination. Streaming current methods for characterizing surface zeta potential of free-standing membranes will be described in detail as well as the derivation of zeta potential from streaming current and streaming potential. Since the streaming
current method was developed for nonconductive materials, complications have arisen when it was applied to porous materials or conductive materials. Methods for correcting the influence of membrane surface conductance and bulk conductance during streaming current measurement will be discussed.

Layer-by-layer assembly has been proposed as an effective surface modification technique. To evaluate LBL assembly’s potential to improve membrane antifouling properties during desalination process, current antifouling strategies and antifouling materials will be reviewed. Furthermore, salt annealing treatment and its effect on LBL will be briefly discussed at the end of this literature review.

2.2 Water binding in polymer membranes and correlation to transport properties

2.2.1 Proton conducting polymer membranes for hydrogen and methanol fuel cells

Grove demonstrated the conversion of chemical energy into electrical energy over 170 years ago using a hydrogen battery he called a voltaic battery. Fuel cells that use hydrogen to produce electricity have promoted a very attractive concept of the “hydrogen economy”. Hydrogen as an energy carrier is promising because its combustion is environmental friendly and does not release pollutants or carbon dioxide. Hydrogen also has a high energy density (658 kcal L\(^{-1}\)) and engines running on hydrogen have reached an efficiency of 42%. On the other hand, direct methanol fuel cells (DMFC) have been brought into focus because methanol is a liquid at room temperature and has even higher energy density than liquid hydrogen (3800 kcal L\(^{-1}\)). Besides, methanol does not require fuel processing. DMFCs are ideal power sources for portable and mobile applications because their energy density is greater than Li-ion batteries.
Figure 2-1 displays the diagram for a proton exchange membrane fuel cell. The solid polymer proton exchange membrane (PEM) is employed to separate the fuel from the oxidant. The early PEM materials, such as sulfonated polystyrene-divinylbenzene copolymer, were expensive and suffered oxidative degradation. The introduction of Nafion® (Figure 2-2), a perfluorosulfonic polymer, by DuPont has greatly improved the performance of fuel cells and commercial applications possible.
However, Nafion® still has some disadvantages such as high cost of production, low conductivity at low water content, and low mechanical strength at higher temperatures. Additionally, the development of DMFC requires PEMs that have low methanol permeability and Nafion® suffers from high methanol permeation. In DMFCs, methanol crossover from the anode to the cathode can hamper oxygen reduction by occupying a part of the active catalyst sites and reduce cell voltage by direct reaction between methanol and oxygen, which generates a mixed potential. Additional water are being generated through the reaction and that requires an expensive water management system.

The search for a high performance PEM is ongoing. Ideal PEM materials require high proton conductivity, low swelling, low gas and methanol permeability as well as stability. Research is still being conducted to understand the transport phenomena through PEMs and new ways are being explored to improve PEM transport properties.

Proton conduction occurs through two mechanisms: the vehicle mechanism involves the migration of hydrated protons that move in concert with water, and the Grotthuss “hopping” mechanism is where the protons diffuse through the hydrogen bonding network by hopping between adjacent water molecules. Proton transport, both by the vehicle mechanism and the Grotthuss mechanism, is greatly influenced by the water motion and hydrogen bonding dynamics.
inside the membrane. The transport of methanol and other small-molecule permeation through the PEMs are also affected by the motion of water inside the membrane. Thus our research interest is the study of water binding inside the polymer membranes and its correlation to membrane transport properties.

2.2.2 The correlation between water binding and membrane transport properties

The presence of water in polymer membranes has been found to have significant influence on the membrane properties. The water content and its dynamic motion in a polymer matrix, or commonly the state of water, can increase the free volume in the system, promote chain mobility and disrupt hydrogen bonding, increase the diffusion of small molecules and ions through the polymer and act as a plasticizer to decrease the glass transition temperature ($T_g$). In a simple description, water absorbed in polymers has been cataloged based on a distribution of three states: [1] nonfreezing water, water that is strongly bound to polymer which does not crystallize and shows no thermal transition by differential scanning calorimetry (DSC); [2] freezable bound water, water that is weakly bound to the polymer chain and has a melting temperature lower than that of pure water in DSC experiments; and [3] free water, unbound water in the polymer which displays similar thermal properties to pure water. The distribution of water in these three states is affected by polymer chemical and physical properties, pH, temperature, and other environmental parameters. While there is likely a continuous distribution of hydrogen bond interactions, rotational motions, and translational self-diffusion coefficients for water in polymers, simple descriptions of the behavior of water in polymers has served to correlate water behavior to membrane properties.

In addition to calorimetry, a variety of techniques have been used to characterize the state of absorbed water and its influence on polymer properties. For example, pulsed field gradient
nuclear magnetic resonance (PFG-NMR) has been used to measure the water self-diffusion coefficient in a wide range of polymers.\textsuperscript{7,8} Additionally, NMR relaxation in terms of $T_1$ and $T_2$ were analyzed to obtain a quantitative measure of the distribution of the three states of water.\textsuperscript{33,34} Solid state NMR can be used to verify the plasticizing effects of water by examining the polymer mobility.\textsuperscript{13} Fourier transform infrared spectroscopy (FTIR) can be used to investigate the structure and dynamics of water absorbed.\textsuperscript{9–11} Positron annihilation lifetime spectroscopy (PALS) helps to probe the free volume of polymer systems.\textsuperscript{12,13}

The water uptake and water environment in proton-conducting membranes, especially Nafion\textsuperscript{®}, have been largely investigated and discussed.\textsuperscript{2,35,36} As water is absorbed into the Nafion\textsuperscript{®} membrane, a portion of the water solvates the sulfonate groups and is confined within the first hydration sphere of the ions. After the primary hydration of sulfonate groups, the addition of more water expands the hydrophilic domain and leads to formation of water-filled domains where proton, water, and other transport occurs.\textsuperscript{4} Zawodzinski, et al. have conducted a comparative study of water uptake by ionic fuel cell membranes including Nafion\textsuperscript{®} and their transport properties such as diffusion coefficient of water, conductivity and electro-osmotic drag.\textsuperscript{2,3,37,38} In their studies, it was found that there are two regions in the water sorption isotherm. First, there is a region of relatively little increase of water sorption with increasing water vapor activity ($a_{\text{H}_2\text{O}} = 0.14$ to 0.75). This region 1 corresponds to uptake of water solvating the ionic groups of the polymer. As water vapor activity further increases ($a_{\text{H}_2\text{O}} > 0.75$), there is a region of greater increase of water sorption with increasing water activity. This region 2 corresponds to water which fills the pores and swells the membrane, Figure 2-3.
Figure 2-3. Water sorption versus water vapor activity for Nafion® and other ionic polymer membranes.38

The water that is not associated with ion hydration tends to have properties akin to bulk water with observable freezing/melting transitions, and nearly bulk-like rotational and translational diffusion coefficients.5 The amount of water in the membrane and its interactions with the polymer can affect the membrane’s structure, such as the topology of the hydrophilic domains and their sizes.39 Also, the water-polymer interactions determine the properties of the absorbed water such as its hydrogen bond dynamics,10 dielectric constant,26 and self-diffusion coefficient.3 Since ion and molecular diffusion occurs through the water phase in these materials, the membrane transport performance is influenced by the water-polymer interactions.26

Nafion®’s transport properties, for example the water self-diffusion coefficient, the D₂O ²H T₁ relaxation time, and proton conductivity, are shown to strongly correlate to the hydration level of the membrane and one-another.1-4 Zawodzinski, et al. have compared the diffusion coefficient of H⁺ derived from NMR measurement and calculated from proton mobility with the
diffusion coefficient of water. It was found that at low water uptake, these two numbers are similar. But as the water content of the membrane increased, the diffusion coefficient of water and the diffusion coefficient of protons diverged. This finding indicates that at low hydration level, the mobilities of protons and water are both intimately related to one another and the vehicle mechanism must dominate. At higher hydration level, the hopping (Grothus) mechanism is enhanced by the more “bulk-like” water thus the transport of H\(^+\) is faster than the diffusion of water.

Kim, et al. demonstrated that the interactions between the absorbed water and the polymer membrane are a stronger indicator of the membrane transport properties rather than the total water content on a mass basis.\(^{34}\) Using DSC and \(^1\)H PFG-NMR, they measured the depression of the T\(_g\) caused by the non-freezing, strongly bound water. Disulfonated poly(arylene ether sulfone) copolymers and Nafion\(^\circledR\) showed distinctly different water-polymer interactions as characterized by the T\(_g\) response of the hydrated polymer with increasing water content. Nafion\(^\circledR\), which interacted weakly with water showed little plasticization and a high fraction of the absorbed water had a measureable melting transition around 0 \(^\circ\)C. The disulfonated poly(arylene ether sulfone) copolymers showed increased plasticization and required significantly more absorbed water than Nafion\(^\circledR\) before a melting transition was observed. The membrane transport properties including electro-osmotic drag and methanol permeability could be rationalized based on each polymer’s chemical structure and interaction with water.

Hibbs, et al. employed PFG-NMR to measure the water self-diffusion coefficient and DSC to measure the water melting endotherm to quantify the mobility and binding of water to sulfonated and quaternary ammonium functionalized poly(phenylene)s.\(^5\) These authors observed that quaternary ammonium bearing polymers interacted less strongly with water as evidenced by high self-diffusion coefficients and greater water melting endotherms. They then related these
measures of the water-polymer interaction to conductivity and pressure-driven water permeability of the membrane.\(^5\)

Holdcroft, et al. have also employed DSC to probe the behavior of water in proton exchange membranes and described the absorbed water as freezable water and nonfreezable water, based on their thermal transition characteristics. They reported that proton conductivity and methanol permeability of novel PEMs increased with the content of freezable water and attributed the increase to the improved mobility of protons and the enhanced network of hydrophilic domain in fully hydrated membranes.\(^{40,41}\) It was also revealed that ~8-14 H\(_2\)O per sulfonic acid group did not freeze and nonfreezable water was still able to transport protons.\(^{41}\)

To better characterize the dynamics of water within a membrane and its effect on proton transport kinetics, Fayer, et al. employed FTIR and fluorescence spectroscopy to investigate the hydrogen bond network dynamics of water confined in the hydrophilic regions of Nafion\(^\circledast\).\(^9,10,42\) Falk and Fayer interpreted the broad OD stretch peak (2553 - 2590 cm\(^{-1}\)) in Nafion\(^\circledast\) as a signature of hydrogen bonding interactions within the membrane.\(^9,10,39\) They also interpreted the high frequency shoulder (2695 cm\(^{-1}\)) of the OD stretch peak as an indication that these water molecules were experiencing a nonpolar environment and were probably in contact with the fluorocarbon backbone. Moilanen and Fayer found that the OD stretch for water absorbed in Nafion\(^\circledast\) displayed a blue shift with respect to bulk water, Figure 2-4.\(^9,10\) It was reported that upon dehydration of Nafion\(^\circledast\), the maximum of the OD stretch peak shifted to higher frequency. The blue shift of OD stretch maximum for water absorbed in Nafion\(^\circledast\) with respect to the position of the OD stretch in bulk water showed that the mean strength of hydrogen bonds was substantially lower for water absorbed in Nafion\(^\circledast\) compared to in liquid water.
Dilute HOD in H$_2$O was employed as a probe for the environment experienced by the water absorbed in ion exchange membranes. Using dilute HOD can greatly simplify the interpretation of the spectra by avoiding Fermi resonances arising from the overlapping fundamentals and overtones of pure H$_2$O and D$_2$O, Figure 2-5. Moreover, the spectrum of dilute HOD in H$_2$O is also free from intermolecular coupling of vibrations thus has narrower bands of simple shapes.
Figure 2-5. IR vibration frequencies of the fundamental, overtone and combination bands of H₂O, D₂O and HOD in liquid water.⁴³

2.2.3 Water binding for reverse osmosis membranes

Though many works have been carried out concerning the state of water absorbed and the transport properties of proton exchange membranes, relatively few investigations have focused on the state of water in reverse osmosis (RO) membranes. Reverse osmosis is a membrane-mediated process which employs a hydrostatic pressure greater than the osmotic pressure of the solution to create a chemical potential difference across the membrane that drives the solvent to the low concentration side of the membrane while retaining the solute in the high concentration side of the membrane.⁴⁴ Two membrane transport properties are the main criteria for assessing RO membranes’ performance: water permeability and salt rejection.⁴⁵ New designs of RO membranes aim to increase water permeability and salt rejection in order to realize more efficient production with lower cost. Therefore, fundamental research on membrane transport mechanisms and the
influence of membrane composition on water permeability and salt rejection will provide
guidance for future materials development in this field.

De Pinho, et al. used attenuated total reflectance Fourier transform infrared spectroscopy
(ATR-FTIR) to characterize the structure of water in the active layer of RO membranes and
correlated these measurements with the membrane’s permeation properties.\textsuperscript{46,47} They monitored
the position of the OH stretch band in films hydrated with pure H\textsubscript{2}O. Shift of OH stretch band to
lower wavenumber upon increasing hydration was observed. They suggested that the shift to
lower wavenumber represented the hydrogen bonding strength and the interactions between the
water molecules increased and it was brought about by the increase in water cluster size. They
found that lightly clustered water species, weakly hydrogen-bonded to the polymer hydroxyl
groups, predominated in the skin layer of the RO membranes. However, they correlated water
structure mostly to the size of the pores that varied with treatment methods and asserted that
lower values of rejection were obtained for increasing size of the water clusters. The water
structure with variations in polymer composition was not discussed.

2.3 \textbf{Reverse osmosis membrane for water purification}

2.3.1 \textbf{Water scarcity and desalination}

According to the World Health Organization, currently 1.2 billion people live in
conditions that lack access to clean, safe water, and 500 million people are approaching this
situation.\textsuperscript{48} Water scarcity already affects every continent and will be the main problem to be
faced by many countries in the 21st century, Figure 2-6.
Population growth and the exhaustion of readily available fresh water resources further deepen the problem. Global population is rising by 1.1 % a year,\textsuperscript{50} while water use has been growing at more than twice the rate of population growth with agriculture irrigation and industry use the leading factors in water consumption.\textsuperscript{51} On the other hand, human activities have brought a great number of pollutants into water supplies, for example, heavy metal and dichlorodiphenyltrichloroethane (DDT), making previously safe water supplies unreliable and requiring more widespread disinfection and decontamination. Also many freshwater aquifers are being overdrawn, resulting in salt water intrusion along coastal regions. Accessible ground water resources are decreasing, and the remaining supplies are becoming increasingly brackish. It has been projected that by 2025, water withdrawals will increase by 50 % in developing countries and
18% in developed countries, Figure 2-7, and two-thirds of the world population will be living in water-stressed countries and regions.\textsuperscript{52}

Figure 2-7. Spreading water shortage.\textsuperscript{49}

Alternative water resources options such as wastewater reuse and desalination have been extensively explored. Wastewater reuse has been providing water for agriculture irrigation, industrial cooling water, industrial process water, municipal gardening, augmentation of natural/artificial streams, and other non-consumption activities, while the production of drinking quality water often employs desalination.\textsuperscript{53}

Of the 1.4 billion km\textsuperscript{3} total volume of water on Earth, only 2.5 percent is fresh water. However, around 97.5% is seawater or brackish water.\textsuperscript{49} If properly employed, seawater and brackish water desalination will offer a vast and steady supply of high-quality water, without impairing natural freshwater ecosystems.\textsuperscript{54} Humankind has been obtaining fresh water through thermal desalination (distillation) for hundreds of years. With the advancements of thermal desalination technology such as multi-effect distillation (MED) and multi-stage flash (MSF), large-scale municipal drinking water distillation plants have been established and in production since the 1950s.\textsuperscript{55} However, thermal desalination consumes a substantial amount of energy and
results in significant greenhouse gases emission. Today, about half of the world’s desalination capacity is still using thermal desalination and these plants locate mostly in counties in Middle East due to easily accessible fossil fuel resources.

On the other hand, membrane-facilitated water purification such as RO, nanofiltration (NF), and electrodialysis (ED) have undergone drastic improvement over the past 40 years. Reverse osmosis as a desalination method requires much less energy than thermal distillation and has now become the primary technology for new desalination plants. With innovative membrane materials and engineering designs that help recover energy, currently seawater reverse osmosis has been able to operate at an energy consumption rate of 1.8 kWh m$^{-3}$ on a controlled pilot-scale system at 50% recovery. With RO technology, fresh water can now be produced from seawater at one-half of the cost of distillation. Brackish water desalination is even less expensive due to the lower pressure requirement because of the lower salinity of brackish water (1,000 – 10,000 mg L$^{-1}$ TDS) compared to seawater (10,000 – 60,000 mg L$^{-1}$ TDS). By 2009, approximately 50% of the world’s desalination plants were RO plants.

In the following section, the mechanism and the recent development of reverse osmosis desalination will be introduced in details.

### 2.3.2 Theories for reverse osmosis

Reverse osmosis is one of the membrane-facilitated filtration processes. When a hydrostatic pressure greater than the osmotic pressure of the solution is applied to a semipermeable membrane, a chemical potential difference is created across the membrane that drives the solvent to the low concentration side of the membrane while retaining the solute in the high concentration side of the membrane.
Filtration membranes such as RO, NF, ultrafiltration (UF) and microfiltration (MF) can be classified according to their pore diameters and the contaminants they are able to reject, Figure 2-8. Membranes with large size pores realize filtration through pore flow, where the fluid is forced through the membrane by pressure and the separation is accomplished via a size-sieving mechanism. When membrane pore size becomes small enough, as in the case of nanofiltration membrane, membrane surface charge also plays a role and the membrane will display low to moderate rejection of higher valent ions.\textsuperscript{59-61}

![Diagram showing pore diameters and filtration mechanisms](image)

Figure 2-8. Range of nominal pore diameters for commercially available membranes and the species they are used to filter.\textsuperscript{62}

However, the polymer materials of RO membranes form a layered, web-like structure and do not have distinct pores that traverse the membranes. Water transports through RO membrane via solution-diffusion mechanism and RO membranes can reject even monovalent ions.\textsuperscript{63,64} In the solution-diffusion model, water first absorbs on the membrane surface, then diffuses through the thickness of the membrane, and desorbs from the permeate surface of the membrane. The difference between pore-flow mechanism and solution-diffusion mechanism is demonstrated in Figure 2-9.
In the practice of reverse osmosis, the flux of water and salt can be described as follows:

\[ N_A = A(\Delta p - \Delta \pi) \]  
\[ N_B = B(C_{\text{feed}} - C_{\text{permeate}}) \]

where \( N_A \) is water flux through the membrane, \( N_B \) is the salt flux across the membrane, \( \Delta p \) is the transmembrane pressure difference and \( \Delta \pi \) the osmotic pressure difference between the feed and the permeate. \( C_{\text{feed}} \) and \( C_{\text{permeate}} \) are the salt concentration in the feed solution and permeate solution respectively. \( A \) and \( B \) are constants that depend on membrane characteristics but they are not material properties of the membrane. Based on solution-diffusion model of water transport through RO membrane, \( A \) and \( B \) can be described by:

\[ A = \frac{D_w S_w V_w}{RT} \]
\[ B = \frac{D_s K_s}{l} \]

where \( D_w \) is the water diffusivity, \( S_w \) is the water solubility, \( V_w \) is the water partial molar volume, \( R \) is the ideal gas constant, \( T \) is the operating temperature, \( D_s \) is the salt diffusivity, \( K_s \) is the salt diffusivity.
partition coefficient between the solution and membrane phases, and \( l \) is the membrane thickness.

The osmotic pressure for a thermodynamically ideal solution can be defined as:

\[
\pi = CRT
\]  
(2-5)

where \( C \) is the salt concentration. Therefore:

\[
\Delta\pi = (C_{\text{feed}} - C_{\text{permeate}})RT
\]  
(2-6)

Besides \( A \) and \( B \), two other parameters are often used to describe RO membrane performance: water permeability \( P_w \) and salt rejection \( R_{\text{NaCl}} \):

\[
P_w = \frac{N_A l}{A t \Delta p}
\]  
(2-7)

where \( A \) is the permeation area of the membrane and \( t \) is the permeation time. \( \Delta p \)

\[
R_{\text{NaCl}} = \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \times 100\%
\]  
(2-8)

### 2.3.3 Materials and membrane design employed in reverse osmosis

The idea of employing reverse osmosis for desalination was proposed by Merten 50 years ago. \(^{67}\) In 1959, Reid and coworkers demonstrated that cellulose acetate (CA) had excellent salt rejection performance. \(^{68,69}\) However, the membrane they used was relatively thick, 4-22 \( \mu \)m, and displayed such low flux that it was not practical for real-world applications. Not until Loeb and Sourirajan made a breakthrough with wet annealing cellulose acetate membranes after casting did reverse osmosis become a viable process for desalination. \(^{70}\) These researchers achieved much higher flux than those reported by Reid while maintaining high salt rejection. Loeb and Sourirajan’s membrane was examined by Riley and an “asymmetric” morphology was observed where a thin dense skin layer (~100 – 200 nm) was supported by a thick porous layer. \(^{71}\) Lonsdale, Merten, and Riley proposed the solution-diffusion mechanism for reverse osmosis process and this simple but classic theory has been proven quite effective for describing desalination by
reverse osmosis.\textsuperscript{63,67,72,73} During the 1960-1970s, cellulose acetate and other polymers were employed in hollow fiber membranes with an asymmetric structure and were commercialized for desalination.

Currently, the desalination market is dominated by thin film composite (TFC) membranes made from aromatic polyamides. A thin film composite reverse osmosis membrane usually consists of three layers, a woven or nonwoven support fabric made of polyester, a microporous support made of asymmetric polysulfone, and an ultrathin polyamide barrier layer, Figure 2-10.

![Schematic diagram of a thin film composite membrane.\textsuperscript{74}](image)

The ultrathin selective barrier layer is formed through interfacial polymerization. Aromatic polyamides with a crosslinked structure synthesized from m-phenylene diamine (mPD) and trimesoyl chloride (TMC) are the most frequently used materials, Figure 2-11.\textsuperscript{75} This system, along with subtle variations, have dominated the membrane desalination market for about 30 years. Crosslinked aromatic polyamides exceed previous materials such as cellulose acetate due to higher flux, higher rejection, wider operational pH range, higher operational temperature and excellent hydrolytic stability. But polyamides still suffer from poor tolerance to chlorine.
2.3.4 Shortcomings of current RO materials

At present, cellulose acetate (CA) and aromatic polyamides (PA) are the two main classes of polymers used for commercial RO membranes. However, they both have shortcomings. CA membranes undergo compaction at higher temperatures and hydrolyze over time. The rate of hydrolysis is at a minimum in the pH range of 4-6, thus CA membranes are limited to operation in a relatively narrow pH range. PA membranes, despite being stable over a wider range of pH
values than CA membranes, are prone to oxidative degradation and suffer significant performance deterioration when exposed to oxidizing agents such as chlorine. Since chlorine is essential in the disinfection of drinking water, feed water needs to be dechlorinated before going through an RO process using PA membranes. After desalination, though, the water needs to be rechlorinated before distributed through municipal system. Keeping PA membranes free from chlorine adds significant additional costs to water purification.

Although several approaches have been proposed to increase the chlorine resistance of polyamide, such as replacing chlorine sensitive amidic hydrogen on the amide linkages with other moieties, or replacing the aromatic ring bonded to the amide nitrogen with aliphatic chain or cyclics, the outcomes have not been satisfying since most approaches displayed weakened membrane desalination performance.

2.3.5 The search for better RO membrane materials

In the search for desalination membrane materials with good chlorine tolerance, polysulfone has attracted attention because it does not contain the amide linkages that are sensitive to attack by aqueous chlorine. To overcome the hydrophobicity of polysulfone membranes, sulfonation and functionalization with quaternary ammonium moieties have been employed to increase the hydrophilicity of the material and enable high rates of water transport. Particularly, sulfonated polysulfone has shown promising selective ion transport properties and high tolerance to aqueous chlorine over a broad range of pH values.

While most researchers have previously synthesized sulfonated polysulfone through postpolymerization sulfonation methods, the difficulties of precise sulfonation control and the varying reaction chemistry on the aromatic backbone have made the process hard to reproduce. McGrath and Freeman have developed sulfonated polysulfone-based materials via direct
copolymers synthesized from sulfonated monomers that offer better control of the sulfonation position and degree of sulfonation, Figure 2-12. The resulting materials displayed controlled IEC and water uptake. The water and salt permeabilities were correlated with water uptake in these materials. Most importantly, thin film composite (TFC) membranes prepared from direct copolymerized sulfonated polysulfone has demonstrated superior chlorine resistance compared to polyamide-based TFCs. As shown in Figure 2-13, the water permeability and salt rejection were stable for sulfonated polysulfone membranes when exposed to chlorine while they both decreased significantly over time for commercial crosslinked polyamide membranes.

Figure 2-12. Synthesis of a phenoxide-endcapped disulfonated biphenol-based poly(arylene ether sulfone) copolymer.
Figure 2-13. The effect of chlorine exposure on NaCl rejection and water permeability for commercial crosslinked polyamide membrane (SW30HR) and thin film composite membranes of sulfonated polysulfone (BPS-40H TFC).
2.4 Streaming current characterization for zeta potential

2.4.1 Zeta potential

Fouling processes are strongly influenced by the surface charge properties of the membrane in contact with the raw water and the species suspended in the feed solution.86–89 Also, electrostatic interactions between ions to be rejected and the membrane charge plays an important role in ion separation based on Donnan exclusion. For a charged membrane, ions with the same charge are excluded and thus the salt transport through the membrane is hindered.90

Zeta potential, which provides useful information about the surface charge properties of the membrane in solution, is an important parameter in various applications such as microfluidics,91–93 colloid chemistry,94,95 and membrane fouling.96 The zeta potential is influenced by surface composition as well as solution properties such as the nature of the ions, ionic strength, and pH.20,96

When a solid surface is brought into contact with an aqueous solution, most materials will acquire a surface charge either due to the dissociation of surface ionic groups, the preferential adsorption of one type of ion from the aqueous solution, or some other charging mechanism.20 The electrostatic charge on the solid surface will attract counterions and repel coions in the vicinity of the surface. The electric double layer (EDL) is a region close to the charged surface in which there is an excess of counterions to neutralize the surface charge.97 As shown in Figure 2-14, in the liquid layer adjacent to the solid surface, termed the Stern layer, ions are strongly attracted to the surface charge and are immobile.98 Potential at the Stern plane is called Stern potential, \( \psi^d \).

Further away from the surface in the diffuse layer, ions are less affected by electrostatic interactions near the solid surface and the net charge density gradually decreases to that of the
bulk liquid. The diffuse layer can flow under the influence of tangential stress and the shear plane is defined where the diffuse layer “slips” or flows past the charged surface. The electrical potential at the shear plane, which can be measured experimentally, is defined as the zeta potential, \( \zeta \). Since the electrical potential at the solid surface \( \psi^0 \) cannot be measured directly, zeta potential is often the most valuable characterization of double-layer properties.

Because the system is electroneutral, the charge density at the surface \( \sigma^0 \), the charge density of the Stern layer \( \sigma^S \), and the charge density within the diffusive part of the electric double layer \( \sigma^d \) should compensate each other:

\[
\sigma^0 + \sigma^S + \sigma^d = 0
\]  

(2-9)

The thickness of the EDL, the Debye length \( \kappa^{-1} \), is defined as:

\[
\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}
\]  

(2-10)

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the dielectric constant of the electrolyte solution, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( N_A \) is the Avogadro number, \( e \) is the elementary charge and \( I \) is the ionic strength of the electrolyte.

\[
I = \frac{1}{2} \sum z_i^2 c_i
\]  

(2-11)

where \( z_i \) is the valence and \( c_i \) is the concentration of species i.
2.4.2 Studies of membrane zeta potential

Streaming potential characterization has been carried out on several commercial nanofiltration (NF) membranes and reverse osmosis (RO) membranes by Elimelech, Childress, and Peeters to investigate the influence of solution chemistry on membrane surface charge. Additionally, zeta potential has been used to rationalize membrane retention mechanisms and fouling properties. Studies dealing with solution ion type and concentration, solution pH, surfactant, and natural organic matter (NOM) have been carried out. In most cases, a change of zeta potential is explained by considering the dissociation of surface functional groups or the preferential adsorption of ions and macromolecules from solution.

Other studies have focused on how membrane chemical composition influences the zeta potential of the membrane surface where different types of materials have different relationships between zeta potential and pH. Hinke and Staude have characterized the zeta potentials of chemically modified polysulfone microporous membranes and have shown distinctive differences between polysulfone membranes with neutral functional groups, such as chloromethyl moieties,
methyl esters, and amines. At low pH, membranes with neutral functional groups displayed negative zeta potentials due to the adsorption of anions from the solution while the membranes with tethered amines displayed positive zeta potentials due to protonation of the amine surface groups.\textsuperscript{104} Werner and Jacobasch studied a series of sulfonated poly(ethersulfone) hollow fiber membranes with different degrees of sulfonation and observed that as the degree of sulfonation increased, the zeta potential became less negative.\textsuperscript{105} Mockel, et al. reported a similar trend for carboxylated polysulfone membranes.\textsuperscript{106} Both of these research groups explained their results on membranes with tethered negative charges by considering the extraordinary hydrophilicity of the acid groups that increased the thickness of the interfacial swelling layer at the membranes’ surface as the degree of substitution was increased. As the thickness of the swelling layer increased, the shear plane moved towards the solution bulk and a lower zeta potential was obtained on samples with a higher degree of tethered ions.

2.4.3 Streaming potential/current measurement for zeta potential characterization

A number of techniques for measuring the zeta potential have been developed based on one of the three electrokinetic effects: electrophoresis, electroosmosis, and streaming potential, out of which streaming potential, or streaming current, is the most suitable for flat membrane surfaces.\textsuperscript{20,99,107}

In the streaming potential technique, a pressure differential, $\Delta P$, is applied between the ends of a channel or capillary containing electrolyte to induce hydrodynamic flow. The ions in the diffuse layer of the EDL are carried in the direction of the flow, resulting in an electrical current defined as the streaming current, $I_s$. The streaming current can be measured when the electrical potential difference between the two ends of the channel is zero.
At open circuit, the streaming potential, $E_s$, generated by the hydrodynamic flow of electrolyte is the potential difference between the ends of the channel which induces a flow of ions in the opposite direction of the hydraulic flow, defined as the conduction current $I_c$. Streaming potential is measured when the electrical flow reaches a steady state and the conduction current equals the streaming current, making the total electrical current in the channel zero. Figure 2-15 displays a slit microchannel geometry usually employed for the streaming potential measurement; $L$ is the length of channel, $W$ is the width of the channel, $h$ is the channel height, and $d_m$ is the thickness of the membrane.

Figure 2-15. Parallel plate microchannel geometry for streaming current measurements.

The Smoluchowski equation describes the relationship between zeta potential ($\zeta$) and streaming potential (Eq 2-12) or streaming current (Eq 2-13):\(^{100}\)

$$\zeta = \frac{dE_s}{dP} \cdot \frac{\eta}{\varepsilon \varepsilon_0} \cdot \frac{L}{W h R}$$ \hspace{1cm} (2-12)

$$\zeta = \frac{dI_s}{dP} \cdot \frac{\eta}{\varepsilon \varepsilon_0} \cdot \frac{L}{W h} = \frac{dI_s}{dP} \cdot \frac{\eta}{\varepsilon \varepsilon_0} \cdot \lambda_0 R$$ \hspace{1cm} (2-13)
where \( \frac{dE}{dP} \) is the change in streaming potential with pressure, \( \frac{dI}{dP} \) is the change in streaming current versus pressure, \( R \) is the resistance of the measuring cell, \( \eta \) is the electrolyte viscosity, \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon \) is the dielectric constant of the electrolyte.

Eq 2-14 is obtained through integration of the product of the volume charge density, \( \rho \), and velocity, \( V \), of the electrolyte across the channel. In this case, \( \rho \) can be expressed as the one-dimensional variant of the Poisson equation (Eq 2-15):

\[
I_s = 2W \int_{y=0}^{y=h/2} \rho(y)V(y)dy
\]

\[
\rho(y) = -\varepsilon_0 \frac{d^2\Psi}{dy^2}
\]

where \( y \) is the distance from the center plane of the channel and \( \Psi \) is the electrical potential at any position \( y \). We can assume that \( \Psi \) and \( d\Psi/dy \) become zero at \( y = 0 \) and designate \( \Psi \) at \( y = h/2 \) as the zeta potential, \( \zeta \), then Eq 2-14 could be rewritten and Eq 2-16 is derived.

\[
I_s = -\frac{\Delta P \varepsilon e \varepsilon_0 h W \zeta}{\eta L}
\] 

### 2.4.4 Methods for correcting the effect of membrane surface conductance and bulk conductance

Though the Smoluchowski equation is widely accepted, it does not take into account surface conductance. Surface conduction is the excess electric conduction that takes place in solid–liquid interfaces owing to the charge carrier accumulation in the electric double layer. Surface conduction becomes important and nonnegligible when \( \zeta \)-potential is moderately large (> 50 mV).\textsuperscript{109}
The Fairbrother-Mastin procedure for eliminating the contribution of surface conductance is based on the assumption that surface conductance is suppressed at sufficiently high electrolyte concentration.\textsuperscript{110} The conductivity term in Eq 2-12 and Eq 2-13 is replaced by:

$$\lambda_0 = \frac{\lambda H R H}{R}$$  \hspace{1cm} (2-17)

where $R H$ is the resistance of the channel when the cell is filled with a solution of high salt concentration, $\lambda H$ is the conductivity of this solution, and $R$ is the resistance of the channel when filled with the measurement solution.

Yaroshchuk and Ribitsch\textsuperscript{111} have pointed out for certain materials such as porous membranes, the conduction current $I_c$ does not necessarily take the same path as the streaming current. If the conduction current circulates through the membrane body, then the membrane wall conductance cannot be eliminated in the simple Fairbrother-Mastin procedure because it is proportional to the conductance in the channel and will not be suppressed. Yaroshchuk and Ribitsch described the streaming current/potential cell as a “sandwich” composed of the channel and two conducting layers with the total electrical conductance (surface conductance is neglected) being:

$$\frac{1}{R} = \frac{W h}{L} \lambda_0 + 2 \frac{W h_m}{L} \lambda_m$$  \hspace{1cm} (2-18)

where $h_m$ is the thickness of the membrane and $\lambda_m$ is its conductivity. Substituting Eq 2-18 into Eq 2-12 leads to:

$$\frac{dE_s}{dp} = \frac{\varepsilon \varepsilon_o \zeta}{\eta \lambda_0} \frac{1}{1 + \frac{\lambda_m h_m}{\lambda_0 h}}$$  \hspace{1cm} (2-19)

In Eq 2-19, the reciprocal of $dE/dP$ is a linear function of cell height, $h$. If the measurement is carried out at several channel heights, it is possible to perform a linear extrapolation to infinitely large channel heights and a correct value of $\zeta$ can be determined. In Yaroshchuk and Ribitsch’s analysis, they assumed that during the streaming current
measurement, there would be no conduction current in the membrane body, thus the streaming current was not affected by membrane conductance and did not need the correction relating to cell height.

Given the ohmic behavior of the streaming channel observed in the previous studies, we set out to test whether the conductance of ion-containing membranes in parallel with the electrolyte channel could be described in a similar fashion using a parallel resistance model. In our investigations, streaming current was measured and the zeta potential was obtained via Eq 2-16. Our results showed that the streaming current measurement was affected by the membrane conductance and the influence of the membrane must be taken into account when trying to interpret the results and obtain information about the zeta potential behavior of materials that are ion conductive.

2.5 Antifouling surface modification for reverse osmosis membranes

2.5.1 Fouling in membrane facilitated water purification

Fouling is the adsorption and accumulation of contaminants on a surface, such as colloidal particles, dissolved organics and salts. Biological fouling could also occur where microbial cells attach to surface, multiply and form biofilms through extra-cellular polymeric substances (EPSs). Protein and polysaccharide adsorption play an important role in biofouling because they alter the hydrophilicity and roughness of the substrate, eventually affecting the bacteria deposition kinetics.

Fouling and biofouling are relevant in a wide range of applications, including biomedical implants, biosensors, food packaging, ship hulls and membranes used in pressure-driven processes such as RO, NF, UF, and MO.
In RO, foulants such as aluminosilicate clays and humic acids accumulate on the membrane surface, leading to the reduction of through-membrane flux and an increase in energy consumption.\textsuperscript{96,117} Shown in Figure 2-16 is an example where an RO membrane was fouled with bacteria inoculated in the feed water, the flux declined with permeation time, and the salt passage performance also worsened.\textsuperscript{118}

![Graph showing flux decline and salt passage with bacteria inoculation](image)

**Figure 2-16.** Flux decline and salt passage increase with bacteria inoculated in the feed water for different period of time for a commercial RO membrane, LFC-1 (Hydranautics, Oceanside, CA).\textsuperscript{118}

Fouled membranes require frequent cleaning with chemicals such as sodium hypochlorite solution, which shortens membrane lifetime. The fouling mitigation processes and accommodation of the decreased productivity of the membranes increase the maintenance and operating costs of the water treatment process. Methods like pretreatment of the process fluid, adjustment of operating design and conditions have been developed and employed since the early 1960s and they can reduce membrane fouling to a certain extent.\textsuperscript{119} The modification of
membrane surface is another route to mitigate fouling and a variety of strategies and materials have been studied.

2.5.2 Strategies for reducing fouling

Generally speaking, there are three strategies for designing antifouling especially anti-biofouling surfaces. Firstly, the “fouling release” strategy is based on minimizing the intermolecular forces or interactions between foulants and the surfaces so that the foulants are easily released under low shear stresses. This strategy is more applicable to marine antifouling as the water flow relative to the ship hull when the ship is moving provides the necessary shear force for releasing the foulants.

The second strategy is to design a surface or surface coating that will degrade the absorbed microbial contamination through the release of biocidal agents, or the use of polycations, enzymes, nanomaterials, and photoactive agents. The antimicrobial route has significant relevance for medical applications since reducing the microbial contamination on medical material surfaces greatly eliminates the risk of infection and prevents subsequent medical complications.

The third approach and the most relevant to membrane facilitated water purification, is the design of a surface that prevents the foulants from attaching. A variety of strategies or materials have been proposed and quite a few of them showed potential. Empirical evidence has shown that there are several surface characteristics that are important to prevent fouling.
2.5.3 Surface characteristics that affect fouling

2.5.3.1 Surface roughness

Smother surfaces typically display lower fouling rates than rough surfaces. Elimelech, et al. have examined the colloidal fouling of several commercial RO and NF membranes and found that the results are nearly perfectly correlated with membrane surface roughness, regardless of other physical parameters of the membranes and operating conditions. The enhancement of fouling was attributed to the increased surface roughness because the colloidal particles are prone to accumulate at the valleys of the rough membrane surface.

2.5.3.2 Surface hydrophilicity

Hydrophilicity of the surface has been shown to help reduce fouling. Figure 2-17 displays that for a series of polysulfone membranes, after fouling the decline of flux was higher for surfaces with higher contact angle. Park, et al. synthesized a series of polysulfone-poly(ethylene oxide) random copolymer having different content of poly(ethylene oxide) (PEO). They found that higher PEO contents yielded surfaces that were more hydrophilic and these hydrophilic surfaces fouled less with emulsified oil.
Figure 2-17. After protein fouling, the flux decline of a series of polysulfone membranes increases with increasing contact angle.\textsuperscript{126}

Immobilizing PEO is one of the most often employed approaches to increase the surface fouling resistance.\textsuperscript{128,129} However, PEO is dissolvable in water and other solvents, which limits its application significantly. Routes such as physical adsorption, chemical grafting, and gelation have been employed to stabilize PEO on a surface.

The use of PEGylated polymers, for example copolymer with PEG side chains, PEG-like hyperbranched polymer, and self-assembled monolayers (SAMs) with only a few EG units per molecules have all shown good resistance to protein and cell adsorption.\textsuperscript{130–132} Experiments on SAMs of oligo(ethylene oxide) support the hypothesis that the formation of a hydration layer near a hydrophilic surface is more meaningful to fouling resistance than the steric repulsion offered by long PEG chains.\textsuperscript{133}
2.5.3.3 Surface charge

Surfaces which contain a nanoscale homogenous mixture of balanced charge groups have demonstrated superior antifouling performance. It is suggested that this kind of mixed charge surfaces achieve fouling resistance because both charge groups are strongly hydrated through ionic solvation.

Zwitterionic molecules, which contain a positively charged functional group and a negatively charged functional group in close proximity, Figure 2-18, are ideal for creating nanoscale heterogeneity in charge composition. Chen, et al. have synthesized zwitterionic poly(sulfobetaine methacrylate) (polySBMA) with sulfonate group and ammonium group on the same side chain. The resulting polymer surface with a mixture of oppositely charged groups displayed much less protein adsorption than methyl-terminated SAMs or oligo(ethylene glycol)-terminated SAMs.\textsuperscript{134}
On the other hand, SAMs with various counter-charged terminal groups of different valence are also highly resistant to protein adsorption. Furthermore, Chen and Jiang have prepared hydrogels from positively charged and negatively charge compounds. The resulting
polyampholyte materials with a uniform distribution of mixed charged groups in different side chains at the nanometer scale are excellent candidates for nonfouling materials.$^{138}$

**2.5.4 Layer-by-layer assembly for antifouling surface modification**

Layer-by-layer assembly (LBL), which is the alternate adsorption of oppositely charged species from aqueous solution, Figure 2-19, has several advantages for constructing thin polymer films.$^{139}$ These types of layers are easy to process, low cost, and there is a variety of polymers and functionalities that can be incorporated into the layered systems.$^{140}$

![Scheme for the assembly of LBL](image)

*Figure 2-19. Scheme for the assembly of LBL.$^{139}$*
Researchers have studied LBL assembly coatings and explored their potential as an antifouling surface modification method. For example, to prevent marine biofouling, layer-by-layer spray-coating of poly(acrylic acid) and polyethylenimine polyelectrolytes was prepared and has been shown to effectively reduce the settlement of spores of Ulva.\textsuperscript{141} LBL assemblies containing silver nanoparticles have been designed by Dai and Bruening that exhibited antimicrobial activity.\textsuperscript{142} For desalination, a LBL assembly of sodium alginate and chitosan were deposited on the surface of cellulose acetate (CA) nanofiltration membranes. The modified membranes were found to retain their desalination abilities better after bovine serum albumin (BSA) fouling than the unmodified CA membranes.\textsuperscript{143}

Recently it has been found that PEO-based poly(urethane)s LBL assembly displayed stability in water, salt water and sodium hydroxide solutions.\textsuperscript{144} Thus it drew our interest to test the antifouling properties of the PEO-based poly(urethane)s LBL assembly and investigate its potential as an antifouling surface modification for membrane facilitated water treatment and other applications.

\subsection*{2.5.5 Salt annealing of LBL assembly}

Salt annealing of LBL assemblies was found to increase the surface smoothness and promote interdiffusion between layers. Schlenoff, et al. have salt annealed polystyrenesulfonate (PSS)/poly(diallyldimethylammonium chloride) (PDADMA) LBL assemblies and found that their surface roughness decreased by about 80\% (Root mean square roughness factors decreased from 20 nm to around 3 nm) after salt annealing in 1 M NaCl for 4 h, Figure 2-20.\textsuperscript{145} Studies performed on these same PSS/ PDADMA LBL systems have also shown that salt annealing promoted the interdiffusion and mixing between layers as revealed by neutron reflectometry. The effect became more significant with longer exposure time to salt solution.\textsuperscript{146} Promoted mixing of
layers may lead to a more neutrally charged surface consisting of a mixture of charge groups. Since smoothness and neutral charge of the surface can both help reduce fouling, we are interested to investigate the effect of salt annealing on the antifouling performance of PEO-based poly(urethane)s LBL assemblies.

Figure 2-20. Surface topology of PSS/PDADMA LBL before and after salt annealing.\textsuperscript{145}
2.6 Conclusions

Sulfonated polysulfone has shown great promise for making reverse osmosis membrane with improved chlorine resistance and it attracts a lot of interest to study its desalination performances. Extensive researches have been carried out regarding water binding in polymer membranes and their transport properties, therefore investigating the water-binding in polysulfone membranes and make correlation to their desalination performances will be an interesting and meaningful topic. FTIR has been employed to study the water binding in Nafion®. FTIR characterization provides information of both water absorbed in the membrane and the membrane material itself. The use of dilute HOD in H$_2$O as FTIR probe successfully avoids Fermi resonance and makes accurate characterization of the water environment inside the membrane possible.

In Chapters 4 and 5, our studies on water binding in polymer membranes will be discussed. FTIR was employed to investigate the water binding in sulfonated and quaternary ammonium functionalized poly(phenylsulfone) and their desalination performance were studied and compared. Crosslinked polymer membrane of acidic polymer with perfluorosulfonate side groups as well as quaternary ammonium and imidazolium functionalized polystyrene were also studied.

To investigate the surface charge of ionic poly(phenylsulfone) membranes which influence their fouling properties, streaming current measurement were carried out on these membranes with varying IEC and conductivity. Method to correct the effect of membrane bulk conductance has been proposed by Yaroshchuk, et al.\textsuperscript{111,147} However, their method is only applicable to streaming potential measurement. Our study focused on streaming current measurement and showed unique influence of membrane conductivity as well as membrane thickness. The results and discussion will be presented in Chapter 6.
Lay-by-layer assembly of PEO-based polyurethanes helps incorporate hydrophilic PEO segment on to a surface, which will benefit antifouling properties. Furthermore, in past researches it has been shown that salt annealing on LBL assembly will reduce surface roughness, promote the interdiffusion between layers. Since smoothness and homogenous mixture of charge groups are both features that have been shown to help reduce fouling, we are very interested in the effect of salt annealing on LBL assembly antifouling performances. Our studies on LBL surface modification and salt annealing of LBL assembly will be presented in Chapter 7.
Chapter 3
Experimental Procedures for Sample Preparation and Characterization

3.1 Introduction

This chapter first introduces the structures and general properties of the polymer materials investigated throughout this dissertation. The procedures for casting polymer membranes as well as assembling layer-by-layer thin polymer films are described in details. Techniques employed for characterization are introduced as well as characterization conditions. Dynamic vapor sorption (DVS) microbalance and quartz crystal microbalance with dissipation monitoring (QCM-D) were employed to measure polymer membrane water uptake. Fourier transform infrared spectroscopy (FITR) was used for probing the water-water and water-polymer interactions inside polymer membranes using transmission geometry in a flow-through cell. Attenuated total reflectance (ATR) mode of FTIR helped monitoring thin film properties and kinetic surface absorption processes. Streaming current measurements were employed for characterizing surface zeta potential.

3.2 Materials

AEM and CEM membranes

For water-binding and surface zeta potential work, the cation exchange membranes (CEM) and anion exchange membranes (AEM) were synthesized from functionalized RADEL® R-5500 poly(phenylsulfone) which was kindly donated by Solvay Advanced Polymers, LLC.
For CEMs, a series of sulfonated poly(phenylsulfone) was prepared through post-sulfonation with trimethylsilyl chlorosulfonate (Aldrich, 99%) in tetrachloroethane (Aldrich, >98%) using a modified reference procedure.\textsuperscript{148} The poly(phenylsulfone) was dried and dissolved in tetrachloroethane at room temperature. Trimethylsilyl chlorosulfonate was carefully added to the solution at 40°C. A reaction followed for 24–98 h while Ar was bubbled into the solution. The solution was then cooled to room temperature and poured into methanol. The precipitated polymer was further washed with methanol and later washed with water in a Soxhlet extractor for 16 h then dried.

For AEMs, the polymers were prepared through chloromethylation and amination of poly(phenylsulfone). 18.02g RADEL\textsuperscript{®} R-5500 poly(phenylsulfone) and 1,1,2,2-tetrachloroethane (450 mL) were mixed and heated to 80 °C. The mixture was kept in argon atmosphere until the complete dissolvation of the polymer, and then cooled to room temperature. 199 ml (2.2 mol) dimethoxymethane in 200 ml 1,1,2,2-tetrachloroethane was added over the course of two hours to avoid precipitation of the polymer. Then 82 mL (1.1 mol) thionyl chloride was added slowly. 6.13 g (45 mmol) ZnCl\textsubscript{2} in 45 ml dry tetrahydrofuran was added. Heat was released during the adding of ZnCl\textsubscript{2}. The reaction was heated to 60 °C with stirring. The degree of functionalization (the number of chloromethyl group per repeating unit) was monitored by $^1$H NMR and the resulting polymer was isolated. The reaction mixture was precipitated in methanol, collected by filtration, and extracted in a Soxhlet extractor using methanol as solvents.\textsuperscript{149}

Membranes from RADEL\textsuperscript{®} precursors were cast in the chloromethylated form. The membranes were converted to quaternary ammonium form by immersion in 45 % aqueous trimethylamine for 48 h, then immersion in 1 M KOH for 48 h followed by complete rinsing and storage in water exposed to air.
The repeat unit for sulfonated poly(phenylsulfone) CEMs (sPS) and aminated poly(phenylsulfone) AEMs (aPS) are shown in Figure 3-1 and their resulting properties are summarized in Table 3-1.

Figure 3-1. Repeat unit of sulfonated poly(phenylsulfone) CEM (sPS) and aminated poly(phenylsulfone) AEM (aPS) where R is either sulfonic acid or trimethylbenzyl quaternary ammonium bicarbonate functional groups or H.

Table 3-1. Properties of sulfonated poly(phenylsulfone) (sPS) and aminated poly(phenylsulfone) (aPS).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>DF_{NMR}^a</th>
<th>Ion exchange capacity (IEC) (mmol g^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-I</td>
<td>0.26</td>
<td>0.6</td>
</tr>
<tr>
<td>sPS-II</td>
<td>0.46</td>
<td>1.1</td>
</tr>
<tr>
<td>sPS-III</td>
<td>0.73</td>
<td>1.6</td>
</tr>
<tr>
<td>sPS-IV</td>
<td>0.93</td>
<td>2.0</td>
</tr>
<tr>
<td>sPS-V</td>
<td>1.28</td>
<td>2.5</td>
</tr>
<tr>
<td>aPS-I</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>aPS-II</td>
<td>0.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>
For casting polymer membranes, the sulfonated poly(phenylsulfone) CEMs (sPS) and chloromethylated RADEL® with different degrees of chloromethylation (for preparing AEMs) were dissolved in dimethylformamide (DMF) and the polymer solutions were cast onto glass plates and dried at 50 ºC in a convection oven for 6 h, then in vacuo at 50 ºC for 12 h. After drying, the glass plates with membranes were soaked in DI water to swell the membranes and detach them from the glass surface. The CEMs were then treated in a 50 ºC bath of 0.5 M H₂SO₄ for 24 h to ensure full protonation of the sample. The free standing membranes of chloromethylated RADEL® were soaked in a 45 (w/w) % solution of trimethylamine in water for 48 h at room temperature to convert the chloromethyl groups to quaternary ammonium groups. Afterwards, the AEMs were soaked in 1M KOH at room temperature for 48 h to exchange the chloride ions for hydroxide ions. Finally, both CEMs and AEMs were rinsed with Millipore 18.5 MΩ water and were stored in DI water in poly(ethylene) vessels to maintain hydration until characterization. When stored in ambient environment, the quaternary ammonium hydroxide groups of AEMs gradually transformed into bicarbonate form due to CO₂ uptake of the samples.¹⁴⁹,¹⁵⁰

For zeta potential characterization, CEMs with thicknesses ranging from 20 μm to 120 μm were obtained by varying the polymer concentration in the casting solution. Dilute solutions of sulfonated poly(phenylsulfone) were also cast on a KAPTON® polyimide membrane substrate to form very thin layers (less than 5 μm) of sulfonated poly(phenylsulfone) for zeta potential measurement.
Crosslinked fluoropolymers networks

The copolymers of vinylidene fluoride and perfluoro(4-methyl-3,6-dioxane-7-ene) sulfonyl fluoride containing amino end-groups, denoted P(VDF-PFSVE), were synthesized by Xu, et al.\textsuperscript{14} The chemical structure of this material is displayed in Figure 3-2.

![Chemical structure of P(VDF-PFSVE)](image)

Figure 3-2. Amino terminated P(VDF-PFSVE).

The prepared amino-terminated polymers underwent crosslinking reactions with 1,3,5-benzene triisocyanate to form proton conductive networks. The crosslinked membranes showed extremely low methanol permeability, while maintaining the same order of magnitude in conductivity as Nafion\textsuperscript{®}, Table 3-2.\textsuperscript{15} These membranes’ exceptional high electrochemical selectivity (the ratio of proton conductivity to methanol permeability) attracted great interest. Therefore the water binding in P(VDF-PFSVE) crosslinked membranes were investigated. The water dynamics and hydrogen bonding network of water absorbed in the membrane were probed and used to rationalize the excellent selectivity.
Table 3-2. Properties of P(VDF-PFSVE) membranes and Nafion®.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ion exchange capacity (IEC) (mmol g⁻¹)</th>
<th>Water uptake (wt. %)</th>
<th>Proton conductivity (S cm⁻¹)</th>
<th>Methanol permeability (cm² s⁻¹)</th>
<th>Electrochemical selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-I</td>
<td>0.45</td>
<td>4</td>
<td>0.004</td>
<td>1.54×10⁻⁹</td>
<td>3.6×10⁶</td>
</tr>
<tr>
<td>PVDF-II</td>
<td>0.87</td>
<td>14</td>
<td>0.018</td>
<td>8.96×10⁻⁹</td>
<td>2.0×10⁶</td>
</tr>
<tr>
<td>PVDF-III</td>
<td>0.97</td>
<td>19</td>
<td>0.044</td>
<td>5.57×10⁻⁸</td>
<td>7.9×10⁵</td>
</tr>
<tr>
<td>PVDF-IV</td>
<td>1.14</td>
<td>26</td>
<td>0.066</td>
<td>9.91×10⁻⁷</td>
<td>6.7×10⁴</td>
</tr>
<tr>
<td>Nafion®</td>
<td>0.91</td>
<td>29</td>
<td>0.084</td>
<td>1.98×10⁻⁶</td>
<td>4.2×10⁴</td>
</tr>
</tbody>
</table>

Polystyrene copolymers and homopolymers with different ionic functional groups

To investigate the effect of phase separation as well as different ionic groups, polystyrene homopolymers and copolymers with quaternary ammonium group or imidazolium group were synthesized. The polystyrene copolymers were also prepared with different degree of functionalization. For polystyrene homopolymers with quaternary ammonium functional group (PS-QA) or imidazole functional group (PS-Im) and polystyrene copolymers with quaternary ammonium functional group (PS-b-PVBQA) or imidazole functional group (PS-b-PVBIIm), their chemical structures are displayed in Figure 3-3. Their properties were listed in Table 3-3.
Figure 3-3. Molecular structure of polystyrene homopolymers with quaternary ammonium functional group (PS-QA) or imidazole functional group (PS-Im) and polystyrene copolymers with quaternary ammonium functional group (PS-b-PVBQA) or imidazole functional group (PS-b-PVBIm).
Table 3-3. Properties of polystyrene homopolymers and copolymers.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ion exchange capacity (IEC) (mmol g⁻¹)</th>
<th>Water uptake (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-QA</td>
<td>4.80</td>
<td>118 %</td>
</tr>
<tr>
<td>PS-b-PVBQA-1</td>
<td>0.69</td>
<td>4.4 %</td>
</tr>
<tr>
<td>PS-b-PVBQA-2</td>
<td>1.24</td>
<td>10.6 %</td>
</tr>
<tr>
<td>PS-Im</td>
<td>3.28</td>
<td></td>
</tr>
<tr>
<td>PS-b-PVBIm-1</td>
<td>0.81</td>
<td>5.0 %</td>
</tr>
<tr>
<td>Ps-b-PVBIm-2</td>
<td>1.23</td>
<td>9.4 %</td>
</tr>
</tbody>
</table>

Polystyrene polymers were cast onto CaF₂ windows for FTIR characterization and on gold coated quartz crystal for QCM-D measurements. For FTIR characterization, 7 wt % solutions were used to obtain thick films. For QCM-D characterization, 0.25 wt % solutions were used for casting to obtain very thin films.

PS-Im was cast in the hood from water solution, then annealed in vacuum oven for 24 h at 129 °C. PS-b-PVBIm polymers were dissolved in THF first, then cast in the hood and covered with petri dish to allow slow drying overnight. After drying the PS-b-PVBIm polymer films were annealed in vacuum oven at 150 °C for 3h then slowly decreased to room temperature. PS-QA was cast from propanol alcohol solution then dried in ambient environment. PS-b-PVBQA membranes were cast from 10:1 toluene/propanol alcohol solution then dried in ambient environment.
Layer by layer assembly surface coatings

For layer-by-layer assembly surface modification studies, quaternary ammonium functionalized and sulfonated PEO-based poly(urethane)s (QA-PEO and Sulf-PEO) were synthesized according to a modified reference procedure.\textsuperscript{144,153} The molecular structures of the aminated and sulfonated PEO-based poly(urethane)s are displayed in Figure 3-4.

![Molecular structure](image)

Figure 3-4. Molecular structure of (a) quaternary ammonium functionalized PEO-based poly(urethane) (QA-PEO) and (b) sulfonated PEO-based poly(urethane) (Sulf-PEO).

LBL assemblies were deposited on silicon wafer substrates or ZnSe crystals. Silicon wafers were used as the substrate for zeta potential measurements. All silicon wafers were soaked
in methanol for 24 h then wiped clean with a lab wipe before use. For ATR-FTIR, LBL layers were assembled on 50 mm ZnSe crystals (New Era Enterprises, Vineland, NJ) used in a horizontal ATR (New Era Enterprises, Vineland, NJ) flow cell. ZnSe crystals were cleaned with methanol, ethanol, and methyl ethyl ketone sequentially using non-residue cotton swabs (Puritan Medical Products, Guilford, ME). All crystals were then cleaned with UV Ozone (Novascan, Ames, IA) under a N₂ purge for 20 min.

Aqueous solutions of sulfonated and aminated PEO-based poly(urethane)s (20 mM based on repeat unit) were prepared by stirring the polymer in 18.5 MΩ water for 12 h until fully dissolved. Cleaned substrates were first immersed in aminated PEO-based poly(urethane)solution for 15 min, followed by 1 min, 2 min, and 1 min rinsing in clean 18.5 MΩ water. The substrates were then immersed in sulfonated PEO-based poly(urethane) solution for 15 min, followed by the same rinsing routine in 18.5 MΩ water. The process was repeated to obtain thin films up to 6 bilayers with one layer of QA-PEO and one layer of Sulf-PEO yielding one bilayer.

3.3 Water uptake and hydration number

Water uptake of ionic poly(phenylsulfone) membranes was measured using a TA Instruments Q5000SA dynamic water vapor sorption (DVS) microbalance at 30 °C between relative humidities of 20% and 95%. Water uptake of polystyrene homopolymers and copolymers were measured using a quartz crystal microbalance with dissipation monitoring (QCM-D) at room temperature between relative humidities of 0% to 100%.

The hydration number (λ), or the number of water molecules per ionic group, was calculated from:

\[
\lambda = \left( \frac{m_{RH} - m_0}{M_{H_2O}} \right) \times \left( \frac{1000}{m_0 \times IEC} \right) \tag{3-1}
\]
where \( m_{RH} \) is the sample mass at a given RH, \( m_0 \) is the mass of the dry sample, \( M_{H_2O} \) is the molecular mass of water, and \( IEC \) is the ion exchange capacity.

3.4 Salt transport and water permeability of sulfonated poly(phenylsulfone) CEMs and aminated poly(phenylsulfone) AEMs

The water permeation and sodium chloride rejection measurement of sulfonated poly(phenylsulfone) CEMs and aminated poly(phenylsulfone) AEMs membranes were conducted in a dead end stirred cell (Sterlitech Corp., Kent, WA) at 25 °C using a 2000 ppm NaCl solution under constant pressure of 800 psi maintained by a high pressure regulator connected to a \( \text{N}_2 \) gas cylinder. The concentration of the permeate solution was measured by a calibrated conductivity probe (Ultrameter II, Myron L Co., Carlsbad, CA). The salt rejection, \( R_{NaCl} \), of the membrane was defined as:

\[
R_{NaCl} = \frac{c_f - c_p}{c_f} \times 100
\]  

(3-2)

where \( c_f \) is the concentration of the feed solution, \( c_p \) is the concentration of permeate solution. The permeate mass was also measured as a function of time. The water permeability was computed from the linear portion of the flux versus time curve from:

\[
P_w = \frac{V_{H_2O}d}{A \cdot t \cdot \Delta P}
\]  

(3-3)

where \( V_{H_2O} \) is the volumetric water transport across the membrane, (the slope of permeate mass vs. time), \( d \) and \( A \) are the thickness and area of the membrane, respectively, \( t \) is the permeation time and \( \Delta P \) is the applied pressure.66
3.5 Fourier transform infrared spectroscopy (FTIR) characterization of poly(phenylsulfone) membranes and polystyrene membranes

Thin films of AEMs and CEMs as well as polystyrene homopolymers and copolymers (~5 μm) were cast onto CaF₂ windows, dried as described above, then sealed in a FTIR transmission cell (New Era Enterprises, Vineland, NJ). Humid air containing 5 mol % D₂O with controlled relative humidity (RH) generated by mixing dew point humidified gas stream and dry gas streams was flowed (20 std. cm³ s⁻¹) through the cell while simultaneous FTIR spectra were recorded. The membrane sample was allowed to equilibrate at each RH (20 min to 1 h) and the transmission spectrum was collected using a Bruker (Billerica, MA) VERTEX 70 with an MCT detector. The spectra were monitored at each RH until they remain stable over a 5 min period. Each FTIR spectrum was taken at 2 cm⁻¹ resolution and 100 scans were collected. Origin software was used to fit two Gaussian peaks in the OD stretch region of 2700 cm⁻¹ to 2400 cm⁻¹. Peak fitting was conducted using local least squares method.

The spectra of an empty transmission cell in ambient environment and after dry air flow for 30 min were recorded. The two spectra were subtracted to obtain the water vapor spectrum under ambient conditions. The water vapor spectrum was then subtracted from the measured sample spectra to eliminate the ambient water rotation bands.

3.6 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) characterization of P(VDF-PFSVE) membranes.

P(VDF-PFSVE) membrane samples were equilibrated under different relative humidity of humidified air containing 50 % D₂O. The FTIR spectra of the membranes were recorded in attenuated total reflectance (ATR) mode with 2 cm⁻¹ resolution and 100 scans from 4000 cm⁻¹ to 650 cm⁻¹ using a Bruker (Billerica, MA) VERTEX 70 with a liquid nitrogen-cooled MCT
detector. P(VDF-PFSVE) membranes soaked in 50 % D2O solution were also measured in ATR-FTIR geometry. Membranes were taken out of the solution and the surface water was blotted away using laboratory wipes. The membranes were then quickly pressed onto ATR crystal for measurement. The spectrum of a clean ATR ZnSe crystal taken at the time of the sample measurement was used as a reference.

ATR ZnSe crystal was cleaned using non-residue cotton swabs (Puritan medical products, Guilford) with ethanol, dichloromethane and methyl ethyl ketone sequentially, followed by three dry cotton swab wipes to reduce solvent residual.

3.7 Streaming current and zeta potential

A SurPASS® (Anton Paar GmbH, Graz, Austria) electrokinetic analyzer was used to measure the streaming current as a function of the applied channel pressure cross a range of pH values. The slit-type channel was 2 cm in length, 1 cm in width and had a variable cell height that was set to approximately 100 μm (as indicated by the pressure/flow rate relationship through the cell) for all experiments. Flow was induced in the measurement cell by linearly ramping the differential pressure from 0 to 300 mbar in both directions. Two cycles of pressure ramping in each direction were conducted and the average slope of streaming current versus pressure, \(dI/dP\), value for all four cycles was used to compute the zeta potential after the raw data confirmed a linear relationship between the applied pressure and the measured streaming current, Figure 3-5. A 0.001 M KCl solution was used as the electrolyte and HCl (0.1 M) and NaOH (0.1 M) were used to adjust the pH. Before measurements, membranes were placed under a constant flow of 0.001 M KCl for at least 30 min to allow the ion exchange process to reach equilibrium. Samples were rinsed for 3 min at each pH point before the zeta potential was measured. The zeta potential
(ζ) of the membrane was computed using the Smoluchowski equation (Eq 3-4) from the measured average \( dI_s/dP \) values.

\[
\zeta = \frac{dI_s}{dP} \cdot \frac{\eta}{\varepsilon_0} \cdot \frac{L}{Wh}
\]  

(3-4)

where \( dI_s/dP \) is the change in streaming current versus pressure, \( \eta \) is the electrolyte viscosity, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon \) is the dielectric constant of the electrolyte, \( L \) is the length of the measuring cell, \( W \) is the width of the measuring cell and \( h \) is the height of the measuring cell.

Figure 3-5. Streaming current \( I_s \) versus applied pressure \( P \) for a poly(phenylsulfone) membrane.

To characterize the surface charge of free-standing films, two identical polymer samples were mounted on sample holders of the adjustable gap cell of the SurPASS system forming a slit-type channel between two sample surfaces.

LBL assemblies were first deposited on silicon wafer pieces (2 cm x 1 cm). After the desired number of layers were deposited, two silicon wafers with identical LBL assemblies were mounted into the adjustable gap cell and the surface zeta potential was characterized.
3.8 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) characterization of LBL assemblies

ATR-FTIR was employed to characterize the LBL assembly, its stability, and its protein and polysaccharide adsorption performance. After each layer was deposited on the ZnSe crystal surface, the spectrum of the LBL assembly was recorded and referenced to the clean crystal spectrum. FTIR spectra of LBL assemblies before and after different treatments (salt annealing, protein adsorption) were also monitored. All spectra were recorded with 2 cm$^{-1}$ resolution and 100 scans from 4000 cm$^{-1}$ to 650 cm$^{-1}$, using a liquid nitrogen-cooled MCT detector.

The spectra of a clean ZnSe crystal in ambient environment and in the flow cell under dry air flow for 30 min were recorded. The two spectra were subtracted to obtain the water vapor spectrum under ambient conditions. The water vapor spectrum was then subtracted from the measured spectra to eliminate the ambient water rotation bands.

3.9 Salt annealing of LBL assembly

The influence of salt annealing on the LBL assemblies was investigated by comparing the ATR-FTIR spectra and surface charge (zeta potential) of the assembly before and after exposure to salt solutions. LBL assemblies were prepared on ZnSe crystals and characterized in ATR-FTIR using a horizontal ATR-FTIR flow cell (New Era Enterprises, Vineland, NJ). The assemblies were sequentially exposed to 5 mL min$^{-1}$ flows of 18.5 MΩ water, NaCl solution (0.5 M, 1 M, 2 M and 3 M), and 18.5 MΩ water. The 18.5 MΩ water rinsing steps before and after salt treatment were performed for 1 h. Salt solution treatment was performed for 2 h. After treatment the LBL assembly was dried. The ATR-FTIR spectrum was recorded and compared to the spectrum of the sample before treatment.
For zeta potential characterization, LBL assemblies were deposited on silicon wafers. After soaking in 18.5 MΩ water for 1 h, the silicon wafers with the LBL films were soaked in 1 M NaCl solution for 2 h followed by 1 h soaking in pure 18.5 MΩ water. The zeta potential of the original and salt treated LBL assemblies were then characterized using the SurPASS system.

### 3.10 Protein and polysaccharide adsorption on the surface of LBL assembly

To investigate the influence of salt annealing on LBL assembly adsorption properties, protein and polysaccharide adsorption characterization were performed before and after the salt annealing. LBL assemblies with 5 layers (QA-PEO capped) or 6 layers (Sulf-PEO capped) were prepared on ZnSe crystals and mounted into a flow cell for ATR-FTIR measurement. Spectra were recorded every 3 min during sequential 5 mL min⁻¹ flow of 18.5 MΩ water, adsorbate solution, and then 18.5 MΩ water for 1 h each. After the adsorption experiment, LBL assemblies with adsorbed protein or polysaccharide were dried and spectra were recorded again. The same adsorption experiments were also carried out on LBL assemblies after 2 h annealing in 1 M NaCl solution. Protein adsorption measurements were performed with 200 mg L⁻¹ bovine serum albumin (BSA) (Sigma Aldrich, St. Louis, MO) in PBS buffer solution (pH 7.4). Polysaccharide adsorptions were performed with 2 g L⁻¹ sodium alginate (Sigma Aldrich, ST. Louis, MO) solution.

To obtain the mass of the protein and polysaccharide adsorbed, calibration of the FTIR spectra intensity versus mass was carried out. Solutions of protein or polysaccharide with known concentration and volume were dropped onto the ZnSe crystal surface. After the solution completely evaporated, a thin layer of the solute was left on the crystal surface. The mass of the solute per unit area of the surface was calculated based on the amount of solution dropped and the surface area of the ZnSe crystal. The FTIR spectrum was taken of the solute layer and the solute
signature peak intensity was correlated with the mass of the solute. After calibration with different amounts of solute, the relationship between FTIR spectra intensity and the adsorbed species mass was obtained. For bovine serum albumin, the 1547 cm\(^{-1}\) amide II peak was chosen for calibration, Figure 3-6. For sodium alginate, the 1041 cm\(^{-1}\) OH bend was chosen.

Figure 3-6. Amide II IR peak intensity versus surface mass density for BSA with best fit line through origin.
Chapter 4
Water Binding in Sulfonated and Aminated Poly(phenylsulfone)

4.1 Introduction

This chapter will discuss the investigation of the water-water and water-polymer interactions in sulfonated poly(phenylsulfone) (CEM) and quaternary ammonium functionalized poly(phenylsulfone) (AEM). These measurements help to rationalize the transport properties of the membranes because all transport occurs in the aqueous phase of polymer. Therefore, if the behavior of water is monitored, the movement of species through that water can be better understood.

FTIR was employed to probe the OD stretch vibration of water absorbed in the polymer membrane. The strength of the hydrogen bond which is influenced by the group hydrogen bonded to the HOD water molecule will affect the OD vibrational frequency. Based on the observed OD stretch frequency, information regarding the water-water and water-polymer interactions can be extracted and compared between polymers containing different functional groups. Transport properties of the AEM and CEM membranes that are relevant to desalination performance were studied and qualitative correlation were made to the water-binding in the membranes.

Additionally, the FTIR spectra of polymer membranes also contain vibrational peaks of certain functional groups in the polymer backbone. When there are water molecules hydrogen bonded to these sites, the bond vibration energy will be affected, result in a change of the vibrational frequency. By comparing FTIR spectra of dry and hydrated polymer membranes, the interactions between water and polymer can be detected through the peak shifts in the polymer fingerprint.
4.2 The OD stretch vibration of water absorbed in polymer membranes

Table 4-1. Properties of sulfonated poly(phenylsulfone) (sPS) and aminated poly(phenylsulfone) (aPS).

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ion exchange capacity (IEC) (mmol g⁻¹)</th>
<th>Water uptake (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS-II</td>
<td>1.1</td>
<td>13.3</td>
</tr>
<tr>
<td>sPS-IV</td>
<td>2.0</td>
<td>28.1</td>
</tr>
<tr>
<td>sPS-V</td>
<td>2.5</td>
<td>47.8</td>
</tr>
<tr>
<td>aPS-I</td>
<td>0.7</td>
<td>11.7</td>
</tr>
<tr>
<td>aPS-II</td>
<td>1.6</td>
<td>22.2</td>
</tr>
<tr>
<td>aPS-III</td>
<td>2.4</td>
<td>75.7</td>
</tr>
</tbody>
</table>

AEMs and CEMs selected for water binding study are listed in Table 4-1 as well as their IEC and water uptake. In the FTIR characterization of membranes hydrated with 5 % D₂O in H₂O, a broad peak in the OD stretch region between 2700 and 2400 cm⁻¹ with a high frequency shoulder at around 2640 - 2619 cm⁻¹ was observed at all RHs for both AEMs and CEMs, Figure 3-2.
Figure 4-1. (a). The OD stretch peak of sPS-II (1.1 mmol g\textsuperscript{-1}) at a \( \lambda \) of 4.1, sPS-IV (2.0 mmol g\textsuperscript{-1}) at a \( \lambda \) of 4.1 and sPS-V (2.5 mmol g\textsuperscript{-1}) at a \( \lambda \) of 4.6. (b). The OD stretch peak of aPS-I (0.7 mmol g\textsuperscript{-1}) at a \( \lambda \) of 5.6, aPS-II (1.6 mmol g\textsuperscript{-1}) at a \( \lambda \) of 4.3 and aPS-III (2.4 mmol g\textsuperscript{-1}) at a \( \lambda \) of 5.5. Hydration was obtained for each membrane by introducing the sample to 70% RH.

The spectra in Figure 4-2 of all AEMs and CEMs equilibrated at 70% RH were fit with two Gaussian peaks over a range of 2700 cm\textsuperscript{-1} to 2400 cm\textsuperscript{-1}. The lower frequency peak captured the position of the OD stretch and the higher frequency peak corresponded to the OD shoulder, which we interpreted as OD in a more hydrophobic environment.\textsuperscript{10} The peak deconvolution results (subpeak position and area) are shown in Table 4-2.
Figure 4-2. The OD stretch peak deconvolution of aPS-I (0.7 mmol g\(^{-1}\)) at a \(\lambda\) of 5.6, aPS-II (1.6 mmol g\(^{-1}\)) at a \(\lambda\) of 4.3, aPS-III (2.4 mmol g\(^{-1}\)) at a \(\lambda\) of 5.5, sPS-II (1.1 mmol g\(^{-1}\)) at a \(\lambda\) of 4.1, sPS-IV (2.0 mmol g\(^{-1}\)) at a \(\lambda\) of 4.1 and sPS-V (2.5 mmol g\(^{-1}\)) at a \(\lambda\) of 4.6. Hydration was obtained for each membrane by introducing the sample to 70% RH.
Table 4-2. OD stretch peak and shoulder frequencies and areas.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Main OD stretch position</th>
<th>Main OD stretch area</th>
<th>OD shoulder position</th>
<th>OD shoulder area</th>
<th>Shoulder to main stretch area ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>aPS-I</td>
<td>2515</td>
<td>3.2</td>
<td>2635</td>
<td>0.5</td>
<td>0.15</td>
</tr>
<tr>
<td>aPS-II</td>
<td>2509</td>
<td>16.0</td>
<td>2630</td>
<td>1.9</td>
<td>0.12</td>
</tr>
<tr>
<td>aPS-III</td>
<td>2510</td>
<td>49.1</td>
<td>2640</td>
<td>4.8</td>
<td>0.10</td>
</tr>
<tr>
<td>sPS-II</td>
<td>2553</td>
<td>16.6</td>
<td>2633</td>
<td>2.4</td>
<td>0.15</td>
</tr>
<tr>
<td>sPS-IV</td>
<td>2550</td>
<td>12.2</td>
<td>2628</td>
<td>0.9</td>
<td>0.08</td>
</tr>
<tr>
<td>sPS-V</td>
<td>2549</td>
<td>6.0</td>
<td>2619</td>
<td>0.2</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Different ionic functional groups will have distinct effects on the hydrogen bond network of water. Therefore, the difference between main OD stretch vibrational frequency of AEMs (2509 – 2515 cm\(^{-1}\)) and CEMs (2549 – 2553 cm\(^{-1}\)) reflects that water interacts differently with sulfonate or quaternary ammonium ionic groups, Table 4-2. The maximum intensity of the OD stretch occurs at a lower frequency in AEMs compared to CEMs, indicating that water is less bound in AEMs, which supports previous NMR studies.

Previous research conducted on water solvating cations and anions has shown that for water molecules directly surrounding a Na\(^+\) cation, the OH groups point away from the cation and are expected to form O-H···O hydrogen bonds with bulk water molecules. As a result, the water molecules solvating cations show very similar dynamics as bulk water and do not change with different cations. For water solvating anions, the O-H groups point toward the anion, forming direct hydrogen bonds with the anion and their dynamics vary with the species of anions. The research on water solvating cations and anions agrees with our finding that OD
stretch vibration frequency of AEMs was very close to that of bulk water (2509 cm$^{-1}$) while for CEMs the frequency displayed a blue shift comparing to bulk water.

Sulfonated poly(phenylsulfone) and aminated poly(phenylsulfone) have the same backbone composition but different ionic functional groups which leads to different ionic domain morphologies.$^{155}$ The shoulder frequency in the OD stretch region may be an indicator of the water in contact with polymer backbone in both AEMs and CEMs. The high frequency shoulders in the FTIR spectra of CEMs and AEMs occurred at significantly lower frequency than that of Nafion® (2695 cm$^{-1}$), Table 4-2. The high-frequency shoulder of Nafion® has a peak absorption frequency close to that of gas-phase HOD, 2724 cm$^{-1}$. Falk and Fayer interpreted the high frequency shoulder as an indication that these water molecules experienced a nonpolar environment and were probably in contact with the fluorocarbon backbone.$^{10,39}$ While Nafion®’s backbone is very hydrophobic and nonpolar, poly(phenylsulfone) has a less hydrophobic and more polarizable backbone. Thus, water molecules in contact with the poly(phenylsulfone) backbone in CEMs or AEMs displayed a lower OD stretch shoulder frequency compared to water in contact with Nafion®’s backbone. The higher OD shoulder frequency in AEMs (2630 – 2640 cm$^{-1}$) could result from a more dispersed water phase compared to the more clustered morphology of CEMs (2619 – 2633 cm$^{-1}$) as indicated by SAXS experiments in Hickner and Tudryn’s study.$^{155}$

The ratio of the shoulder area to the area of the OD stretch main peak decreased as IEC increased for both AEMs and CEMs, Figure 4-3. For higher IEC samples, more water takes part in solvating the ionic groups and swelling the hydrophilic domain thus the portion of water in contact with polymer backbone decreases. At higher IECs, AEMs also displayed a higher fraction of water that was in contact with the polymer backbone compared to CEMs.
Figure 4-3. The ratio of shoulder area to OD main stretch peak area for AEMs (▪) and CEMs (□).

### 4.3 Transport properties of AEMs and CEMs

Salt rejection, $R_{\text{NaCl}}$, and water permeability, $P_w$ of the AEMs and CEMs were measured to investigate the influence of ion content and type on the membrane transport properties, Figure 4-4.
Figure 4-4. Water permeability and salt rejection rate $R_{\text{NaCl}}$ versus ion exchange capacity (IEC) for AEMs (■) and CEMs (□).

Figure 4-4 shows that the permeability and rejection are inversely related for all materials. This tradeoff has been seen in many investigations of separation membranes, and was codified by upper bound observations.\(^{159-161}\) Polymers that are more permeable are generally less selective and vice versa. The results showed that as the membrane IEC increased, the water permeability of the membrane increased accordingly while the salt rejection decreased. The increase of water and salt transport with an increase in IEC resulted from higher water content in membranes with greater IEC yielding enlarged and better interconnected hydrophilic domains for water and salt transport. AEMs exhibited higher water permeability and lower rejection than CEMs with the same IEC. This trend in desalination performance is supported by the FTIR results demonstrating that the water in the hydrophilic domains of AEMs is less confined by the presence of the ionic group and is therefore more mobile.
4.4 Fingerprint region spectra shift upon hydration

Water molecules can interact with moieties on the polymer backbone which will shift the vibrational frequency of polymer functional groups in the fingerprint region compared to dry films, Figure 4-5, if there is sufficiently strong interaction. When a dry state spectrum is subtracted from the spectrum of a hydrated polymer, a derivative peak is obtained which characterizes the shift in the center of mass of the peak. The derivative maximum corresponds to the increasing interaction and the derivative minimum corresponds to the decreasing noninteracting functional groups on the polymer backbone, Figure 4-6. Thus, the magnitude of the derivative peak is an indicator of the increased interaction between water and polymer backbone upon hydration. While the peak shift is usually small (2-3 cm\(^{-1}\)) and very hard to accurately quantify, the magnitude of the derivative peak can provide us with a direct and clear demonstration of the population change in different vibration energy state.

Figure 4-5. The 1152 cm\(^{-1}\) diaryl sulfone vibration in the fingerprint region of sPS-V CEM under 0 % RH and 70 % RH.
Figure 4-6. The derivative peak of 1152 cm\(^{-1}\) diaryl sulfone in the fingerprint region of aPS-I AEM (black) and sPS-III CEM (gray) (70 % RH spectra ratioed to 0 % RH spectra).

All spectra were normalized by the intensity of the diaryl sulfone peak (1152 cm\(^{-1}\)) since the density of sulfone functional groups was relatively constant in each material. Derivative peaks were then obtained by subtracting dry state spectra (0 % RH) from the wet state spectra (70 % RH). Using this analysis procedure, the effects of water interacting with the polymer backbone could be quantified, Figure 4-7.

The normalized derivative peak magnitude versus membrane water uptake is displayed in Figure 4-7 for both AEMs and CEMs. It is clear that for CEMs, the water interacts less with polymer backbone as IEC and the water uptake increase. As the hydrophilic region enlarges and becomes better interconnected, more of the water absorbed is residing in the hydrophilic region and less of the water is still in contact with polymer backbone. While for the AEMs, water-polymer backbone interaction increases with the water uptake. The analysis of derivative peaks may give an indication of how water is dispersed within the polymer matrix and may be correlated to future measurements on membrane morphology and ionic group distribution.
Figure 4-7. The magnitude of derivative peak (1152 cm\(^{-1}\) diaryl sulfone) after normalization versus water uptake for AEMs (■) and CEMs (□).

**4.5 Conclusions**

By monitoring the OD stretch vibration in HOD-doped H\(_2\)O at 2700 to 2400 cm\(^{-1}\) using FTIR, information about the water-polymer interactions in ion exchange membranes was extracted and correlated to membrane transport performances. It was found by monitoring the OD stretch main peaks that water in quaternary ammonium functionalized AEMs interacted less with the functional groups and the AEMs exhibited higher water and salt transport due to less bound water. The high frequency shoulder of OD stretch peak showed the portion of water that was interacting with polymer backbone. Information about water-polymer backbone interaction could also be extracted from the peak shifts of the polymer backbone functional groups in fingerprint region. It was found that in CEMs water interacted with polymer backbone less strongly as IEC increases, while for AEMs the interaction became stronger. The difference in water-polymer backbone interaction could result from a more dispersed water phase in AEMs compared to the more clustered morphology in CEMs.
Chapter 5

Water Binding in Ion-functionalized Membranes

5.1 Introduction

For direct methanol fuel cells (DMFCs), research is being conducted to develop materials that have low methanol permeability and yet possess reasonably high conductivity. Several strategies have been attempted to reduce methanol permeability such as synthesizing sulfonated aromatic polymers where the methanol transport is lower by the presence of smaller hydrophilic domains compared to polyperfluorosulfonic acid membranes and incorporating inorganic additives into Nafion® and other polymer matrices to block methanol diffusion. Also crosslinked polymers and blends have been studied which decrease methanol permeability via restricting the water adsorption of PEMs.

In low methanol permeability membranes, the challenge remains that decreased conductivity usually accompanies reduced methanol permeability and therefore, the overall electrochemical selectivity is not improved. Electrochemical selectivity (\(E_s\)) is the ratio between proton conductivity \(\sigma_{\text{H}^+}\) and methanol permeability \(P_{\text{CH}_3\text{OH}}\):

\[
E_s = \frac{\sigma_{\text{H}^+}}{P_{\text{H}_2\text{O}}}
\]  

Xu, et al. have developed highly selective proton conductive networks based on chain-end functionalized polymers with perfluorosulfonate side groups. They first synthesized copolymers of vinylidene fluoride and perfluoro(4-methyl-3,6-dioxane-7-ene) sulfonyl fluoride containing amino end-groups. Then the amino-terminated P(VDF-PFSVE) copolymer was cross-linked through the formation of urea linkages and finally the sulfonyl fluoride groups was hydrolyzed to generate sulfonic acid groups. Chain-end crosslinking preserves the main-chain structure. The polymers have excellent electrochemical stability and superior acidity, and
crosslinking preserves the continuity of the proton conduction channel during swelling. The resulting P(VDF-PFSVE) crosslinked polymer membranes have displayed lower methanol permeability than Nafion® but maintained reasonable proton conductivity.

To explain the properties of these crosslinked P(VDF-PFSVE) polymer membranes, we investigated the water binding in the polymers and made correlations between the water behavior and membrane selectivity. Using FTIR, it was found that the interactions between water absorbed and the P(VDF-PFSVE) polymers became stronger with increasing IEC as well as increasing water content. The lack of bulk-like water in the crosslinked P(VDF-PFSVE) samples compared to Nafion® explained the low methanol permeability because the strongly bound water was not able to facilitate methanol transport. At the same time, the bound water still maintained some level of proton transport to yield highly selective membranes.

Phase separation plays an important role in the swelling and ion conductivity of ion-containing polymer membrane. We endeavored to investigate the water binding in membranes with different ionic phase separated morphologies. Specifically, we investigated homopolymers and block copolymers with ionic functional groups and characterized their interactions with water using FTIR. In this study, quaternary ammonium or imidazolium groups were tethered to poly(styrene) backbones. It was found that the homopolymers contained more bulk-like water due to a higher degree of functionalization compared to block copolymers. For block copolymers, the content of bulk like water increased with increasing IEC. Block copolymers with imidazolium groups displayed a higher fraction of bound water compared to quaternary ammonium functionalized polystyrene block copolymers.
5.2 Water binding in crosslinked P(VDF-PFSVE) membranes

5.2.1 Methanol permeability and proton conductivity

The proton conductivity and methanol permeability of P(VDF-PFSVE) membranes and Nafion\textsuperscript{®} are displayed in Table 5-1.\textsuperscript{14,15} It is clear that the proton conductivity increased with increasing IEC for P(VDF-PFSVE) membranes. PVDF-II, III, and IV membranes exhibited proton conductivity that was close or higher than 0.02 S cm\textsuperscript{-1}, due to high concentrations of PFSVE and the strong acidity of perfluorosulfonic acid groups. Nafion\textsuperscript{®} displayed higher proton conductivity than the P(VDF-PFSVE) membranes due to its higher water uptake and the phase separation in Nafion\textsuperscript{®}.\textsuperscript{15} However, the methanol permeability was significantly lower in P(VDF-PFSVE) membranes compared to Nafion\textsuperscript{®}, which resulted in higher electrochemical selectivity, Figure 5-1.

Table 5-1. Water uptake and transport properties of P(VDF-PFSVE) membranes and Nafion\textsuperscript{®}.\textsuperscript{14,15}

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Water uptake (wt. %)</th>
<th>Proton conductivity (S cm\textsuperscript{-1})</th>
<th>Methanol permeability (cm\textsuperscript{2} s\textsuperscript{-1})</th>
<th>Electrochemical selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-I</td>
<td>4 %</td>
<td>0.004</td>
<td>1.54×10\textsuperscript{-9}</td>
<td>3.6×10\textsuperscript{6}</td>
</tr>
<tr>
<td>PVDF-II</td>
<td>14 %</td>
<td>0.018</td>
<td>8.96×10\textsuperscript{-9}</td>
<td>2.0×10\textsuperscript{6}</td>
</tr>
<tr>
<td>PVDF-III</td>
<td>19 %</td>
<td>0.044</td>
<td>5.57×10\textsuperscript{-8}</td>
<td>7.9×10\textsuperscript{5}</td>
</tr>
<tr>
<td>PVDF-IV</td>
<td>26 %</td>
<td>0.066</td>
<td>9.91×10\textsuperscript{-7}</td>
<td>6.7×10\textsuperscript{4}</td>
</tr>
<tr>
<td>Nafion\textsuperscript{®}</td>
<td>29 %</td>
<td>0.084</td>
<td>1.98×10\textsuperscript{-6}</td>
<td>4.2×10\textsuperscript{4}</td>
</tr>
</tbody>
</table>
To investigate the water-binding in the P(VDF-PFSVE) membranes, FTIR was employed to monitor the OD stretch peak of water absorbed in the polymers. Dilute D$_2$O in water was used to avoid Fermi resonance in pure H$_2$O or pure D$_2$O which can influence the peak position as well as peak intensity. However, for the P(VDF-PFSVE) membrane series, the ATR-FTIR mode of spectral collection had to be employed due to the thickness of the crosslinked membrane, which made transmission collection of FTIR spectra impossible. In order to get strong and clear OD stretch signal in ATR-FTIR mode, 50 % D$_2$O in water was used to hydrate the membranes and the pure liquid signal with 50 % D$_2$O was also characterized.

The spectra of membranes equilibrated at different RH were compared and it was clear that the OD stretch peak shifted to higher frequency with increasing RH. An example is shown.

Figure 5-1. Electrochemical selectivity of the crosslinked P(VDF-PFSVE) membranes and Nafion.$^{15}$
for PVDF-IV membrane, Figure 5-2. For Nafion®, the OD stretch shifted to lower frequency with increasing RH due to the increase of bulk like water in Nafion®.9,10 For P(VDF-PFSVE) membranes, the shifting to higher frequency demonstrated the presence of more bound water with increasing RH due to strong water-polymer interactions.

Figure 5-2. The OD stretch peak of PVDF-IV membrane equilibrated under different RH.

To differentiate between the bulk-like water and the bound water, peak deconvolution was performed to obtain OD stretch peaks for these two states of water. All sample spectra were extracted from 2750 cm\(^{-1}\) to 2385 cm\(^{-1}\) and baselined using a two point baseline. Two peaks were fitted under the main OD stretch area with one peak maximum fixed 2484 cm\(^{-1}\), the OD stretch vibration frequency of 50 % D\(_2\)O in bulk water, Figure 5-3.

The low frequency peak at 2484 cm\(^{-1}\) represented OD stretch peak of bulk-like water, or water molecules hydrogen bonded to other water molecules. The high frequency peak represented
the bound water or water molecules that were associated with the polymer through hydrogen bonds or other interactions.

Figure 5-3. Peak fitting of the OD stretch region for PVDF-IV. (Black: original OD stretch vibration spectrum. Green: fitted sub peaks. Red: fitted OD peak.)

The peak deconvolution showing the bound water to bulk-like water peak area ratio are shown in Table 5-2. The bound water to bulk-like water ratio increased with increasing IEC. As discussed in Chapter 4 for functionalized poly(phenylsulfone) samples, the content of bulk-like water increased with increasing IEC as more water was involved in solvating the ionic groups and swelling the hydrophilic domains. Oppositely, there was a higher content of bound water in higher IEC P(VDF-PFSVE) membrane samples.
Table 5-2. Peak deconvolution results for PVDF-II, PVDF-III and PVDF-IV membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Position</th>
<th>Peak area</th>
<th>FWHM</th>
<th>Area ratio (high frequency peak to low frequency peak)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-II</td>
<td>2484</td>
<td>0.13</td>
<td>118.5</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>2568</td>
<td>0.1</td>
<td>120.7</td>
<td></td>
</tr>
<tr>
<td>PVDF-III</td>
<td>2484</td>
<td>1.19</td>
<td>116.8</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>2569</td>
<td>1.15</td>
<td>140.2</td>
<td></td>
</tr>
<tr>
<td>PVDF-IV</td>
<td>2484</td>
<td>2.64</td>
<td>115.4</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>2567</td>
<td>2.8</td>
<td>138.7</td>
<td></td>
</tr>
</tbody>
</table>

Methanol transports through interconnected hydrophilic regions filled with bulk-like water. For crosslinked P(VDF-PFSVE) membranes, the lack of bulk-like water compared to Nafion® rationalized their hindered methanol transport and lower methanol permeability. On the other hand, there was a large content of bound water in P(VDF-PFSVE) membranes. Even though these water molecules were bound to the polymer ionic group or polymer backbone, there was enough water to support proton conductivity. Thus, the proton transport was facilitated by the bound water and the methanol transport was suppressed, therefore the membranes displayed overall high proton conductivity.

5.3 Water binding in poly(styrene)-based homopolymers and block copolymers with quaternary ammonium and imidazolium functional groups

Poly(styrene)-based homopolymers and block copolymers with quaternary ammonium and imidazolium functional groups in Cl⁻ form¹⁵¹,¹⁵² were hydrated with humidified air containing
5 % D₂O and FTIR spectra were recorded. The OD stretch peak was monitored to obtain information regarding the water binding within the polymer membranes.

To quantify the content of bulk-like water and bound water, the OD stretch peak spectra between 2400 cm⁻¹ and 2650 cm⁻¹ were extracted and baselined. Two peaks were fitted under the OD stretch region with one peak corresponding to bulk-like water (peak frequency fixed at 2509 cm⁻¹, the OD stretch frequency for bulk water containing 5 % D₂O). For low IEC polystyrene copolymers, peaks at 2582, 2603 and 2632 cm⁻¹ corresponding to monosubstituted benzene rings were also fitted under the OD stretch peak.

Displayed in Figure 5-4 are examples of the OD stretch vibration peak deconvolution. The low frequency peak at 2509 cm⁻¹ represents the contribution from bulk-like water while the high frequency peak represents bound water. The area ratio between these two peaks was compared for homopolymers and block copolymers, Table 5-3.

The area ratios from peak deconvolution for the samples are listed in Table 5-3. The area ratio of the high frequency peak to the low frequency peak reflects the content of bound water compare to bulk-like water. Higher ratio indicates that a membrane contains more bound water.

It is clear that homopolymers contained a lower amount of bound water compare to the block copolymers. Due to the high degree of functionalization in homopolymers, they had much higher water uptake than the copolymers. Thus the amount of bulk-like water was relatively high in homopolymers. For block copolymers, the content of bound water was lower for higher IEC membranes because the higher concentration of ionic groups resulted in enlarged hydrophilic domains and a higher fraction of bulk like water. Additionally, the hydrophobic/hydrophilic phase boundaries in the block copolymers could influence the water binding in these samples.
Figure 5-4. Peak deconvolution of the OD stretch region for PS-Im and PS-b-PVBIm copolymers. (Black: original OD stretch vibration spectrum. Green: fitted sub peaks. Red: fitted OD peak.)
Table 5-3. Peak deconvolution results for PS-QA, PS-b-PVBQA, PS-Im and PS-b-PVBIm membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Position</th>
<th>Peak area</th>
<th>FWHM</th>
<th>Area ratio (high frequency peak to low frequency peak)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-QA</td>
<td>2509</td>
<td>12</td>
<td>102.2</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>2548</td>
<td>1.2</td>
<td>51.2</td>
<td></td>
</tr>
<tr>
<td>PS-b-PVBQA-1</td>
<td>2509</td>
<td>2.9</td>
<td>104.4</td>
<td>0.175</td>
</tr>
<tr>
<td></td>
<td>2557</td>
<td>0.5</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2582</td>
<td>0.05</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2603</td>
<td>0.1</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2632</td>
<td>0.16</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>PS-b-PVBQA-2</td>
<td>2509</td>
<td>9.4</td>
<td>116.4</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>2557</td>
<td>1.5</td>
<td>95.6</td>
<td></td>
</tr>
<tr>
<td>PS-Im</td>
<td>2509</td>
<td>16.7</td>
<td>144.6</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>2530</td>
<td>3.2</td>
<td>80.3</td>
<td></td>
</tr>
<tr>
<td>PS-b-PVBIm-1</td>
<td>2509</td>
<td>1.6</td>
<td>90.6</td>
<td>0.803</td>
</tr>
<tr>
<td></td>
<td>2542</td>
<td>1.3</td>
<td>116.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2582</td>
<td>0.04</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2603</td>
<td>0.1</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2634</td>
<td>0.21</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>PS-b-PVBIm-2</td>
<td>2509</td>
<td>3.5</td>
<td>104</td>
<td>0.594</td>
</tr>
<tr>
<td></td>
<td>2542</td>
<td>2.1</td>
<td>127.1</td>
<td></td>
</tr>
</tbody>
</table>
It is also worth noting that polymers containing the imidazole group displayed a higher content of bound water compared to polymers containing quaternary ammonium functional groups. Based on the position of the bound water OD peak, the interaction between water and imidazole was stronger than the interaction between water and quaternary ammonium, thus the imidazole functionalized polymers contained more bound water.

The difference in phase segregation between PS-b-PVBQA and PS-b-PVBI can also be the reason of more bound water in PS-b-PVBI. For example, PS-b-PVBI could have smaller size hydrophilic domains thus less bulk like water. But without characterization of the phase separated morphology, the effect of phase segregation on water-binding for these samples has yet to be determined.

5.4 Conclusions

Crosslinked P(VDF-PFSVE) membranes displayed better electrochemical selectivity than Nafion® while having relatively high proton conductivity and were good candidates for direct methanol fuel cell membranes. To understand their superior performance, FTIR was employed to monitor the OD stretch of water absorbed in the membrane and obtain information about water binding within the polymer membranes. It was found that P(VDF-PFSVE) membranes contained more bound water with increasing relative humidity or increasing IEC compared to minimally hydrated or low IEC samples. The lack of bulk-like water explained their low methanol permeability. There was enough bound water to facilitate proton transport while still impeding the methanol transport.

The water binding in ionically functionalized polystyrene-based homopolymers and block copolymers was studied and compared to determine ionic type and phase separation effects on water-polymer interactions. It was observed that homopolymers contained more bulk-like
water due to a higher degree of functionalization and higher water uptake than the block copolymers. For block copolymers, the content of bound water decreased with increasing IEC. When comparing the influence of different ionic functional groups, it was found that imidazolium chloride functionalized polymers displayed a higher content of bound water compared to quaternary ammonium chloride functionalized polymers. The fact that water interacted stronger with the imidazole group compared to the quaternary ammonium groups explained the OD water binding.
Chapter 6

Streaming Current Measurement for Characterizing Zeta Potential of Ionic Polymer Membranes

6.1 Introduction

This chapter will discuss applying the streaming current measurement, which is traditionally employed for characterizing the zeta potential of non-conductive materials, to ionic polymer membranes with relatively high conductivity. The ionic polymer membrane surface charge group density should increase with increasing ion exchange capacity (IEC) of the bulk membrane, up to ionic dilution due to too high water swelling, leading to increases in the magnitude of the surface charge with IEC. However, during the steaming current measurement, we observed that the surface zeta potential first became more negative with increasing IEC, and then became less negative when the IEC was further increased. Besides IEC, the thickness of the membrane was also shown to have an influence on the measured zeta potential where thicker membranes had smaller zeta potentials.

Membrane ionic conductance was taken into consideration and offered a reasonable explanation for the effects that IEC and thickness had on measured zeta potential. Different from non-conductive materials, ions concentrated in the area adjacent to the conductive membrane surface could partially back flow through the ionic polymer membrane during streaming current measurement, resulting in a smaller net streaming current in the fluid channel, Figure 6-1.
Figure 6-1. Illustration of the streaming current generated by electrolyte flow through the channel and the back flow current through the membrane bulk.

Linear regression regarding membrane thickness was proposed as a method to correct the effect of conductivity on measured streaming current and proven feasible. Measurement of thin film zeta potential confirmed the thickness effects and supported thickness-corrected zeta potential analysis.

### 6.2 Measured zeta potential versus IEC and membrane thickness

The computed zeta potentials from streaming current measurements of the sulfonated poly(phenylsulfone) membranes with thicknesses of approximately 20 - 30 µm were negative at high pH and became less negative as pH decreased, Figure 6-2. This increase in zeta potential with a decrease in pH could be explained by the promoted protonation of sulfonic acid groups in a lower pH environment leading to more contact ion pairs which did not contribute to the surface charge. A similar trend of less negative zeta potential was observed for neutral surfaces that tend to attract anions. When pH decreased, the absorption of cations was enhanced thus a less negative surface charge was measured.
At pH 5, the zeta potentials computed directly from the measured streaming current for each sample became more negative as the IEC of the membrane increased up to 1.1 mmol g\(^{-1}\). When the IEC exceeded 1.1 mmol g\(^{-1}\), the computed zeta potentials became less negative with increasing IEC, Figure 6-3. For surfaces without ionizable groups, the adsorption of ions from solution can result in surface charges comparable to those of surfaces with tethered ionizable groups.\(^{35}\) Often, anion adsorption to hydrophobic surfaces (because of the anions minimal hydration shell compared to cations) causes the surface to display a negative zeta potential. The surface adsorption of ions changes with pH and thus the computed zeta potentials are a function of solution pH and often solution composition. In this series of experiments on polymers with fixed ionic charges, the surfaces with low ionizable functional group density displayed more negative zeta potentials compared to the unfunctionalized polymer surface. It is reasonable to
assume that membranes with negatively charged sulfonate groups covalently bound to the polymer should have a comparable or more negative zeta potential than their unsulfonated analog. At low IECs, the functional group ionization on the surface of the membrane lowered the measured zeta potential compared to the unfunctionalized surface, e.g. in Figure 6-3 the zeta potential of the unfunctionalized surface was about -40 mV at pH 5, while the zeta potential for the surface of a membrane with 0.6 mmol g⁻¹ IEC was -52 mV and decreased to -72 mV for a membrane with 1.1 mmol g⁻¹ sulfonate groups. When the fixed charge density (IEC) of the membranes increased further, the conductance of the membranes had an influence on the measured streaming currents so the computation of zeta potential directly from the streaming current was not valid, as will be discussed in the following paragraphs.

![Graph showing zeta potential at pH 5 versus IEC for the series of sulfonated poly(phenylsulfone) membranes.](image)

Figure 6-3. Zeta potential at pH 5 versus IEC for the series of sulfonated poly(phenylsulfone) membranes.
Figure 6-4. Zeta potential versus pH for (a) sPS-II (IEC: 1.1 mmol g\(^{-1}\)) and (b) sPS-IV (IEC: 2.0 mmol g\(^{-1}\)) membranes of different thickness \(d_m\).
Werner, et al. also reported the phenomenon of decreasing zeta potential with increasing IEC in their streaming potential measurements on sulfonated poly(ethersulfone) membranes: the zeta potential for less substituted poly(ethersulfone) membranes was more negative than for materials with higher ionic substitution\(^{18}\). They explained this trend by hypothesizing that the sulfonic acid groups increased the thickness of the swelling layer at the membranes’ surface and changed the location of the shear plane. Their interpretation does not explain the phenomena observed in the present experiments. First of all, the more negative zeta potential of sPS-II (IEC 1.1 mmol g\(^{-1}\)) compared to sPS-I (0.6 mmol g\(^{-1}\)) did not fit their explanation. Secondly, a correlation between measured zeta potential and membrane thickness was observed, Figure 6-4. This data cannot be rationalized by the increased thickness of the swelling layer at the surface of the membranes, since all of the membranes were of the same material with the same membrane/solution interface.

Figure 6-4 shows that the computed zeta potential versus pH curves trend toward zero with increasing thickness of membranes of the same composition. The hydrophilicity of sulfonic acid groups, per Werner, et al.’s explanation, is not able to account for the change in zeta potential with membrane thickness, so the effect cannot be just at the surface. From the prospective of membrane conductivity through the thickness of the sample, the trend is clearly in accordance with the data presented in Figure 6-2 and Figure 6-3 where samples with lower resistance (higher thickness or higher ion conductivity) displayed less negative zeta potential values.

### 6.3 The influence of membrane conductance

Based on these observations, instead of membrane hydrophilicity and swelling at the interface, membrane conductivity appears to be an important factor in the streaming current
measurement and thus the calculation of zeta potential. In the slit microchannel geometry used in these experiments, the electrolyte flow sheared away the ions in the diffuse layer of the surface and induced a streaming current. In the case of a non-conductive channel boundary, the amount of ions driven by the hydrodynamic force to the end of the channel will be measured by drawing the current off through a low impedance electronic circuit, which short-circuits the return path through the conducting liquid.\textsuperscript{15} The zeta potential is calculated from the measured streaming current and the dimensions of the cross section of the slit channel. But with the sulfonated poly(phenylsulfone) membranes in this study and Werner, et al.’s sulfonated poly(ethersulfone) membranes, the conductivity of the membrane bulk is comparable to, or greater than the conductivity of the electrolyte in the channel. As a result, the ions driven by hydrodynamic force could flow back through the membrane due to the potential difference generated by the streaming current, leading to a smaller value of streaming current measured between the two ends of the channel as shown in Figure 6-1. In the case of a conductive membrane, the highest resistance path is through the electrolyte solution, so ionic current will naturally flow through the conductive membrane bulk instead of in the electrolyte channel. As shown in Eq 6-1, the original streaming current $I$ is reduced by the backflow current through the membrane $I_m$, resulting in a smaller measured streaming current $I_s$. Accordingly, the calculated zeta potential would become smaller when significant back flow of current occurs through the ion-conductive membrane.

\[ I_s = I - 2I_m \]  \hspace{1cm} (6-1)

Using this framework of a conductive path through the membrane, the change of zeta potential with IEC or membrane thickness is explicit. As IEC increases, membrane conductivity increases and membrane resistance decreases. Thus, more ions back flow through the membrane bulk, resulting in a smaller measured streaming current and a smaller computed zeta potential. For membranes of the same IEC polymer, as membrane thickness increases, membrane resistance also decreases which will decrease the streaming current accordingly. Since the surface properties
do not change with membrane thickness, the backflow current, \( I_m \), must be a function of membrane thickness to explain the data shown here. Previous work has demonstrated that the streaming channel can be treated as ohmic,\(^{32} \) so in the simplest ohmic model for the membrane resistance, we can use a linear extrapolation of \( d_m \) to determine if a parallel ohmic resistance description is sufficient for the materials and conditions examined.

We are not the first to observe an influence of membrane conductivity on the streaming current and steaming potential measurements. A series of studies have been carried out on “soft surfaces” such as chemically crosslinked gels and adsorbed layers of polymers or polyelectrolyte, which allow ion penetration and limited solvent flow within the polymer matrix.\(^{169–175} \) The soft surface layer’s intrinsic charge and permeability to ions allow counterions to reside inside the layer bulk and partly screen the fixed charge. The counterions inside the polymer layer are mobile and migrate under the action of the tangential field to give a surface current. Ohshima and Kondo first developed a model to describe the counterion distribution and potential drop across the polymer layer.\(^{173–175} \) Dukhin, et al. further extended the model for incomplete dissociation of functional groups under different pH.\(^{171,172} \)

However, according to their description, the mobility of counterions inside the soft layer and the flow developed within the layer contributed to the total streaming current.\(^{169,170} \) Oppositely, we have observed a decrease of streaming current caused by current inside the membrane. Therefore, instead of their view of flow inside the porous layer which is in the same direction of the bulk electrolyte flow, our assumption of a conductive path that allows ions to back flow through the membrane is more applicable to the materials studied here.

On the other hand, their discussion regarding the influence of membrane conductivity only involved streaming potential measurement. Thus an investigation on streaming current and the influence of membrane conductivity is much needed.
6.4 Correction for the effect of membrane conductance

For the Radel and sPS-I (IEC: 0.6 mmol g\(^{-1}\)) samples, the membrane conductivities were low, and the conductivity influence on the measured streaming current was small. There was only a small decrease of measured streaming current with increasing membrane thickness for Radel and sPS-I membranes, Figure 6-5. For sPS-I and sPS-II membranes with thicknesses of 20 - 30 μm, sPS-I membrane displayed a less negative zeta potential than sPS-II. This result reflected the lower density of sulfonate groups in sPS-I compared to sPS-II and their bulk conductivities were small enough not to have a large effect on the streaming current. These two samples containing negatively-charged sulfonate groups displayed measured zeta potentials more negative than that of the unsulfonated membrane.

Figure 6-5. Measured streaming current at pH 5 as a function of applied pressure \(dl/dP\) versus membrane thickness \(d_m\) for Radel (△), sPS-I (●), sPS-II (◇), and sPS-IV (■) membranes.
The measured $dI/dP$ values at pH 5 were plotted as a function of sample thickness ($d_m$) and extrapolated to zero membrane thickness (membrane resistance infinite), as shown in Figure 6-5. Linear regression with respect to $d_m$ would eliminate the influence of $I_m$ and resulted in the original streaming current without the influence of membrane conductance. The corrected $dI/dP$ values and the accordingly corrected zeta potential ($\zeta_c$) values displayed a different trend, Error! Not a valid bookmark self-reference., than was shown previously in Figure 6-3. For the corrected results, membranes of higher IEC had more negative zeta potentials as shown in Figure 6-6 which was in agreement with the expectation that higher IEC membranes contained more negatively charged functional groups and thus should display a more negative zeta potential.

Table 6-1. The measured and corrected values of $dI/dP$ and zeta potential for Radel, sPS-I, sPS-II and sPS-IV membrane of sample thicknesses of 20 - 30 μm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$dI/dP$ (mA/mbar)</th>
<th>$\zeta$ (mV)</th>
<th>Corrected $dI/dP$ (mA/mbar)</th>
<th>$\zeta_c$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radel</td>
<td>-1.8*10^{-7}</td>
<td>-40.9</td>
<td>-2.0*10^{-7}</td>
<td>-49.7</td>
</tr>
<tr>
<td>sPS-I</td>
<td>-2.1*10^{-7}</td>
<td>-51.6</td>
<td>-2.4*10^{-7}</td>
<td>-59.6</td>
</tr>
<tr>
<td>sPS-II</td>
<td>-2.6*10^{-7}</td>
<td>-71.8</td>
<td>-3.5*10^{-7}</td>
<td>-97.7</td>
</tr>
<tr>
<td>sPS-IV</td>
<td>-1.3*10^{-7}</td>
<td>-34.6</td>
<td>-4.4*10^{-7}</td>
<td>-116.7</td>
</tr>
</tbody>
</table>
6.5 Zeta potential of thin polymer membranes

Additional measurements on thin (~5 µm) sulfonated poly(phenylsulfone) films on KAPTON® substrates also supported the thickness-corrected results obtained on 15 - 90 µm films. A more negative zeta potential was computed from streaming current measurements on the thin-film sample with higher IEC, Figure 6-7. As the membrane became thin enough, the effect of membrane conductivity was minimized and the zeta potential was predominately determined by surface charge density, or by extension, the polymer IEC. These results, along with the data presented in Figure 6-5 demonstrated that the entire membrane resistance must be taken into account in the streaming current analysis and the membrane resistance may be treated as ohmic. Simply considering the surface hydration or other polymer/electrolyte interfacial phenomena is
not sufficient to capture the data presented here. The deviation between thin film zeta potential and the corrected zeta potential extrapolated to zero membrane thickness still showed the influence of membrane conductance, even though the effect is small in the case of thin films.

![Zeta potential versus pH for thin films, sPS-II (■) and sPS-IV (▲), on Kapton substrates.](image)

Figure 6-7. Zeta potential versus pH for thin films, sPS-II (■) and sPS-IV (▲), on Kapton substrates.

### 6.6 Conclusions

Accurately characterizing zeta potential has been an important issue for investigating the charging behavior of solid surfaces in contact with aqueous solutions. During the zeta potential measurements of sulfonated poly(phenylsulfone) membranes, we found that membrane bulk conductivity could induce large perturbations of the measured streaming current, and thus the computed zeta potential, for ion-conductive membranes. Both membrane IEC and membrane thickness affected membrane conductance thus had an influence on the measured membrane zeta
potential. Streaming current measurements on thin membranes supported the argument.

Measuring membrane zeta potential at different membrane thicknesses and using a parallel ohmic resistance model to eliminate the influence of bulk conductivity has proven to be a feasible route to obtain results that reflect the membrane composition.
Chapter 7

Layer-by-Layer Assembly for Surface Antifouling Modification

7.1 Introduction

In this chapter the potential of layer-by-layer (LBL) assembly as a surface antifouling coating is discussed. This study acquired a better understanding of the structures, properties and performances of LBL assemblies under desalination and fouling conditions. It would benefit future antifouling materials development and techniques to interrogate surface modification layers.

Anionic and cationic poly(ethylene oxide)-based poly(urethane)s were electrostatically assembled into thin layer-by-layer (LBL) films and successfully incorporated hydrophilic PEO segment that are beneficial to antifouling onto a surface. The resulting coating was proven stable in water and salt solutions up to 3 M. The PEO-based poly(urethane)s LBL assembly surface displayed lower bovine serum albumin adsorption than ionic poly(phenylsulfone) which was employed in reverse osmosis.

Using ATR-FTIR, the properties of the LBL assembly were monitored during the assembly process. It was found after six (6) layers the assembly ceased to grow due to lower surface overcharging of thicker films as confirmed by zeta potential measurements. The effect of salt annealing on the LBL assembly was also studied by ATR-FTIR and surface charge characterization. It was revealed that the assemblies went through internal restructuring after immersion in salt solution. Interdiffusion between layers was promoted by breaking of the ionic bonds between the anionic and cationic polymers and the surface charge became closer to neutral due to mixing of the polymers.
ATR-FTIR is a powerful tool for studying the kinetic adsorption of different species onto the LBL surface. The protein and polysaccharide adsorption behaviors on LBL assembly before and after salt annealing were studied and discussed. Bovine serum albumin displayed very different behavior from sodium alginate, reflecting the role surface charge and surface charge group distribution played in their adsorption.

7.2 Layer-by-layer assembly process

In FTIR spectra of the LBL assemblies, the signature peaks of the PEO-based poly(urethane)s, including the carbonyl C=O stretching vibration ($\nu$) at 1701 cm$^{-1}$, -CH$_2$- symmetrical and asymmetrical stretching vibration ($\nu_s$ and $\nu_a$) at 2918 cm$^{-1}$ and 2850 cm$^{-1}$, C=C stretching vibration ($\nu$) of ring between 1625 cm$^{-1}$ and 1430 cm$^{-1}$, and ether C-O-C stretching vibration ($\nu$) at 1112 cm$^{-1}$ were clearly resolved, Figure 7-1. Additionally, the 1223 cm$^{-1}$ asymmetrical ($\nu_a$) and the 1036 cm$^{-1}$ symmetrical stretching vibration ($\nu_s$) of hydrated sulfonic acid groups could be observed. Peak positions and assignments are listed in Table 7-1. In these spectra, a cleaned ZnSe crystal spectrum was used as a reference. The negative peaks in the spectrum shown in Figure 7-1 indicated that surface species were displaced from the crystal upon LBL assembly. The negative peaks are in the 3620 cm$^{-1}$ to 2950 cm$^{-1}$ and 1580 cm$^{-1}$ regions of the spectrum indicating that species containing OH and carbonyl moieties (likely residuals from the cleaning solvents) were displaced. Displacement of surface species demonstrated the presence of strong bonds between the LBL assemblies and the ZnSe crystal.
Figure 7-1. FTIR spectrum of 4 bilayers of LBL film on ZnSe crystal and its main features.

Table 7-1. Signature IR peaks of PEO-based polyurethane(s) LBL.

<table>
<thead>
<tr>
<th>Number</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2918</td>
<td>-CH(_2)- symmetrical stretching vibration</td>
</tr>
<tr>
<td>2</td>
<td>2859</td>
<td>-CH(_2)- asymmetrical stretching vibration</td>
</tr>
<tr>
<td>3</td>
<td>1703</td>
<td>C=O stretching vibration</td>
</tr>
<tr>
<td>4-7</td>
<td>1617, 1537, 1463</td>
<td>C=C stretching of ring</td>
</tr>
<tr>
<td>8</td>
<td>1112</td>
<td>C-O-C stretching vibration</td>
</tr>
<tr>
<td>7, 9</td>
<td>1223, 1036</td>
<td>SO(_3^−)H(_3)O(^+) asymmetrical and symmetrical stretching vibration</td>
</tr>
</tbody>
</table>
Figure 7-2. FTIR spectra of alkyl peaks (left) and carbonyl peaks (right) as LBL layers were deposited.

Figure 7-3. The intensity of alkyl peaks at 2859 cm\(^{-1}\) (left) and carbonyl peaks at 1703 cm\(^{-1}\) (right) versus layer number.

A cleaned ZnSe crystal was alternately exposed to the anionic and cationic PEO solutions as described in the experimental section. The addition of single layers during LBL assembly was resolved in the multireflection geometry used for ATR-FTIR experiments. Figure 7-2 shows the increasing intensity of alkyl and carbonyl peaks as layers were deposited on the ZnSe crystal surface.
The intensity of the 2859 cm$^{-1}$ and 1703 cm$^{-1}$ bands are plotted in Figure 7-3, which shows that the LBL assembly ceased growth after about 6 layers (3 bilayers).

![Zeta Potential Plot](image)

Figure 7-4. Zeta potential ($\zeta$) of the LBL assembly for sequential surface layers.

Overcharging is known to control the growth of LBL assemblies.$^{176,177}$ Figure 7-4 shows the zeta potential of the silicon wafer substrate (0 layer number) and the assembly as a function of layer. The silicon wafer substrate was negatively charged. After the first QA-PEO layer was deposited, the surface charge became positive. Following the deposition of the next Sulf-PEO layer, the surface charge became negative again. This repeated alternation of surface charge during LBL assembly was observed in other LBL systems as well.$^{178-180}$ To enable layer deposition, the outermost surface must possess an excess charge which is the driving force for absorption of the next layer. Each deposited layer in turn leads to an overcompensation of the previous charge excess.$^{176,177}$
However, after 6 layers, it was observed that the magnitude of the surface charge was greatly reduced. Layer intermixing is known to occur in LBL assemblies. Figure 7-4 shows that interpenetration of the layers eventually diminished the surface overcharge, reducing the surface zeta potential greatly after 6 layers. This reduction in excess surface charge lead to the weakening of the electrostatic forces that governed assembly, and consequently, the growth of the assembly stopped. Because the copolymers in this study have a low density of ions along the backbone and highly mobile PEO segments, the rearrangement of the layers during assembly is feasible. For low layer numbers, the rearrangement is constrained by the substrate. But for thick enough films, the layers are able to rearrange and the surface overcharging is decreased.

7.3 The effect of salt annealing on LBL assembly

These LBL assemblies have shown surprising stability during processing in aqueous base and salt solutions. It is possible that salt annealing of the LBL assemblies would promote further interdiffusion of the Sulf-PEO and QA-PEO polymers to create a more uniformly mixed charge surface which is known to display antifouling character. Therefore the effect of salt annealing on LBL assembly was investigated.

Figure 7-5 shows that little of the polymer from the LBL assembly was lost after exposure to 3 M NaCl solution for 1 h and rinsing with DI water for 1 h. The intensity of the main bands of the base polymer PEO-based poly(urethane)s, for example 1701 cm⁻¹ C=O stretching and C=C stretching ring modes at 1617, 1537 and 1463 cm⁻¹, did not significantly decrease with salt treatment. However, significant restructuring of the film occurred as indicated by the changes in the 1263 and 1074 cm⁻¹ regions corresponding to the sulfonic acid groups.
Figure 7-5. FTIR spectra of 3 bilayers LBL film. Black: before salt treatment; Red: after 1 h soaking in 3 M NaCl solution.
Figure 7-6. FTIR spectra showing a peak at 1263 cm\(^{-1}\) appeared after 0.5 M and 2 M salt solution treatment. Black: before salt treatment; Red: after salt treatment.

Treatment of the LBL film in water had no significant effect on the spectrum, while soaking the films in salt solution lead to the appearance of two peaks, 1263 cm\(^{-1}\) and 1074 cm\(^{-1}\), corresponding to sulfonic acid salts SO\(_3\)M\(^+\), with a higher concentration of salt leading to a more dramatic change in 1263 cm\(^{-1}\) and 1074 cm\(^{-1}\) peaks. The change of 1263 cm\(^{-1}\) peak is depicted in Figure 7-6. These structural changes indicated that salt ions from the solutions did break some of the electrostatic crosslinks in the film and associated to any remaining unpaired sulfate groups which resulted in free
sulfonic acid salts. However, the films still had enough electrostatic bonds left to hold the polymer chains on the surface and the assemblies did not disintegrate during immersion in salt solutions.

Figure 7-7. FTIR spectra of 5 layers LBL assembly before salt annealing (black line), after 1 M NaCl salt annealing for 2 h then rinse with DI water for 3 min (blue line) and 1 h (red line).

In FTIR spectra of LBL assemblies before and after salt annealing and after short or long periods of 18.5 MΩ water rinsing, Figure 7-7, it was observed that the OH band intensity increased after salt annealing and remained relatively constant whether the assembly was rinsed for 3 min or 1 h in water. The water content of the LBL assembly increased after the electrostatic crosslinks were disrupted in the film by salt treatment. Schlenoff, et al. have also observed LBL assembly swelled on exposure to salt solution with salt ions breaking the ionic crosslinks. In our study, the PEO-based polyurethane LBL investigated in this study was constructed using polymer solutions with no added
salt during assembly. After exposure to salt solution, salt ions were absorbed into the assemblies and broke some of the electrostatic crosslinks. The LBL assemblies became more hydrophilic and the effect is irreversible.

Figure 7-8. ζ potential at pH 5 of 5 layers (positive surface) and 6 layers (negative surface) LBL assembly before and after 1 M NaCl solution treatment for 2h.

Figure 7-8 displays the zeta potential at pH 5 of 5 or 6 layer LBL assemblies surfaces before and after 2 h salt annealing in 1 M NaCl solution. Before salt annealing, the 5 layer LBL assembly capped with QA-PEO possessed a positive surface charge while the 6 layer LBL assembly capped with Sulf-PEO had a negative surface charge. Upon exposure to salt solution, salt ions came into the LBL assembly and broke the polymer electrostatic crosslinks. Salt annealing promoted the interdiffusion of polymer chains between different layers, leading to a more neutral surface charge.
7.4 Bovine serum albumin (BSA) adsorption on LBL assemblies and ionic poly(phenylsulfone) surfaces

Protein (bovine serum albumin) and polysaccharide (sodium alginate) adsorption were performed on LBL assemblies with differently charged capping layers to evaluate their potential as an antifouling surface modification.

Bovine serum albumin (BSA) adsorption on LBL assemblies with Sulf-PEO (IEC: 2.37 mmol g\(^{-1}\)) or QA-PEO (IEC: 2.05 mmol g\(^{-1}\)) capping layer was compared to the BSA adsorption on anionic poly(phenylsulfone) (IEC: 2.5 mmol g\(^{-1}\)) or cationic poly(phenylsulfone) (IEC 2.1 mmol g\(^{-1}\)) membranes, Figure 7-9. PEO-based poly(urethane)s LBL assembly displayed much less BSA adsorption than the poly(phenylsulfone) thin films, which are considered candidates for water treatment membranes.\(^{45,66,82,181}\) This comparison demonstrated good potential of PEO-based poly(urethane) LBL as an antifouling coating for reverse osmosis membranes due to the strong hydrophilicity of PEO segment and stability afforded by the electrostatic assembly of the layers.

The QA-PEO capped positively charged surface displayed more protein adsorption than Sulf-PEO capped negatively charged surface. Protein adsorption was also greater on an aminated poly(phenylsulfone) surface compared to the sulfonated poly(phenylsulfone) surface. These results were expected because at neutral pH used in these experiments, BSA (isoelectric point pH 4.7) was negatively charged and prone to adsorb to a positive surface.
BSA adsorption performance was also compared between LBL assemblies with different capping layers and Sulf-PEO and QA-PEO thin films, Figure 7-10, a. BSA adsorption on the LBL assembly with QA-PEO capping layer was about twice of that on the QA-PEO thin film. On the other hand, the BSA adsorption behavior on negatively capped LBL assembly and sulf-PEO thin film were almost the same save for the slower adsorption rate on sulf-PEO caped LBL assembly. BSA molecules have been found to incorporate into the LBL assembly if the capping layer is positively charged, but not if the capping layer is negatively charged. The greater BSA adsorption amount on QA-PEO capped LBL could be attributed to the fact that for positively capped LBL assemblies, BSA molecules were absorbed into the LBL layers. It is been observed in our experiments that for QA-
PEO capped LBL, the BSA adsorption amount increased with LBL thickness. While for Sulf-PEO capped LBL, the BSA adsorption amount did not alter with LBL thickness, Figure 7-10, b.

Figure 7-10. (a) BSA adsorption kinetics on Sulf-PEO and QA-PEO thin film surfaces as well as PEO-based poly(urethane)s LBL assembly surfaces with different capping layer. (b) BSA adsorption amount at 1 h on PEO-based poly(urethane)s LBL assembly surfaces versus number of layers. Black: QA-PEO capped LBL; Red: Sulf-PEO capped LBL.
7.5 Protein and polysaccharide adsorption on salt annealed LBL assemblies

To investigate the effect of salt annealing on the protein and polysaccharide adsorption performance of the LBL assemblies, BSA and sodium alginate adsorption were conducted on LBL assembly surfaces before and after salt treatment. The influence of salt annealing on BSA and sodium alginate adsorption were rather different.

![BSA Adsorption](image)

Figure 7-11. Total BSA adsorption amount after 1 h on LBL assembly surfaces with different capping layer, before and after 1 M NaCl treatment of 2 h.

The BSA adsorption before and after salt annealing, Figure 7-11, reflected the surface charge of LBL assembly before and after salt annealing. Reduced positive surface charge lead to less BSA adsorption due to the decreasing electrostatic attraction between the positively charged surface and the negatively charged (at pH 5) BSA. Reduced negative surface charge presented the opposite effect,
leading to more BSA adsorption due to less electrostatic repulsion by the surface with the lower negative surface charge.

For most cases, the BSA adsorption kinetic data was fitted to the Langmuir isotherm, here we found a pseudo-second-order model described our adsorption data better. This may be an indication that after the rapid initial adsorption, the conformation of BSA molecules gradually became distorted on interaction with the surface.\textsuperscript{183}

All adsorption kinetics were fitted with a pseudo-second-order model (Eq 7-1) as displayed in Figure 7-12.\textsuperscript{184}

\[ q_t = \frac{q_e^2 k t}{1 + q_e k t} \]

(7-1)

where \( q_t \) is the adsorption amount at time \( t \), \( q_e \) is the equilibrium adsorption amount and \( k \) is the adsorption rate. The fitted parameters were presented in Table 7-2.

Figure 7-12. BSA adsorption kinetics and pseudo-second-order fit (dash line). (■) QA-PEO capped LBL; (○) Sulf-PEO capped LBL; (▲) QA-PEO capped LBL after salt annealing; (▼) Sulf-PEO capped LBL after salt annealing.
Table 7-2. Fitted parameters of BSA adsorption kinetics on different surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$q_e$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>QA-PEO capped</td>
<td>0.23</td>
<td>0.93</td>
</tr>
<tr>
<td>QA-PEO capped salt annealed</td>
<td>0.17</td>
<td>2.67</td>
</tr>
<tr>
<td>Sulf-PEO capped</td>
<td>0.16</td>
<td>1.09</td>
</tr>
<tr>
<td>Sulf-PEO capped salt annealed</td>
<td>0.19</td>
<td>1.81</td>
</tr>
</tbody>
</table>

After salt treatment, adsorption rate, $k$, increased likely due to the smoother surface and easier to access adsorption sites. The $q_e$ change followed the surface charge change before and after salt annealing. The results suggested that surface charge polarity played an important role in BSA adsorption.

On the other hand, after salt annealing, sodium alginate adsorption increased greatly on both sulfonated and aminated PEO-based poly(urethane)s capped surfaces, Figure 7-13.
Figure 7-13. Total sodium alginate adsorption amount after 1 h on LBL assembly surfaces with different capping layer, before and after 1 M NaCl treatment of 2 h.

The large difference of sodium alginate adsorption on untreated and salt treated surfaces could possibly be explained by the strong electrostatic interaction between sodium alginate molecules and the surface cationic groups. We speculated that on Sulf-PEO capped surface, the positively-charged QA density was small, leading to lower adsorption. On QA-PEO capped surface, the sodium alginate chain rearranged to maximize the interaction between sodium alginate and surface quaternary ammonium groups to occupy more adjacent adsorption sites, leading to only a small increase of adsorption. After salt annealing, the homogeneous mixing between positive and negative charges may have hindered the rearrangement of sodium alginate chain thus leading to higher sodium alginate adsorption.
7.6 Conclusions

LBL modification was employed to effectively incorporate hydrophilic PEO onto a surface using the electrostatic attraction of ionic PEO-based poly(urethane)s. Sequential addition was shown to cease after 6 layers due to a decrease in surface overcharging caused by interlayer mixing of the anionic and cationic polymers, which was confirmed by zeta potential measurements. Salt annealing was found to promote the mixing between layers, leading to a more neutrally charged surface and higher hydration of the LBL assembly. However, the restructuring of the layers only moderately decreased the protein adsorption. Investigation of protein and polysaccharide adsorption behaviors on LBL assemblies before and after salt annealing found that BSA adsorption was greatly affected by surface charge polarity. Sodium alginate adsorption was influenced by electrostatic interaction with the surface as well as surface distribution of charge groups.
8.1 Conclusions

8.1.1 Water binding and transport properties in polymer membranes

Membrane transport properties, such as proton conductivity, methanol, water, and salt permeability, are essential for applications in advanced energy devices and membrane-facilitated water purification. Elucidating the factors that influence the transport of different species through the membrane and investigating how these relationships control membrane selectivity will further our understanding of the fundamental factors governing transport mechanisms and greatly benefit future materials design.

Using FTIR, we focused on sulfonated and quaternary ammonium functionalized poly(phenylsulfone) membranes and investigated the behavior of water absorbed in the polymers. Membrane desalination performance of the samples revealed that the quaternary ammonium functionalized poly(phenylsulfone) (AEMs) displayed higher water flux and lower salt rejection than the sulfonated poly(phenylsulfone) (CEMs). The observation of water binding by FTIR suggested that water was more loosely bound in AEMs than in CEMs and behaved more like bulk water. The OD stretch peak frequency in AEMs was around 2510 cm\(^{-1}\) (OD stretch frequency of 5 % D\(_2\)O in H\(_2\)O mixture, 2509 cm\(^{-1}\)) and the OD stretch peak frequency in CEMs was around 2550 cm\(^{-1}\). Both water and salt ions diffuse through the membrane hydrophilic domains, thus less bound water in AEMs agrees well with transport properties measurements.

The OD stretch peak in DOH-doped H\(_2\)O had a high frequency shoulder corresponding to the fraction of the water that was in contact with polymer backbone. Through deconvolution of the
spectrum in the OD region, the high frequency shoulder peak area can be obtained, corresponding to the portion of water that is in contact with polymer backbone. On the other hand, by monitoring polymer backbone IR peaks in the fingerprint region and their shifts when comparing the dry membrane spectrum with the wet membrane spectrum, the interactions between water and the polymer backbone have been detected. The difference of water-polymer backbone interactions between AEMs and CEMs are a result of the different ion clustering in each system where CEMs display concentrated ionic domains and AEMs have a more dispersed ionic structure.

The method of using FTIR to monitor OD stretch of water absorbed in polymer membranes was applied to other polymer systems containing ionic groups. Crosslinked P(VDF-PFSVE) membranes are promising candidates for direct methanol fuel cell due to their good electrochemical selectivity and relatively high proton conductivity. It was found that P(VDF-PFSVE) membranes contained more bound water with increasing relative humidity or increasing IEC as evidenced by the OD stretch peak shifting to higher frequency with increasing hydration or IEC. The lack of bulk-like water explained their low methanol permeability. The presence of bound water still facilitated proton conductivity due to these polymers’ high water uptake.

To understand the influence of membrane morphology and different ionic groups on water binding, polystyrene homopolymers and block copolymers having quaternary ammonium functional groups or imidazolium groups were synthesized and studied. It was observed that the bulk-like water content was higher in homopolymers due to their higher degree of functionalization and higher water uptake. For block copolymers, the bound water content decreased with increasing IEC. It was found that water interacted more strongly with the imidazolium group compared to the quaternary ammonium groups as evidenced by the lower frequency of OD stretch for imidazolium polymers (homopolymer at 2530 cm\(^{-1}\), copolymers at 2542 cm\(^{-1}\)) than for quaternary ammonium polymers (homopolymer at 2548 cm\(^{-1}\), copolymers at 2557 cm\(^{-1}\)).
8.1.2 Membrane surface charge characterization

Zeta potential, as a parameter representing surface charge, has been studied in membrane fouling research and membrane desalination work. In fouling studies, membrane surface charge can influence the adsorption of charged fouling species. For desalination purposes, membrane charge is important because the surface charge will affect salt partition through Donnan exclusion.

There are several techniques available for characterizing zeta potential. Streaming current measurement, most often used for free standing membranes, was developed for non-conductive membrane materials. Polymers with ionic functional groups have been employed in desalination and other applications where their ionic moieties play an important role in water passage and salt exclusion. In our characterization of sulfonated poly(phenylsulfone) membranes having a range of ion exchange capacity (IEC), membrane conductance was found to influence the streaming current. With increasing IEC or increasing membrane thickness, the resistance of membrane decreased and the zeta potential became closer to zero. A hypothesis was proposed where part of the streaming current generated by a shearing hydrodynamic flow parallel to the membrane surface would back flow through the membrane bulk, reducing the total streaming current. Zeta potential measurements on thin polymer films supported this hypothesis. Linear regression with regard to membrane thickness was proposed as a method to correct the membrane conductance effect.

8.1.3 Membrane surface modification to combat fouling

Layer-by-layer assembly of sulfonated and quaternary ammonium functionalized PEO-based poly(urethane)s was employed for surface antifouling modification. The resulting LBL assembly was stable in both water and NaCl solution up to 3 M concentration. By monitoring the LBL assembly during the layer deposition process, it was found that the surface zeta potential became positive or
negative according to the last layer deposited. Thus the surface charge of the assembly could be tuned by choosing the capping layer of the assembly. After 6 layers were deposited, the surface charge decreased. FTIR characterization showed that the LBL growth plateaued after 6 layers. The diminishing surface charge was correlated to the ceasing LBL growth and interlayer mixing for thicker films was proposed as the mechanism for the self-limiting deposition behavior. Due to the hydrophilicity of the PEO segments, surfaces coated with PEO-based poly(urethane)s LBL displayed lower protein adsorption compared to sulfonated and aminated poly(phenylsulfone) without PEO, which are materials employed in reverse osmosis membranes.

Salt annealing was employed to further modify the LBL assembly. It was found that salt annealing promoted the interdiffusion between layers, leading to a more neutral surface. After salt annealing, some of the electrostatic crosslinks between polymer chains were broken and the hydration of the LBL assembly increased.

Although it was proposed that a surface consisting of a homogenous blend of different charges but displays an overall neutral charge will resist fouling better, in our studies with bovine serum albumin (protein) and sodium alginate (polysaccharide), only BSA adsorption on positively charge LBL assembly surface decreased after salt annealing. Bovine serum albumin adsorption was dictated by the surface charge polarity while sodium alginate adsorption was affected by both the surface charge and the surface charge group distribution.

8.2 Future Research

8.2.1 The influence of LBL surface modification on membrane desalination performance

For reverse osmosis membranes, the thin surface barrier layer plays an important role in the rejection of salt ions and flux of water through the membrane. When modifying the membrane
surface through layer-by-layer assembly, the change to the membrane desalination performance could potentially be significant. Thus it is essential to evaluate membrane desalination performance in addition to antifouling properties after LBL surface modification.

Studies have been performed on LBL modified nanofiltration membranes.\textsuperscript{143,185} NF membranes exhibited higher flux and lower rejection of monovalent ions compared to RO membranes. The change of monovalent ion rejection after LBL modification of NF membrane surfaces varies with ion type to be excluded, the number of LBL layers deposited, and salt concentration in the feed solution. Water flux through the membrane also showed a dependence on feed solution conditions and thickness of LBL layers. Thus the effect of LBL surface modification on desalination behavior is sensitive to the exact materials and conditions and further work in this area using the techniques described in this thesis will help to clarify the mechanisms of how LBL layers influence desalination performance.

LBL assemblies have also been explored as the active layer of NF and RO membranes.\textsuperscript{186–188} Viable performance for seawater and brackish water desalination have been achieved. Therefore, it is believed that with a suitable choice of polyelectrolytes, and a careful optimization of preparation and operation conditions, LBL assembly can be used for RO membrane surface modification without weakening membrane desalination performance. Furthermore, separation performance can be optimized through control over the LBL assembly and the details of the materials employed.

8.2.2 Crosslinking of LBL assembly

It has been demonstrated that crosslinking of the LBL assembly through methods of thermal treatment,\textsuperscript{189} ultraviolet (UV) irradiation,\textsuperscript{190} and chemical reaction\textsuperscript{191} enhanced the stability and mechanical strength of the layers. For desalination applications, pH stability and long-term stability
are essential. Therefore, it will be interesting to study the improvement of LBL surface modification stability through crosslinking under desalination conditions.

Advincula, et al. have prepared ion-permselective ultrathin films by LBL assembly and photo-crosslinking of benzophenone-modified poly(acrylic acid) (PAA-BP) and poly(allylamine hydrochloride) (PAH-BP). The multilayer structure and composition was preserved by photo-crosslinking, forming highly stable membrane films. Moreover, by controlling the pH of the solutions during the LBL assembly process, the ion selectivity could be tuned.

Park, et al. explored thermally-crosslinked LBL assemblies of cationic poly(allylamine hydrochloride) (PAH) and anionic poly(acrylic acid) (PAA) and tested their ion rejection and permeate flux. Crosslinking was realized through thermal treatment of PAA/PAH LBL assemblies formed under controlled pH. The crosslinking reaction between the carboxylic acid and amine groups stabilized the films. After thermal treatment, the thickness of the LBL assembly when immersed in water significantly decreased due to restricted swelling. The crosslinked LBL membranes displayed an improved ion rejection and decreased flux compared to untreated LBL membranes. Their result suggested that the optimal structures for desalination membranes should contain a large amount of freely charged groups with densely-packed structures via crosslinking.

In conclusion, crosslinking of LBL assembly offers enhancement of film stability as well as control over the transport properties. By carefully choosing crosslinking methods and LBL assembly process conditions, overall performance improvement of the membrane after LBL surface modification can be achieved.
8.2.3 Characterization of water binding in thin polymer films

Thin polymer films have distinctively different properties from bulk polymer films. It has been demonstrated that for films with thickness in the nanometer scale, the properties of the polymer vary with thickness. The influence of substrate on thin film properties is also large, Figure 8-1.

![Graph showing Tg versus thickness for PMMA thin films on silicon oxide or silicon oxide treated with hexamethyldisilizane (HMDS).](image)

Figure 8-1. Tg versus thickness for PMMA thin films on silicon oxide or silicon oxide treated with hexamethyldisilizane (HMDS).104

Accurate measurements of thin polymer film properties such as water diffusion coefficient and proton conductivity will be meaningful to applications like fuel cells and thin film composite membranes for desalination.

The thin barrier layer of thin film composite (TFC) membranes, usually a few hundred nanometers in thickness, is very important to membrane desalination performance. The water flux and salt rejection strongly depend on the physiochemical properties of the selective layer, for example, surface charge, surface roughness, selectivity and permeability. To better understand the transport properties of the surface selective layer such as aromatic polyamides, characterization of water
binding could be applied to the thin film. However, there is the challenge that the selective layer is extremely thin compared to the polysulfone (40 µm) and polyester (120 µm) supports. To study the thin selective layer without the interference of the thick support, grazing angle FTIR could be employed which has the ability to monitor the monomolecular layer. Specular reflectance at high “grazing” angles (around 80 ° from normal to the surface) enhances the infrared signal and improves the sensitivity. The properties of thin LBL assemblies especially water binding could also be studied using grazing angle FTIR provided that they are deposited on solid reflective surfaces. Thin film properties are a rich area of study and more vibrational spectroscopic characterization of these unique films will provide detailed insights into the mechanisms that control their properties.

8.2.4 Surface charge changes during fouling

Deposition of protein and extracellular polymeric substance (EPS) on surfaces alters the hydrophilicity, roughness, and surface charge of the original membranes, affecting the subsequent fouling and microorganism settlement.

Studies have been performed on the influence of membrane surface charge on initial rate of fouling for reverse osmosis and nanofiltration membranes. However, after the initial deposition of foulants, the surface will be changed by the foulant layer and further accumulation of foulants will be primarily determined by the interactions (hydrophilic, hydrophobic or electrostatic) between bulk foulants and foulants deposited on the surface. Foulant-foulant interactions also influence the fouling layer structure such as thickness and compactness, which determine the hydraulic resistance of the fouling layer thus influencing the flux of the fouled membrane.

Foulant-foulant intermolecular adhesion forces has been investigated using AFM for alginate and natural organic matter (NOM) fouling on aromatic polyamide thin film composite RO membrane
surfaces. After evaluation of the RO fouling rate, a remarkable correlation was observed between the measured adhesion force and the fouling rate.

Bovine serum albumin (BSA) fouling of reverse osmosis membranes has also been studied. It was observed that at pH near the isoelectric point (IEP) of BSA, where electrostatic repulsion between BSA molecules was the weakest, fouling of the RO membrane by BSA was the most severe. It is clear that electrostatic interactions play an essential part during the fouling by charged species.

To better understand the role surface charge plays during fouling, it will be interesting to characterize surface charge after the initial deposition of foulants and during the subsequent foulant adsorption. This type of study will further our understanding of the fouling process and benefit antifouling work. There has been an attempt to characterize electrokinetic properties of a microfiltration polysulfone membrane fouled by latex particles. For biofouling in membrane facilitated water purification, streaming current characterization of membrane fouled by proteins and EPS is worth pursuing in the future.
Appendix

A. OD stretch vibration FTIR spectra and peak deconvolution for P(VDF-PFSVE) membranes

Figure 1. OD stretch vibration for P(VDF-PFSVE) membranes at different RH containing 50 % D$_2$O.
Figure 2. Peak deconvolution for OD stretch vibration spectra of P(VDF-PFSVE) membranes soaked in 50 % D₂O. (Black: original OD stretch vibration spectrum. Green: fitted sub peaks. Red: fitted OD peak.)
B. OD stretch vibration spectra deconvolution for polystyrene polymer membranes

Figure 3. Peak deconvolution for OD stretch vibration spectra of imidazolium functionalized polystyrene homopolymer (PS-Im) and copolymers (PS-b-PVBIm). (Black: original OD stretch vibration spectrum. Green: fitted sub peaks. Red: fitted OD peak.)
Figure 4. Peak deconvolution for OD stretch vibration spectra of quaternary ammonium functionalized polystyrene homopolymer (PS-QA) and copolymers (PS-b-PVBQA). (Black: original OD stretch vibration spectrum. Green: fitted sub peaks. Red: fitted OD peak.)
C. Modeling of streaming current measurement of ionic polymer membrane using COMSOL

COMSOL Multiphysics, a finite element analysis software, was employed to simulate the streaming current phenomenon in a slot-type channel as a simulated environment for the experimental streaming current measurements. A simplified 2D model was used to represent the actual 3D channel. The walls of the channel were formed by ionic polymer membrane and the electrolyte solution flowed through the slit channel between the membrane surfaces. The objective was to simulate the hydrodynamic flow and the streaming current along the channel when a certain pressure was applied. Also the influence of membrane conductance on the resulting streaming current was investigated.

Displayed in Figure 5 is a schematic depicting the cross section of the slit channel for streaming current measurement. To represent the setup of the channel better, the ratio between channel length and channel height was reduced in this plot. The actual size of the channel modeled was 2 cm in length and 1 cm in width (not reflected in the 2D model). The height of the channel was 100 μm. The thickness of the membrane is variable so the membrane conductance can be adjusted through changing the membrane thickness.

![Figure 5. The channel geometry of the model.](image)

Figure 6 is the 2D model geometry with the domains and boundaries labeled by numbers. Domain 2, 4 and 5 are the channel filled with electrolyte solution and domain 1 and 3 are the membrane walls. To reduce the number of mesh elements for simulation, the model was simplified...
compared to the realistic case by: (1) the height of the channel was increased to $1 \times 10^{-3}$ m and (2) the electric double layer thickness $\lambda_D$ was enlarged to $1 \times 10^{-4}$ m.

In the streaming current experiment, the channel was filled with a dilute electrolyte solution (0.001 M KCl). To simulate the hydrodynamic flow in the channel, the Laminar Flow module of COMSOL was employed for domains 2, 4 and 5 to obtain the velocity of the flow at any point of the channel when a certain pressure $p$ was applied to the end of the channel. Navier-Stokes equations (Eq 1 and Eq 2) were incorporated in Laminar Flow module for calculation of the velocity field:

\[
\rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[ -\mathbf{p} I + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) I \right] + \mathbf{F} \tag{1}
\]

\[
\nabla \cdot (\rho \mathbf{u}) = 0 \tag{2}
\]

where $\rho$ and $\mu$ are the density and dynamic viscosity of the electrolyte solution respectively, $\mathbf{u}$ is the velocity field having $u, v, w$ in the $x, y, z$ directions respectively, $p$ is the pressure applied to the channel, $I$ is the identity matrix and $\mathbf{F}$ is the external force.

The properties of the electrolyte solution were required for accurate simulation. Listed in Table 1 are the constants employed in the Laminar Flow module. Listed in Table 2 are the boundary conditions defined in the module.
Table 1. Properties of the electrolyte solution employed in the Laminar Flow module.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Parameter Name</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>rho</td>
<td>1000.07456[kg/m^3]</td>
<td>Density</td>
</tr>
<tr>
<td>$\mu$</td>
<td>eta</td>
<td>8.443e-4[Pa*s]</td>
<td>Dynamic Viscosity</td>
</tr>
<tr>
<td>$p$</td>
<td>p_0</td>
<td>3[mbar]</td>
<td>Inlet pressure</td>
</tr>
</tbody>
</table>

Table 2. Boundary conditions for Laminar flow module on domain 2.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 3, 4, 5, 7, 8, 10, 12, 13, 14</td>
<td>No slip</td>
</tr>
<tr>
<td>2</td>
<td>Inlet, pressure p_0</td>
</tr>
<tr>
<td>11</td>
<td>Outlet, pressure 0</td>
</tr>
</tbody>
</table>

After solving the Navier-Stokes equations, the velocity field $u$ inside the channel can be obtained and plotted using the graphic feature of COMSOL. Figure 7 displayed the velocity field computed for $p_0 = 3$ mbar. The color scheme represented the magnitude of the velocity. Inside the slit channel, the velocity varied along the y direction as expected for flow in a channel with no slip boundary conditions.
Figure 7. Velocity field computed using COMSOL Laminar Flow module.

To further study the streaming current, the charge density, \( \rho_v \), distribution in the channel resulting from membrane surface electric double layer needs to be defined in order to calculate the streaming current produced by the hydrodynamic flow. The potential in the bulk solution \( \psi_0 \) was defined as zero, the potential at the membrane-solution interface was approximated using zeta potential \( \zeta \). Therefore, the charge density inside the channel can be obtained using the Debye-Huckel approximation form of the Poison-Boltzmann equation. (Eq 3)

\[
\rho_v = -\varepsilon_r \varepsilon_0 \zeta \kappa^2 \exp(-\kappa x)
\]

(3)

where \( \varepsilon_r \) is the relative permittivity of the electrolyte solution, \( \varepsilon_0 \) is the permittivity of vacuum, \( \zeta \) is the zeta potential of the membrane surface, \( \kappa \) is the Debye-Huckel parameter, and \( x \) is the distance from the membrane surface. \( \kappa \), the Debye-Huckel parameter, is the reciprocal of the Debye length \( \lambda_D \), determined from the properties of the electrolyte solution. (Eq 4)
\[ \lambda_D = \kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}} \]  

(4)

where \( I \) is the ionic strength of the electrolyte, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature in kelvins, \( N_A \) is the Avogadro number, and \( e \) is the elementary charge.

The Electric Currents module in COMSOL was employed for simulation of the streaming current. Coupling the velocity field \( u \) and the charge density \( \rho_v \) inside the channel, streaming current \( I_s \) can be calculated. \( u \times \rho_v \) was implemented into the model as the external current density.

To study the influence of the membrane wall conductance, the membrane properties were defined and the membrane regions were treated as a conductive domain. List in Table 3 are all the parameters employed in the Electric Currents module. The boundary conditions are listed in Table 4.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Parameter Name</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_r )</td>
<td>eps_r</td>
<td>77.51</td>
<td>Relative permittivity of electrolyte solution</td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>epsilon</td>
<td>( 8.85 \times 10^{-12} ) [F/m]</td>
<td>Permittivity of vacuum</td>
</tr>
<tr>
<td>( \rho_e )</td>
<td>sig</td>
<td>17[mS/m]</td>
<td>Conductivity of the electrolyte solution</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>zeta</td>
<td>25[mV]</td>
<td>Zeta potential of membrane</td>
</tr>
<tr>
<td>( \lambda_D )</td>
<td>debyel</td>
<td>( 1 \times 10^{-4} ) [m]</td>
<td>Debye length</td>
</tr>
<tr>
<td>( \rho_w )</td>
<td>sigwall</td>
<td>variable</td>
<td>Conductivity of the membrane wall</td>
</tr>
</tbody>
</table>
Table 4. Boundary conditions for Electric Currents module.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>6, 9</td>
<td>Electric insulation</td>
</tr>
<tr>
<td>1, 2, 3, 10, 11, 12</td>
<td>Ground</td>
</tr>
<tr>
<td>4, 5, 7, 8, 13, 14</td>
<td>Electric continuity</td>
</tr>
</tbody>
</table>

Over all five domains, electric conservation condition was applied, where:

\[ D = \varepsilon_r \varepsilon_0 E \]  \hspace{1cm} (5)

where \( D \) is the dielectric displacement and \( E \) is the electric field over all the domains. Figure 8 displayed the x component of the current density simulated for \( p_0 = 3 \text{mbar}, \rho_w = 0.1032 \text{ S/cm} \) and membrane thickness = \( 5 \times 10^{-4} \text{ m} \).

![Figure 8. Current density x component computed using Laminar Flow module and Electric Currents module.](image-url)
To study the influence of membrane conductance on measured streaming current, currents at the three boundaries of outlet (10, 11, 12) were integrated to represent the streaming current $I_s$.

Membrane conductivity and membrane thickness were varied systematically, resulting in different membrane conductance. The values chosen for membrane conductivity and membrane thickness were listed in Table 5 as well as the streaming current simulated. The streaming current values were also plotted in Figure 9.

Table 5. Varying membrane conductivity and membrane thickness as well as the streaming current simulated for each case.

<table>
<thead>
<tr>
<th>Conductivity (S/cm)</th>
<th>0.01093</th>
<th>0.1032</th>
<th>0.2475</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>5.30e-6 A/m</td>
<td>2.27e-6 A/m</td>
<td>1.75e-6 A/m</td>
</tr>
<tr>
<td>0.0003</td>
<td>4.10e-6 A/m</td>
<td>1.64e-6 A/m</td>
<td>1.35e-6 A/m</td>
</tr>
<tr>
<td>0.0005</td>
<td>1.74e-6 A/m</td>
<td>1.19e-6 A/m</td>
<td>1.15e-6 A/m</td>
</tr>
</tbody>
</table>
It is clear from our simulations that increased membrane conductance lowered the calculated streaming current as observed in the experimental data in Chapter 6. The higher the membrane conductivity and the thicker the membrane, the higher the membrane conductance. Higher membrane conductance resulted in smaller streaming current, which supported our hypothesis that the conductive membrane regions allowed some of the current to back flow through the membrane bulk and eventually reduced the streaming current.

Overall, these simulation results qualitatively mirrored our experimental data. Further refinements to the model are necessary to try to calculate the zeta potential from first principles and more accurately represent the experimental geometry for better quantitative agreement between experiment and simulation.
References


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VITA

He Xie was born on August 10th, 1985 in Nanping, China. She received her Bachelors of Science degree in Materials Science and Engineering from Tsinghua University in June of 2007. She began her graduate studies at the Pennsylvania State University in August of 2007 under the guidance of Dr. Michael Hickner pursuing a doctorates degree in Materials Science and Engineering. Her dissertation work involves the water binding and transport properties of ionic polymer membranes, characterization of membrane surface charge and antifouling modification using layer-by-layer assembly. She started an internship with Dow Water & Process Solutions since March 2012, working on seawater reverse osmosis membranes.