Interfacial Engineering of Bipolar Junctions for Electrochemical Processes

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INTERFACIAL ENGINEERING OF BIPOLAR JUNCTIONS FOR ELECTROCHEMICAL PROCESSES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by

Subarna Kole
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Abstract

Water and energy scarcity are two of the main problems the world is facing today. A number of industrial processes like chemical manufacturing plants, energy production, electricity generation are heavily dependent on availability of a reliable source of water. Similarly, every step of water collection, treatment, and distribution, is an energy intensive process. The efficient use of electrochemical devices can help tackle some of these problems.

Bipolar membranes (BPMs) have historically been deployed in electrodialysis setups for mineral acid and base production. The need to have disparate pH environments in electrochemical cells, and prevent species crossover, have motivated researchers to examine BPMs as an electrolyte separator. BPMs have the unique capability to split water into protons and hydroxide ions charge carriers in addition to conducting those ions in opposite directions to maintain current flow in the electrochemical setup. Most materials related research for BPMs has focused on water-dissociation catalysts. There are few reports that investigate the importance of high-quality bipolar junction interfaces for improving water-splitting in BPMs. This Dissertation studies how tuning bipolar junction interfaces affect the kinetics for water splitting in addition to ionomer conductivity. In the first part of the work, BPMs with systematically varied interfacial area values were prepared using soft lithography. Polarization experiments with the new, micropatterned interface BPMs reveal a 250 mV reduction in the on-set potential when increasing the interfacial area by 2.2x and a 15% increase in current density at 2 V. This approach was conducive for making BPMs with different chemistries ranging from perfluorinated AEMs and CEMs to alkaline stable, ether-free poly(arylene) hydrocarbon AEMs. These polymer chemistries are more robust for fuel cell and electrolysis applications.
Nanopatterned surface ion exchange membranes (IEMs) have also been prepared using block copolymer (BCP) lithography. These membranes were demonstrated to have up to 5% improvement in through-plane conductivity without affecting the permselectivity of the membrane. Finally, modification of bipolar junctions in electrode surfaces was shown to impact the microstructures of anion exchange ionomer (AEI) thin films, leading to enhanced conductivity.

Overall, this dissertation demonstrates that improving the properties of IEMs and ionomer-electrode interactions play a crucial role in improving the performance of electrochemical processes used to address problems in the water-energy nexus.
Chapter 1. Introduction

1.1. Background

Reducing society’s reliance on fossil for energy is today’s foremost challenge to mitigate climate change. According to the latest report (2017) published by International Energy Agency (IEA) (Figure 1), vast majority of our energy demand is met by coal, oil and gas. These three sources contributed to a little more than 11,000 Mtoe (Million tonnes of Oil Equivalent) of energy in 2016 or 82.3% of the total energy demand. This number is projected to increase to about 13,000 Mtoe in 2040 due to the ever-increasing energy demand even though the technologies for extracting energy from renewable resources keep on improving. The major factors behind our dependence on the conventional energy sources include low cost and reliability of these sources of energy compared to solar and wind that depend on the location, climate, and limited

Figure 1. World energy consumption report, 2017 (International Energy Outlook)
infrastructure due to their high initial cost of setting up. The continued use of fossil fuels may lead to irreversible climate change.

The other major challenge faced by the world today is limited availability of water for drinking, energy production, agriculture, etc. Water and energy requirements are intertwined in a way that the scarcity of one of them directly affects the other. Energy production and electricity generation requires water, and on the other hand, the extraction and delivery of water utilizes energy. This codependence between water and energy systems is known as the water-energy nexus. Figure 2 below outlines this codependence in detail.

![Figure 2. Co-dependency between water and energy systems](image)

### 1.2. Motivation for this work

Electrochemical devices have the potential to significantly reduce our dependence on fossil fuels. The use of more efficient ion exchange membranes (IEMs) in fuel cells, for example, can increase their efficiency and make them more viable for use in portable (public transport, light
duty transportation) and stationary (residential heat and power, power backup) applications.

Nafion™, a cation exchange membrane (CEM), is the most common IEM used in hydrogen fuel cells today. Bipolar membranes (BPMs) and anion exchange membranes (AEMs) are a different subset of IEMs that complement CEMs. Nafion™ is the most widely used IEM as its excellent oxidative stability and conductivity is needed for the chloro-alkali process – an industrial operation used to manufacture chlorine and caustic soda. Similarly, Nafion™, and other perfluorosulfonic acid analogues, are used as proton exchange membranes (PEMs) in commercial, low-temperature water electrolyzers for hydrogen production and fuel cells. The chemical structure of Nafion™ is shown in Figure 3 and the structure of an AEM is shown in Figure 4.

![Figure 3. Nafion™ structure](image)

AEMs and BPMs are not as prevalent in the chemical industrially as they are only needed for commercial electrodialysis units; and as such, they are not as technologically mature. However, there is interest in developing BPMs and AEMs further for low-temperature fuel cell and water
electrolyzers, in addition to other emerging technologies like carbon dioxide (CO\textsubscript{2})/carbon monoxide (CO) electrolyzers. AEMs have seen tremendous development in the past 5 years because fuel cells and water electrolyzers that operate in alkaline media do not require expensive platinum group metals for the necessary redox reactions and they can use low-cost stainless steel bipolar plates. These technologies operated under acidic environment with Nafion\textsuperscript{TM} necessitate costly graphitic carbon flow fields. BPMs have several potential advantages when used in a hydrogen fuel cell configuration such as disparate pH conditions between the electrodes that enable optimal conditions for the reactions and formation of water in the bipolar junction that can spur self-humidifying fuel cells. IEMs are also being explored for water purification via membrane capacitive deionization, electrodialysis and electrodeionization processes.

1.3. Electrochemistry concepts

All electrochemical processes share some common characteristics: two electrodes (cathode and anode) separated by a conductive electrolyte – which can be a liquid or a solid (membrane, ionomer film or a ceramic material).\textsuperscript{7} One of the electrodes (cathode, for e.g.) is the site of the reaction of interest. The other electrode (anode, in this case) is used to close the circuit and enables current flow for the opposite reaction.

In an ideal world, the resistance of an electrochemical circuit can be calculated by Ohm’s law (Equation 1) where the circuit has only one resistive element, \( R \):

\[
R = E/I
\]  

\( E \) = voltage  

\( I \) = current
However, in an electrochemical circuit, more complex elements are exhibited. To calculate the resistance of a complex circuit, impedance of the system must be considered instead of just the resistance. Impedance is the ability of the circuit to resist the flow of the electrical current.

Unlike the traditional definition of resistance, impedance does not assume that the current and the voltage are in phase with each other. To calculate the impedance, the current and the potential must be presented as complex functions (Equations 2 and 3) where the response is shifted by the phase angle.\(^8\)

\[
I = I_0 \exp(j \omega t - \varphi)
\]

(2)

\[
E = E_0 \exp(j \omega t)
\]

(3)

\[j = \sqrt{(-1)}\]

\[\omega = \text{angular frequency}\]

\[t = \text{time}\]

\[\varphi = \text{phase shift}\]

Using these equations, the impedance \((Z)\) can be calculated as follows:

\[
Z = \frac{E_0}{I_0} \exp(j \varphi) = \frac{E_0}{I_0} (\cos \varphi + j \sin \varphi) = Z_0 (\cos \varphi + j \sin \varphi)
\]

(4)

The expression for the impedance is presented as a complex number containing a real part and an imaginary part. The complex conjugate can be presented on a Nyquist plot by plotting the real part on the x-axis and the imaginary part on the y-axis. Figure 5 shows an example Nyquist plot. The vectors on the Nyquist plot present the total magnitude of the resistance and the capacitance components of the circuit.

Because the Nyquist plot cannot tell the frequency used to scan the impedance, the Bode plot can be more informative. In a Bode plot the frequency is plotted on the x-axis and both the values of
the impendence and the phase shift is plotted on the y-axis as shown in Figure 6. In order to extract the film resistance and double layer capacitance, it is essential to fit the experimental data to circuit equivalent model. The detailed procedure and expressions used for calculating film conductivity are mentioned in latter sections.\textsuperscript{9}

![Figure 5. An example of a Nyquist plot (Source: Instruments, G., Basics of electrochemical impedance spectroscopy. G. Instruments, Complex impedance in Corrosion 2007, 1-30)](image1)

![Figure 6. An example of a Bode plot (Source: Instruments, G., Basics of electrochemical impedance spectroscopy. G. Instruments, Complex impedance in Corrosion 2007, 1-30)](image2)
1.4. Ion exchange membranes (IEMs)

IEMs are the key components of electrochemical devices employing a thin, solid-state electrolyte separator. The thickness of an IEM typically ranges from 10 µm to 300 µm. IEMs allow the selective transport of a particular type of ion through its cross-section in presence of chemical potential gradient or electrochemical potential gradient. IEMs can be classified into several categories based on the material of construction, type of ions it allows to pass through it, surface design/patterning and method of preparation.\textsuperscript{10}

IEMs typically consist of a polymer matrix with charged groups fixed to the polymer backbone, and oppositely charged mobile ions to balance the fixed charges. In a cation exchange membrane (CEM), fixed negative charges are in equilibrium with positively charged mobile ions and vice versa in case of anion exchange membranes (AEMs). The mobile ions are also known as counterions.\textsuperscript{11} If a CEM is placed in a salt solution, negatively charged ions in the solution (also known as coions) are excluded from the membrane due to similar electric charge of the fixed groups, allowing only positively charged ions to pass through the membrane. This principal is known as Donnan exclusion. By the same principle, AEMs exclude positively charged ions from the polymer matrix and as a result, only negatively charged ions can pass through it. Figure 7 presents the structure of a polymeric CEM. Bipolar membranes (BPMs) consist of a CEM and AEM appended to each other. BPMs can dissociate water at the AEM-CEM interface, which is known as the bipolar junction. An electric field, known as a space charge region, is created in the bipolar junction due to the tethered anions in the CEM and the tethered cations in the AEM. The oppositely charged tethered ions give rise to an electric field and is similar to a charged capacitor.
Transport of ions across an AEM or CEM is governed by Donnan equilibrium theory. In simple words, Donnan equilibrium states that when a semi-permeable membrane is present in an electrolytic solution, distribution of mobile ions takes place in a way to make the electrochemical potential equal in each phase. Donnan equilibrium is responsible for high selectivity of anions in an AEM. Conversely, it is also responsible for selectivity of cations in a CEM while excluding anions from the membrane phase.\textsuperscript{12}

The performance of AEMs and CEMs is measured in terms of its ionic conductivity, permselectivity, ion exchange capacity, mechanical, chemical and thermal stability. The ionic conductivity of IEMs affects the ohmic overpotential and the energy efficiency in electrochemical processes. Through-plane conductivity characterization of IEMs is more relevant for electrochemical devices, as the membrane acts as a separator between the anode and cathode, and we are concerned about the ions flowing across the membrane cross section to travel from

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{membrane.png}
\caption{A microscopic illustration of a polymeric cation exchange membrane\textsuperscript{11}}
\end{figure}
one electrode to the other. In-plane conductivities are often reported in literature; however, if the membrane is anisotropic, it is important to distinguish between the two of them. Figure 8 highlights the differences between these two conductivities.

In-plane ionic conductivity and resistance are related as follows:

\[ \sigma = \frac{d}{L \cdot W \cdot R} \]  

(5)

\[ \text{ASR} = \frac{L}{\sigma} \]  

(6)

\( \sigma \) = in-plane ionic conductivity of the membrane

\( d \) = distance between the electrodes where the potential drop is measured

\( L \) = membrane thickness

\( W \) = width of the membrane in the conductivity probe

\( R \) = in-plane membrane resistance

\( \text{ASR} \) = Area specific resistance

Area specific resistance or ASR of an IEM extracted from low frequency EIS data includes contributions from the ohmic overpotential, concentration losses, polarization losses and reactant crossover.

Through-plane conductivity of an IEM is measured from its high frequency resistance (HFR) derived from its electrochemical impedance spectroscopy (EIS) using the following expression:

\[ \sigma_{t-p} = \frac{L}{R_{t-p} \cdot A \cdot \text{ASR}_{cell}} \]  

(7)

\( \sigma_{t-p} \) = through-plane conductivity

\( L \) = membrane thickness

\( R_{t-p} \) = through-plane membrane resistance

\( A \) = active area of the membrane
\[ \text{ASR}_{\text{cell}} = \text{Area specific resistance of the cell without the membrane (in presence of electrolyte)} \]

Figure 8. Directions for conductivity measurement in an IEM

In an IEM, majority of the electric current is carried by counterions. The fraction of current carried by each ionic species is known as its transference number. It can be calculated by the membranes’ junction potential when separating two electrolyte solutions of different concentrations as follows:

\[
E = \frac{RT}{zF} \left[ T_{\text{counter}} \ln \left( \frac{a_{\text{counter}}^{\text{conc}}}{a_{\text{counter}}^{\text{dil}}} \right) - T_{\text{co}} \ln \left( \frac{a_{\text{co}}^{\text{conc}}}{a_{\text{co}}^{\text{dil}}} \right) \right]
\]

\[ E = \text{junction potential across the IEM} \]

\[ T_{\text{counter}} + T_{\text{co}} = 1 \]

\[ T_{\text{counter}} \text{ or } T_{\text{co}} = \text{the transference number of an IEM for the corresponding counterion or coion respectively} \]

\[ R = \text{Universal gas constant} \]

\[ F = \text{Faraday’s constant} \]

\[ z = \text{valence for the ions} \]

\[ a_{\text{counter}}^{\text{conc}} = \text{activity coefficient for the counterion in the concentrated electrolyte solution} \]
\( \alpha_{\text{counter}}^{\text{dil}} = \) activity coefficient for the counterion in the dilute electrolyte solution

\( \alpha_{\text{co}}^{\text{conc}} = \) activity coefficient for the coion in the concentrated electrolyte solution

\( \alpha_{\text{co}}^{\text{dil}} = \) activity coefficient for the coion in the dilute electrolyte solution

The permselectivity of IEMs is defined as its ability to distinguish between cations and anions. In an ideal IEM, permselectivity is 1 due to the complete exclusion of coions from the membrane phase. However, most IEMs have permselectivity lower than 1. It is calculated from the transference numbers of the coions and counterions in the membrane and external electrolyte solutions using the following equations:\(^{14}\)

\[
\varphi_{cm} = \frac{T_{cm} - T_c}{T_a}
\]

\[
\varphi_{am} = \frac{T_{am} - T_a}{T_c}
\]

\( \varphi_{am} \) or \( \varphi_{cm} \) = the permselectivity of the AEM or CEM

\( T_a \) or \( T_c \) = transference number for anion or cation in the solution phase respectively.

\( T_{a am} \) or \( T_{c cm} \) = transference number for anion in the AEM or cation in the CEM respectively.

Ion exchange capacity (IEC) of IEMs represent the total number of fixed charges or functional groups present in the polymer matrix and is expressed in milliequivalents per gram of the polymer. It can be calculated by titration or determined from the NMR spectrum of the polymer.\(^{10}\)

Water uptake of an IEM is also an important property especially in desalination and electrodialysis applications and is calculated as:
\[ W = \frac{w_2 - w_1}{w_1} \times 100\% \]  

(12)

W = water uptake of the IEM

w₁ = weight of dry membrane

w₂ = weight of membrane after immersion in deionized (DI) water for 24 hr

1.5. Theory of water dissociation in bipolar membranes

As mentioned in section 1.4, BPMs are a special class of IEMs, prepared by appending a CEM to an AEM. The shared interface between the two membranes may feature a water-dissociation catalyst. One of the most important processes in a BPM is the dissociation of water at its interface (Figure 9) which has several applications like production of acid/base from salt solutions and performing water electrolysis with an acidic cathode and alkaline anode (i.e., non-PGM electrocatalyst for OER and a low PGM loading for HER). ¹⁵,¹⁶

Figure 9. Dissociation of water at BPM interface
When an electric field is applied between the electrodes connected to a bipolar membrane kept in a salt solution, there is a movement of ions from one electrode to the other. The direction in which ions move depend on the polarity of the applied external voltage. In forward bias configuration, the AEM is adjacent to the cathode and CEM is placed near the anode, while in reverse bias configuration, AEM is adjacent to the anode and CEM is placed near the cathode.\textsuperscript{17}
It can be seen in Figure 10a that there is a movement of ions towards the interface in forward bias configuration. This happens because the anion exchange layer (AEL) in the BPM is almost impermeable to the mobile cations in the solution, and as a result they cannot reach the cathode. Similarly, the cation exchange layer (CEL) prevents mobile anions from reaching the anode. Hence, ionic species get accumulated at the interface. This configuration is useful for running a hydrogen fuel cell as the protons and hydroxide ions can combine at the interface to produce water and provide hydration for the membrane which is needed for mediating ion transport.

Figure 10b shows a BPM in reverse bias configuration with the ions moving away from the interface under the influence of external voltage. This leads to the depletion of ions from the interface at higher voltages. If the applied reverse bias voltage is sufficiently high, splitting of water molecules present at the interface takes place, leading to the formation of protons and hydroxide ions. These ions can participate in charge-transfer reactions at the electrodes or pH adjust the anolyte and catholyte chambers. The voltage where water splitting starts to occur is known as the onset potential ($E_{\text{onset}}$) and the thermodynamic minimum is 0.83 V ($E_j$) for a BPM.\textsuperscript{18} The thermodynamic minimum value of 0.83 V is obtained from the following equation when activities are 1 and experiments are performed at 25 °C:

$$E_j = \frac{RT}{F} \ln(a_{H^+}^{\text{PEM}}a_{OH^-}^{\text{AEM}}) - \frac{RT}{F} \ln(K_w)$$ (13)

where $R$ = universal gas constant, $T$ = temperature, $F$ = Faraday constant, $a_{H^+}^{\text{PEM}}$ = activity of protons in the PEM, $a_{OH^-}^{\text{AEM}}$ = activity of hydroxide ions in the AEM and $K_w$ = water dissociation constant.
Several theories exist for understanding the mechanism for water dissociation in bipolar junction interfaces. The most widely accepted among them states that water dissociation takes place due to the second Wien effect (dissociation principle of weak acids) and a strong electric field at the junction that assists with protonation/deprotonation of functional groups.\(^\text{18}\)

Figure 11 shows the polarization (current-voltage relationship) behavior of a BPM under reverse bias. At low voltages, there is a linear relationship between the voltage and current. In this part of the curve, the current is almost exclusively due to the movement of salt ions present in the solution. The dissociation rate of water molecules is extremely low in this region of the curve. Hence, the current arising from the movement of protons and hydroxide ions is kinetically limited. This process continues until the salt ions are depleted from the BPM interface. The current density at this point is known as the first limiting current density \(i_{\text{lim1}}\). Any further increase in current density can only take place by dissociation of water molecules at the
interface. This happens when the onset potential \( (U_{\text{diss}}) \) for water dissociation is reached. At this voltage, the concentration of proton and hydroxide ions rapidly increase due to electric field enhanced (EFE) water dissociation. The current arising from the products of water dissociation in this part of the curve is governed by mixed control (both kinetic and transport limitations). At extremely high voltages, the current density reaches a second limiting value \((i_{\text{lim2}})\). At these voltages, the delivery of water molecules from the solution to the BPM interface is not fast enough to match the rapid dissociation rate at the interface. Hence, in this part of the curve, current arising from protons and hydroxide ions is transport limited.

The Nernst-Planck-Poisson equation is used to model the transport of ions at the interface of a BPM. It is a mass conservation equation for charged particles that considers the diffusion of ions under concentration gradient and migration of ions under electrostatic forces. The Poisson equation accounts for the space charge at the interface due to unbalanced fixed charges on the AEM and CEM at either side of the interface.\(^{12}\)

\[
j_i = - D_i \left( \nabla c_i + z_i F c_i \nabla \phi_{BPJ} \right) \quad (14)
\]

\[
\nabla j_i = -\frac{dc_i}{dt} \quad (15)
\]

\[
- \varepsilon \nabla^2 \phi_{BPJ} = \rho \quad (16)
\]

\( j_i \) = flux of the ionic species \( i \)

\( D_i \) = diffusion coefficient of \( i \)

\( c_i \) = concentration of \( i \)

\( z_i \) = valence of ion

\( F \) = Faraday constant

\( \phi_{BPJ} \) = local potential at the BPM interface (bipolar junction)
\( t = \) time

\( \varepsilon = \) permittivity of the medium (IEM)

\( \rho = \) density of fixed charges

where equations 14, 15 and 16 are Nernst-Planck, continuity, and Poisson’s equations, respectively.

Figure 12. Diffusion of water to the interface and electro-osmotic drag of water away from the interface.

1.6. Lithography as a tool for patterning IEM surfaces

In the previous section, different types of IEMs based on the polarity of fixed charges present in the polymer matrix are discussed. IEMs can also be categorized as flat or profiled/patterned surface membranes. Patterned surface IEMs are of particular interest in many applications because changing the surface design of an IEM can result in improved mass transfer of ionic species due to an increase in the available surface area without compromising its electrochemical (permselectivity, IEC) and mechanical (tensile strength) properties.\(^{19}\)
Lithography (from ancient Greek words: lithos 'stone', and graphein 'to write') is a versatile process that allows us to prepare IEMs with surface feature sizes anywhere between a few hundred micrometers to a few nanometers. Optical and block copolymer (BCP) lithography are two of the most mature lithography technologies for generating patterns on substrate surfaces. Optical lithography is commonly employed when the desired lateral feature sizes on the membrane surface are relatively large (minimum of few hundred nanometers). The popularity of this technique stems from the fact that it is a versatile process that can be used for patterning many different membrane chemistries with varied feature shapes and sizes. Optical lithography relies on the modification of a photosensitive component (photoresist) when exposed to photons. Most modern optical lithography techniques use ultraviolet radiation passing through a photomask to selectively modify certain areas of the photoresist surface to obtain a patterned substrate. Alternatively, maskless optical lithography employs direct laser writing to focus ultraviolet radiation on a specific part of the photoresist surface and prepare the desired pattern. The minimum feature size that can be obtained by this method is hence dictated by the wavelength of ultraviolet radiation. After generating patterns on the photoresist, poly(dimethylsiloxane) (PDMS) melt is poured on it and allowed to cure. The advantage of PDMS molds generated by the soft lithography process is that they are reusable and can be used with several different membrane chemistries like hydrocarbon and perfluorinated membranes. The PDMS molds also maintain their structures and integrity with common solvent like IPA, water, NMP, DMF, DMAc used to prepare the ionomer solutions.

To achieve smaller lateral feature sizes, block copolymer (BCP) lithography is a promising technology that allows us to prepare IEMs with surface features sizes in the range of 3 to 50 nm.
depending on the periodicity of the self-assembled block copolymer.\textsuperscript{22, 23} BCPs are a special class of polymers that are composed of two or more chemically dissimilar chains connected end to end by covalent bonds. Owing to the differences in chemical properties of the chains or blocks, they microphase separate under favorable conditions like suitable temperature, neutral layer etc. Poly(styrene)-\textit{block}-poly(methylmethacrylate) or PS-b-PMMA is one of the most studied block copolymers for BCP lithography.\textsuperscript{21} The popularity of PS-b-PMMA stems from the fact that it can be readily self-assembled at temperatures above the glass transition (\textgreater{}105 °C) to form perpendicular lamella or cylinders depending on volume fraction of the blocks (Figure 13). This BCP does not require solvent vapor annealing for self-assembly, a more complex and cost prohibitive process in some cases, and a top layer to provide a non-preferential condition at the free surface. The neutral layer used in this process is a random copolymer of styrene and methylmethacrylate (PS-\textit{r}-PMMA), and it can be prepared by a simple nitroxide mediated polymerization (NMP) of the monomers. The etch contrast between the styrene and MMA blocks also makes it viable to transfer the pattern onto substrates (ion exchange membranes).\textsuperscript{24, 25}

Figure 13. PS-b-PMMA film self-assembly into polystyrene and polymethylmethacrylate blocks resulting in fingerprint lamella pattern on thermal annealing
1.7. Electrochemical devices

Most electrochemical devices fall under the category of energy conversion/storage, membrane-based separation and chemical synthesis. Fuel cells convert chemical energy into electrical energy by means of an electrochemical reaction, similar to a battery. Main difference between a battery and fuel cell is that batteries need to be recharged or replaced once the fuel runs out, but fuel cells can keep working indefinitely (in theory) as long as there is fuel supply. Fuel cells gained popularity in the 1950s after NASA used them in their Gemini spaceflight. The main components of a fuel cell are: fuel, oxidant and ion exchange membrane/electrolyte to facilitate the transfer of ions from one electrode to the other.\(^{26}\) Fuel cells are classified into different categories such as: proton exchange membrane fuel cells (PEMFCs), anion exchange membrane fuel cells (AEMFCs), solid oxide fuel cells (SOFCs), phosphoric acid fuel cells, aqueous alkaline electrolyte fuel cells, and molten carbonate fuel cells.\(^{27}\) Hydrogen based proton exchange membrane fuel cells (PEMFCs) are one the most common fuel cells studied and sold commercially. In case of PEMFCs, hydrogen acts as the fuel, pure oxygen or air acts as the oxidant and a proton exchange membrane acts as the channel for transport of protons generated at the anode to the cathode. Figure 14 shows the operation of a PEMFC/AEMFC.
Bipolar membrane fuel cells (BPMFC) are another class of fuel cells that uses a BPM as the membrane separator. Using a BPM allows the anode and cathode reactions to take place at disparate pH values, providing the optimum conditions for improved reaction kinetics at each electrode. Additionally, self-humidification of the cell takes place due to water formation at the interface, as shown in Figure 15, when operated in forward bias.\textsuperscript{28, 29}

![Figure 14. PEM/AEM based hydrogen fuel cell operation](image1)

**Figure 14.** PEM/AEM based hydrogen fuel cell operation

![Figure 15. BPM fuel cell under forward bias with self-humidification of the cell due to formation of water at the interface](image2)

**Figure 15.** BPM fuel cell under forward bias with self-humidification of the cell due to formation of water at the interface
Water electrolyzers are another class of electrochemical devices that are commonly employed for hydrogen production for application in fuel cells. Nafion™ based PEM electrolyzers have traditionally been used but BPM based water electrolyzers are becoming increasingly popular as they allow the anode and cathode to operate at different pH conditions within the same cell leading to improved reaction kinetics at both electrodes. Electro dialysis is another common process that utilizes ion exchange membranes. Bipolar electrodialysis uses both bipolar membranes and IEMs to synthesize mineral acids (sulfuric acid, nitric acid, hydrofluoric acid), bases (sodium hydroxide, potassium hydroxide, ammonium hydroxide), and organic acids (lactic acid, citric acid, tartaric acid. It is particularly useful for converting waste brine from desalination processes into valuable products.

Figure 16. Bipolar membrane electrodialysis to produce sulfuric acid and sodium hydroxide from brine solution

Bipolar membrane electrodialysis (BMED) is one of the most mature applications of a BPM (Figure 16). It is commonly employed to synthesize mineral acids, bases, and organic acids from
their aqueous salt solutions. An important example of BMED is in chlor-alkali process to produce sodium hydroxide and chlorine from sodium chloride solution.\textsuperscript{30}

1.8. **Electrode surface modification with oppositely charged ionomers**

The interaction between electrodes or electrocatalyst surface with ionomers are extremely important for efficient reactant delivery, product removal and charge transfer reaction kinetics at the electrode-ionomer interface of an electrochemical device.\textsuperscript{31} The behavior of thin films of ionomers on electrode surfaces are, in general, different from bulk membrane properties. Hence, a part of this dissertation is dedicated to studying electrode-ionomer interactions with anion exchange ionomers (AEIs) electrostatically bound to cation exchange polypeptides grafted to electrode surfaces (i.e., modification of the electrocatalyst surfaces). Additionally, modification of the electrocatalyst surfaces may result in enhanced ionic conductivity of the ionomer film. Electrocatalyst surfaces can be modified using random copolymers (brush polymers), nanoparticles, self-assembling monolayers (SAMs) and peptides.\textsuperscript{32-34} Elastin like peptides (EPIs) are a special category of peptides that have a fixed number of amino acids in a specific order attached end to end with peptide bonds. EPIs can self-assemble in different orientations and give different elastic properties and can be manufactured easily in large quantities. Due to these properties, EPIs have been explored for surface modification of electrodes to manipulate ionomer-electrode interfaces.\textsuperscript{35,36} Figure 17 shows an amino acid sequence example of an EPI. Each letter indicates a specific amino acid and X represents any amino acid except proline.
Figure 17. Elastin based peptide

1.9. Summary of the introduction

This introduction has provided a brief overview of electrochemical systems and their main components. IEM types, properties and methods are discussed in further detail. This introduction also details lithographic methods to prepare patterned IEM surface and synthesis of BPMs for water dissociation. The correlation between interfacial area of the bipolar junction of the BPM and the electric field at the junction is derived using mass/charge balance and continuity equations.

This introduction also discussed interactions between ionomer thin films and electrode surfaces and the importance of those interactions. Subsequent chapters will show that modifying ionomer microstructures on electrodes are important to ionic conductivity.
Chapter 2. Research Goals and Hypotheses

Overall, the theory and fundamentals of bipolar membranes for electrochemical systems form the basis of the experiments carried out and the obtained results in this dissertation. The first results Chapter (i.e., Chapter 4) reports a versatile optical lithography process to fabricate a series of micropatterned BPMs with precise control over the interfacial area in the bipolar junction. The main goal of this work was to understand how the polarization behavior, reaction kinetics, and species transport changed as a function of interfacial area in bipolar junction region of BPMs. From the polarization experiments, a 2.28x increase in interfacial area led to a 250 mV reduction in the onset potential. Additionally, the same increase in interfacial area yielded marginal improvements in current density due to the junction region being under kinetics-diffusion control. Finally, the soft lithography approach was also conducive for fabricating BPMs with different chemistries ranging from perfluorinated polymer backbones to alkaline stable poly(arylene) hydrocarbon polymers. These polymer chemistries are better suited for fuel cell and electrolysis applications. The BPM featuring the alkaline stable poly(terphenyl) anion exchange membrane had an onset potential of 0.84 V, which was near the thermodynamic limit, and was about 150 mV lower than a commercially available variant.

Chapter 5 presents work on nanopatterning the surface of IEMs using BCP lithography. The main goal of this work was to see if smaller lateral feature sizes, which give rise to larger interfacial areas, would promote water splitting kinetics in bipolar junction regions. It was also desired to see if the smaller feature sizes reduced interfacial resistance species transport at membrane-liquid interfaces. Although a nanopatterned sulfonated poly(arylene ether ether ketone) (SPEEK) membrane was realized for the first time, it was not yet possible to fabricate
bipolar membranes. This is a future priority. Nevertheless, the electrochemical properties of the nanopatterned SPEEK was tested. Reducing the feature size on membrane surfaces to the nanoscale resulted in a 3 to 5% increase in through-plane conductivity without compromising its permselectivity or mechanical integrity.

Chapter 6 disseminates a way to manipulate the microstructure of thin film anion exchange ionomers (AEIs, which contain tethered cations) on electrode layers using sequence defined, grafted peptides that contain tethered carboxylate anions. The interface between the AEI and the sequence defined peptide represents an electrostatic interaction and bipolar junction region. The main goal of this work was to see how AEI thin film processing and electrostatic interactions at electrode surfaces affect AEI conductivity. In this work, it was discovered that moderately sized microphase separated ionic domains of the AEI, obtained either by peptide modified electrodes (30.0 ± 14.0 nm) or solvent vapor annealing (22.5 ± 5.0 nm), increased thin film in-plane ionic conductivity by a factor of two to three. Interestingly, the use of peptide modified electrodes in conjunction with solvent vapor annealing yields excessively large ionic grains that compromise ionic conductivity. Overall, judicious use of sequence defined peptides adsorbed to electrode surfaces, or solvent vapor annealing, encourage the appropriate microstructures of thin film AEIs resulting in ameliorated ionic conductivity.
Chapter 3. Experimental Methods

This Chapter summarizes the materials and experimental methods for the work presented in subsequent chapters. Synthesis/modification of the polymers used for preparing ionomers is discussed. The methods for preparing PDMS molds and alumina templates for micropatterned and nanopatterned membranes respectively, are detailed. The processing of ionomers into flat, micropatterned and nanopatterned membranes and flat/micropatterned interface BPMs is described. The construction and operation of 2 compartment homemade glass cell for measuring IEM and BPM properties is explained. Further, the procedures used to measure IEM properties like in-plane conductivity, through-plane conductivity, IEC, transference number, permselectivity, and water uptake are outlined. Testing the BPMs to determine their polarization behavior for water splitting is also discussed. Electrochemical impedance spectroscopy (EIS) was deployed during water splitting measurements to elucidate the sources of individual resistances that contribute to polarization behavior. The surfaces and cross-sections of flat, micropatterned and nanopatterned IEMs/BPMs have been imaged using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

The next section focuses on the procedures for depositing thin films of ionomers on electrode surfaces. First, the manufacture procedure of interdigitated electrodes used in this work is shown.

Section 3.1-3.11 of this chapter is reprinted with permission from “Kole, Subarna, et al. “Bipolar membrane polarization behavior with systematically varied interfacial areas in the junction region.” Journal of Materials Chemistry A (2021).”


*co-first authors
The ionomer films on electrode surfaces are modified using peptides and solvent vapor annealing.

The interactions between the peptide and ionomer on the electrode surface are examined using dynamic light scattering and quartz crystal microbalance dissipation (QCM-D). The ionomer films on electrodes were imaged using AFM to observe the change in microstructures because of peptide and solvent vapor annealing modification. FTIR measurements were also carried out to investigate solvent vapor annealing effect on peptide structures. Raman mapping of the IDEs confirmed the uniform distribution of ionomer and peptide over the entire electrode. Finally, ionic conductivity of the ionomer films is measured by extracting resistance values from EIS spectroscopy data.

3.1. Chemicals used for preparation of ionomers

The base polymers for making hydrocarbon poly(arylene ether) CEMs and AEMs were poly(arylene ether ether ketone) (PEEK) from Victrex and Udel® poly(arylene ether sulfone) (M_w = 60,000, ACS grade) from Acros Organics. Another type of hydrocarbon AEM, Orion TM1 polymer (medium molecular weight and an all-carbon backbone poly(arylene) chemistry), was sourced as a powder resin from Orion Polymer. The perfluorinated CEM was prepared from Nafion™ dispersion (20 wt% in alcohol-water mixture) sourced from Ion Power. The perfluorinated AEM, Gen 211b, was prepared by the National Renewable Energy Laboratory (NREL). Other chemicals for modifying the base polymers and fabricating membranes and material characterization using NMR spectroscopy are: chloroform (CHCl_3) (≥ 99.8 %), methanol (MeOH) (≥ 99.8 %), n-methyl-2-pyrrolidone (NMP) (> 99.0 %), 1-methylpyrrolidine (98 %), sulfuric acid (H_2SO_4) (≥ 95 %), chlorotrimethylsilane (≥ 98.0 %), dimethylsulfoxide
(DMSO) (≥ 99.9 %), deuterated dimethylsulfoxide (d6-DMSO) (99.5 %), deuterated chloroform (CDCl₃) (99.6 % D), reagent alcohol (90 % ethanol, 5 % methanol, and 5 % 2-propanol), N,N-dimethylformamide (DMF) (≥ 99.8 %), and isopropanol (≥ 99.5 %) obtained from VWR, paraformaldehyde (reagent grade) and stannic chloride (SnCl₄) from Sigma-Aldrich and N,N-dimethylacetamide (DMAc) (ACS grade) from Alfa Aesar. These were the materials used for preparing flat and patterned IEMs and BPMs.

All chemicals, to make AEI solutions for electrode surface modification studies, except poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) and azobisisobutyronitrile (AIBN), were received from VWR and used as is. These chemicals include chlorobenzene (≥99.5%), n-methyl pyrrolidone (NMP) (>99.0%), n-bromosuccinimide (NBS) (99%), N,N-dimethyl-n-decyl ammonium (>95%), sodium chloride (≥99.0%), sodium hydroxide, 2-butanone (99%), methanol (≥99.8%), chloroform (>99.8%) and 2-propanol (IPA) (>99.5%). PPO was obtained from Polysciences Inc. (Mn: 50k). AIBN (99.5%) was obtained from Sigma Aldrich.

3.2. Synthesis of ionomers

Synthesis of sulfonated poly(arylene ether ether ketone) (SPEEK): PEEK was dissolved in concentrated H₂SO₄ at room temperature and allowed to react for 2 days. The degree of sulfonation (DS) of PEEK was monitored during the reaction by extracting a solution and precipitating it in copious amounts of DI water to neutralize the sulfuric acid. The precipitated polymer was filtered and dried in a fume hood and then analyzed by ¹H NMR using d6-DMSO as the solvent. After the desired DS value was obtained, the SPEEK in H₂SO₄ was precipitated using the said procedure. The CEMs from synthesized SPEEK were prepared by dissolving SPEEK into NMP (5 wt%) and then drop casting the solution onto flat glass plates or
micropatterned PDMS molds placed on a leveled surface in an oven. The solvent was evaporated from the drop casted SPEEK solution by maintaining the oven temperature at 60 °C for 30 hours. Figure 18 shows the reaction scheme for SPEEK synthesis.\textsuperscript{16}

![Figure 18. Synthesis scheme for sulfonated poly(arylene ether ether ketone) (SPEEK) by reacting poly(arylene ether ether ketone) (PEEK) with concentrated sulfuric acid followed by neutralization of NaOH solution.](image)

Synthesis of quaternary ammonium polysulfone (QAPSf): Polysulfone (PSf) was dissolved in chloroform to form a 3 wt% solution. Paraformaldehyde and chlorotrimethylsilane were added to the mixture, and the solution was poured into a round bottom flask. The temperature of the flask was raised to 60 °C. Then, the reaction solution was capped with a rubber septum and placed under a nitrogen blanket. Then, the Lewis acid catalyst, SnCl\textsubscript{4}, was added. The degree of chloromethylation (DC) was monitored by withdrawing 10 mL of solution from the flask at various time periods. For a given time period, the solution was precipitated in methanol (5:1 volume ratio) followed by filtration. The collected solid was dried and analyzed via $^1$H NMR using CDCl\textsubscript{3}. Once the desired DC value was achieved, an identical precipitation procedure was followed for the whole solution after cooling the solution to room temperature. The acquired CMPSf solid was redissolved in CHCl\textsubscript{3} (10 wt%) and then reprecipitated in MeOH.\textsuperscript{39} The reaction scheme for CMPSf synthesis is shown in Figure 19.
Figure 19. Synthesis scheme for QAPSf by i.) chloromethylation of poly(arylene ether) sulfone (PSf) followed by ii.) quaternarization reaction with n-methyl pyrrolidine.

The precursor for PPO based AEI, brominated PPO, was synthesized via free-radical bromination of PPO in the presence of NBS with AIBN as the free radical initiator. A 7 wt% solution of PPO in chlorobenzene was prepared followed by addition of NBS into the solution (1.2 moles to each mole of PPO repeat units). 2 wt% of AIBN, to the amount of PPO dissolved, was added once the reaction temperature of 115 °C was attained. The reaction was carried out for 12 hours at the elevated temperature, then the solution was cooled to room temperature, and precipitated in methanol. The solid BrPPO solid was collected by vacuum filtration and then allowed to dry overnight in a fume hood. The solid was redissolved in chloroform and precipitated in methanol to remove unwanted impurities. The polymer formed was dried in a hood for 24 hours followed by drying under vacuum for 24 hours at room temperature to remove residual solvents. The degree of bromination at the benzyl and aryl positions of PPO (BrPPO)
was determined by $^1$H NMR. Then, a 5 wt% solution of BrPPO in NMP was prepared. To the resulting solution, N,N-dimethyldecyl amine (DMDA) was added to the dissolved BrPPO in the molar ratio of 1:1 (DMDA to bromomethyl groups as determined from $^1$H NMR). The resulting mixture was allowed to react overnight at 40 °C, then cooled to room temperature, and was then drop-casted on a glass plate on a leveled surface to yield a free-standing membrane. The membrane was ion-exchanged from the bromide anion form to the chloride anion by immersion in 1 M sodium chloride for 24 hours followed by excess rinsing with deionized water (18 MΩ, TOC < 10 ppb). The solid membrane material, PPO-QDMDA, was then dissolved at 1 wt%, in a 50-50 mixture of IPA and deionized water. The PPO AEI solution was stored at room temperature. Note: The $^1$H NMR spectrum of PPO-QDMDA substantiated that 100% of the bromomethyl groups were converted to quaternary benzyl ammonium bromide groups. The reaction scheme for this procedure is shown in Figure 20.
3.3. PDMS molds for micropatterned surface IEMs

A silicon submaster, using the procedure by Arges and co-workers, was prepared by a standard photolithography process. In this process, SU-8 2025 resist was diluted with GBL to obtain 55\% solid ratio. This solution was spincoated on to a silicon wafer at 2000 rpm for 45 seconds, soft baked at 95 °C for 30 minutes, cooled in a heat insulating cabinet for 30 minutes, and exposed to 225 mJ cm\(^{-2}\) UV radiation in presence of a chromium mask that has the desired pattern. Immediately after exposure, the silicon wafer was baked for 1 minute at 65 °C followed by 1 minute at 95 °C and allowed to cool slowly for 5 minutes. The wafer was developed by immersion in SU-8 developer for 5 minutes with gentle shaking and agitation, quenched in IPA and dried with nitrogen. The resulting wafer was thermally treated at 95 °C for 10 minutes.
Finally, PDMS was cured on top of the silicon submaster to obtain the micropatterned PDMS mold by using the following procedure: 10 mL PDMS solution (SYLGARD-184) and 1 mL curing agent were thoroughly mixed and poured onto the silicon submaster kept inside a desiccator. Vacuum was slowly applied to the desiccator and held for 30 mins. It was then heated to 75 °C to cure the PDMS mixture for 40 mins. Figure 21 shows a picture of the PDMS mold.

Figure 21. Picture of PDMS mold used for dropcasting ionomers to prepare micropatterned surface IEMs

3.4. Alumina templates for preparing nanopatterned surface IEMs

The materials used for making nanopatterned alumina templates on silica wafer were silicon wafer (Purewafer), poly(styrene-block-methyl methacrylate) \((M_n: 105k–106k \text{ g mol}^{-1}, \text{PDI}: 1.13)\) (Polymer Source Inc.), poly(styrene-block-methyl methacrylate) \((M_n: 132k–68k \text{ g mol}^{-1}, \text{PDI}: 1.01)\) (Polymer Source Inc.), polystyrene-random-poly(methylmethacrylate)-random-polyglycidyl methacrylate (PSrPMMArPG4) containing 76% styrene, toluene (VWR) trimethylaluminum (TMA, Sigma-Aldrich, 97%).

The first step in this process is the self-assembly of block copolymers (BCP) on silicon wafers. 1 wt% solution of the random copolymer PSrPMMArPG44 in toluene is spincoated on wafer
surface at 5000 rpm for 45 s and thermal annealed in presence of nitrogen at 200 °C for 10 min to graft the brush onto the wafer surface. Excess brush was rinsed off from the wafer surface by sonicating in toluene. Next, 1 wt% of the PS-\(b\)-PMMA (105k-106k g mol\(^{-1}\)) solution in toluene was spincoated on to the non-preferential brush surface at 5000 rpm for 45 s and thermal annealed in presence of nitrogen at 200 °C for 48 h. Identical procedure was adopted for self-assembly of PS-\(b\)-PMMA (132k-68k g mol\(^{-1}\)), but the annealing time was reduced to 20 h. Thermal annealing promotes microphase separation of the blocks into perpendicular lamella (PS-\(b\)-PMMA (105k-106k g mol\(^{-1}\))) or perpendicular cylinders (PS-\(b\)-PMMA (132k-68k g mol\(^{-1}\))).

\(\text{Al}_2\text{O}_3\) Atomic Layer Deposition (ALD) was carried out in a bench-top viscous-flow reactor (GEMStar-6 XT\textsuperscript{TM}) by alternate exposure of trimethylaluminum (TMA, Sigma-Aldrich, 97%) and water vapor using \(\text{N}_2\) (UHP, Airgas) as a carrier gas. Both TMA and water reservoirs were kept at room temperature. Five cycles of \(\text{Al}_2\text{O}_3\) ALD were conducted at 130 °C on the block copolymer film. The time sequence of each cycle was 60 s, 120 s, 60 s, and 300 s for TMA exposure, \(\text{N}_2\) purge, water exposure, and \(\text{N}_2\) purge, respectively.

The wafer was then subjected to oxygen dry etching in an Oxford PlasmaLab System 100 RIE tool (50 W RF power, 70 mTorr chamber pressure, 50 sccm gas flow rate, 10 min) to get rid of the polymer on its surface and convert the Al(OH)\(_3\) to alumina. This resulted in silica wafers with alumina nanostructures.

3.5. Processing of ionomers into flat, micropatterned and nanopatterned surface IEMs

The CEMs from synthesized SPEEK were prepared by dissolving SPEEK into NMP (5 wt%) and drop casting the solution onto flat glass plates, micropatterned PDMS molds or nanopatterned alumina templates placed on a leveled surface in an oven. The solvent was
evaporated from the drop casted SPEEK solution by maintaining the oven temperature at 60 °C for 30 hours. To prepare AEMs from the resulting polymer, CMPSf was dissolved in NMP to make a 5 wt% solution. N-methyl-pyrrolidine was added to this solution to convert the chloromethylated groups in CMPSf to quaternary ammonium groups. The ionomer solution was then drop casted on to flat glass plates in an oven at 60 °C for 24 hours. Nafion™ dispersion was diluted with reagent alcohol to make a 10 wt% solution. For every 9 mL of 10 wt% Nafion™ dispersion in reagent alcohol, 1 mL of DMF was added. This solution was drop casted on a flat glass plate or patterned PDMS mold and placed in an oven. The oven temperature was maintained at 60 °C overnight (14 hours) followed by a temperature of 120 °C for 2 hours to evaporate the solvents completely. The perfluorinated AEM was used as is. For the alkaline stable hydrocarbon AEM, Orion TM1 resin was dissolved in DMSO to make a 5 wt% solution and drop casted on a flat glass plate in an oven at 60 °C overnight (14 hours) followed by a temperature of 120 °C for 2 hours to evaporate the solvents completely. After that, the membrane was removed from the plate with the aid of DI water.

3.6. Fabrication of BPMs

For BPMs that contained water dissociation catalysts, a suspension of Al(OH)₃ in DI water was spray painted on the CEM and allowed to dry in a fume hood at room temperature (22 to 25 °C). Catalyst loadings were systematically varied from 0.02 mg cm⁻² to 0.50 mg cm⁻². BPMs were fabricated by hot pressing the flat or patterned CEM with an AEM at 5000 lb and 120 °C in a Carver thermal-mechanical press for 30 min. Then, the BPMs were solvent vapor annealed in a custom-built flow chamber at room temperature in a mixture of saturated 2-butanol (or saturated acetone for perfluorinated BPMs) and dry nitrogen. The flow rates were 5 sccm for each stream and the BPMs were annealed for 1 hour.
Figure 22. (a) Process flow diagram for fabricating micropatterned BPMs with systematically varied interfacial areas in the junction region. (b) Synthesis scheme to prepare nanopatterned ion exchange membranes
After annealing, the saturated solvent vapor stream was set to 0 sccm and the dry nitrogen stream was increased to 250 sccm for 10 minutes to rapidly remove solvent from the BPM.

The flow diagram for preparing micropatterned PDMS molds and micropatterned IEMs/BPMs is shown in Figure 22 (a). The flow diagram for preparing nanopatterned alumina templates and nanopatterned surface IEMs is shown in Figure 22 (b). Figure 23 shows the chemical structures of ionomers used for making BPMs. The following BPM chemistries were prepared: i) SPEEK/QAPSf hydrocarbon BPM ii) SPEEK/Orion TM1 hydrocarbon BPM iii) Nafion™/PF AEM perfluorinated BPM. Figure 24 shows the photographs of various synthesized IEMs and BPMs.
Figure 23. Chemical structures of ionomers used for synthesizing BPMs (a) Sulfonated poly(arylene ether ether ketone) (SPEEK) (b) Quaternary ammonium poly(arylene ether) sulfone (QAPSf) (c) Nafion<sup>TM</sup> (d) Perfluorinated anion exchange membrane (PF AEM) (e) Orion AEM
A homemade 4-point cell (Figure 25) was prepared to test the polarization behavior of BPMs and determine certain electrochemical properties of IEMs. Both compartments were filled with potassium nitrate (1 M KNO₃) salt solutions and separated by the membrane (IEM or BPM). The working electrodes were made of Pt-Ir mesh and connected to working and counter electrodes using platinum wires. Two Ag/AgCl reference electrodes were placed close to either side of the BPM using Luggin capillaries.
Figure 25. (a) Schematic of the 4-point cell used to evaluate BPM polarization behavior; (b) Picture of home-made 4-point cell for polarization experiments.
3.8. Measuring electrochemical properties of the IEMs

The in-plane ionic conductivity ($\sigma$) of AEMs and CEMs were measured with a 4-point platinum probe situated in polytetrafluoroethylene (PTFE) housing. The ionic conductivity measurements were carried out in DI water at room temperature. For measuring AEM hydroxide ion conductivity, the AEMs were ion-exchanged to the hydroxide form using 1 M KOH followed by rinsing with DI water that was bubbled with nitrogen\textsuperscript{43} (for minimizing carbonation of the AEM).\textsuperscript{42} The in-plane resistance of the membranes was measured via electrochemical impedance spectroscopy (EIS). Equation 1 in Chapter 1 was used to determine the ionic conductivity of the AEMs and CEMs from the in-plane resistance. Equation 2 in Chapter 1 was used to determine the ASR of the AEMs and CEMs.

Through-plane conductivity of the IEMs was measured with the help of the 4-point cell. Both compartments were filled with 0.5 M NaCl solution and Ag/AgCl reference electrodes were immersed in them on either side of the IEM. Equation 3 in Chapter 1 was used to calculate the through-plane conductivity of the membranes.

Permselectivity of the AEMs and CEMs were determined from the transference number ($T_i$) of the membranes with the help of equations 4 and 5 in Chapter 1. The $T_i$ was calculated from the membranes’ junction potential when separating 0.1 M NaCl\textsubscript{aq} and 0.01 M NaCl\textsubscript{aq} solutions\textsuperscript{38} in either compartment of the 4-point cell, measured using a multimeter.
3.9. Other properties of the IEMs

The degree of sulfonation (DS) of SPEEK was determined using equation 17 from the $^1$H NMR spectrum of SPEEK in Figure 26.

\[
DS = \frac{4 \times \text{Area}(\delta=7.5 \text{ ppm})}{\text{Area}(\delta=7.65 \text{ to } 8.1 \text{ ppm})}
\]  \hspace{1cm} (17)

Equation 18 provides the calculation for SPEEK’s IEC from the degree of sulfonation.$^{38}$

\[
\text{IEC [meq g}^{-1}] = \frac{1000 \times \text{DS}}{\text{MW}_{\text{PEEK, monomer}} + \text{DS}(\text{MW}_{\text{SO}_3} + \text{MW}_{\text{H}^+} - 1)}
\]  \hspace{1cm} (18)

\(\text{MW}_{\text{PEEK, monomer}}\) = Molecular weight of PEEK repeat unit (g mol$^{-1}$)

\(\text{MW}_{\text{H}^+}\) = Molecular weight of proton (g mol$^{-1}$)

\(\text{MW}_{\text{SO}_3}\) = Molecular weight of SO$_3$ (g mol$^{-1}$)

The degree of chloromethylation (DC) of CMPSf was calculated from its NMR spectrum (Figure 27a) and equation 19.

\[
\text{DC} = \frac{2 \times \text{Area}(\delta=4.5 \text{ ppm})}{\text{Area}(\delta=7.8 \text{ ppm})}
\]  \hspace{1cm} (19)

Conversion of chloromethylated sites to cation sites was calculated from equation 20 using NMR spectrum of QAPSf in Figure 27b and the IEC of QAPSf was calculated$^{44}$ from equation 21.

\[
\text{Conversion} = \frac{\text{Area}(\delta=2.85 \text{ to } 3.15 \text{ ppm})}{2 \times \text{DC} \times \text{Area}(\delta=1.7 \text{ ppm})}
\]  \hspace{1cm} (20)

\[
\text{IEC[meq g}^{-1}] = \frac{1000 \times \text{DC}}{\text{MW}_{\text{PSf, monomer}} + \text{DC}(\text{MW}_{\text{cation}} + \text{MW}_{\text{chloride}} + \text{MW}_{\text{CH}_2} - 1)} \times \text{Conversion}
\]  \hspace{1cm} (21)

\(\text{MW}_{\text{PSf, monomer}}\) = Molecular weight of PSf repeat unit (g mol$^{-1}$)

\(\text{MW}_{\text{cation}}\) = Molecular weight of cation (g mol$^{-1}$)

\(\text{MW}_{\text{chloride}}\) = Molecular weight of chloride ion (g mol$^{-1}$)

\(\text{MW}_{\text{CH}_2}\) = Molecular weight of CH$_2$ (g mol$^{-1}$)
Figure 26. $^1$H NMR spectra of SPEEK (a) used for preparing flat and micropatterned IEMs. The degree of functionalization of sulfonated groups was 0.52 and ion-exchange capacity was 1.65 meq g$^{-1}$ (b) used for preparing nanopatterned IEMs. The degree of functionalization of sulfonated groups was 0.60 and ion-exchange capacity was 1.78 meq g$^{-1}$. 
Figure 27. (a) $^1$H NMR spectra of CMPSf. Degree of chloromethylation was 1.26 (b) $^1$H NMR spectra of QAPSf. The ion-exchange capacity was 2.34 meq g$^{-1}$. 
Figure 28. (a) $^1$H NMR spectrum of BrPPO (b) $^1$H NMR spectra of PPO-QDMDA Cl$^-$. The IEC of PPO-QDMDA in the chloride form was 1.49 mmol g$^{-1}$. 
Equations for determining bromine DF values to benzyl and aryl positions of PPO:

\[
DF_{\text{Br to benzyl}} = \frac{\text{Area(}\delta \approx 4.3)}{\text{Area(}\delta \approx 6.4 - 7.0) + 2 \cdot \text{Area(}\delta = 6.0 - 6.4)}
\]  
(22)

\[
DF_{\text{Br to aryl}} = \frac{2 \cdot \text{Area}(\delta \approx 6.0 - 6.4)}{\text{Area}(\delta \approx 6.4 - 7.0) + 2 \cdot \text{Area}(\delta \approx 6.0 - 6.4)}
\]  
(23)

Equation for determining DF values of bromomethylated groups to PPO:

\[
DF_{\text{CH}_2\text{Br}} = \frac{\text{Area}(\delta \approx 4.4)}{\text{Area}(\delta \approx 6.4 - 7.0)}
\]  
(24)

Conversion of brominated sites to cation sites:

\[
\text{Conversion} = \frac{\text{Area}_{\text{cation substituent}}(\delta)}{\text{Ratio} \cdot \text{Area}_{\text{benzylcation substituent}}(\delta)}
\]  
(25)

\[
\text{Ratio} = \frac{\# \text{ of protons for cation substituent}}{\# \text{ of protons for PPO substituent}}
\]  
(26)

IEC of PPO-QDMDA in the chloride form is calculated by integrating the \(^1\text{H}\) NMR spectra of PPO-QDMDA (Figure 28) and knowing the DF value and using equation 27.\(^{43,45}\)

Theor. IEC \([\text{mmol g}^{-1}]\)

\[
= \frac{\text{DF}_{\text{benzyl}} \cdot 1000 \cdot \text{Conversion}}{\text{MW}_{\text{PPO monomer}} + \text{DF}_{\text{benzyl}} \cdot (\text{MW}_{\text{cation}} + \text{MW}_{\text{chloride}} - 1) + \text{DF}_{\text{aryl}} \cdot (\text{MW}_{\text{bromine atom}} - 1)}
\]  
(27)

The IEC of other ionomers were provided by their manufacturers.

Water uptake of the membranes was calculated as a percentage in weight change of the dry membranes before and after immersion in DI water for 24 hours using equation 12 in Chapter 1.
3.10. Polarization behavior and electrochemical impedance spectroscopy of flat and micropatterned BPMs for water dissociation

The 4-point cell was connected to a Gamry Reference 3000 Potentiostat/Galvanostat for obtaining the polarization curves of BPMs. Polarization curves were obtained by running chronoamperometry experiments on the BPMs in the voltage range of 0-3 V with a step size of 0.1 V. The voltage was held at a constant value for 15 seconds and the final steady state current at each step was recorded.

Figure 29 shows the method for determining onset potential for water splitting in BPMs. “Onset Of Slope” application in Origin 2020 was used to draw tangents in linear parts of the pol curve immediately before and after the point of onset potential. The application then calculates the intersection point of the slopes.16

Electrochemical impedance spectroscopy (EIS) was performed in galvanostatic mode across the frequency range of 100,000 Hz to 0.01 Hz to measure in-plane resistance and apparent rate constant for water dissociation ($k_d^{app}$) by data fitting of EIS curve (Figure 30) in the low frequency regime of the Nyquist plot. The alternating current perturbation was 1 mA and ten data points were collected per decade of frequency values.39 An electric circuit equivalent (ECE) model based on literature46 was used to fit the EIS data and extract the values of individual circuit elements. The ECE model is discussed in detail in Section 4.3 of Chapter 4.
Figure 29. 2-tangent method for determining onset potential for water splitting.

Figure 30. An example of the extraction of $k_d^{app}$ from Gerischer element by data fitting of EIS curve in the low frequency regime of the Nyquist plot.

3.11. SEM and AFM imaging of membrane surfaces/cross-sections and substrates for preparing nanopatterns

A FEI Quanta 3D FEG FIB/SEM imaged the surface and cross section of membranes with a backscattered electron detector. The membrane surfaces and cross sections were sputtered with 20 nm of platinum for micropatterned IEMs and 10 nm of platinum for nanopatterned IEMs to
enhance the imaging contrast. The working distance for imaging ranged from 3 mm to 18 mm and accelerating voltage for imaging was 5 kV for micropatterned IEMs (working distance of 3 mm to 3.2 mm and 2 kV accelerating voltage for nanopatterned IEMs).^{16}

Atomic force microscopy (AFM) was performed using a Horiba SmartSPM 1000 in the tapping mode using uncoated Si cantilevers (ACTA-SS, k = 37 N m$^{-1}$, 125 $\mu$m length) operating at a resonant frequency of 287 kHz and free amplitude of 30 nm to image alumina templates containing nanostructures and carry out an etch test and determine the best parameters for synthesizing nanopatterned BPMs.

### 3.12. Interdigitated electrode (IDE) substrates manufacture

The materials used for IDE manufacture were S1813 photoresist (Microchem), MF-319 developer solution (Microchem), silicon wafers with 1 $\mu$m thick thermally grown oxide layer (WRS Materials), gold pellets (ACI Alloys, 99.999%), titanium pellets (RDM, 99.999%), NMP (>99.0%, VWR) and acetone (>99.5%, VWR).

The photoresist was spincoated on to silicon wafers. Photoresist coated wafer was baked at 115 °C and placed in a mask aligner with a chromium mask of the IDE design and the resist was exposed to 225 mJ/cm$^2$ of UV light. After the exposure, the wafer was immersed in the developer for 30 seconds with gentle shaking followed by quenching with excess deionized water and nitrogen drying. 15 nm titanium was thermally evaporated on to the patterned wafers followed by 135 nm of gold. The remainder of the resist on the wafer substrates was lifted-off by immersing in acetone and placing in an ultra-sonic bath for 5 minutes. The acetone was then replaced, immersed wafer was placed in an ultra-sonic bath again for 5 minutes. Afterwards, the
wafer was immersed in NMP solvent at 60 °C for 5 minutes. The resulting IDEs were rinsed excessively with deionized water and then dried with nitrogen.\textsuperscript{23}

Figure 31. (a) Geometric dimensions of the gold IDEs (b) photograph of the IDE
3.13. Synthesis of peptide sequence and modification of ionomer films on electrode surfaces

The peptide sequence CVPGEG (>97%, GenScript) was used (supplied by Renner lab, Case Western Reserve University). It featured a negatively charged guest residue glutamic acid (E), to bind to the positively charged AEI through electrostatic interactions. The peptide was acylated and amidated to isolate the negatively charged guest residue.\textsuperscript{36,40}

To prepare the peptide on IDE substrates, the IDE samples were first rinsed with DI water, then immersed in 10 $\mu$g/mL peptide sodium hydroxide solution (10 mM NaOH) and allowed to incubate on a rocker for 1 hr. After peptide incubation, the IDE samples were immersed in 10 mM NaOH solution and incubated for 1 hour on a rocker to rinse off loosely-bound peptide, followed by rinsing with DI water to remove rest of the NaOH solution. All IDE samples were dried in nitrogen gas after the final rinse. To prepare PPO-QDMDA AEI thin layers on substrates with or without peptides, PPO-QDMDA chloride (1 wt% in 2-propanol/DI H\textsubscript{2}O) was added to 10 mM solutions of sodium hydroxide (NaOH) to yield a concentration of 10 $\mu$g mL\textsuperscript{-1} of AEI in solution. The substrates were immersed in this diluted AEI solution for 2 hours for AEI adsorption to the substrate surface. Then, the substrates were immersed in 10 mM NaOH solution overnight to rinse away excess material, followed by rinsing with excess DI H\textsubscript{2}O, and drying with nitrogen gas. The process for depositing peptide sequence and ionomer is detailed in Figure 32.
Figure 32. Process of using peptides to assemble AEI layers onto substrates. A.) Amino acid sequence of thiol-terminated elastin like peptides bound to gold with a detailed view of the negatively charged guest residue (E) functional group; B.) Chemical structure of PPO-QDMDA AEI added to the substrate surfaces; C.) Process for peptide and/or AEI deposition on to IDEs (identical process used for gold QCM/coated-wafers or SiOx wafers).

A home-built solvent vapor annealing (SVA) chamber exposed the IDE samples to 2-butanone (VWR, 99%) vapor to alter the microstructure of the samples. This is a similar chamber reported by Arges et al.\textsuperscript{23} Solvent vapor annealing was carried out at 20 °C with a mixture of saturated 2-butanone (150 sccm – saturated vapor pressure of 10.4 kPa) and pure, dry nitrogen gas (5 sccm). The samples were exposed to this flowrate for 2 hours. At the end of 2 hours, the saturated 2-butanone stream was terminated, and the dry nitrogen stream had its flow rate increased to 250 sccm to rapidly remove the solvent and to quench the microstructure.
3.14. Study of AEI-peptide interactions

A preliminarily evaluation of the peptide and AEI interactions (observed from particle aggregation) was performed by dynamic light scattering (DynaPro NanoStar, controlled by software Dynamics 7.1.9, 0.2 to 2500 nm range). The hydrodynamic radius changes of the peptide sequence CVPGEG (2 mg mL\(^{-1}\) in DI water) in the solution of AEI (1:1 molar concentration ratio to peptide) were compared to a sequence with neutral guest residue CVPGVG, at 90° scattering angle and a fixed wavelength of 662 nm. All tests were performed at 25 °C, triplicated (n=3).

A quartz crystal microbalance with dissipation (QCM-D, Q-Sense Explorer, controlled by Q-Soft integrated software from Biolin Scientific) was used to investigate the interactions between peptide and AEI to a gold surface in aqueous hydroxide solutions, where the frequency shifts and energy dissipation are monitored with time.\(^{47}\) Experiments were carried out in a flow module at 150 μL min\(^{-1}\) and 18 °C with clean gold coated sensors (QSX 301, 5 MHz, Biolin Scientific). A 10 mM NaOH solution served as the baseline and a solution of 10 μg mL\(^{-1}\) peptide in 10 mM NaOH was utilized to functionalize the gold. Experimental runs consisted of introducing solutions and allowing them to come to equilibrium before a new solution was added. All runs began with a stable baseline solution (below 0.5 Hz frequency shifts over 10 minutes) followed by a peptide solution, then a rinse with baseline solution to remove unbound peptide. After the peptide rinse, a 10 μg mL\(^{-1}\) solution of AEI in 10 mM NaOH was used and a baseline solution served as the final rinse. The third overtone (15 MHz) was used in data analysis of rigid films. All experiments were performed in triplicate (n=3), unless otherwise noted. All QCM-D data were analyzed by QSense Dfind Software (Biolin Scientific). For AEI assembled on gold
without peptide, the Dfind Smartfit function was utilized (which is based on the Voigt model) to estimate mass, thickness, viscosity and the elastic modulus. The model is appropriate for significant dissipation shifts and/or well-separated frequency shifts for the different harmonics. The QCM-D data gathered for AEI assembled without peptide was represented well by the viscoelastic model (goodness of fit > 0.9 on average), while the data gathered for the AEI assembled on the peptide layer was not (goodness of fit ~0.4 on average). Therefore, the Composite Sauerbrey model was used for analyzing the AEI layer assembled on the peptide anchored to the gold sensors since the dissipation shift was negligible. This model calculates the film thickness according to the Sauerbrey equation using a weighted average of all harmonics. Using the assumed density values of the AEI polymer and peptide (1.06 g cm$^{-3}$ for AEI, based upon PPO density value, and 1.10 g cm$^{-3}$ for the CVPGEG peptide, based on hydrated protein density found in the Dfind Software), the mass uptake was converted to film thickness.

### 3.15. AFM imaging and analysis of AEI microstructures on IDE substrates

An atomic force microscope (AFM, Dimension 3100, Veeco Digital Instruments by Bruker, USA) was used to investigate the surface morphology of AEI assembled on gold sensors and IDE samples. A silicon cantilever (NCHV-A, Bruker, USA) with spring constant of 40 N m$^{-1}$, nominal radius of 8 nm and resonant frequency of 328 kHz were used. Height and phase images were collected in tapping mode with scan rate of 1 Hz, resolution of 512×512 pixels and scan size of 500×500 nm$^2$. All the samples were placed in the AFM chamber at room temperature in air. NanoScope Analysis 1.50 (Bruker, USA) was used for image analysis. The phase separated grain diameters were measured using ImageJ. The right corner quarter of phase images was used for analysis, and all grains in that section were counted. If the grain is elliptical, the major axis is
used. The analysis was performed on 11 grains for AEI assembled without peptide (one sample), and 13 grains for AEI assembled with peptide (one sample).  

3.16. FTIR characterization of peptide structure  
The secondary structure of peptide when assembled on a gold QCM sensor was characterized by Fourier-transform infrared spectroscopy (FTIR). Measurements were performed using a Nicolet iS50R FTIR (ThermoFisher Scientific) spectrometer, equipped with a mercury cadmium telluride (MCT) detector and a VeeMAX III accessory at 80°. The MCT was cooled with liquid nitrogen and the system was purged with pure nitrogen gas for 30 min before all experiments. The sensors were made by following the same procedure as samples for QCM-D, with one exposed to DI water and another to 2-butaone. The background spectra were taken on a clean bare gold sensor, and subtracted from spectra taken with the assembled peptide, all spectra were collected with 2000 scans.

3.17. Raman spectroscopy and mapping of IDEs and peptide coated IDEs  
Raman spectra and maps were collected on a Renishaw inVia Reflex Raman Microscope operated in surface enhanced Raman scattering (SERS) mode. The wavelength of laser used for the experiments was 785 nm with a wavenumber scan range of 0-2000 cm⁻¹ and exposure time of 10 sec. Bare IDE was used as background. Same settings were used to obtain the maps. A 50 μm x 50 μm area was scanned with step size of 10 μm in both x and y directions. Data was processed using WiRE (Windows-based Raman Environment) software.
3.18. AEI film conductivity experiments

The AEI and adsorbed peptide (if applicable) on the electrode pads of the IDE substrate was scraped away using a cotton Q-tip to make electrical connections. The polymer film resistance was determined using electrochemical impedance spectroscopy (EIS - Gamry 3000 Ref Potentiostat/Galvanostat with a frequency response analyzer). The frequency range was set from 100,000 to 1 Hz with an oscillatory amplitude of 0.1 mA. An electric circuit equivalent (ECE) model (Figure 52B) was used to fit the impedance data and determine the AEI electrical resistance. The ionic conductivity was determined from the ionomer electrical resistance using equation 28 and the dimensions of the IDE (Figure 31).

\[ \sigma = \frac{1}{R} \cdot \frac{d}{l(N-1)t} \]  

(28)

\( \sigma \): in-plane ionic conductivity

\( R \): in-plane ionic film resistance

\( d \): Spacing between teeth on IDE (100 μm)

\( l \): Length of teeth on IDE (4500 μm)

\( t \): AEI film thickness on IDE substrate

\( N \): # of teeth on IDE substrate
Chapter 4. Scaling the Interfacial Area of a Bipolar Membrane Junction to the Onset Potential and Current for Water Dissociation

4.1. Introduction

In a BPM, the CEM contains a polyanion and the AEM features a polycation. The oppositely charged polymers at a polyanion-polycation shared interface have been described as an abrupt junction that is analogous to p-n junctions found in semiconductor devices.\textsuperscript{17, 18} However, it is important to note here that there are some differences in these two systems arising due to difference in size of charged particles and variations in concentration/mobility of ions or charges.\textsuperscript{52, 53} The opposite charges at the AEM-CEM interface impose a local electric field that can be augmented with an externally applied electric field for dissociating water into hydronium and hydroxide ion charge carriers via second Wien effect.\textsuperscript{14, 54, 55}

Effective water splitting at the bipolar junction interface, often measured through the onset potential for water splitting and the current density for water splitting at a particular cell voltage,\textsuperscript{15} depends on bulk AEM and CEM properties as well as other factors like the type of water dissociation catalyst present at the interface and quality of polycation-polyanion interface. In the recent years, due to a wide range of IEMs with different functionalities and stabilities to choose from, it is possible to tailor BPMs specific to a particular application or operating conditions (temperature, pH).\textsuperscript{52}

\hspace{1cm}

This chapter is reprinted with permission from “Kole, Subarna, et al. “Bipolar membrane polarization behavior with systematically varied interfacial areas in the junction region.” \textit{Journal of Materials Chemistry A} (2021).”
There are numerous types of water dissociation catalysts used in bipolar junctions and they often include materials with weakly basic or acidic moieties (e.g., poly(vinylpyridine) and poly(acrylic acid), graphene oxide and metal hydroxides).

The quality of polycation-polyanion interface depends on the fabrication method of the BPM. Large distances between the fixed charges in the bipolar junction region, potentially caused by air bubbles or particles, deteriorate the effective width of the local electric field. The consequence of a poor interface necessitates larger cell voltages for dissociating water in BPMs. Hence, making adequate interfacial contact between the polycation and polyanion in BPMs, is paramount for minimizing BPM polarization.

Most materials related research about BPMs has focused on developing and evaluating water dissociation catalysts. BPM fabrication and manufacture has received less attention. The lamination of AEM and CEM together through a mechanical hot press makes it difficult to mitigate the inclusion of air bubbles at the interface that compromise BPM performance. The direct application of polycation or polyanion dissolved in solution on the oppositely charged membrane also has challenges as it requires that the one polymer be soluble (or dispersed well in a solvent) while the receiving oppositely charged membrane being insoluble to the solvent and resisting swelling during the application process. The direct application process has mainly relied upon liquid solution deposition, aerosolized spray deposition, or spin-coating approaches. More recently, Pintauro and co-workers, and others, have created intimate, 3D bipolar junctions through electrospinning a polyanion or polycation followed by depositing a water dissociation catalyst and electrospinning the oppositely charged polymer. Then, the layered
electrospun mats were exposed to solvent vapor to form a compact bipolar junction. The 3D bipolar junction BPMs displayed superior performance, in terms of onset potential and current density at a particular cell voltage, when compared to a commercially available BPM (Fumasep®). Although it is recognized that increasing the interfacial surface area between the polycations and polyanions in BPMs improves the current density and onset potential for water splitting, it is unclear how these metrics scale with interfacial area.

4.2. Objectives

In this work, the process of soft lithography was adopted for preparing BPMs with systematically varied interfacial areas. This methodology was inspired from previous reports that micropatterned surfaces of CEMs (e.g., Nafion™) and AEMs for increasing the interfacial area between the electrode and membrane in catalyzed coated membranes (CCMs) used in low-temperature fuel cells. The increased interfacial area resulted in a reduction of charge-transfer resistances for hydrogen oxidation and oxygen reduction reactions. The micropatterned CEMs from soft lithography were deposited with a water dissociation catalyst (aluminum hydroxide (Al(OH)₃) nanoparticles) followed by a thermal-mechanical press with an AEM to prepare BPMs. To ensure adequate interfacial contact in the bipolar junction, the BPMs were solvent annealed in a custom-built flow chamber that is traditionally used for solvent annealing thin film block copolymers. A 4-point electrochemical cell was then used to assess the water splitting kinetics in micropatterned and non-patterned BPMs.
Figure 33. Comparison of this work with previous reports (a) Previous work done by Pintauro et. al. to prepare high interfacial area BPM using electrospinning$^{15}$ (b) Preparation of systematically varied interfacial area BPMs via soft-lithography.
4.3. Results and discussions

Table 1. Properties of AEMs and CEMs used in BPMs

<table>
<thead>
<tr>
<th>Membrane</th>
<th>SPEEK</th>
<th>QAPSf</th>
<th>Nafion™</th>
<th>PF AEM</th>
<th>Orion AEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>26.7±3.8</td>
<td>37.3±6.4</td>
<td>24.7±3.0</td>
<td>28.3±3.5</td>
<td>37.0±3.6</td>
</tr>
<tr>
<td>σ (mS cm(^{-1}))(^a)</td>
<td>110±1.0</td>
<td>59±1.2</td>
<td>100±0.1</td>
<td>15±0.5</td>
<td>50±0.0</td>
</tr>
<tr>
<td>ASR (Ω-cm(^2))(^a)</td>
<td>0.025±0.0</td>
<td>0.063±0.01</td>
<td>0.025±0.0</td>
<td>0.189±0.03</td>
<td>0.074±0.0</td>
</tr>
<tr>
<td>Transference number(^b)</td>
<td>0.96±0.0</td>
<td>1.00±0.0</td>
<td>1.00±0.0</td>
<td>0.96±0.1</td>
<td>0.80±0.0</td>
</tr>
<tr>
<td>Permselectivity(^b)</td>
<td>0.94±0.0</td>
<td>1.00±0.0</td>
<td>1.00±0.0</td>
<td>0.94±0.1</td>
<td>0.70±0.1</td>
</tr>
<tr>
<td>IEC (meq g(^{-1}))(^b)</td>
<td>1.65±0.06</td>
<td>2.34±0.02</td>
<td>0.91(^c)</td>
<td>0.91(^c)</td>
<td>2.1(^c)</td>
</tr>
<tr>
<td>Water uptake (%)(^b)</td>
<td>5.0±5.3</td>
<td>38.4±2.5</td>
<td>51.4±37.3</td>
<td>27.6±2.7</td>
<td>11.8±2.2</td>
</tr>
</tbody>
</table>

\(^a\)Measured in the proton or hydroxide ion form; \(^b\)Measured in the sodium ion form or chloride ion form; \(^c\)Value provided by the manufacturer

Table 1 presents the individual properties of AEMs and CEMs used to fabricate BPMs. These properties include membrane thickness, ionic conductivity, transference number and permselectivity for the counterion, ion-exchange capacity (IEC), and water uptake. The individual AEMs and CEMs are below 50 µm in thickness and the resulting BPMs are less than 125 µm in thickness. The commercial baseline variant, the Fumasep\(^®\) BPM from Fumatech, was 195 µm thick.

Table 2. Thicknesses of various BPMs used in this work

<table>
<thead>
<tr>
<th>BPM chemistry</th>
<th>Thickness (flat BPM)</th>
<th>Thickness (patterned BPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEEK/QAPSf BPM</td>
<td>70 µm</td>
<td>74 µm</td>
</tr>
<tr>
<td>Nafion™/PF AEM BPM</td>
<td>91 µm</td>
<td>104 µm</td>
</tr>
<tr>
<td>SPEEK/Orion AEM BPM</td>
<td>119 µm</td>
<td>124 µm</td>
</tr>
</tbody>
</table>
Table 2 provides the thickness values for all BPMs studied in this report. Surface patterning did not significantly alter the BPM thickness (< 8% than the average value for all BPMs prepared for a given chemistry). Thicker membranes have the undesired consequence of greater area specific resistance (ASR) values that can compromise cell efficiency. Further, the poly(arylene ether) and perfluorinated AEMs and CEMs have permselectivity values over 0.9 making them excellent candidates for mitigating co-ion leakage in electrochemical cells. The Orion AEM had a slightly lower permselectivity value (0.8). Despite this shortcoming, it will be shown later that this AEM paired with the more permselective SPEEK results in a BPM with low co-ion leakage and thus minimal crossover current. The ionic conductivity in every variant is over 15 mS cm\(^{-1}\) in DI water. Using the ionic conductivity values and the membrane thickness values, the ASR values were calculated (Table 1) and the highest ASR value was 0.189 \(\Omega\)-cm\(^2\). It is worth noting that the ohmic drop from the BPMs composed of individual AEMs and CEMs will be regulated by the highest ASR value of the CEM or AEM material in the BPM. This is caused by iso-neutrality constraints. For instance, every proton gated from the CEM side in a BPM is accompanied by a hydroxide ion from the opposite AEM side. The limitation of ion migration will be important for understanding BPM performance in the mixed control region of the polarization curves. Overall, the ASR values, as well as the low water uptake values, demonstrate that the AEMs and CEMs are good candidates for fabricating BPMs.

The availability of selective and low-resistant AEMs and CEMs made it possible to fabricate BPMs with systematically varied interfacial areas using soft-lithography. In this report, a particular interfacial area value is expressed as the normalized interfacial area (NIA) value – which is the interfacial area divided by the geometric area calculated from the geometry of the
silicon template. Previous research has shown that direct thermal lamination of AEMs and CEMs can lead to poor performing BPMs when compared to direct drop casting or spray deposition of one type of ion-containing polymer onto the oppositely charged polymer membrane. Initial studies attempted the spray deposition approach to fabricate BPMs using a quaternary benzyl ammonium poly(2,6-dimethyl 1,4-phenylene oxide) (QAPPO) dissolved in a water-2-propanol mixture (1 to 5 wt% in a 50:50 solvent mixture). However, the water-alcohol mixture containing QAPPO swelled the receiving SPEEK CEM during BPM fabrication. Similarly, the dilute PF AEM solutions (1 to 5 wt% in an alcohol-water-DMAc 40:40:20 mixture) swelled the receiving Nafion™ CEM. Due to these challenges, the direct spray deposition approach was abandoned, and the drop casting approach was not pursued further.

To produce mechanically robust and high quality BPMs, a thermal-mechanical lamination process was adopted followed by solvent vapor annealing to ensure good interfacial contact between the polycation and polyanion in the junction region. For controlled studies that generated BPMs without a water dissociation catalyst, the spray deposition step of Al(OH)₃ in water on top of the CEM was skipped. Additionally, the solvent vapor annealing step was skipped for controlled studies that examined BPMs without the additional processing step to ensure good interfacial contact between the oppositely charged polymers.
Figure 34. (a) Electron micrographs of the membranes’ cross-section at each stage of the SPEEK/QAPSf hydrocarbon BPM fabrication process: SPEEK CEM with topographical patterns, after spray deposition of catalyst layer on patterned side, thermal-mechanical press of SPEEK CEM and QAPSf AEM (formation of BPM), and after solvent annealing the BPM. (b) Electron micrographs of the surface of micropatterned SPEEK with different well diameters. Below these micrographs, the normalized interfacial area (NIA) values are provided. Smaller feature sizes gave larger normalized interfacial area values.
Figure 35. (a) Electron micrographs of the surface of micropatterned Nafion™ with different well diameters. (b) Cross-sectional electron micrographs at each stage of the all perfluorinated BPM fabrication process: Nafion™ CEM with topographical patterns, after spray deposition of catalyst layer on patterned side, thermal-mechanical press of Nafion™ with PF AEM, and after solvent annealing the BPM. (c) Cross-sectional electron micrographs at each stage of the SPEEK/Orion hydrocarbon BPM fabrication process: SPEEK CEM with topographical patterns, after spray deposition of catalyst layer on patterned side, thermal-mechanical press of SPEEK with Orion AEM (formation of SPEEK/Orion BPM), and after solvent annealing the BPM.
Figure 34a provides the cross-sectional SEM images of: SPEEK CEM with topographical patterns, followed by spray deposition of Al(OH)$_3$ nanoparticles on to the SPEEK CEM, thermal-mechanical pressing the SPEEK CEM with a QAPSf AEM, and then solvent vapor annealing of the resultant BPM. The cross-sectional SEM image of the micropatterned SPEEK-QAPSf BPM after the thermal-mechanical press demonstrates that the QAPSf did not fill in the topographical wells in the CEM completely. The presence of the topographical features in these electron micrographs demonstrate that surface patterns, and their interfacial area, are maintained after thermal-mechanical pressing. Hence, the NIA values calculated from the geometric patterns observed on the CEM surfaces were used for probing how interface area affects water splitting in BPMs in subsequent experiments. However, the thermal-mechanical pressing process may have slightly altered the NIA values. After solvent vapor annealing, the surface patterns are no longer observed in the cross-sectional SEM image and a compact interfacial polycation-polyanion layer (i.e., a bipolar junction) was formed.

The generation of topographical patterns on SPEEK and Nafion$^\text{TM}$ were produced from PDMS molds that were generated from soft lithography techniques. The surface patterns of the CEMs were defined by chromium mask used in the photolithography exposure step. Figure 34b shows top-down SEM images of SPEEK with 80, 40, 33 and 20 $\mu$m topographical well diameters and the resultant NIA values they produce. A smaller well diameter generates a larger NIA value.

Figure 35a shows SEM surface images of micropatterned Nafion$^\text{TM}$. Figure 35b provides the cross-sectional SEM images during the fabrication of all-perfluorinated BPMs from Nafion$^\text{TM}$
and PF AEM. Figure 35c shows the cross-sectional SEM images during the fabrication of a hydrocarbon, alkaline resilient BPM with Orion AEM paired with SPEEK.

An advantage of the PDMS molds generated by the soft lithography process is that they are reusable and can be used with both CEM chemistries of SPEEK and NafionTM. They can also be used with the AEM chemistries of QAPSf, PF AEM, Orion AEM, and QAPPO. Each one of these AEM or CEM chemistries were dissolved in either NMP, DMAc, DMF, alcohol, or alcohol-water mixtures. The PDMS molds maintain their structures and integrity with those solvents.

Overall, Figure 34 and Figure 35 demonstrate a versatile and robust process to produce CEMs with systematically defined topographical micropatterns that are subsequently used to fabricate BPMs with good interfacial contact. Systematically changing the surface pattern feature size allowed control over the NIA value in the bipolar junction region in BPMs. Additionally, the resultant PDMS mold from soft lithography were compatible with a multitude of AEM and CEM chemistries and solvents used to dissolve those polymers. Prior to exploring how interfacial area of bipolar junction interfaces impact the Figures of Merit for BPM performance, it is necessary to discuss the importance of a water dissociation catalyst and solvent vapor annealing on BPM performance. Figure 36 presents the polarization behavior of a commercially available BPM, Fumasep®, and 4 different types of SPEEK/QAPSf variants with planar interfaces that featured no water dissociation catalyst and a water dissociation catalyst, and that were solvent vapor annealed and non-annealed.
Figure 36. Polarization curves for non-patterned (i.e., planar interfaces) SPEEK/QAPSf BPMs with and without Al(OH)$_3$ nanoparticle water dissociation catalysts and with and without solvent vapor annealing processing. Error bars correspond to the standard error for n=3 independent samples.

The current response before the onset potential (below 1-1.5V), which typically becomes flat and mimics a limiting current, hails from the diffusion of co-ion crossover. The higher the permselectivity of the polymers used in the BPM resulted in BPMs with a low crossover current density value. To illustrate how electrolyte crossover impacts polarization behavior, a BPM with sub-mm hole was tested in the 4-point cell setup. The presence of a small hole gave a linear current response across the BPM voltage drop (Figure 37), and this crossover current obfuscates the contribution from water-splitting in the BPM (i.e., no limiting current can be seen before the onset potential for water splitting). It leads to poor current utilization in bipolar electrodialysis as some of the current is not being used for water-splitting.
With respect to the SPEEK/QAPSf BPMs that did not contain a water dissociation catalyst, both BPMs displayed low current responses (< 15 mA cm$^{-2}$) in Figure 37 across the voltage range up to 3 V. Additionally, onset potentials for these BPMs were not clearly apparent as a rapid increase in current was not observed over the voltage range. Comparing the BPMs with a catalyst at the bipolar junction interface (SPEEK/QAPSf and Fumasep® BPM) to those without a catalyst (SPEEK/QAPSf), demonstrates that a water dissociation catalyst greatly increases water splitting in the bipolar junction region.
Figure 38. Effect of catalyst loading on (a) flat and (b) patterned SPEEK/QAPSf BPMs.
It is worth noting that Al(OH)$_3$ nanoparticle catalyst loading at the BPM interface (patterned and not-patterned) does not impact the polarization behavior for SPEEK/QAPSf BPMs. The other key observation in Figure 36 is that solvent vapor annealing of the planar interface SPEEK/QAPSf BPMs reduced the onset potential by 300 mV and increased the current density response by 70% at 2 V (to 19 mA cm$^{-2}$ from 11 mA cm$^{-2}$). As seen in Figure 34 for the micropatterned SPEEK/QAPSf BPM variants, solvent vapor annealing allows for improved interfacial contact between the polycation and polyanion in the junction region. The solvent vapor annealing process plasticizes$^{71}$ the individual AEMs and CEMs at the interface allowing these polymers to interpenetrate and improves interfacial contact. This improved interfacial contact renders a greater concentration of effective bipolar junctions that work in tandem with the water dissociation catalyst to reduce the energy barrier for water splitting. The mathematical scaling relationships between effective bipolar junction concentrations and the onset potential for water splitting will be elaborated on in greater detail for the BPMs with systematically varied interfacial area values.

It is important to note that the current density and onset potential for water splitting of the SPEEK/QAPSf BPM is comparable or exceeds values mentioned in the literature.$^{53, 58, 61, 63, 72-77}$ There are a few instances where current density values can be substantially higher (e.g. a few hundred mA cm$^{-2}$), but this is most likely attributed to the cell design - which is often custom built as no commercially available BPM testing cells exist. Hence, the newly fabricated BPMs were benchmarked against a commercially available material (e.g., Fumasep$^\text{®}$ BPM by Fumatech).
Overall, Figure 36 highlights the importance of water dissociation catalysts and interfacial contact for producing functional BPMs. Without a water dissociation catalyst, SPEEK/QAPSf BPMs perform extremely poorly. The good interfacial contact in the bipolar junction region of SPEEK/QAPSf BPMs, enabled by solvent vapor annealing, leads to a substantial reduction in onset potential and increase in current density. However, the best performing SPEEK/QAPSf BPM with a planar interface had a higher onset potential, by 200 mV, and lower current response than the Fumasep® BPM. Despite these shortcomings, the SPEEK/QAPSf had greatly reduced co-ion leakage values compared to Fumasep® BPM. This indicates that the SPEEK/QAPSf would be better at curtailing crossover current in electrochemical devices. The lower co-ion leakage of the SPEEK/QAPSf hails from their good permselectivity values (> 0.9; Table 1. Properties of AEMs and CEMs used in BPMs). The next few paragraphs will show that BPMs can be improved further by increasing the bipolar junction interfacial area through micropatterning the membrane surfaces and adopting alternative AEM chemistries.

Figure 39a presents the polarization curves for water splitting of SPEEK/QAPSf BPMs with different NIA values. This Figure also contains the polarization behavior of the Fumasep® BPM as a reference. Figure 39b gives the polarization curves for the SPEEK/QAPSf BPM at NIA values of 1 and 2.28 (i.e., smallest and largest only) to highlight how the extreme of NIA values affect onset potential. Because each BPM displayed some current contribution from ionic species crossover (i.e., the limiting current observed before the onset potential), Figure 39c subtracted the crossover current contribution from the polarization data. It is clear from Figure 39b and c that the BPM with larger interfacial areas had a smaller onset potential.
Figure 39. a.) Polarization curves for micropatterned and non-patterned SPEEK/QAPSf BPMs and Fumasep® BPM. The legend provides the NIA values with respect to the non-patterned, planar SPEEK/QAPSf BPM interface. b.) Onset potential determination for patterned SPEEK/QAPSf BPMs with NIA = 1 and 2.28. c.) Polarization curves for micropatterned and non-patterned SPEEK/QAPSf BPMs and Fumasep® BPM with crossover current subtracted. This plot is zoomed in near the onset potential and error bars are removed for clarity. Increased NIA values for the SPEEK/QAPSf BPMs reduced the onset potential d.) The onset potential (right y-axis) and current density values at 1.5 V (left y-axis) for SPEEK/QAPSf BPMs versus NIA values. Note: All SPEEK/QAPSf BPMs contained an Al(OH)₃ water dissociation catalyst and were solvent vapor annealed. Error bars correspond to the standard error for n=3 independent samples.
Figure 40. Onset potential for water splitting in SPEEK/QAPSf BPMs of various NIA values.
Figure 39d plots onset potential and current density for water splitting at 1.5 V from polarization experiments with SPEEK/QAPSf BPMs that have systematically varied NIA values (Figure 40a-e provides the determined onset potential for individual BPM curves). Figure 39d conveys a 250 mV reduction in the onset potential when increasing the NIA values to 1.95 and 2.28. This Figure also demonstrates 20% to 50% larger current density values at 1.5 V for most BPMs when increasing NIA values (i.e., NIA = 1.48, 1.95, and 2.28); however, the current density at larger cell voltages (e.g., 2 V and 3 V) only occurred for NIA = 2.28.

To better understand the changes in resistances and water splitting kinetics in the bipolar junction region, in-situ EIS was carried out with a background voltage of 2 V. EIS with this background voltage ensured the BPM was splitting water and was in the mixed-controlled regime. The electric circuit equivalent (ECE) model (Figure 41a) proposed by Mallouk and co-workers was adopted for extracting the resistance value associated with water splitting ($R_w$) and the circuit element, Gerisher element ($R_G$), that included both the apparent water dissociation reaction constant ($k_d^{app}$) and diffusion coefficient of ions ($D_{ion}$) away from the bipolar junction interface.

$R_G$ scales to approximately $\sim 1/\sqrt{k_d^{app} D_{ion}}$. It is assumed that micropatterning the surface of the membranes does not impact bulk transport properties of the membranes, such as $D_{ion}$, and thus any reduction in $R_G$ is primarily ascribed to a larger $k_d^{app}$ value. Figure 41b shows the ECE model fit to the Nyquist plot from a micropatterned SPEEK/QAPSf BPM (NIA of 1.95) with a water dissociation catalyst and that was solvent annealed. Figure 41c plots $R_w$ and the $k_d^{app}$ as a function of the normalized area in the bipolar junction of the BPMs. $k_d^{app}$ was extracted from the Gerisher element and data fitting of the impedance data in the low frequency regime (Figure 30).
Figure 41. a.) Electrochemical equivalent circuit (ECE) used to model water dissociation in a BPM. b.) Nyquist plot of representative EIS data of water splitting in SPEEK/QAPSf patterned BPM with ECE model fit. (NIA=1.95) c.) Plot of $R_w$ and $k_d^{app}$ (apparent, forward water dissociation reaction rate constant) versus NIA value.
$R_w$ decreased with increasing interfacial area and it was inversely commensurate (i.e., a 2x increase in NIA gave a 50% reduction in $R_w$). $k_d^{app}$ was also promoted with increasing interfacial area, especially when examining NIA values greater than 1; but sometimes it decreased from one NIA value to the other (e.g., it went down from NIA = 1.95 to NIA = 2.28). Similar to observations made by Mallouk and co-workers,\textsuperscript{46} the reduction in $R_w$ correlated better with improved water-splitting in BPMs rather than $k_d^{app}$. Their work also showed similar water splitting performance between a 3D electrospun BPM versus a 2D BPM despite the 3D electrospun BPM having 2x to 3x lower $k_d^{app}$ value.

Hence, $k_d^{app}$ extracted from electric circuit equivalents featuring a Gerischer element may not be a good parameter for understanding BPM water splitting kinetics and motivates future work that probes $k_d^{app}$ in bipolar junction regions.

Figure 42a conveys polarization behavior of following micropatterned BPMs (NIA = 2.28): Nafion®/PF AEM, SPEEK/QAPSf, and SPEEK/Orion AEM. These BPMs all had Al(OH)$_3$ as a water dissociation catalyst and were solvent annealed. The impetus of fabricating BPMs with PF AEM and Orion AEM hails from their excellent alkaline stability in 1 M KOH or greater at temperatures of 80 °C for prolonged periods of time.\textsuperscript{78} QAPSf is known to suffer from backbone and cation degradation\textsuperscript{79} in 1 M KOH at 60 °C and a similar variant has only been shown to be stable in 2 M NaOH at 40 °C.\textsuperscript{80} Work by Pintauro and co-workers has used quaternary ammonium benzyl poly(2,6-dimethyl 1,4-phenylene oxide) (QAPPO) AEMs in their BPMs. This AEM chemistry is also unstable in 1 M KOH at 60 °C. Hence, functional BPMs have been fabricated with alkaline resilient AEMs.
From Figure 42a, the SPEEK/Orion AEM BPM had the lowest onset potential (0.84 V) of all the BPMs tested – including 150 mV lower than the commercial Fumasep® BPM. The observed onset potential for the SPEEK/Orion AEM BPM is near the thermodynamically predicted value based upon the water dissociation constant ($K_w$). The excellent polarization behavior of SPEEK/Orion AEM BPM may be partially ascribed to the Orion AEM’s low water uptake leading to less swelling of the BPM interface; and thus, maintenance of quality interface that has good contact. The micropatterned all-perfluorinated BPM from Nafion™/PF AEM displayed similar polarization as the micropatterned SPEEK/QAPSf BPM up to 1.3 V. After 1.3 V, the all-perfluorinated BPM gave a smaller increase in current when ramping up the voltage. The lower IEC values of the perfluorinated materials give rise to a lower $E_{loc}$ value. Plus, the higher ASR values of the PF AEM incurred a larger ohmic penalty when extracting greater current density values. It is important to note that the linear regime after the onset potential in polarization curves corresponds to mixed control (i.e., it is governed by both reaction kinetics and diffusion of water to the interface and migration of ions away from the interface).
Figure 42. (a) Polarization curves for micropatterned BPMs with different membrane chemistries. (b) Polarization behavior of Fumasep® and SPEEK/Orion AEM BPMs with the crossover current subtracted.
Although the current density values are larger for Fumasep® BPM in Figure 42a, it is also apparent that the crossover current is quite large for Fumasep® BPM and negligible for SPEEK/Orion AEM BPMs. Figure 42b plots the polarization behavior of Fumasep® BPM and SPEEK/Orion AEM BPMs with the crossover current contribution subtracted. This plot demonstrates that the SPEEK/Orion AEM BPM gives current density values for water-splitting that are similar to the Fumasep® BPM up to 1.5 V. Hence, the newly prepared BPMs dissociate water to hydroxide ions and hydronium ions as well as the commercial baseline material.

Additionally, it is important to recognize that the micropatterned SPEEK/Orion AEM BPM has a lower crossover current values when compared to Fumasep® and this is an important quality for current utilization in BPM electrodialysis.

Finally, it is important to highlight that the Nafion™/PF AEM, SPEEK/Orion and SPEEK/QAPSf BPMs are composed of perfluorinated or poly(arylene) chemistries that are known to tolerate chlorine solutions. The oxidative stability of these BPMs allows the use of cleaning solutions to overcome fouling problems such as bio-films and/or surfactants. Overall, the SPEEK/Orion AEM BPM and all-perfluorinated BPMs are promising candidates for applications that require harsh environments (e.g., extreme pH values, oxidizers, and elevated temperatures).
Figure 43. Onset overpotential for water dissociation as a function of local electric field for various BPMs of varying NIA values and IEC values.

Figure 43 plots \( \eta_{WD} \), determined from equation 19 in Chapter 1, against the \( E_{loc} \) value, which was calculated by using the known interfacial area values and constants for \( t_{dw} \), \( \varepsilon \) and \( \rho_{BPJ} \). The values shown in Figure 43 are on the same order of magnitude as reported in the literature\(^{18} \) (i.e., \( \sim 1 \times 10^8 \text{ V m}^{-1} \)) and equation 19 bares similarity to the equation used by Kohl and co-workers\(^{82} \) except equation 19 here captures interfacial area. \( t_{dw} \) used in equation 19 was 20 nm based on literature precedent.\(^{53} \) \( \varepsilon \) was based upon available values for Nafion\(^{TM} \)\(^{83} \) and hydrocarbon anion exchange and cation exchange membranes\(^{83} \). \( \varepsilon \) can also be calculated by the weighted average between the polymer materials and water as described in our previous work\(^{35} \) and others\(^{84} \). \( \rho_{BPJ} \) was based on the lowest IEC value between the AEM and CEM. The lower IEC value was selected because it dictates the number of oppositely charged pairs that can form in the bipolar
junction region. IEC was converted to density by multiplying by the density of the membrane material (1.40 g cm\(^{-3}\) for hydrocarbon\(^{38}\) and 1.58 g cm\(^{-3}\) for perfluorinated polymers like Nafion\(^{TM}\)).\(^{39}\) This conversion resulted in a \(\rho_{IEM}\) values that ranged from \(1.23 \times 10^2\) C cm\(^{-3}\) to \(2.96 \times 10^2\) C cm\(^{-3}\) depending on the IEC value used (see equation 32 for an example calculation).

Equation 33 is an example calculation for \(E_{loc}\). Figure 43 shows that \(\eta_{WD}\) decreases with increasing the magnitude of \(E_{loc}\). This trend supports that the greater interfacial area increases the strength of \(E_{loc}\) that is responsible for the 250 mV drop in onset potential observed in Figure 40b.

Density of fixed charges in the bipolar junction (\(\rho_{BPJ}\)) was calculated from the average IEC value of AEM and CEM material and density of the membrane material. The calculation for SPEEK/QAPSf BPM is shown below (equation 29):

\[
\rho_{BPJ} = IEC \cdot \rho \cdot F = 1.65 \frac{mmol}{g} \times 0.001 \frac{mol}{mmol} \times 1.4 \frac{g}{cm^3} \times 96485 \frac{C}{mol} = 2.23 \times 10^2 \frac{C}{cm^3}
\]  

\(IEC\) = Lowest value between the AEM and CEM variant used to make a BPM. 1.65 meq g\(^{-1}\) for SPEEK/QAPSf and SPEEK/Orion BMs

\(\rho = 1.4\) g cm\(^{-3}\) (density of membrane material)\(^{85}\)

\(F = 96,485\) C mol\(^{-1}\) (Faraday’s constant)

The local electric field for water splitting at the bipolar junction interface was calculated as shown below for SPEEK/QAPSf BPM (NIA = 1.00) in equation 30:

\[
E_{loc} = \frac{\rho_{BPJ} A_{int} t_{dw}}{\varepsilon} = \frac{\rho_{BPJ} A_{int} t_{dw}}{\varepsilon} \frac{2.23 \times 10^2 \frac{C}{cm^3} \times 1.27 cm^2 \times 20 nm}{40 \times 885 \times 10^{-12} \frac{C}{V^{-1}m^{-1}}} = 1.6 \times 10^{-8} \frac{V}{m}
\]

\(A_{int}\) = interfacial area of the BPM

\(t_{dw}\) = depletion width thickness

\(\varepsilon = \) permittivity of the hydrated polymer

The limited increase in current density (20 to 50\%) with the largest NIA value BPM (NIA = 2.28) was ascribed to mixed kinetics-diffusion control. Using Faraday’s Law of Electrolysis
(equation 34), the change in mass per time can be estimated by the $VdC_{H_2O}/dt$. Writing the water species conservation of mass equation in the bipolar junction region (equation 31) and assuming i.) no convection and Fick’s 2nd Law of Diffusion and ii.) a first-order reaction rate law for water splitting (equation 32), the current response in Faraday’s Law is controlled both by reaction kinetics and diffusion of water to the interface (equation 33). Inspection of equation 33 reveals that the current density response is not explicitly related to interfacial area. The parameter of interfacial area is captured indirectly in $k_{d}^{app}$ because EIS experiments showed that larger NIA values increased $k_{d}^{app}$ (Figure 41c), but there was some scatter in the upward trend. Hence, improving the current density in the interfacial region of bipolar junctions may require a substantial gain in $k_{d}^{app}$ (e.g., 2 orders of magnitude) while also curtailing any diffusion limitations. The small to negligible increase in current density for BPMs with smaller NIA values (e.g., 1.19 and 1.48) were attributed to diffusion resistances dominating over kinetics. Once the $k_{d}^{app}$ value increased by 10-20x, increases in current density occurred.

$$i = -\frac{F}{A_{int}} \frac{\Delta m_i}{\Delta t} = -\frac{F \cdot V}{A_{int}} \frac{dC_{H_2O}}{dt}$$  \hspace{1cm} (31)$$

$$\frac{dC_{H_2O}}{dt} = -\nabla \cdot N_{H_2O} + R_{H_2O}$$  \hspace{1cm} (32)$$

$-\nabla \cdot N_{H_2O}$ is simplified to $-D_{H_2O} \frac{d^2C_{H_2O}}{dx^2}$ because convection is negligible and 1-D transport is assumed.

$$H_2O \xrightarrow{BPI} H^+ + OH^-$$

$$R_{H_2O} = u_{H_2O}r_{H_2O} = -k_{d}^{app}C_{H_2O}$$  \hspace{1cm} (33)$$

$u_{H_2O}$: stoichiometric coefficient for water is -1.

$$i = F \cdot t_{dw} \cdot \left(D_{H_2O} \frac{d^2C_{H_2O}}{dx^2} + k_{d}^{app}C_{H_2O} \right)$$  \hspace{1cm} (34)$$
4.4. Conclusions

BPMs with systematically controlled interfacial areas were fabricated via soft lithography. This approach for manufacturing BPMs was conducive for a multitude of materials chemistries that are known to have excellent chemical stability at extreme pH values, elevated temperatures (up to 80 °C), and in the presence of oxidizers. By using micropatterned interfaces for SPEEK/QAPsf BPMs, the interfacial area was increased up to 2.28x resulting in a 250 mV reduction in onset potential and 50% improvement in current density at 1.5 V over the non-patterned/flat BPM variant. EIS and simple physics models revealed that the increase in interfacial area amplifies the junction region electric field resulting in lower resistance values for water dissociation ($R_w$) and a larger apparent water dissociation reaction rate constants ($k_d^{app}$).

The best BPM material was comprised of SPEEK CEM and Orion AEM and this material showed an onset potential at 0.84 V, which was near the thermodynamic minimum, while also displaying significantly lower crossover current when compared against a commercial variant BPM (Fumasep®). Future work will look to fabricate CEM or AEM surfaces with smaller patterned feature sizes in addition to incorporating the respective interfaces with more appropriate metal oxide catalysts. The role of bonding and adhesion in the fabrication of BPMs with high surface area interfaces also requires further investigation – especially in the context of potential mixing and complexation between oppositely charge polymers (e.g., similar to what is observed coacervate materials)\textsuperscript{86} and their effect on water splitting in BPMs. These activities may lead to BPMs that facilitate large current density values and thus overcoming barriers that currently stymie BPMs from being deployed in established and emerging electrochemical energy conversion technologies.
4.5. Future work

The future work, in this project, will involve further reducing the size of micropatterns on the PDMS submasters prepared using optical lithography. The minimum lateral feature size that can be obtained by this method is limited by the wavelength of UV light. Hence, it is challenging to make feature sizes that are less than 700 nm. Future work attempts to attain a BPM with good, intimate contact of the polycation-polyanion at these reduced interfacial feature sizes. By developing a nanopatterning IEM platform, one can determine how the BPM polarization behavior changes with even larger interfacial area values. This idea is conveyed in Figure 44.

![Figure 44](image)

Figure 44. Postulated results for BPM onset potential and current density when reducing the pattern feature size further that increases the interfacial area (aka normalized area) in the junction region.
Chapter 5. Nanopatterned Surface Ion Exchange Membranes using BCP Lithography

5.1. Introduction

Polymeric exchange membranes (IEMs) are key component in many electrochemical processes like electrodialysis, flow batteries, fuel cells, and water and carbon dioxide electrolyzers. For these processes, IEM materials need to display low area specific resistance (i.e., high ionic conductivity), robust mechanical properties and thermal and chemical stability. Despite the various electrochemical processes having some similar requirements for IEMs, there are nuanced property requirement differences for IEMs between different technologies – e.g., fuel cell and electrolyzer IEMs need good integration with electrodes and low interfacial resistances between the IEM and electrodes. High mobility of ions, especially in alkaline fuel cells and extreme pH/ high temperature stability are also important. Conversely, IEMs for electrodialysis for electrochemical separations need to excellent permselectivity and resist fouling. Bipolar membrane electrodialysis (BMED) is becoming an important technology for production of inorganic acids and bases but low permselectivity of these membranes often limit their large-scale applications. Other applications such as redox flow batteries for energy storage require IEMs with high conductivity and low crossover ratio.

Most IEM research relates to the manipulation of materials chemistry, ionic loading (i.e., on-exchange capacity) and macromolecular architecture for tuning the aforementioned properties of ionic conductivity, mechanical integrity, permselectivity, and stability (chemical, electrochemical, and thermal). Addressing surface features and patterns on an IEM and their impact on membrane properties are a more recent field of study. There are several reports that suggest that modifying the surface design features of IEMs such as shape and orientation

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while keeping the material properties unchanged, often results in significant improvement in device performance. For example, studies have shown that replacing flat IEMs with patterned or profiled IEMs in electrodialysis reduces mass transfer limitations by increasing the available surface area on the membrane.

In this work, for the first time, a method to prepare nanopatterned IEMs using BCP lithography is reported. PS-b-PMMA is used to carry out the self-assembly, due high etch contrast of the blocks and relatively simple self-assembly process compared to other BCPs. To transfer the pattern from BCP substrate to free standing polymer electrolyte membranes, the self-assembled BCP layer is exposed to trimethylaluminum (TMA) and water using a sequential infiltration synthesis (SIS) process. TMA reacts selectively with the PMMA block, resulting in the formation of aluminum hydroxide layer. In the next step, the sample is etched in presence of O₂ to remove all organic matter. This process also converts aluminum hydroxide to alumina resulting in a nanopatterned alumina template. This template is used as a mold to drop cast ionomer solutions like SPEEK. Similar procedure was attempted to prepare nanopatterned surface Nafion® IEMs. However, SEM and AFM imaging confirmed that the patterns did not get transferred from the alumina templates on to the Nafion® membrane surface. Electrochemical properties of the nanopatterned membrane such as conductivity, permselectivity and ion exchange capacity are measured and compared to a similar membrane with flat surface.

5.2. Objectives

The main objectives of this work are to establish a versatile methodology to prepare nanopatterned surface IEMs that can be used for synthesizing a number of different membrane
chemistries and pattern shape and sizes and relate nanopattern feature, size, and morphology to electrochemical properties of the IEM.

5.3. Results and discussions

An etch test was performed to determine the optimal conditions to prepare the nanopatterned alumina templates, specifically the BCP concentration for spicoating on to the wafers and the oxygen etching time in the reactive ion etching (RIE). Figure 45 presents 2D and 3D AFM height maps of alumina nanostructures on silica wafers acquired after the oxygen reactive ion etching step. It can be seen clearly from Figure 45b that the alumina nanostructures are well defined when the 1.0 wt % BCP solution is used along with 10 min O₂ etching. Hence, the same conditions are used for preparing templates to dropcast SPEEK membranes with lamella and cylinder nanostructures.
Figure 45. 2D AFM height maps and 3D AFM maps of alumina nanostructures on silica wafers at different concentrations of spincoated BCP and etch times (a) 1.0 wt % BCP, 1 min etch time (b) 1.0 wt % BCP, 10 min etch time (c) 1.5 wt % BCP, 1 min etch time (d) 1.5 wt % BCP, 10 min etch time; Scale bar in (a) 2D map corresponds to 0.5 μm and applies to all AFM 2D maps.

(figure cont'd.)
Figure 46. Surface SEM micrographs at each step of nanopatterned IEM synthesis process (a) PS-\textit{b}-PMMA (105-106k) self-assembly on silica wafer resulting in fingerprint lamellae pattern, (b) PS-\textit{b}-PMMA (132-68k) self-assembly on silica wafer resulting in perpendicular cylinder pattern, (c) lamellar alumina nanostructures on silica wafer, (d) cylindrical alumina nanostructures on silica wafer, (e) nanopatterned SPEEK membrane with lamellar nanopattern, and (f) nanopatterned SPEEK membrane with cylindrical nanopattern. Scale bar in (a) corresponds to 0.5 μm and applies to all electron micrographs.

(figure cont'd.)
Figure 46 presents the surface SEM micrographs at each stage of the nanopatterned IEM synthesis process for lamellar and cylindrical features starting from BCP self-assembly on silicon wafer (Figure 46a and b), alumina nanostructures on the wafer (Figure 46c and d) and finally surface images of SPEEK membrane (Figure 46e and f) prepared by drop casting SPEEK ionomer solution on the alumina nanostructures. The nanopatterned cylindrical features obtained on the membrane surface in Figure 46f is not as well defined as its lamellar counterpart in Figure 46e. Hence, there is a need to optimize various process conditions like BCP concentration, SIS parameters (number of cycles), O2 RIE time etc. to get well defined nanopatterned features on the membrane surface in the final step. For measuring electrochemical properties of the SPEEK membranes, only lamella patterned IEMs have been used.

Table 3 lists the measured electrochemical properties of the nanopatterned SPEEK membrane and it has been compared with the flat and micropatterned surface SPEEK IEMs prepared by
drop casting ionomer solution on flat glass plate and micropatterned PDMS mold respectively, as discussed in the previous sections. Thickness of each type of membrane is approximately the same within the margin of error. This helped us to accurately judge the effect of surface patterning on membrane properties. There is an improvement in through-plane conductivity of the IEMs as the lateral feature sizes on the IEM surface are reduced, effectively increasing the membrane surface area due to reduced mass transfer limitations. The permselectivity and membrane transference number remain unchanged after surface patterning. The IEC values in all three cases are same as it is an intrinsic property of the membrane and is unaffected by surface features. Finally, the water uptake ratios were not severely affected.

Table 3. Comparison of the flat, micropatterned and nanopatterned SPEEEK properties

<table>
<thead>
<tr>
<th></th>
<th>Nanopatterned IEM</th>
<th>Micropatterned IEM</th>
<th>Flat IEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>83.7±7.1</td>
<td>76±4</td>
<td>85.3±3.2</td>
</tr>
<tr>
<td>$\sigma_{\text{T-P}}$ (mS cm$^{-1}$) $^a$</td>
<td>97.0±0.1</td>
<td>94.0±0.3</td>
<td>92.6±0.0</td>
</tr>
<tr>
<td>Transference number $^b$</td>
<td>1.0±0.0</td>
<td>1.0±0.0</td>
<td>1.00±0.0</td>
</tr>
<tr>
<td>Permselectivity $^b$</td>
<td>1.0±0.0</td>
<td>1.0±0.0</td>
<td>1.00±0.0</td>
</tr>
<tr>
<td>IEC (meq g$^{-1}$) $^b$</td>
<td>1.8±0.06</td>
<td></td>
<td></td>
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<tr>
<td>Water uptake (%) $^b$</td>
<td>6.0±4.2</td>
<td>6.0±5.7</td>
<td>5.0±5.3</td>
</tr>
</tbody>
</table>

$^a$ Measured in the proton or hydroxide ion form. $^b$ Measured in the sodium ion form or chloride ion form

5.4. Conclusions

In this work, nanopatterned surface IEMs using BCP lithography were prepared. This is the first report of preparing a nanopatterned IEM from a bottom-up, molecular self-assembly method. The self-assembled block copolymer patterns were successfully transferred to free standing SPEEEK membranes. Reducing the feature size on SPEEK from micropattern to nanopattern resulted in 3 to 5% increase in through-plane conductivity over micropattern and flat membranes without compromising the permselectivity of the membrane.
5.5. Future work

In the future, a wide variety of IEMs can be synthesized with various surface architectures and feature sizes using the same methodology discussed in this chapter. Further, this method may also be expanded to prepare BPMs by spray painting a water dissociation catalyst followed by oppositely charged ionomer solution on the nanopatterned IEM surface. It might be hard to make good interfacial in the BPM contact due to the small crevasses on the surfaces. Another application is to make catalyzed coated membranes by sputtering (or other physical or chemical vapor deposition) of electrocatalysts.98
Chapter 6. Peptide Modification of Electrocatalyst Surfaces for Controlling Anion Exchange Ionomer Thin Film Microstructures

6.1. Introduction

Anion exchange membrane fuel cells and water electrolyzers (AEMFCs and AEMWEs) are modular electrochemical energy storage and conversion technologies that have garnered significant interest as alternatives to commercialized proton exchange membrane devices. The alkaline environment expands the palette of electrocatalyst materials, particularly non-precious group metals, for the necessary redox reactions. The electrocatalysts, in many instances, make up a significant portion of the capital costs of these technologies when manufactured at large volumes. Proton exchange membrane fuel cells and water electrolyzers are costly due to their use of platinum group metals making widespread proliferation difficult. Their acidic environment restricts the type of electrocatalyst they can use because there are few alternatives to platinum group metals that are both high performing and stable in acid. Alkaline fuel cells and water electrolyzers using a liquid electrolyte are both mature and commercialized technologies that operate effectively with low cost silver and nickel metal based electrocatalysts, but the liquid electrolyte is undesirable as it can suffer from carbonation leading to precipitates that clog porous electrodes and the liquid electrolyte is not conducive to a thin cell design and may cause shunt currents.

While there are several reviews dedicated to developing AEMs with alkaline resiliency in base baths at elevated temperatures, as well as a plethora of reports on catalyst research in alkaline medium, a neglected area of materials research for AEMFCs and AEMWEs is the understanding of how AEIs interact with electrode and electrocatalyst surfaces. These interactions have strong implications for ion conductivity in electrode layers in addition to influencing reactant delivery and product removal to electrode surfaces and charge-transfer reactions. With respect to AEM based fuel cells and electrolyzers, the breakthrough in peak power density of AEMFCs over 1 W cm\(^{-2}\) with hydrogen and oxygen (or over 0.8 W cm\(^{-2}\) with clean air) are ascribed to several factors that include new AEIs in electrode layers (e.g., ETFE-AEI powders). Hence, electrode ionomers have a profound impact on fuel cell and electrolyzer performance and stability, and thus serves as motivation for this work. Some unanswered questions in the field, which we address in this study, include: how do the surfaces of electrodes impact AEI microstructure configurations? And as a result, how do the different microstructure configurations of AEIs in electrode layers, which may be different than bulk membrane materials, govern ionic conductivity?

This work reports the microstructure and ionic conductivity of an AEI model material, as a thin film, interfaced with a model electrode material (i.e., gold) with and without peptide modification and when processed via solvent vapor annealing. Previous studies by Renner and co-workers have shown that sequence defined bound peptides can alter interactions and microstructure arrangements of Nafion\(^{\text{®}}\) with electrode surfaces. While other surface modifications have been used to control the interactions with co-polymers (e.g. polymer brushes), peptides are an attractive option because they are easily tunable, and possess well-
defined secondary structures. This work done in collaboration with Renner lab at CWRU\textsuperscript{23, 126} has shown that solvent vapor annealing facilitates microphase separation between ionic and non-ionic domains in diblock, anion conducting copolymer electrolytes. Solvent vapor annealing lowers the glass transition of the polymer film below room temperature through solvent plasticization. The plasticized film becomes a polymer melt and it can now diffuse and reorganize itself into a thermodynamically favorable microstructure.\textsuperscript{127} Zihang Su from Renner lab at CWRU synthesized the peptide sequence and characterized the AEI-peptide-electrode interactions using FTIR, AFM imaging, DLS and QCM-D. IDE fabrication, ionomer synthesis, conductivity measurements and Raman spectroscopy were carried out at Arges lab at LSU.

6.2. Objectives

The overall goal of this study was to characterize the effect of biomolecular surface modifications with and without solvent annealing on the microstructure configurations of AEIs and subsequent ionic conductivity. The model AEI in this report is a random copolymer brush of poly(2,6-dimethyl 1,4-phenylene oxide) featuring quaternary benzyl N, N-dimethyl-n-decyl ammonium hydroxide/carbonate/bicarbonate anions (PPO-QDMDA). This material was selected because of its ease of preparation from commercially available polymers\textsuperscript{45, 128} and its ability to microphase separate due the hydrophobic brush tails in the N,N-dimethyl-n-decyl ammonium moiety.\textsuperscript{129, 130} In addition, this class of PPO AEMs with alkyl brush tails has reasonable alkaline stability at 60 °C. Our work herein highlights thiol-terminated peptides, featuring anionic moieties, anchored to electrode and substrate surfaces which generate favorable microphase separated grains in the PPO based AEI. The negatively charged anionic moiety on the peptide sequence connects to the quaternary ammonium group in the AEI, forming a bipolar junction. Unlike the bipolar junctions formed in BPM work, in this case, the effect of bipolar junctions on
AEI microphase separation and ionic conductivity is studied. However, water-splitting in this junction region may also be possible and it could be explored in future work. The results demonstrate the utility of both biomolecular modification and solvent vapor annealing for controlling the microphase separation of AEIs.

6.3. Results and discussions

To characterize the adsorption phenomena of CVPPEG and PPO-QDMDA AEI to gold, QCM-D was used to sense the mass uptake and the retention of the deposited layers on a gold-coated AT cut quartz crystal. Figure 47 presents the shift in frequency and dissipation from QCM-D experiments that examined AEI adsorption in the presence or absence of surface bound CVPPEG peptide. The negative frequency shift corresponds to the sensor gaining mass. The baseline solution and carrier for all components tested, was dilute aqueous sodium hydroxide (NaOH). Figure 47a shows a representative experiment where a gold-coated sensor without peptide is exposed to an AEI solution and Figure 47b shows a representative experiment where a gold-coated sensor with peptide is exposed to the AEI solution. Both samples experience negative frequency shifts in the presence of AEI, indicating the formation of an AEI layer.
Figure 47. QCM-D monitoring of frequency (black) and dissipation (grey) shifts versus time for A) PPO-QDMDA AEI adsorption on to a gold sensor, and B) CVPGEG peptide adsorption followed by PPO-QDMDA AEI adsorption on to a gold sensor. The third overtone is shown.

Generally, the AEI assembled on the bare gold electrode had large shifts in dissipation, and was modeled as a viscoelastic film\(^{131}\) (goodness of fit > 0.9 on average), whereas the AEI assembled on the peptide has small dissipation shifts, and did not fit the viscoelastic model (goodness of fit 0.4 on average). This implies that the AEI film formed on the substrate with bound peptide had a different structure and is more rigid than the AEI film formed on gold without the peptide. The final rinse steps showed minimal frequency reverse or dissipation change over time this indicated that the deposited peptide and AEI films were stable on the gold-based QCM substrate.
Figure 48. QCM-D experiments monitoring frequency (black) and dissipation (grey) shifts versus time for a.) PPO-QDMDA AEI adsorption on to a gold coated sensor, and b.) CVPGEG peptide adsorption followed by PPO-QDMDA AEI adsorption on to a gold coated sensor. The third overtone is shown.
Figure 49. Average values of frequency (grey) and dissipation (teal) shifts for the third overtone of QCM-D data shown in Figure S1. Error bars represent standard error.

Figure 48 provides the changes in frequency and dissipation versus time for all experiments, including repeats and Figure 49 summarizes the frequency and dissipation shifts on average for the final assembled AEI layers on gold versus bound peptide.

Table 4. Mass loading, estimated thickness values, and viscoelastic properties of AEI films calculated from QCM-D data. Values reported are the average and the error bars represent the standard error of parameters calculated from three separate QCM trials (n=3).

<table>
<thead>
<tr>
<th></th>
<th>Mass Loading (ng/cm²)</th>
<th>Thickness (nm)</th>
<th>Viscosity (µPa*s)</th>
<th>Elastic Modulus (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEI on gold</td>
<td>3100 ± 700</td>
<td>30 ± 7</td>
<td>2800 ± 260</td>
<td>14 ± 5</td>
</tr>
<tr>
<td>AEI on peptide</td>
<td>1200 ± 300</td>
<td>11 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4 summarizes the mass uptake, AEI film thickness, and AEI viscoelastic properties estimated from the QCM-D data. Note that the AEI film thicknesses reported from QCM-D data do not include the peptide layer, which was estimated to be < 1 nm.

Table 5. Film thickness results from ellipsometry (n=2). Error bars are the absolute difference from the average.

<table>
<thead>
<tr>
<th></th>
<th>Film thickness on silica substrate (nm)</th>
<th>Film thickness on gold coated wafer substrate (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not annealed</td>
<td>Solvent annealed</td>
</tr>
<tr>
<td>AEI without peptide</td>
<td>21 ± 1</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>AEI with peptide</td>
<td>22 ± 2</td>
<td>22 ± 1</td>
</tr>
</tbody>
</table>

Table 5 reports the film thickness values of the AEI on adsorbed on to gold and silica substrates with and without a peptide layer from ellipsometry. Furthermore, this Table contains film thickness values for samples that underwent solvent vapor annealing with 2-butanone (note: 2-butanone liquid was observed to solubilize PPO-QDMDA at 50 mg mL⁻¹). The QCM-D results showed variation in film thickness for the AEI on the gold QCM substrates with and without peptide (range of 11 to 30 nm). Film thickness results by ellipsometry on silica substrates were more precise (range of 21 to 23 nm). However, the film thickness values by ellipsometry of the AEI on gold coated wafers displayed a larger range (18 to 27 nm). It is important to note that the QCM-D measurements are made in a liquid flow environment, whereas the ellipsometry measurements are done in ambient air post-adsorption and solvent vapor annealing (if applicable). Despite the variances between the two independent methods, the thickness values were close. Generally, the AEI/peptide-AEI films have a thickness value that ranges from 10 to 30 nm on gold substrates. The adsorbed layers were roughly 20 nm in thickness on average on silica substrates.
The QCM-D results substantiate that the peptide layer and AEI adsorbed to the gold substrates, while the ellipsometry results demonstrate peptide and AEI adsorption to both gold and silica substrates. The peptide adsorption is attributed to the thiol moiety in the terminal cysteine group which binds to the gold and silica surfaces. The AEI adsorption to peptide containing substrates partially arises from the quaternary ammonium moieties along the PPO backbone forming electrostatic interactions with the glutamate (E) residue (i.e., a carboxylate moiety) in the peptide chain. The electrostatic interactions anchor the AEI to the peptide that is bound to the substrate surface.

![Dynamic light scattering data demonstrating interaction between CVPGEp peptide and PPO-QDMDA AEI in solution. A significant increase hydrodynamic radius was observed in solutions of DI water with CVPGEp peptide and AEI compared to individual solutions of peptide and AEI, and a peptide without a negatively charged guest residue (CVPGVG). (*) represents $p < 0.10$ comparing CVPGEp + AEI with CVPGVG + AEI, two-tailed $t$-test, $n=3$.](image)

Figure 50. Dynamic light scattering data demonstrating interaction between CVPGEp peptide and PPO-QDMDA AEI in solution. A significant increase hydrodynamic radius was observed in solutions of DI water with CVPGEp peptide and AEI compared to individual solutions of peptide and AEI, and a peptide without a negatively charged guest residue (CVPGVG). (*) represents $p < 0.10$ comparing CVPGEp + AEI with CVPGVG + AEI, two-tailed $t$-test, $n=3$. 
Figure 50 verified the electrostatic interactions between the peptide CVPGEG and PPO-QDMDA AEI in liquid solution using dynamic light scattering. For the substrates not containing the peptide, the quaternary ammonium groups are also known to adsorb to gold\(^{134}\) and silica\(^{135}\).

The role of electrostatic interactions in AEI assembly on bare gold and peptide functionalized gold was further confirmed by performing QCM-D in 10 mM sulfuric acid (Figure 51) where much lower frequency shifts were observed in both cases.

The deposition process of peptides and AEI through immersion in dilute NaOH solutions was shown to be successful for the preparation of thin AEI films on electrode type substrates. These thin films mimic the ionomer layers observed in electrodes of fuel cell and electrolyzer applications.
Figure 52. A.) Nyquist plot of representative EIS data of the four different AEI samples on IDEs and B.) ECE model of peptide and PPO-QDMDA AEI layer on IDE. The ECE model was used to extract the AEI resistance value.

After successful confirmation of the adsorption of AEI layers to bare and peptide-modified gold electrode surfaces, the in-plane ionic conductivity of the AEI films on IDEs were investigated using galvanostatic electrochemical impedance spectroscopy (EIS). The IDE substrates consisted
of gold electrode teeth on silicon wafer substrates that contained a 1 μm thick electron insulating thermally grown silica layer (i.e., silica substrate). The IDE material composition was selected due to our previous observations that the AEI adsorbed both to gold and silica. Figure 52A shows representative Nyquist plots from EIS with the AEI samples covered in a drop of liquid deionized water. Four different type of samples’ impedance behavior are plotted in Figure 52A: i.) AEI with peptide and no solvent vapor annealing, ii.) AEI without peptide and no solvent vapor annealing, iii.) AEI with peptide and solvent vapor annealing, and iv.) AEI without peptide and no solvent vapor annealing. The diameter of the semi-circles in Figure 52A corresponds to the samples’ in-plane resistance from ionic conduction within the AEI layer.

Reports by Karan and co-workers, Patel and co-workers, and others, have shown that the semi-circle diameter corresponds to ionic migration resistance.\textsuperscript{6, 33, 136-140} Figure 52B is the electric circuit equivalent (ECE) model used to fit the data in the Nyquist plot to extract the in-plane resistance attributed to ionic conductance.

Table 6 provides the modeled in-plane resistance values of the AEI samples and it also reports the calculated in-plane ionic conductivity from the resistance values. The samples with the AEI film assembled on a peptide layer, but not solvent annealed, displayed one of the highest ionic conductivity values (32 ± 12 mS cm\textsuperscript{-1}). A statistically equivalent ionic conductivity value was attained (22 ± 7 mS cm\textsuperscript{-1}) with AEI without peptide, but solvent annealed. Conversely, the AEI film without peptide or solvent vapor annealing yielded a significantly lower ionic conductivity value of (10 ± 2 mS cm\textsuperscript{-1}). The AEI film with peptide and solvent annealed displayed a similarly
low ionic conductivity value \( (10 \pm 2 \text{ mS cm}^{-1}) \) to the AEI without the peptide sample but not solvent annealed.

Table 6. In-plane resistance and ionic conductivity \( (\sigma) \) values of AEIs on IDE substrates. Error bars are the standard error for \( n=3 \) independent samples.

<table>
<thead>
<tr>
<th>R_1 (k\Omega)</th>
<th>( \sigma ) (mS cm(^{-1}))</th>
<th>R_1 (k\Omega)</th>
<th>( \sigma ) (mS cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEI with peptide</td>
<td>Not annealed: 18 \pm 7</td>
<td>32 \pm 12</td>
<td>Solvent annealed: 46 \pm 8</td>
</tr>
<tr>
<td>AEI with no peptide</td>
<td>52 \pm 9</td>
<td>10 \pm 2</td>
<td>24 \pm 8</td>
</tr>
</tbody>
</table>

* Thickness value used for ionic conductivity determination came from ellipsometry experiments

Table 6 highlight that peptide modified electrodes and solvent vapor annealing are extremely influential on the ionic conductivity of AEIs. For the AEI with the peptide modified electrode, but not solvent annealed, the gain in ionic conductivity cannot be accounted by the carboxylate moieties in the peptide. The peptide layer is very thin (i.e., not a large amount of material) and it features a low ion-exchange capacity value (1.66 mmol g\(^{-1}\)). Hence, it lacks the quantity of fixed charge carriers to augment the ionic conductivity. Second, the carboxylate group binds a small fraction of the quaternary ammonium groups in the PPO-QDMDA AEI and the rinse step will wash away the released HCl from the adsorption process (i.e., hydronium comes from the peptide and the chloride counterion comes from the quaternary ammonium in PPO-QDMDA). Because the number of carboxylate groups is smaller compared to the AEI, it is assumed that all the hydronium counterions are removed. Hence, this also explains why the peptide layer cannot contribute to the ionic conductivity. It can only bind the AEI through electrostatic interactions, as verified by Figure 50 via dynamic light scattering. To understand why the peptide and solvent
vapor annealing processing impacted ionic conductivity of the AEI thin films, the microstructures of the AEI samples were investigated by tapping mode AFM.

Figure 53. AFM micrographs of A.) height (left) and phase (right) images of PPO-QDMDA AEI on gold substrates; B.) height (left) and phase (right) images of CVPGEG peptide on gold substrate with PPO-QDMDA AEI layer assembled on top.

Figure 53A and B present the AFM topography and phase images of the AEI films on the QCM gold substrates with and without a peptide layer. The AEI layer deposited on the gold QCM sensor without a peptide displayed smaller phase separated grains (light circles in phase image) when compared with the phase images of AEI assembled on a peptide layer (Figure 53B). The sample with AEI assembled on gold without peptide produced grains that were 14 ± 1 nm versus the sample with AEI assembled on peptide which produced grains that were 31 ± 2 nm.

Interestingly, the AEI sample with the peptide underneath showed more uniformity in the AFM
height images when compared to the AEI on gold by itself. Recall, that the QCM results indicated that there was more AEI mass uptake during the adsorption process for the electrode without the peptide. Hence, the mass uptake data and AFM height image in Figure 53A indicates that more mass uptake does not necessarily result in more uniform deposition of the AEI layer. It is clear from Figure 53A and B that the film uniformity and grain microstructure for the AEI differ if a peptide is present on the gold surface. Overall, the AFM images inform why the AEI with the peptide underneath may yield higher ionic conductivity. However, it is important to note that the IDE substrates contain gold electrodes and a silica layer between the gold electrodes. The difference in the IDE samples could cause varying microstructures, and thus the microstructures of the AEI on the IDEs were interrogated by AFM.

Figure 54 A to D present the AFM phase images of AEI microstructures on IDEs in the areas with gold electrodes and the areas with the silica substrate. Figure 54A is the assembled AEI sample with no peptide and not solvent annealed, and Figure 54B is the assembled AEI sample with no peptide that was solvent annealed. Figure 54C represents the AEI sample assembled on peptide without solvent annealing, and Figure 54D is the AEI assembled on a peptide layer that was solvent annealed with 2-butanone. It is assumed the dark spots in most of the phase images for Figure 54 correspond to the ionic domains. It is clear from the AFM images in the silica regions of the IDE that the AEI by itself appear to have the smallest microphase separated ionic grains (18 nm to 24 nm), while the AEI with the peptide and the AEI by itself but solvent annealed have slightly larger ionic grains (20 nm to 35 nm). Recall that the AEI assembled with a peptide, but not annealed, and the AEI by itself, but annealed, displayed roughly a two- to three-fold increase in ionic conductivity over the AEI by itself and not annealed.
Figure 54. AFM micrographs of A.) PPO-QDMDA AEI layer, non-annealed, B.) PPO-QDMDA AEI layer, solvent annealed, C.) PPO-QDMDA AEI layer on CVPGE G peptide, and D.) PPO-QDMDA AEI layer on CVPGE G peptide and solvent annealed. Left images are the AEI on the gold part of the IDE and the right images are the AEI on the silica part of the IDE.
The substantial increase in ionic conductivity for the samples in Figure 54B and C is attributed to their larger ionic grains in the silica regions of the IDEs. It is clear that the increase in ionic grains, spurred by the peptide modified electrodes and solvent vapor annealing, resulted in higher ionic conductivity. However, this trend has limitations. The AFM phase image of the assembled AEI on a peptide layer and solvent annealed (Figure 54D) displayed excessively large ionic grains of 30 to 65 nm. This sample was observed to have low ionic conductivity that is similar to the AEI by itself and not-annealed. Hence, appropriately sized ionic grains afforded the best ionic conductivity for thin film PPO-QDMDA AEI samples (see Figure 55).

Figure 55. Ionic conductivity versus AEI ionic domain size on the SiOx region of the IDE. The y-error bars represent the standard error while the x-error bars correspond to the range of ionic grain sizes seen in the right column of Figure 4.
To probe the effect of solvent vapor annealing on the peptide structure itself, FTIR measurements were taken on gold QCM sensors with an assembled peptide layer. A sample exposed to DI water was compared to a sample exposed to 2-butane, the same solvent used in vapor annealing. The results shown in Figure 56 feature a peak around 1675 cm$^{-1}$ in both samples, which was observed previously with a similar peptide, and suggests that a $\beta$-turn structure is present even after exposure to 2-butane. Similarly, Thomas et al. observed the preservation of secondary structure in larger proteins after exposure to solvent vapor annealing. These data indicate that the differences in microphase structure observed are not due structural modifications in the peptide.

The AEI on the gold portion of the IDEs showed different coverage and microphase behavior than the AEI in the silica regions if no peptide was applied to the substrate (Figure 54A and B). Conversely, the peptide modified electrodes caused the AEI to yield the same coverage uniformity and microstructure arrangement for samples solvent annealed or not (Figure 54C and D). These images provide further evidence explaining why the AEI on the peptide layer but not annealed displayed the highest ionic conductivity on average: i.) the sample had appropriately
sized ionic domains and ii.) the AEI was uniformly covered on the gold and silica portion of the IDEs.

Figure 55 summarizes the trends between ionic conductivity and the sized ionic domains. Although Figure 55 suggests that an optimal ionic grain size may give the best ionic conductivity for PPO-QDMDA (a 2- to 3-fold improvement over the lowest value attained), it is important to note that other reports highlight that smaller ionic domains give higher ionic conductivity\textsuperscript{142, 143} or ionic grain size does not impact ionic conductivity at all\textsuperscript{144}.

The difficulty in correlating ionic grain size to ionic conductivity relates to the control of other structural factors such as percolation and tortuosity\textsuperscript{22, 126}. The work here is starting point to manipulate microstructures of AEIs with peptides and solvent vapor annealing. Other AEI systems, such as block copolymers, that are more conducive to long-range order and connectivity\textsuperscript{59} will be pursued in future studies with modified electrode surfaces to definitively understand how grain size impacts ionic conductivity.

Figure 57A-E present Raman Spectra and maps of the peptide on the IDE before addition of AEI. These results substantiated uniform coverage of the peptide over the IDE leading to uniform AEI microstructure across the IDE. Recall that the AFM images of AEI on gold QCM sensors (Figure 53A and B) also substantiated that the AEI had better coverage and larger grains when the gold was modified with an adsorbed peptide.
Figure 57. A) Places on the IDE for Raman spectra collection; B) Raman spectra for areas that contain SiO\textsubscript{x} surface. At 196 cm\textsuperscript{-1} a signal associated with the peptide was present because no signal was given for SiO\textsubscript{x} at that Raman shift; C) Raman spectra for areas that contain Au surface. At 500 cm\textsuperscript{-1}, a signal associated with the peptide was detected, but Au did not provide a signal at that Raman shift. D) and E) are localized Raman spectra maps (given as contour plots) at 10 µm resolution over a 50 µm x 50 µm area on Au (196 cm\textsuperscript{-1}) and silica (500 cm\textsuperscript{-1}). Both the macroscopic Raman spectra (B & C) and the localized Raman maps (D & E) substantiate uniform peptide coverage over the IDE.
It is important to note that the morphologies of the AEI on the gold QCM sensors were different than the gold portion of the IDEs. This may be due to the gold surfaces being different: the gold on IDEs is ~2X rougher in comparison to the gold on QCM-D sensors according to AFM topography images (images and roughness factors shown in Figure 58). We also speculate the difference in gold surface roughness is the reason the grains are sometimes represented by a different color (light vs. dark) in Figure 53 and Figure 54, as topography has been shown to affect phase imaging.¹⁴⁵

Figure 58. AFM topography images of A) bare gold QCM sensor and B) bare gold of IDE. The power spectral density (PSD) is reported which is an indicator for surface roughness. One sample was analyzed in multiple locations with similar results.

6.4. Conclusions

Sequence defined peptides, featuring a carboxylate moiety, anchored to a surface generated better ionomer coverage and larger microphase separated ionic grains compared to samples with AEI films assembled without the peptides. In turn, the appropriately sized ionic grains that formed on the peptide layer substantially improved thin film ionic conductivity by a factor of three compared to samples without peptide. When the samples were solvent vapor annealed,
appropriately sized ionic grains were observed in the microphase separated PPO-QDMHA AEI assembled without a peptide, but nonuniform coverage persisted. Lastly, a combination of peptide modified electrodes and solvent vapor annealing resulted in large AEI ionic domains that were as big as 65 nm, but the larger domains proved catastrophic to AEI conductivity. Generally, these results show that both biomolecular modifications and solvent vapor annealing can be used to control the microphase separation of AEIs on solid surfaces to discover important structure-property information, such as ideal grain size for ionic conductivity.

6.5. Future work

Future work will take advantage of discovery by exploring the rich design space enabled by different peptide sequences in combination with different solvent vapor annealing conditions, AEI block copolymer designs, and electrode potential to achieve new microphase separated structures and to investigate their functional properties.
Chapter 7. Conclusions

This dissertation demonstrates that IEMs/ionomers are a key component of electrochemical systems and improving the performance of IEMs and ionomer-electrode interactions can lead to significant improvement in the efficiency of devices such as electrolyzers, fuel cells and flow batteries. There are many areas where membrane performance may be improved: material chemistry, type of catalyst and surface patterning. Several membrane/ionomer chemistries have been researched over the years, from hydrocarbon based polyarylene to perfluorinated backbone polymers. Similarly, in case of BPMs, different combinations of AEM and CEM and interfacial catalyst layer have been studied. This work looked at the interfacial design aspects of BPMs by micropatterning the junction region using an optical lithography method. The effect of normalized interfacial areas on the water dissociation properties of the BPM were studied, in terms of onset potential and current density at a fixed voltage. The results clearly demonstrate an improvement in BPM water dissociation performance in the junction regions on increasing interfacial areas.

The next section also looked at patterning membrane surfaces, and focused on BCP lithography to make nanopatterned IEMs. Various electrochemical properties of nanopatterned IEM were measured and compared with micropatterned and flat surface membranes. Some properties like through-plane membrane conductivity showed an improvement on reducing the lateral feature sizes on membrane surfaces, while other properties like permselectivity did not change. This can have implications in electrochemical devices where patterning membrane surface can be employed as a simple method to improve its conductivity without compromising on other electrochemical and material properties.
The final project in this dissertation examines AEI-electrode interactions and their modification using sequence defined peptides and solvent vapor annealing. It was observed that peptide interaction and solvent vapor annealing changed the microstructures of AEI thin films on electrode surfaces, resulting in alteration of AEI film domain size. It is important because ionomer films are responsible for effective reactant delivery, product removal and charge transfer reactions on electrode surfaces. The results show that an optimum AEI domain size resulted in highest conductivity of the AEI films. This can have important implications in AEI based fuel cell and water electrolyzer performance.
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Peptide-Modified Electrode Surfaces for Promoting Anion Exchange Ionomer Microphase Separation and Ionic Conductivity

Author: Zhang Su, Subarna Kale, Leigh C. Harden, et al

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References


54. Simons, R., Electric field effects on proton transfer between ionizable groups and water in ion exchange membranes. Electrochimica Acta 1984, 29 (2), 151-158.


67. Arges, C. G.; Kambe, Y.; Dolejsi, M.; Wu, G.-P.; Segal-Pertz, T.; Ren, J.; Cao, C.; Craig, G. S.; Nealey, P. F., Interconnected ionic domains enhance conductivity in microphase


77. Xu, J.; Amorim, I.; Li, Y.; Li, J.; Yu, Z.; Zhang, B.; Araujo, A.; Zhang, N.; Liu, L., Stable overall water splitting in an asymmetric acid/alkaline electrolyzer comprising a bipolar...


Vita

Subarna Kole was born in Arambagh, India. She graduated with a Bachelor’s Degree in Chemical Engineering from National Institute of Technology, Raipur. Her undergraduate research work was based on synthesis and characterization of Ceria nanoparticles. After that, she pursued her Masters’ at Oklahoma State University, where she worked on a microfluidic facility to investigate the generation of emulsions in petroleum industry during crude oil production. Her interest in research motivated her to pursue PhD at Louisiana State University. During her PhD, she worked on projects to explore and improve the performance of ion exchange membranes for applications in electrochemical devices such as fuel cells, electrolyzers, flow batteries and study ionomer-electrode interactions in these devices, in the Arges Laboratory in collaboration with Case Western Reserve University, Cleaveland, Ohio. Besides research, she enjoys traveling, painting, and jogging.