Identification of Low Potential Onset of Concentration Polarization and Concentration Polarization Mitigation in Water Desalination Membranes

THESIS

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Abstract

Identification of concentration polarization regimes in nanocapillary array membranes for electrokinetically driven flow was investigated in a parametric study varying both nominal pore diameter (10, 50, 100 nm) and potassium phosphate buffer solution concentration (0.2, 1, 10 mM) used as the background electrolyte. The applied voltage for the electrokinetic flow was kept below 1 V (tested range from 10-750 mV) and was chosen to conduct experiments in a regime where minimal Faradaic or charge transfer reactions occur for transport across nanopores. Methylene blue at a concentration of 0.14 mM was used as a tracking dye to indicate the transport of charged carriers in the presence of these relatively low applied potentials. An electrical circuit model of the nanopore and the surrounding solution was developed. For an electrokinetic radius of 3.56 or less, the concentration time gradient of dye indicates onset of concentration polarization regimes.

Mitigation of polarization was performed with commercial forward osmosis (FO) membranes in permeation cells using a new electrical mitigation method that has been developed as part of this work. Initial proof-of-concept experiments show that for the membranes tested, a flux enhancement of over 40% was achieved.
Dedication

This document is dedicated to my family, thank you for all your support.
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1. Introduction

1.1. Thesis Objective

The goal of the work presented in this thesis is to identify concentration polarization onset regimes in membrane separation processes, specifically through a broad parametric study of water desalination membranes. Once the concentration polarization onset regimes have been identified, a low energy consumption method to mitigate concentration polarization is proposed, and a proof-of-concept for polarization reduction or mitigation demonstration was shown.

1.2. Background

Membranes play an important role in the functioning of everyone’s day to day life. For example, the skin, lungs, kidneys, and numerous other biological systems and processes employ membranes to separate biological functions and clean vital liquids in our bodies in an efficient manner. Consequently, membranes are defined as a physical barrier that separates two media of the same or different phases and may allow preferential transport of one species over another. Membranes can be broadly classified into two categories, organic and inorganic. Organic membranes are made from polymers or biological materials, and inorganic membranes could be made using metals, semiconductors, or insulators that are primarily non-carbon containing materials.

In an attempt to mirror the energy efficiency and separation effectiveness of biological membranes, artificial membranes have been developed for processing a myriad of fluids in the pharmaceutical, food, and water industries, to name a few. Purification of
liquids and gases by membrane processing is attractive for several reasons. As an example, membrane processing generally produces high purity permeates, and since processing is not thermal, i.e., temperature is not used to drive purification processes, flavors and aromas in food are preserved and enzyme activity is retained [1].

As membrane separation processes develop, concentration gradients form at the surface as the rejected feed components build up near the membrane on the reject side [2]. Initial fouling is usually manifested as a phenomenon known as concentration polarization, which forms a higher concentration layer at a membrane surface as seen in Figure 1.

![Concentration Polarization](image)

Figure 1: Concentration boundary layer formed by concentration polarization on a membrane surface [3]. The figure shows the development of the concentration polarization boundary layer for cross-flow over the membrane, with the permeate passing through the membrane as shown.

This boundary layer causes flux impediment due to the rise in local concentration of species. This, in turn, leads to an increased local osmotic pressure at the membrane surface, which causes a decrease in the effective driving pressure [4, 5]. As the fouling continues to develop, particles can adhere to the membrane surface causing scaling, which occurs when solid phase precipitates out of the solution, or biofilm formation. In
addition to flux impediment, biofilms can act as a source of permeate contamination. This denser, more impeding layer can be termed a cake or gel layer as shown in Figure 2 [2].

![Cake Formation (N_F > N_{Fc})](image)

Figure 2: The figure shows the same membrane as in Figure 1, but depicts the process of membrane fouling that is initiated by concentration polarization. The cake layer is a dense particle layer adjacent to the membrane surface. This layer can irreversibly foul the membrane as the polarization layer remains over the membrane surface [3].

As the cake or scale layer continues to build, it can become permanently attached to the membrane surface causing irreversible fouling that diminishes the flux through the membrane, which cannot be recovered even after the membrane is cleaned. Cake or gel layer formation occurs at a critical pressure and solute or particle concentration at the membrane surface. Gel layer formation can lead to a long term and sometimes irreversible efficiency reduction [3]. Concentration polarization initiates gel layer formation; however, in processes such as reverse osmosis, nanofiltration, and select ultrafiltration separations, the particles being separated out (generally ions or macromolecules) are too small to form traditional gel layers. Consequently, with ions and non-fouling macromolecules, the polarization layer behaves as if there is an additional or virtual membrane at the physical membrane surface as depicted in Figure 3. The higher
osmotic pressure through the coupled virtual and real membrane system creates a larger requirement for the driving force of the separation process to overcome, thereby decreasing the separation efficiency. Note, while this description is qualitative, Chapter 3 presents a detailed quantitative analysis for the development of the concentration polarization layers subject to the experimental conditions listed in Chapter 2.

![Unimpeded Membrane](image1.png) ![After concentration polarization onset](image2.png)

Figure 3: Schematic depicting the effect of concentration polarization. After the onset of concentration polarization, the system at hand behaves as if there were additional membranes added. Consequently, the easiest conceptual framework for visualizing concentration polarization is to recognize the presence of virtual membranes.

As concentration polarization and cake layer formation develop for ions and non-fouling macromolecules, an integrated treatment of these phenomena has been suggested. Here, the cake layer is defined as the point when the solute molecules are structured and the Brownian motion ceases. These thermodynamic conditions are defined mathematically as:

\[
N_F = \frac{4\pi a_p^3(\Delta P - \Delta \pi - \mu R_m J)}{3kT}
\]  

(1)

where \(N_F\) is termed the filtration number, \(a_p\) is the particle radius, \(\Delta P\) is the applied pressure, \(\Delta \pi\) is the osmotic pressure, \(\mu\) is the solvent viscosity, \(R_m\) is the membrane...
resistance, $k$ is Boltzmann’s constant, $T$ is temperature, and $J_i$ is the permeate flux [3]. Note that larger particle size will cause $N_F$ to grow rapidly due to the cubic dependence of $N_F$ on $\alpha_p$.

As separation or filtration processes progress, the local concentration gradients formed at the membrane surface are caused due to the different permeation rates of the solution components. Differences in permeation rates are determined by properties of species in solution and interactions with the electronic double layer (EDL) due to charge interactions between ions, solvents, and the membrane walls. More depth on the EDL can be found on page 8.

Since concentration polarization is inherently an interfacial phenomenon, it has been observed in many different cases and applications. These include, but are not limited to, artificial and biological membranes as well as ion selective interfaces in micro- and nanoscale devices. Significant concentration polarization occurs in systems independent of the driving force used, whether pressure or electrokinetically driven. The important factor is the ratio of rejected solutes that form concentration gradients at the solid-liquid interface either due to a membrane or micro/nanoscale interface. This ratio is what forms the areas of concentration at the membrane surface or interface that differs from the bulk concentration. The effects of concentration polarization can be more easily imaged in electrokinetic micro- and nanoscale devices than for membrane systems. An example of the effects of concentration polarization is presented in an experimental study and shown as enrichment depletion zones in Figure 4.
Figure 4: Enrichment/depletion zones in an electrokinetically driven micro/nanoscale device identified by increased or decreased fluorescence of the marker dye. These zones have been considered as evidence of polarization at the interface of micro- and nanochannels. Adapted from [6].

As seen in Figure 4, strong enrichment and depletion zones form at the micro/nanoscale interface. These zones were imaged in Figure 4 with fluorescent dyes. The direct consequence of concentration polarization in micro- and nanoscale devices with electrokinetic flow is on the magnitude of electrically based sensor measurements. As with pressure driven membrane separations, in addition to increasing energy requirements of the system, concentration polarization shifts the current density readings, thus adversely affecting the accuracy if only calibrated for the ohmic region.

1.3. Membrane Separation Processes

Flow through a membrane is commonly described using the solution-diffusion model, which was proposed in the nineteenth century and became popular in the 1940s. This model states that the permeants dissolve into the membrane and diffuse through it at different rates, based on their diffusivity within the membrane, membrane pore size, and concentration of permeants on each side of the membrane [7]. Permeation through
membranes can be written in a general form, as shown in equation 2, which allows for any of the driving forces to be written as a chemical potential gradient.

\[ J_i = -L_i \frac{d\mu_i}{dx} \]  

(2)

where \( L_i \) is the coefficient of proportionality that relates the chemical potential driving force to the flux, and \( \frac{d\mu_i}{dx} \) is the chemical potential gradient. For an osmotic process where concentration gradient is the only driving force, Fick’s first law of diffusion shown in equation 3 can be used to describe flux through the membrane.

\[ J_i = -D_i \frac{dc_i}{dx} \]  

(3)

where \( J_i \) is the flux of component \( i \), \( D_i \) is the diffusion coefficient, and \( \frac{dc_i}{dx} \) is the concentration gradient of component \( i \). For the reverse osmosis process, which is pressure-driven separation against the concentration gradient, it can be shown that the flux through a membrane can be described as follows [7].

\[ J_i = \frac{K_i D_i}{l} \left[ c_{io} - c_{il} \exp \left( \frac{-v_i (\Delta p - \Delta \pi)}{RT} \right) \right] \]  

(4)

where \( c_{io} \) is the concentration of solvent at the membrane surface on the feed side, which is water in the case defined here, \( c_{il} \) is the concentration of salt, \( K_i \) is the sorption coefficient, \( l \) is the width of the membrane, \( v_i \) is the molar volume, \( \Delta p \) is the applied pressure, \( \Delta \pi \) is the osmotic pressure created by the difference in the concentration of salt on each side of the membrane, and \( T \) is the temperature [8]. From equation 4, the amount of pressure required to separate a solution into components can be found based on the osmotic pressure across the membrane for a given flux value.
1.4. Concentration Polarization Effects

Selectivity of membranes is determined by pore size, membrane surface charge, and solution composition. Pore size in the membrane rejects particles and solutes by physical filtration, i.e., particles larger than the pore opening diameter are left behind, whereas, membrane surface charge and solution composition lead to the formation of the electric double layer (EDL) as shown in Figure 5.

![Electric Double Layer Diagram](image)

Figure 5: The schematic here shows the electric double layer structure at a solid/liquid interface with immobile Inner Helmholtz plane, Stern layer, and Outer Helmholtz plane before reaching the diffuse or bulk layer [9].

A wall surface becomes charged when exposed to the ionic fluids (e.g., seawater or brackish water), and this charged surface will in turn be screened by a layer of counterions. This screening layer is commonly known as the electric double layer (EDL), where the...
counter-ions in the “Stern layer” are immobilized by short-range attractive forces at the surface, and the mobile counter-ions in the “diffuse layer” have only electrostatic interactions with the charged surface. The boundary between the Stern and diffuse layers is the shear plane, and the overall thickness of the EDL is about five times the Debye screening length, $\lambda_D$, which varies from Ångstroms for aqueous electrolyte solutions at molar concentrations of $O(1 \text{ M})$ to nearly 1 micron for pure water. Note that the EDL is a model of the counter-ion distribution, and accurately representing the charge distribution in the layer of counter-ions screening the charged wall may require more than two layers. Generally, in macro-scale flows (for example, millimeter scale or larger characteristic lengths), the effect of the EDL on the flow is negligible. However, as the surface area to volume ratio increases, the effects of the EDL can be significant. The Boltzmann distribution can be used to describe the distribution of charged particles near a flat charged surface with equation 5.

$$n_i = n_i^\infty e^{-\left(\frac{z_i e \phi}{k_b T}\right)}$$  \hspace{1cm} (5)

where $n_i$ is number of ions of type $i$ at the surface, $n_i^\infty$ is the number of ions of type $i$ in the bulk, $z_i$ is the charge of the ion, $e$ is the charge of an electron, $\phi$ is the electrical field potential at the point in the liquid, $k_b$ is Boltzmann’s constant, and $T$ is temperature. [10]

From this equation, it can be seen that the potential distribution from the surface wall into bulk fluid follows an exponential decay. The layer of charged particles directly next to the surface is termed the compact or Stern layer, is generally considered immobile, and is typically a few Angstroms thick, as described above. [10] From a combination of the Boltzmann distribution described above and the Poisson equation, the shielding length of the electric double layer is defined in equation 6.
\[ \lambda_D = \sqrt{\frac{\varepsilon_e RT}{F^2 z_i^2 c_i}} \]  

(6)

where \( \varepsilon_e \) is the electric permittivity of the medium, \( R \) is the gas constant, \( F \) is Faraday’s constant, and \( c_i \) is the concentration of ion \( i \). Investigation of equation 6 shows that Debye length is dependent on concentration of the electrolyte used. For a symmetric monovalent electrolyte, for concentrations ranging from 0.33 \( \mu \)M to 1 M Debye length ranges from 0.3 to 530 nm, respectively.

Concentration polarization is especially problematic in cases employing highly permeable membranes or high molecular weight solvents which can be seen by examining the stagnant boundary layer case describing the polarization modulus, \( M \).

\[ M = \frac{C_w}{C_b} = e^{\left(\frac{J_i \delta}{D}\right)} \]  

(7)

where \( C_w \) is the concentration of the solute at the membrane surface, \( C_b \) is the concentration of the solute in the bulk solution on the retentate side, \( J_i \) is the flux of solute \( i \), \( \delta \) is the boundary layer thickness, and \( D \) is the solute diffusivity in the solution. [11]. Equation (7) shows that \( M \) increases exponentially with increasing solute flux.

When voltage is used as the driving force for these separations and the flow through the membrane is measured by the ensuing current, a characteristic voltage/current curve arises during membrane separation processes as shown in Figure 6 [12]. The curve shown in Figure 6 has been considered representative of polarization onset once the current-voltage relationship deviates from the first linear or ohmic region.
Figure 6: The characteristic shape of the current-voltage plot for onset operation of membranes with concentration polarization. Ohmic, limiting, and overlimiting current/voltage relationships develop for an electrokinetically driven ion exchange membrane (adapted from [12]). Note that the predicted overlimiting regime slope is smaller in magnitude than that of the ohmic region.

Initially the current/voltage relationship in such a system has an ohmic relationship, as seen in region I, as characterized by the linear dependence of current flow on applied voltage. As the voltage is increased, concentration polarization begins to impede the flow and the voltage increases without any response from the current flow, as shown in region II, termed the limiting regime. As the voltage continues to increase, an overlimiting regime is reached where the voltage-current relationship resumes a linear response, although at a different slope than in the ohmic regime [12]. Studies have suggested that if the membrane surface has patches of varying ion conductance, the electric field in the adjacent solution layer is distorted. The interaction of space charges with the electric field gives rise to a spatially inhomogeneous bulk force which is bound to set the fluid in the depletion diffusion layer in motion [12]. Electroconvection, with a
complex circulatory pattern (with a typical vortex size ranging from that of the typical spacing between the conducting parts at the membrane surface and up) results, causing mixing. The overlimiting conductance is observed when electroconvection becomes dominant over molecular diffusion in the depletion unstirred layer [12].

Another method of evaluating the restrictiveness of the polarization layer is characterization of the diffusivity with respect to the thickness of the diffusion layer, $\delta$ [13].

$$p^\delta = \frac{D}{\delta}$$

(8)

where $P$ is permeability and $D$ is the diffusion coefficient. Since the thickness of the layer determines the permeability and is dependent on the species diffusivity, the restrictiveness can be calculated from the amount of time to create or eliminate the solute adjacent to the membrane barrier [13]. It should also be noted that the solute concentration, $C$, within the polarization layer can be described as follows [13].

$$C(x) = C_s e^{-\frac{\nu x}{D} + \frac{a x^3}{3D}}$$

(9)

where $D$ is the diffusion coefficient, $\nu$ is the linear velocity of the osmotic volume flow, $x$ is the distance from the surface, and $a$ is the stirring parameter [13].

1.5. Applications

Although concentration polarization impacts almost every industry using membrane separation processes, the application chosen for this thesis is focused on the water processing industry due to water’s relationship to quality of life and survival for humans.
Recent reports and various publications have emphasized the importance of clean water for not only public health, but also for energy and security needs [14, 15, 16, 17]. Consider the following statistics that present a sobering picture of the current state of water supplies and the importance of advancing the science and technology to increase freshwater supplies. Based on World Health Organization (WHO) reports, nearly 2.4 million people die every year due to contaminated water, and a child under the age of five dies every 20 seconds. The most common waterborne diseases, affecting millions of people worldwide, are malaria, cholera, and diarrhea. In addition, it has been estimated that over 20 million people are affected by arsenic poisoning in the Bengal region of the Indian subcontinent (including Bangladesh). Given these brief statistics, it is not surprising that there is a renewed focus on developing new technologies for water purification [15, 18]. In addition to traditional contaminants found in water sources, a new class of emerging contaminants also threatens water quality in many regions. Many of these contaminants are not regulated due to lack of information with regard to exposure effects. Current contaminants identified are as follows:

- Fuel oxygenates (i.e. methyl tert-butyl ether, MTBE)
- N-nitrosodimethylamine (NDMA)
- Perchlorate
- Chromate

Parts of this chapter appear in [57]
• Veterinary medications that originate from concentrated animal-feeding operations
• Pharmaceutical and personal care products (PPCPs)
• Nanoparticles [19]

Among the many challenges that exist toward generating high quality potable water, desalination of salt water has been identified as a key step toward making progress for developing sustainable sources for fresh water [20]. However, to create effective desalination and subsequent distribution strategies, it is important to review how the water is distributed around the planet. The total available water on Earth is approximately $1.4 \times 10^{21}$ liters (or about 332,500,000 mi$^3$). Of this seemingly enormous water supply, over 99% is currently inaccessible to human use, and more than 97% of the Earth’s water exists in oceans, bays, seas, and saline aquifers as large reservoirs of salt water. In fact, several estimates place the approximate supply of usable fresh water at $\sim 0.7\%$ or about $9.8 \times 10^{18}$ liters. While this may appear to be a large number, accounting for population increase, demands on freshwater for agriculture, industry, potentially changing climate, declining fresh water quality from worldwide contamination via industrial, municipal, and agricultural discharge, and increasing energy needs leads to a rather bleak picture for future availability of clean water for human use.

Consider a recent editorial review [20] which reports data from the World Meteorological Organization (WMO), the combination of uneven population and water distribution is causing rapidly increasing water withdrawal rates as a fraction of total
available water (Figure 7) and projects that by 2025 (only 14 years from now) most of the world’s population will be facing serious water stresses and shortages.

Figure 7: Water withdrawal rate as a percentage of total available water, projected till 2025 [20].

Therefore, the ability to affordably and sustainably desalinate water can resolve many of the impending and projected water crises.

1.5.1. Review of Existing Water Desalination Methods

A huge variety of water desalination methods exist. In this section, a brief review for the most common methods is presented; therefore, not all techniques or references are included in this section. However, the reader is pointed to several review articles and books along with a broad variety of literature to allow further reading given the reader’s specific interests.

1.5.1.1. Theoretical Minimum Energy Requirement for Water Desalination

Consider an equilibrium analysis for the process of water desalination. From the second law of thermodynamics, for reversible processes the amount of energy required is
independent of the method used [21]. As a consequence, given the starting salinity of water and the target salinity of de-salted water, it is possible to calculate a theoretical minimum amount of energy required for water desalination. This exercise may appear academic, but is of value since the energy-water nexus [22, 23] is a major consideration towards evaluating the current state of water desalination technologies and also towards identifying new technologies. Consider an ideal compressor for moving water vapor from a tank of sea water (typically assumed at ~ 35,000 ppm or milligrams/liter salinity) to a tank of fresh water (typically assumed at ~ 500 ppm salinity) [21]. Using these conditions, the minimum energy requirement for water desalination at 25°C with a recovery rate of zero (i.e. negligibly small amount of water produced from a near infinite amount of sea water), is 0.70 kWh/m³ [21]. Recovery rate is defined as the ratio of freshwater produced to the inlet salt water. For a viable system, recovery ratios must be maximized in contrast to the waste or brine streams. Increasing the recovery rates to 25, 50, and 75% of fresh water product requires theoretical energy minimums of 0.81, 0.97, and 1.29 kWh/m³ respectively [15]. Based on an average water consumption of 466 m³/year [24], if all water demands were met at the theoretical desalination minimum the additional increase in energy cost would range from 378 to 602 kWh/year for recovery rates of 25-75%, respectively. Considering the average annual energy consumption of a U.S. household at 11,496 kWh [25], this amounts to an increase of 3-5% annual energy use. Therefore, in principle it should be possible to remove salt from water in an efficient manner with low energy consumption. However, several challenges exist to achieving these theoretical limits.
1.5.1.2. Challenges to Desalination Processes

Inherent irreversibilities present in real systems typically drive the energy requirements higher than the theoretical minima. Some of these irreversibilities relate to the presence of organics and particulates, and varying pH and salinity of source waters. Others relate to operation of mechanical and electrical equipment at varying energy efficiencies. The varying source water content can lead to scale formation and deposition or membrane fouling in desalination plants [26]. In order to mitigate these problems, desalination plants often employ extensive pre-treatment steps involving intensive chemical treatment processes including precipitation, flocculation, lime softening, ion-exchange columns, or mechanical processes such as aeration and sedimentation. For example, in order to minimize scaling, pre-treatment of feed water by introducing an acid followed by CO₂ degassing have shown to be effective methods of preventing alkaline scale formation [26]. Anti-scalants are particularly popular due to their effectiveness at low concentrations; the chief chemical families from which anti-scalants have been developed from are condensed polyphosphates, organophosphonates, and polyelectrolytes. Of these three classes of compounds, polyphosphates are most economical while effectively retarding scale formation and offering corrosion protection [26]. Organophosphonates are suitable for a wider range of operating pH and temperature conditions than polyphosphates [26]. The main consequence of all pre-treatment processes is that all of these involve increased energy consumption and material costs regardless of the specific desalination methodology employed. There is also growing concern that the rejection of these pre-treatment chemicals poses environmental threats
due to their toxicity. The subsequent treatment, if required, to remove the anti-scalants also consumes energy.

1.5.1.3. Common Separation Methods

About 88% of the available desalination production capacity employs either reverse osmosis (RO) or multi-stage flash (MSF) distillation processes for fresh water production from either brackish or seawater [27]. Other main technologies include multi-effect distillation (MED), vapor compression (VC), and electrodialysis (ED) [27]. The primary energy requirement for multi-stage flash, multi-effect distillation, and vapor compression is in the form of thermal energy, while reverse osmosis requires primarily mechanical energy, and electrodialysis requires primarily electrical energy. Other methods such as solar distillation, freezing, gas hydrate processes, membrane distillation, capacitive deionization, and ion exchange are used for desalination, but current technology levels for these processes find limited use and are not commercially viable on a world-wide scale for widespread implementation.

Table 1: Energy consumption and capacity needed for various desalination methods

<table>
<thead>
<tr>
<th>Process</th>
<th>MSF</th>
<th>MED/TVC</th>
<th>RO</th>
<th>ED*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Consumption (kJ/l)</td>
<td>290</td>
<td>145-390</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Electricity Consumption (kJ/l)</td>
<td>10.8-18</td>
<td>5.4-9</td>
<td>9-25.2</td>
<td>4.32-9</td>
</tr>
<tr>
<td>Total Energy Consumption (kJ/l)</td>
<td>300.8-308.8</td>
<td>150.9-399</td>
<td>9-25.2</td>
<td>4.32-9</td>
</tr>
<tr>
<td>Production Capacity (m³/day)</td>
<td>&lt;76,000</td>
<td>&lt;36,000</td>
<td>&lt;20,000</td>
<td>&lt;19,000</td>
</tr>
<tr>
<td>Conversion to Freshwater</td>
<td>10-25%</td>
<td>23-33%</td>
<td>20-50%</td>
<td>80-90%</td>
</tr>
<tr>
<td>Total Capacity (m³/day)</td>
<td>304000</td>
<td>109091</td>
<td>40000</td>
<td>21111</td>
</tr>
<tr>
<td>Pretreatment required</td>
<td>little</td>
<td>little</td>
<td>demanding</td>
<td>moderate</td>
</tr>
</tbody>
</table>

*taken for brackish water (3000-10000 ppm); other values are for seawater (32,000-35,000 ppm)
Table 1 summarizes energy consumption of various desalination methods. From an energy consumption standpoint, membrane separations offer the lowest energy input required by at least a factor of six. Thermal processes such as MED and MSF consume the largest amounts of energy, thus they may not be practical from an energy standpoint unless it is coupled with a process that produces a large amount of waste heat.

The pretreatment requirements for reverse osmosis units can include scale control, which can be managed by pH adjustment or an addition of a chemical anti-scalant, thus preventing irreversible scaling damage to the membrane. Prefiltration can also be employed for particulate removal, and disinfection can be used to prevent biofouling when the disinfectant is compatible with the membrane material. The reverse osmosis process can also require post-treatment, depending on the initial water quality to remove dissolved gases and adjust the pH and alkalinity [19]. It should be noted that scaling and corrosion are also major problems for MSF and MED desalination methods, as continued scaling decreases the efficiency of the desalination plant over time.

1.6. Methods of Polarization Reduction

Current methods of concentration polarization can be classified into three broad categories, (i) mechanical, (ii) chemical, and (iii) electrical.

Mechanical methods of polarization reduction include any method that agitates the fluid surrounding the membrane, including but not limited to physical mixing, vibration, and flow pulsing. Chemical methods include chemical surface modification of the membrane or solution to be separated. Electrical methods include applying an electrical, magnetic, or electromagnetic field on or near the membrane in order increase
flux by mitigating concentration polarization. To understand the methods used for concentration polarization reduction, it is useful to investigate the concentration polarization modulus, $c_{io}/c_{ib}$, equation.

$$c_{io} \over c_{ib} = \frac{J_v \delta}{1 + E_o (\exp^{D_i \delta} - 1)}$$  \hspace{1cm} (10)

where $c_{io}/c_{ib}$ is the concentration ratio at the membrane surface over the concentration in the bulk which is referred to as the polarization modulus, $J_v$ is the volume flux through the membrane, $\delta$ is the boundary layer thickness, $D_i$ is the diffusion coefficient of the solute in the fluid, and $E_o$ is the membrane enrichment, or $c_{io}/c_{io}$ or the ratio of concentration at the membrane surface over concentration on the permeate side. From this equation, as flux or boundary layer thickness increases, concentration polarization or $c_{io}/c_{ib}$ also increases. In many systems, the variable that is most readily manipulated is $\delta$, the boundary layer thickness [7]. The maximum flux through a membrane is the flux of deionized water through that membrane, i.e., no salt rejection causing the flux to reduce.

1.6.1. Mechanical Methods of Polarization Reduction

Mechanical methods of CP reduction tend to focus on increasing turbulence in the flow at the membrane surface in order to decrease $\delta$, the boundary layer thickness [7]. Methods of achieving this goal include increasing the fluid velocity at the membrane surface, adding membrane spacers to disturb the flow, or pulsing the feed flow in the system.
Feed spacers have been used to disturb the flow at the membrane surface. Placement of the feed channel spacer in a spiral wound membrane system is shown in Figure 8.

Figure 8: Schematic of a typical spiral wound membrane module [28]. Permeate travels through the membrane to the permeate collection material and out while the feed travels along the feed channel spacer before exiting as a concentrated brine.

In a review investigating a variety of systems using fouling and non-fouling feed solutions, a permeate flux increase between three and five times has been observed with the use of feed spacers [29]. The energy input for this method is in the pressure drop across the spacer as well as the reduced membrane area available for separation due to physical blockage by the feed spacer. Thus this method requires more membrane material for the same amount of product water as well as a larger applied driving force to drive permeate through the membrane. The relationship between feed pressure and membrane productivity, $\xi$, is described in the following equation.

$$\xi = \frac{Q_p}{V_{modP_f}}$$  \hfill (11)
where \( Q_p \) is the permeation rate, \( V_{\text{mod}} \) is the volume of the membrane module, and \( p_f \) is the feed entrance pressure. Using this equation and a sensitivity analysis, pressure losses for a given membrane length \((L)\) over membrane width \((W)\) can be seen in Figure 9.

![Figure 9: The effect of pressure drop across feed spacers on module productivity [29].](image)

Investigation of the graph shown in Figure 9 demonstrates that for a given \( L/W \) ratio, the mass transfer rates increase at the expense of pressure losses. For example, for an \( L/W \) ratio of 3.5, productivity can be reduced by as much as 35%, thus adding to the energy cost of permeation. The pressure drop is caused by an abrupt change in momentum at the spacer surface [30]. Looking at some individual studies, spacer thickness was varied in spiral wound RO systems, using spacer thicknesses between 0.1168 and 0.0508 cm. Six different feed concentrations, ranging from 0-5% NaCl were tested. In each case, the 0.1168 cm spacer thickness achieved a permeate flux of approximately 100% more than the 0.0508 cm spacer thickness case [31]. This experiment is an example of the effects of reduction in membrane area. Although the flux was greater for the 0.1168 cm spacer thickness case than for the 0.0508 cm thickness
case, the increase in permeate volume flow rate for the 0.1168 cm spacer case was only between 30-50% for the NaCl concentrations tested [31].

Schwinge et al. investigated zigzag spacer (Figure 10) effectiveness in ultrafiltration for a crossflow configuration with Dextran.

Figure 10: Schematic of the zigzag spacer investigated in [32]. These types of spacers increase surface turbulence while taking up less useable membrane area. Zigzag spacers are investigated due to their small contact area with the membrane, thus allowing more effective membrane area than a mesh spacer. For the ultrafiltration setup tested, the average increase in flux was between 160-190% for flow rates ranging from 0.5-3 l/min [32]. It should be noted here that of the feed spacer papers presented, the increased pressure drop due to the spacer layers is not explicitly discussed. This aspect is critical since there is no explicit discussion of energy consumption changes due to feed spacer introduction to the set-up. However, inferring from the data in Figure 9, the change is non-linear with pressure drop increasing at near exponential rates at low (< 2) $L/W$ values. Therefore, the increased energy consumption by enhancing turbulence in the
flow due to an increased pressure requirement to drive the flow can (and usually in most practical systems does) outdo the gain from improved flux.

Rios et al. took a different method to inducing turbulence in a tubular membrane for gelatin filtration by dispersing 3 mm diameter stainless steel balls in front of the membrane. This method increased steady state permeate flux by as much as a factor of ten for a fluidized bed porosity of 0.68 over the empty tube [33].

High frequency back-pulsing of a crossflow microfiltration system for bacterial separation has been tested with several different pulse rates and times. For a forward filtration time of 0.2 seconds and a backpulse time of 0.1 seconds, the system achieved approximately 12.5 times flux over the unpulsed system in a ten minute trial [34].

Reduction of concentration polarization has been carried out in many membrane separation systems by rotating disks, rotating membranes, or module vibrations. These ‘dynamic’ filtration systems reduce concentration polarization at the cost of necessitating a complex system that is challenging to develop for high pressure applications (NF or RO) [35]. However, rotating membrane systems such as manufactured by the Novoflow company consume 2.5 to 4.1 kW for their MF and UF systems. A pervaporation vibrating membrane module which operates by vibrating the membrane stack about the axis of the stack is shown in Figure 11 [36].

The method of membrane stack vibration creates high shear rates on the membrane surface and is referred to as vibrational shear enhanced process (VSEP) [36]. VSEP has been shown to increase the mass flux from an average $0.5 \pm 0.1 \times 10^{-6}$ to an
average of $1.0 \pm 0.2 \times 10^{-6}$ g/cm$^2$s with an additional energy input of 5-30 kW depending on system size [36, 35].

![VSEP bench scale schematic](image.png)

**Figure 11:** VSEP bench scale schematic [36]

In another study, the flux enhancement was achieved through direct membrane oscillation combined with turbulence promoters in order to more effectively reduce the boundary layer at the membrane surface. Flux measurements were taken for a no oscillation case, a membrane oscillation case, and a membrane oscillation with turbulence promoters case as seen in Figure 12 [37].

![Flux enhancement results](image.png)

**Figure 12:** Flux enhancement results with and without turbulence promoters versus plain system [37]. Note that the case with oscillations provided approximately 4 times higher flux values while the cases with turbulence promoters and oscillations showed an increase of about 10 times over no oscillation case.
Investigation of Figure 12 shows that the flux enhancement achieved by the membrane oscillation alone is a factor of four, while the combination of oscillation and turbulence promoters achieved a flux enhancement of almost an order of magnitude [37].

Ultrasonic waves have also been used to prevent membrane fouling and increase flux during separation. The sound waves travel by compression and expansion, and at high enough intensities, cause cavitation. Current challenges to this technology include integration of the ultrasound transducers into existing compact membrane module designs as well as the amount of energy lost as heat in these systems. Additionally, membrane lifetime can be a concern with this method as the waves have been shown to damage some types of membrane surfaces. The power intensity used for this process can range from 0.5-6 W/cm². An example of frequency dependence at an intensity of 23 W/cm² is shown below in Figure 13. [38]

![Figure 13: Flux of 0.5 wt.% of milk aqueous solution in cellulose MF membrane at 60 kPa](image)
Although significant flux increases were observed with this system, implementation issues and energy cost are major drawbacks to this solution since the energy required scales linearly with membrane area. Despite higher energy operating budget, mechanical methods such as feed spacers remain popular as they are easy to implement in most commercial systems.

1.6.2. Chemical Methods of Polarization Reduction

Chemical methods of polarization reduction focus on either membrane modification during membrane development or modification of the surface post creation via surface treatment. One method of surface modification is fluorination of membranes. This method has been shown to increase reverse osmosis membrane flux by six times versus an untreated membrane for FT-30 membranes (FilmTec Corp., Minneapolis, MN) while maintaining rejection and membrane lifespan. The mechanism behind this was hypothesized to be due to thinning of the polymer strands of the interfacial rejection layer as shown in Figure 14. [39]

Figure 14: (A) Unexposed SW30HR membrane (B) SW30HR membrane exposed to 15% wt. HF for 11 days [39]
Poly(ethylene glycol) (PEG) solutions have been used to pretreat polysulfone, polyethersulfone, polyacrylonitrile, and polyvinylidenefluoride membranes for a water flux enhancement. Results indicated flux enhancements between 50% and 500% based on membrane material and PEG solution concentration without a decrease in membrane selectivity. [40] However, after the initial flux enhancement experienced during membrane operation, membrane performance was still hindered by concentration polarization, and as the separation continued, the flow decreased back below pretreatment conditions [40]. Although the mechanism for the flux increase demonstrated by the PEG treatment was not discussed, it is probable that PEG makes the membrane surface highly hydrophilic, thus encouraging water entrance into the membrane.

1.6.3. Electrical Methods of Polarization Reduction

Electrical methods offer yet another alternative for reducing concentration polarization. Song et al. developed a protein concentration method by applying a DC electric field across a crossflow electro-ultrafiltration unit. By applying the DC field in such a way that the proteins were drawn away from the membrane, the permeate flux increased from $1.2 \times 10^{-6}$ to $1.6 \times 10^{-6}$ m/s when the electric field was increased from 0 to 3000 V/m [41]. Hermann attempted to increase flow across hyperfiltration and pressurized reverse osmosis membranes with ultrasonic vibration at 120 kHz and with electric excitation from 20 kHz to 200 mHz without success [42]. Other researchers enhanced the flux of a pressure driven oil emulsion separation by applying an electric field of up to 15 kV/m, resulting in a flux increase from 35 l/m$^2$h to 70 l/m$^2$h [43]. In a similar study, the flux was increased from 75 l/m$^2$h to 350 l/m$^2$h for an oily waste water
where the membrane was used as the cathode in a crossflow filtration system for an electric field of 2.4 kV/m (30 V for their setup) [44]. Flux enhancement of a hydrophobically modified water-soluble polymer (HMWSP) was carried out in a crossflow system using polyether sulfone (PES) membranes and an electric field of 16.7 kV/m (at 50 V for their setup) for a flux enhancement of approximately ten times [45]. Rios et al. investigated electro-ultrafiltration of proteins by using ‘step up’ fields of up to 2.4 kV/m (~26.4 V) in increments of 6 kV/m or initial ramps up to each of the field values (i.e. 0.6, 1.2, 1.8, and 2.4 kV/m). For their system, flux was enhanced by approximately 270% for the system without turbulence promoters with the initial ramp method and an electric field of 2.4 kV/m, but for a system with a fluidized bed to promote turbulence, the flux increase was only about 4% [33]. A commercial company, GrahamTek, utilizes both mechanical and electrical methods in their reverse osmosis systems. The electrical component consists of three coils 120° out of phase energized at an alternating field of 2 kHz that are wrapped around the membrane sandwich structure. The mechanical component is an ‘integrated flow distributor’ which creates 1-2 mm air bubbles that are allowed to flow along the membrane surface. This system achieves sustainable fluxes of 22-27 l/m²h for 40-50% recovery rates. From the patent report, a 380 V, 50 Hz power supply is called out to run the electric field on the coils, which is reported to run at a steady 2 A, consuming 760 W of power [46].

1.7. Thesis Deliverables

Concentration polarization is a well-documented issue in membrane processes, requiring more energy as the separation progresses and the boundary layers develop.
Although numerical modeling of concentration polarization induced electroconvection at an ideally permselective ion exchange membrane (which would be the overlapping EDL case) has been shown [12], to this author’s knowledge, concentration polarization’s onset regimes have never been quantified with respect to percentage of pore left open by EDL. In addition, this thesis will demonstrate a new proof-of-concept concentration polarization mitigation method. The method will use a low voltage AC field applied to the membrane surface in a forward osmosis membrane permeation cell. This type of mitigation is desirable due to its lack of moving parts, thus creating systems that are robust and relatively undemanding in maintenance requirements.

This thesis is organized in the following manner. Chapter 2 details methods of the concentration polarization identification experiments as well as the concentration polarization mitigation experiments. Chapter 3 presents and discusses first, the results from the concentration polarization identification experiments, followed by the concentration polarization mitigation work. Chapter 4 presents conclusions and identifies keys areas of projected future work for both concentration polarization identification and concentration polarization mitigation work.
2. Methods

2.1. Concentration Polarization Identification Experimental Methods

Concentration polarization identification experiments were performed using track etched, PVP coated polycarbonate membranes (diameter 25 mm) with pore sizes 10 nm, 50 nm, and 100 nm (GE Osmonics). The membranes are referred to as nanocapillary array membranes or NCAMs for this thesis; their properties are listed in Table 2.

Table 2: Properties of experimentally investigated NCAMs

<table>
<thead>
<tr>
<th>Pore Diameter</th>
<th>Pore Density (pores/cm²)</th>
<th>Total Number of Pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm</td>
<td>6.0E+08</td>
<td>1.2E+09</td>
</tr>
<tr>
<td>50 nm</td>
<td>6.0E+08</td>
<td>1.2E+09</td>
</tr>
<tr>
<td>100 nm</td>
<td>4.0E+08</td>
<td>8.0E+08</td>
</tr>
</tbody>
</table>

The NCAM pores are nearly cylindrical with monodisperse diameters forming model structures for the experiments discussed here. As an example, a scanning electron microscope (SEM) image of an NCAM with 100 nm pores is shown in Figure 15.

Figure 15: SEM of NCAM with 100 nm nominal pore size. The dark spots are the pores.
NCAMs were pretreated in DI water for 48 hours and working buffer solution for 4 hours immediately prior to experiment. The membrane pre-treatment process follows a previous report [47]. Current measurement and application of voltages was done using a Gamry Reference 600 in a four electrode setup [48]. Potassium phosphate buffer (pH 7 ± 0.2) in concentrations of 0.2 mM, 1 mM, and 10 mM, was prepared with Millipore 18.2 MΩ deionized water and monobasic and dibasic potassium phosphate salts (Sigma Aldrich, USA). The buffer provides control over electrolyte pH, which is in contrast to most published literature on nanopore transport where the pH of the solution is rarely controlled. This is critical since it is now well-established that surface charge is a major influence on nanoscale transport, and pH can cause changes to surface charge for the channel or pore walls.

Permeation experiments were carried out in a custom cast acrylic permeation cell with a 500 mL solution capacity on each side. The permeation cell was placed within an earth grounded Faraday cage.

Figure 16: Schematic of the experimental setup for the identification of concentration polarization at low applied electric potentials.
Methylene blue (MB) was added to the solution in the source side of the permeation cell at a 0.14 mM concentration. Current was recorded throughout the entire 3600 second experiment at specific time intervals set by the operating software algorithm. Several data points in the first 100 seconds were collected to capture any transient in the current flow. Equal 3 mL samples of solution were extracted with a pipette from both sides of the permeation cell at 0, 8, 15, 30, 45, and 60 minutes (after thoroughly stirring the sides at those times) to conduct optical measurements for verifying MB transport. Ag/AgCl reference electrodes (Bioanalytical Systems) were connected to a high impedance input in the potentiostat, while both the working and counter electrodes were 1 mm diameter gold wires (Alfa Aesar) which had been cleaned using an SC-1 cleaning process as described in Appendix B. Methylene blue is positively charged at the experimental conditions [49]. A detailed experimental procedure is shown in Appendices A and B. Absorptivity of each sample was measured with a Thermo-Scientific Evolution 300 UV-Vis at 665 nm. Beginning with the Beer-Lambert law to relate transmissivity, $T$, and concentration,

$$ T = \frac{I}{I_o} = 10^{-\varepsilon cl} $$ (12)

where $I$ is the intensity of the transmitted light, $I_o$ is the intensity of the incident light, $\varepsilon$ is the molar absorptivity, $c$ is concentration, and $l$ is path length of light. For a liquid,

$$ A = -log_{10}\left(\frac{I}{I_o}\right) $$ (13)

where $A$ is the absorptivity. This relation suggests that for very low concentrations, absorptivity is linear with concentration as below.

$$ A = \varepsilon cl $$ (14)
The absorbance for low concentrations can be considered linear with concentration for fixed molar absorptivity and path length. Thus, solutions of known concentration were prepared in the concentration range of expected permeate values, and the absorptivity measurement of each concentration (repeated in triplicate) was recorded. A linear fit was applied to this data for each of the potassium phosphate buffer concentrations and absorptivity values were converted back to concentration with this method. The experimentally generated calibration curve for the concentrations in the predicted range of permeate values is shown in Figure 17.

![Graph showing absorptivity vs concentration](image)

Figure 17: Experimentally determined absorptivity of 0.2 mM potassium phosphate buffer with varying methylene blue concentrations at 665 nm.
Figure 18: Experimentally determined absorptivity of 1 mM potassium phosphate buffer with varying methylene blue concentrations at 665 nm.

Figure 19: Experimentally determined absorptivity of 10 mM potassium phosphate buffer with varying methylene blue concentrations at 665 nm.
From Figure 17, Figure 18, and Figure 19 it can be seen that for the concentration range of methylene blue, the relationship to absorptivity remains linear. These calibration curves were used to relate the absorptivity measurements back to concentration.

2.2. Concentration Polarization Mitigation Experimental Methods

In addition to identifying regimes where CP onset occurs, proof-of-concept CP mitigation experiments were carried out using forward osmosis membranes. Polyamide-based forward osmosis (FO) membranes provided by Porifera (California, USA) were electrolessly gold plated to render the membrane conductive. Hydraulic Technology Innovations (HTI) also provided cellulose triacetate based FO membranes from their cartridge products, which were also electrolessly gold plated. Flux experiments were performed using the same custom permeation cell (Figure 20) as the polarization identification experiments. DI water was used as the draw solution and 1.5 M NaCl as the feed solution using NaCl (Fisher Scientific, USA) prepared in Millipore DI water (18.6 MΩ). The permeation cell began with 400 mL of feed and draw solutions on their respective sides and the experiment was run for 8 hours. The control case used unplated Porifera membranes, while the experimental case used plated Porifera membranes where the membrane was used as the electrode. A waveform generator (Keithley 3390) is used to apply an electrical field between the gold wire and the conductive membrane in the configuration as shown in Figure 20.
Figure 20: A. Schematic showing the experimental schematic for mitigation of concentration polarization at low applied electric potentials. B. Digital picture of permeation cell running a mitigation experiment.

The electrodes were the conductive membrane and a gold wire placed into the draw side of the solution.
3. Results and Discussion

3.1. Concentration Polarization Identification

The increased energy use and subsequent formation of a cake layer under the conditions discussed in Chapter 1 make concentration polarization a major hindrance for the advancement of membrane separation technology. Identification of polarization onset under the experimental conditions discussed in this thesis will allow increased understanding of flow characteristics through membranes operating with low electrical potential-driven electrokinetic phenomena.

3.1.1. Characteristics of NCAM transport

By varying pore size (10, 50, and 100 nm) and potassium phosphate buffer concentration (10, 1, and 0.2 mM), the concentration time gradient of methylene blue was investigated as a function of pore diameter and EDL thickness dependence as described in Chapter 2. In addition, by varying the applied voltages (0 to 750 mV) for each of these cases, the effect of electric field strength on the concentration time gradient was also quantified. Before discussing the results, it is useful to note that the PVP coating on the polycarbonate-based NCAMs causes the membranes to be hydrophilic instead of hydrophobic as polycarbonate. In addition, the amine group in the PVP coating contains an N atom that is protonated in the pH 7-8 range, causing the membranes to have a positive surface charge for the experimental conditions tested [50].
It should also be noted that although pore densities and nominal diameters would suggest a ratio of 1:25:66.67 for the 10:50:100 nm pores. Previous reports of metal nanowires grown in NCAMs have shown that the nanopores actually have a cigar-like shape leading to a narrower entrance and exit in contrast to the middle part of the nanopore with respect to the nominal pore diameter. Therefore, treating the pore as a straight cylinder can lead to an overestimation of area ratio between NCAMs of different nominal pore diameters [51]. Furthermore, recent electrochemical impedance spectroscopy (EIS) studies also confirm the non-cylindrical shape, finding that for a membrane with 5 nm nominal pore radius (or 10 nm diameter), the pore entrance could range from 2.19-2.49 nm while the diameter in the middle of the pore could range from 4.05-4.61 nm, taking manufacturer’s tolerances into account [47]. Consequently, it should be noted that for the analysis and discussions presented here, variations in pore diameter between the nominal value at the membrane surface and in the middle of the membrane could range from 63-111% and can introduce errors in estimates based on a cylindrical geometry.

Ionic transport through the membranes is also influenced by the EDL, which is correlated as in most nanoscale transport literature, to the Debye length, $\lambda_D$. The electrokinetic radius is a non-dimensional quantity that is the ratio of the radius of the pore to the Debye length (calculated as stated in Chapter 1). It can also be calculated by using the product of the reciprocal of the Debye length, $\kappa$ with the pore radius, $a$. Therefore, for electrokinetic radius $\kappa a > 1$, the EDLs within a nanopore are considered non-interacting or not overlapping. Consequently, overlapping or interacting EDLs occur
at $\kappa a < 1$. For the nominal pore diameters and solution composition in this work, a summary of the Debye length and electrokinetic radius is presented in Table 3.

The electrokinetic radii experimentally investigated ranged from 0.36 (for the EDL overlapped case, 0.2 mM and 10 nm pore) to 21.74. Both the concentration of the potassium phosphate buffer and the methylene blue were taken into account for the solution composition.

Table 3: Summary of calculated Debye length and electrokinetic radius summary for experimental conditions tested

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Debye Length</th>
<th>Pore Size</th>
<th>$\kappa a$</th>
<th>% of pore covered by EDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM</td>
<td>2.30 nm</td>
<td>10 nm</td>
<td>2.17</td>
<td>71%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 nm</td>
<td>10.87</td>
<td>17%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 nm</td>
<td>21.74</td>
<td>9%</td>
</tr>
<tr>
<td>1 mM</td>
<td>7.04 nm</td>
<td>10 nm</td>
<td>0.71</td>
<td>Overlap</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 nm</td>
<td>3.56</td>
<td>49%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 nm</td>
<td>7.11</td>
<td>27%</td>
</tr>
<tr>
<td>0.2 mM</td>
<td>13.83 nm</td>
<td>10 nm</td>
<td>0.36</td>
<td>Overlap</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 nm</td>
<td>1.81</td>
<td>88%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 nm</td>
<td>3.62</td>
<td>54%</td>
</tr>
</tbody>
</table>

It is useful to note that the Debye length increases by 6 times as the buffer concentration is decreased from 10 mM to 0.2 mM. The main consequence of increasing $\lambda_D$ is that electroosmosis begins to dominate flow and electromigration becomes less dominant with decreasing concentration and increasing $\lambda_D$ [52].

The average current densities, defined here as average current over the entire experiment per pore, are presented in Figure 21 and Figure 22 for the applied potential between 250-750 mV, with Figure 22 presenting a more detailed look at the 10 mM
concentration case for all pore diameters tested. Based on the cigar-like geometry of the 
pores, it is not surprising that the current does not scale with the nominal pore radius (or 
square with area) following Ohm’s law, as would be expected for the 50 nm and 100 nm 
pores at all concentrations. Note, that for the 10 nm pore membranes, the 1 mM and 
0.2 mM cases correspond to interacting EDLs, thus changing the expected scaling [52].

Figure 21: Average current densities for 1 mM and 0.2 mM cases for applied potentials 
between 250-750 mV for all three nominal pore diameters. Note that the average density 
does not scale with pore radius as would be expected for the 1 mM, 100 nm and 50 nm 
cases. EDL effects change scaling for the overlapping cases of 0.2 mM, 10 nm and 50 nm 
cases and their subsequent relationship between other cases.
Figure 22: The figure presents average current densities for 10 mM cases to show that for the case when $\kappa a > 1$, measured current values do not scale with nominal pore radius by following Ohm’s law.

The results in Figure 21 and Figure 22 both suggest that the average current voltage relationship over the range presented increases with increasing applied potentials. The data trends reported in Figures 21 and 22 agree with a recent paper investigating noise in solid-state nanopores, in which pore diameters from 6.3 - 51.0 nm [53] were considered, and the current-voltage scaling though increasing linearly was not Ohmic. Previously, pores in nanocapillary array membrane (NCAMs) have been modeled as a parallel RC circuit (Figure 23) [54]. A similar approach is used next to understand the data presented.

Figure 23: Equivalent circuit model of a pore in an NCAM where the $C_{edl}$ is the capacitance of the EDL in the pore and $R_p$ is the resistance of the pore.
In order to model the total measured current, which includes the flow through the nanopore as well as the solution between the nanopore and the reference electrodes, the characteristics of the solution/membrane interface need to also be considered. The solution between the electrode and the nanopore is commonly modeled as a resistor [55]. To account for this in the circuit model, a resistor in series was added to either side of the pore model as seen in Figure 24.

Figure 24: Proposed equivalent circuit model for NCAM including the membrane solution interface. Note $R_s$ is solution resistance, $C_{edl}$ is the capacitance of the EDL in the pore and $R_p$ is the resistance of the pore.

For an electrode setup containing two high impedance inputs connected to the reference electrodes, these two electrodes are modeled as ideal non-polarizable electrodes [56]. For the model circuit, the current can be written as follows.

$$i_{total} = i_\delta + i_{pore}$$  \hspace{1cm} (15)

where $i_{total}$ is the total current measured, $i_\delta$ is the current carried by the boundary layer at the solution/membrane interface, and $i_{pore}$ is the current carried through the pore. Since the pore was modeled as a parallel RC circuit, the terms of the current can be divided as follows,

$$i_{total} = i_\delta + \frac{\nu_{app}}{R_p} + \frac{d}{dt}(C_p\phi_{c,p})$$  \hspace{1cm} (16)
where $v_{app}$ is the voltage applied to the system, $R_p$ is the pore resistance, $C_p$ is the pore capacitance, $\varphi_{c,p}$ is the potential drop within the pore. Since the boundary layer, $\delta$, can be modeled as a resistor, the current flow through this part of the pore should be independent of time as resistance is governed by the ion concentration within the geometrical region in space [56]. The current flow is measured as a function of time. Therefore, the non-oscillating current, measured at the end of the current measurement would correspond to the steady current. The steady current was subtracted from the total measured current, $i_m$, the transient part of the current is remains as shown below.

$$i_t = C_p \frac{d\varphi_{c,p}}{dt} + \varphi_{c,p} \frac{dC_p}{dt}$$  \hspace{1cm} (17)

In order to develop a hypothesis about which of the two terms on the right hand side of equation (15) is dominant, it is useful to examine each term independently.

The driving forces present here are osmotic pressure, electroosmosis, and ion migration, as displayed in Figure 25. First, the $\frac{d\varphi_{c,p}}{dt}$ term, or change in potential drop across the pore in time, will be considered. The potential drop across the nanopore is dependent on the resistance across the pore and the applied electric field as shown in Figure 26 and Figure 27 based on EDL thickness.

![Figure 25: Directions of force vectors involved in the flow through the nanopore. $F_{eo}$ is the electroosmotic force vector, $F_{im}$ is the ion migration force vector, and $F_{op}$ is the osmotic pressure force vector. These arrows display direction only, not magnitude.](image)
The magnitude of osmotic pressure, which is created by the concentration gradient of methylene blue between the source and permeate sides, is $6.7 \times 10^{-6}$ atm. Although small, this is a force that drives transport from source to permeate side when no potential is applied. Electroosmosis, for the case of a positively charged substrate, will drive the highly mobile anions and consequently the flow towards the anode. Ion migration will move charge carriers to the oppositely charged electrode [52].

**Figure 26**: Expected potential drop through a nanopore for a thin EDL. Note that in the case of a thin EDL, ion migration dominates the flow.

**Figure 27**: Expected potential drop through a nanopore with overlapping EDL. Note that for the overlapping case electroosmosis dominates the flow.
From Figure 26 and Figure 27, we can see that the expected potential drop through the membrane is linear in space if the pore shows resistive behavior. However, as has been shown previously [57, 58] velocity and potential profiles in nanochannels and nanopores follow similar functional forms. The work by Bhattacharyya, et al. has shown that the potential distribution within a nanopore with non-interacting EDLs is constant, and can follow a near-parabolic profile for interacting or overlapped EDLs [57]. Therefore, for cases when $\kappa a >= 1$, the $dq/dt$ term can be neglected. This leaves two cases (1 mM and 0.2 mM for the 10 nm nanopores) where the change in potential may be significant.

Conventional models assume pore capacitance remains a constant. However, recent papers [53, 59] have shown that there can be surface charge fluctuations within nanopores. In addition, at low frequencies of the applied electric potential (few Hz or lower), it was reported that the current flow through nanopores is strongly correlated to the total number of charge carriers within the nanopore [59]. In the present case, charge carriers in the nanopore are controlled by the applied potential and the osmotic gradient for methylene blue. Therefore, the capacitance of the pore cannot be assumed to be a constant.

In order to test the above claims, the simplest EDL model was implemented. The Guoy-Chapman EDL model approximates the solution charge as a diffuse layer with ions approximated as point charges that can approach the surface of the nanopore without restriction. From the Poisson-Boltzmann equation, far from the surface the change in
potential over distance from the surface, \( \frac{d\phi}{dx} \), for a multivalent electrolyte can be expressed as follows [48].

\[
\frac{d\phi}{dx} = \sqrt{\frac{2k_B T}{\varepsilon \varepsilon_0}} \sum_i n_i \left[ e^{-\frac{z_i e \phi}{k_B T}} - 1 \right]
\] (18)

where \( k_B \) is Boltzmann’s constant, \( T \) is temperature, \( \varepsilon \) is permittivity of the medium, \( \varepsilon_0 \) is vacuum permittivity, \( e \) is the elementary electron charge, \( z_i \) is the charge on component \( i \), \( n_i \) is the number density of component \( i \). Noting that the charge, \( q \), in the diffuse layer near the surface is expressed as [48]

\[
q = \varepsilon \varepsilon_0 A \left( \frac{d\phi}{dx} \right)_{x=0}
\] (19)

where \( A \) is the area over which the charge resides. Noting that the solution phase surface charge density, \( \sigma^s \), is the negative of the surface charge density on the material surface, \( \sigma^m \), and which can also be expressed as the charge over the area or \( q/A \). With this in mind, \( \sigma^m \) for a multivalent electrolyte follows.

\[
\sigma^m = \sqrt{2\alpha \sum_{i=0}^{l} n_i \left( e^{-\beta_i \phi_0} - 1 \right)}
\] (20)

where \( \alpha = k_B T \varepsilon \varepsilon_0 \), \( \beta_i = \frac{z_i e}{k_B T} \), and the additional variables are defined as above. The capacitance of the EDL, \( C_{edl} \), can be calculated by taking the differential of surface charge density with respect to the potential drop though the EDL in the solution, \( \frac{d\sigma^m}{d\phi_0} \).

\[
C_{edl} = \frac{d\sigma^m}{d\phi_0} = \frac{\alpha \sum_{i=0}^{l} \beta_i n_i e^{-\beta_i \phi_0}}{\sqrt{2\alpha \sum_{i=0}^{l} n_i \left( e^{-\beta_i \phi_0} - 1 \right)}}
\] (21)
where the variables are all defined as immediately above. Since the rest of the terms in the capacitance expression are constants, the surface charge density must be taken as a time dependent term. Differentiating the capacitance expression with respect $t$

$$\frac{dc_{edt}}{dt} = \frac{-a\sum_{i=0}^{I}n_{i}e^{-\beta_{i}\phi_{0}}}{\sqrt{2a\sum_{i=0}^{I}n_{i}(e^{-\beta_{i}\phi_{0}}-1)}} + \frac{-a^{2}\sum_{i=0}^{I}n_{i}e^{-\beta_{i}\phi_{0}}^{2}}{(2a\sum_{i=0}^{I}n_{i}(e^{-\beta_{i}\phi_{0}}-1))^{2}}$$ (22)

where, all the terms are consistent with above definitions. It is interesting to note that the transient capacitance term is dependent on $z_{i}^{2}$, hence ions with multivalent charges have greater influence on transient capacitance behavior than monovalent charges. Since the potassium phosphate buffer solution contains $K^{+}$, $H_{2}PO_{4}^{+}$, and $HPO_{4}^{2-}$, the anion with -2 charge will have the largest influence on the changes to the capacitive term as per equation (17).

In both the 50 and 100 nm case, $\kappa a > 1$ for all experimental conditions and therefore, the pore largely behaves as a resistor with sufficient charge carriers that the capacitive current is not dominant. These trends agree with previously reported results where ion-migration is the dominant transport phenomenon [52]. However, for the 10 nm pores, $\kappa a$ can be less than 1 and the numbers of charge carriers within the nanopore are limited at lower concentrations (1 mM and 0.2 mM respectively). Thus, it is expected that the capacitive component of current plays a more important role. The average of the transient surface charge density, with a line shown at zero for clarity, is presented in Figure 28.
Figure 28: Average transient current for 10 nm pores. The scatter in the current is significantly higher in the 10 mM case than for the 1 mM or 0.2 mM cases.

Figure 28 shows that the transient current data has more scatter about zero for the 10 mM case. As shown by Smeets et al., the noise in nanopores for $\kappa a > 1$ is governed by the number of charge carriers and can increase with an elevated number of charge carriers. Figure 27 qualitatively agrees with the findings reported as at 10 mM concentration the transient current shows a higher degree of scatter in the measured data in contrast to the 1 mM and 0.2 mM cases. Note that the magnitude of the transient current is much lower than the magnitude of the average steady state current. This is expected for a DC bias since the capacitive current would be expected to be much lower in value than the steady state current.

Table 4 shows a summary for the comparison between the averages of these values.
Table 4: Comparison of average transient and steady state currents for the 10 nm case.

<table>
<thead>
<tr>
<th>Applied voltages (mV)</th>
<th>10</th>
<th>75</th>
<th>100</th>
<th>250</th>
<th>500</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM steady state current (A/pore)</td>
<td>1.5E-14</td>
<td>1.4E-13</td>
<td>1.7E-13</td>
<td>4.2E-13</td>
<td>8.2E-13</td>
<td>1.1E-12</td>
</tr>
<tr>
<td>10 mM transient current (A/pore)</td>
<td>8.6E-16</td>
<td>3.6E-15</td>
<td>2.2E-15</td>
<td>-1.6E-16</td>
<td>8.7E-15</td>
<td>-1.0E-14</td>
</tr>
<tr>
<td>1 mM steady state current (A/pore)</td>
<td>6.0E-15</td>
<td>1.3E-14</td>
<td>2.1E-14</td>
<td>4.6E-14</td>
<td>8.5E-14</td>
<td>1.5E-13</td>
</tr>
<tr>
<td>1 mM transient current (A/pore)</td>
<td>7.5E-16</td>
<td>1.1E-15</td>
<td>-2.3E-16</td>
<td>1.1E-15</td>
<td>-9.9E-16</td>
<td>-7.2E-16</td>
</tr>
<tr>
<td>0.2 mM steady state current (A/pore)</td>
<td>4.0E-16</td>
<td>4.9E-15</td>
<td>5.5E-15</td>
<td>1.5E-14</td>
<td>2.0E-14</td>
<td>3.0E-14</td>
</tr>
<tr>
<td>0.2 mM transient current (A/pore)</td>
<td>1.9E-17</td>
<td>7.3E-17</td>
<td>-4.1E-17</td>
<td>-2.7E-15</td>
<td>-6.9E-16</td>
<td>5.4E-15</td>
</tr>
</tbody>
</table>

As the concentration decreases, the transient and steady state currents keep this trend, staying at least one order of magnitude apart from each other. It should also be noted that for the negative currents seen in Table 4, it is expected that the transient current is essentially zero and the negative value is representative of the range of error in the measurements.

Previous studies have shown that the increase in current over the limiting current seen once an over-limiting voltage is reached is caused by convective mixing [12]. Rubinstein and Zaltzmann present a numerical solution of the excess noise generating vortices that would develop as a result of electro-convection in electrokinetic phenomena as shown in Figure 29. From the numerically predicted electro-convection vortices, as applied voltage increases and concentration polarization regimes develop, the noise in the measured current should increase. It should be noted that another source of noise could be hydrolysis, or splitting, of water, which occurs at 1.2 V. Since these experiments were performed with a highest voltage of 750 mV, there should be no hydrolysis noise contribution.
Figure 29: Numerically predicted streamlines of electroconvection vortices formed once the overlimiting region of concentration polarization has developed [12]. A. For time t=1 and B. For time t=3. Note that X is height along the membrane surface and Y=0 is the membrane surface.

In addition, the primary reason for choosing to work at potentials below 1 V is to minimize any charge transfer or Faradaic reactions [56] that can happen in any electrokinetic flow set-up. Minimization of these reactions keeps the species present more consistent, since new species are not being developed by oxidation/reduction reactions within the system.

Beginning with the 10 mM potassium phosphate case (Figure 30) for the 50 nm NCAM, as the applied voltage is increased the noise seen in the current increases as well. Qualitative examination of the data shows noise, characterized by increased scatter also increases with applied potential (see Figure 30).
Figure 30: Recorded current for 10 mM 50 nm cases. Note that significant noise does not develop in the data until an applied voltage of 500 mV.

As the concentration is dropped, the EDL grows and the electrokinetic radius decreases. In addition as the applied voltage and hence applied electric field across the nanopore arrays increase, the flux through the pore is substantially increased. Based on the concentration polarization modulus and the previous work investigating noise in nanopores, it is expected that this should allow earlier onset of concentration polarization regimes, and consequently should be accompanied by more noise or scatter in the measured current data. For the 50 nm 1 mM case, significant noise is seen in the measured current beginning at a 250 mV applied bias.
Figure 31: Recorded current for 1 mM, 50 nm cases. Note that significant noise does not develop in the data until an applied voltage of 250 mV.

As concentration continues to decrease to reach the 0.2 mM condition, the magnitude of the noise in the measured current is expected to increase further. The expected trend holds, and increased noise for a lower magnitude applied voltage is shown for the 0.2 mM buffer case (Figure 32). The scatter seen in the current measurements for the 0.2 mM case when compared to the 10 mM case for the same pore size is much larger. The trends displayed in these three cases are consistent for the 10 nm (Appendix C) and 100 nm (Appendix D) measured currents with respect to both concentration and voltage trends presented in the 50 nm case.
Figure 32: Recorded current for 0.2 mM 50 nm cases. Note that significant noise develops as early as an applied voltage of 100 mV.

Consider the methylene blue used in the source side of the experiments discussed. Since the methylene blue molecule will dissociate into a positively charged methyl blue ion and a negatively charged chloride ion, where the chloride ion is free of color, the movement of methylene blue through the system should be proportional to the current flow. Therefore, overall trends for concentration gradients would be expected to follow the same trends as current in prediction of onset of concentration polarization regimes as described in Figure 6 (see Chapter 1).

For the 10 mM buffer concentration, it is useful to note that the electrokinetic radii are 2.17, 10.87, and 21.74 for 10, 50, and 100 nm pores, respectively. The concentration gradient with time (Figure 33) shows clear ohmic, limiting, and
overlimiting regimes for the 10 nm case as shown by the dashed line for the 10 nm NCAMs. The transition between the Ohmic and limiting regions occurs near \( \sim 100 \text{ mV} \). Both the 50 nm and 100 nm also have similar regions though as seen in Figure 33, the three regions are less clearly defined.

Figure 33: Methylene blue concentration flux for 10 mM potassium phosphate showing clear ohmic, limiting, and overlimiting regimes for the 10 nm case.

Figure 34: Methylene blue concentration flux for 1 mM potassium phosphate showing clear ohmic, limiting, and overlimiting regimes for the 10 and 50 nm cases.
It is noted that for the 10 mM and 1 mM cases, the onset potential of the limiting case moved from 100 mV to 250 mV, respectively (Figure 34).

Figure 35: Methylene blue concentration flux for 0.2 mM potassium phosphate showing clear ohmic, limiting, and overlimiting regimes for the 10 and 50 nm cases.

3.2. Concentration Polarization Mitigation

Concentration polarization mitigation experiments were performed with electrolessly gold plated commercial forward osmosis membrane as shown in Figure 36.

Figure 36: Gold plated HTI forward osmosis membrane on the mesh structure side.
The hypothesis behind these experiments is that if the unstirred layer at the membrane/solution interface was perturbed significantly, concentration polarization could not develop or would be severely limited. Toward this goal, an AC bias was directly applied to the surface of the gold-plated membrane with respect to the solution, to ‘stir’ the EDL. The goal of these experiments is to demonstrate a proof-of-concept low energy consumption concentration polarization mitigation method. As discussed in Chapter 1, mitigation of concentration polarization would not only prevent increased energy use as the CP boundary layer grew, it would prevent the formation of most types of fouling including cake formation. Results for continuous application of the potential to a membrane surface for eight hour flux experiments are summarized and presented in Table 5. These experiments show that the plated membranes performed considerably better than the unplated membranes, as discussed next.

Table 5: Flux enhancement of electrolessly gold plated FO membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Voltage Applied</th>
<th>Flux (L/m²h)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porifera</td>
<td>n/a</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>Plated Porifera</td>
<td>100 Hz, 500 mV</td>
<td>20.3</td>
<td>41.6%</td>
</tr>
<tr>
<td>Commercial Cartridge</td>
<td>n/a</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>Plated Commercial Cartridge</td>
<td>1 kHz, 500 mV</td>
<td>9.8</td>
<td>42%</td>
</tr>
</tbody>
</table>

For the plated Porifera membranes, up to a 41.6% increase in flux was achieved. For the commercial cartridge membranes obtained from Hydration Technology Innovations, a flux increase of 42% was achieved. The initial results reported here suggest that with further optimization over voltage and/or AC frequency, a substantial increase in flux can be achieved for an applied potential of less than 1 V. Note that since power consumption for given resistance to a system scales as voltage squared. Therefore,
in contrast to other active polarization mitigation methods (refer to Chapter 1), the
method demonstrated here can potentially consume orders of magnitude less power. The
quantification of exact power consumption and the benefit over existing methods is part
of on-going experiments, and is beyond the scope of this thesis.
4. Conclusions

It has been shown that for an electrokinetic radius of 3.56 or smaller, CP regimes can be identified from the concentration time gradient of the dye. Conversely, for electrokinetic radii of 7.11 or higher, no such dependence was demonstrated for the range of applied voltages. Initial results showing a 41% increase in flux suggest promise for the method of concentration polarization mitigation presented. Separations using this technology could be far more economically viable than current membrane separation methods. Used in an application such as water treatment, this type of separation would allow a method of safe drinking water procurement without the risks of creating trihalomethanes (THMs) or other disinfection byproducts (DBPs) that are of increasing concern for public health as the knowledge of these chemicals and their toxicity evolves.

4.1. Future Work

For further exploration of the differential capacitance of nanoporous geometry, electrochemical impedance spectroscopy (EIS) could be used to provide a range of frequency based data. This data would allow one to determine whether the change in surface potential with time or the change in capacitance with time was the dominant term in the current measurements. The method presented for concentration polarization mitigation has several development directions to take as listed below.

- Optimization of applied AC field
• Optimization of electrode configuration
• Separation efficiency verification
• Concentration polarization mitigation verification for a pressure-driven flow system
• Investigation of possible faradaic reactions constituents of feed solutions
  • Important for applications where permeate composition is critical
• Investigation of use of combined mitigation methods
  • i.e. Feed spacers and membrane electrode mitigation
Bibliography


[59] R. Smeets, N. Dekker and C. Dekker, "Low-frequency noise in solid-state

Appendix A: Procedure for Methylene Blue Diffusion Experiments

Day Before

1. Get new scintillation vial, rinse with DI water and dry with air gun.
2. Soak membrane in DI water for 48 hours in scintillation vial.

Experiment

1. Get out 1L beaker and rinse with DI.
2. Add 250 mL DI water.
3. After performing calculations for given salt concentration and pH desired, weigh out amount of monobasic and dibasic salt.
4. Record actual amounts of salt used in experimental log.
5. If using the weigh boat container, it can be advantageous to rinse salt from this into the beaker by adding the next 250 mL of DI water.
6. Add the remaining water for a total of 1001.5 mL.
7. Stir well.
9. Pick the membrane up with tweezers. Drain the scintillation vial, and add enough buffer solution to cover membrane. Replace membrane and soak for 4 hours.
10. Rinse boxes and o-rings with IPA.
11. Wipe down boxes and o-rings with IPA soaked clean room cloth.
12. Rinse boxes and o-rings with IPA.
13. Rinse boxes and o-rings with DI.
14. Dry boxes with air gun.
15. Load membrane in boxes so that the shiny side faces the source box. Add soaking solution back to buffer.
16. Separate buffer out into 500 mL volumes.
17. Add 1.5 mL methylene blue (MB) to 500 mL of solution in a beaker. Stir well (at least 30 seconds with stirring rod).
18. Take out enough buffer (permeate side) to get a baseline measurement (two 3 mL samples) and MB doped buffer to maintain a consistent volume between both sides (6 mL)
19. Fill both chambers, keeping track of the source and permeate side.
20. Using micro-pipette, take 3 mL (1,000 microL) of solution from each side at time zero, 8 minutes, 15 minutes, 30 minutes, 45 minutes, and one hour. **Before** taking each sample, both the permeate and the source side need to be stirred at moderate speed for 15 seconds.

21. Samples can be stored in cuvette box until the experiment is finished (60 minutes).

22. **Immediately** after experiment is finished, rinse the reference electrodes with methanol, then soak in methanol for 1 minute. Repeat once before rinsing with DI water and returning electrodes to their storage chamber.

23. Allow the UV-Vis to warm up for 30 minutes and perform UV-Vis measurements.

24. Use the UV-Vis to measure the samples as outlined in UV-Vis procedure sheet. Set the decimal places recorded to 8.

   a. You will have two different sets of measurements and two baselines, one for the permeate side and one for the source side.

25. Immediately after the measurements are recorded, repeat the cleaning process for the boxes. This is extremely important, as leaving this will prevent methylene blue from becoming permanently stuck in boxes and contaminating the experiment.
Appendix B: Procedure for Applied Bias Methylene Blue Experiments

Day Before

1. Get new scintillation vial, rinse with DI water and dry with air gun.
2. Soak membrane in DI water for 48 hours in scintillation vial.

Experiment

1. Get out 1L beaker and rinse with DI.
2. Add 250 mL DI water.
3. After performing calculations for given salt concentration and pH desired, weigh out amount of monobasic and dibasic salt.
4. Record actual amounts of salt used in experimental log.
5. If using the weigh boat container, it can be advantageous to rinse salt from this into the beaker by adding the next 250 mL of DI water.
6. Add the remaining water to total volume of 1.0015 L.
7. Stir well.
9. Pick the membrane up with tweezers. Drain the scintillation vial, and add enough buffer solution to cover membrane. Replace membrane and soak for 4 hours.
10. Rinse boxes and o-rings with IPA.
11. Wipe down boxes and o-rings with IPA soaked clean room cloth.
12. Rinse boxes and o-rings with IPA.
13. Rinse boxes and o-rings with DI.
14. Dry boxes with air gun.
15. SC-1 clean gold wire electrodes.
   a. 100 mL H₂O, 10 mL hydrogen peroxide, 1 mL (added with micropipette) ammonium hydroxide (NH₄OH)
   b. Put onto hotplate at 400°C. Allow temperature of solution to rise to 73°C. (~8 minutes in chemical hood)
   c. Turn hotplate down to 255°C.
d. Leave solution at 73°C for 10 minutes.
e. Remove from solution, rinse with DI.
f. Place electrodes in sealed environment such as Ziploc bag.
g. Cleaning is good for up to 24 hours.

16. **Turn on Gamry 15 minutes before use.**

17. Load membrane in boxes. Add soaking solution back to buffer.

18. Add 500 mL buffer into both sides.

19. Replace box tops. Rinse reference electrodes well with DI water and place in slots in box making sure each tip is centered at the membrane.

20. Make sure ground wire is attached to cage.

21. Attach the white and blue leads to the reference electrodes.

22. On the blue side, add the gold wire electrode using the green lead.

23. On the white side, add the gold wire electrode using the red lead.


25. Experiments-Named Script-Chronoamperometry

26. Call Experiment by date followed by pore size, followed by concentration, followed by pH (i.e. 2_26_2011_100nm_100mM_pH6

27. Record any other pertinent data in the notes section (actual pH, conductivity, ect.)

28. Load membrane in boxes so that the shiny side faces the source box. Add soaking solution back to buffer.

29. Separate buffer out into 500 mL volumes.

30. Add 1.5 mL methylene blue (MB) to 500 mL of solution in a beaker. Stir well (at least 30 seconds with stirring rod).

31. Take out enough buffer (permeate side) to get a baseline measurement (two 3 mL samples) and MB doped buffer to maintain a consistent volume between both sides (6 mL)

32. Fill both chambers, keeping track of the source and permeate side.

33. Using micro-pipette, take 3 mL (1,000 microL) of solution from each side at time zero, 8 minutes, 15 minutes, 30 minutes, 45 minutes, and one hour. **Before** taking each sample, both the permeate and the source side need to be stirred at moderate speed for 15 seconds.

34. Samples can be stored in cuvette box until the experiment is finished (60 minutes).

35. **Immediately** after experiment is finished, rinse the reference electrodes with methanol, then soak in methanol for 1 minute. Repeat once before rinsing with DI water and returning electrodes to their storage chamber.

36. Allow the UV-Vis to warm up for 30 minutes and perform UV-Vis measurements.
37. Use the UV-Vis to measure the samples as outlined in UV-Vis procedure sheet. Set the decimal places recorded to 8.
   a. You will have two different sets of measurements and two baselines, one for the permeate side and one for the source side.
38. Immediately after the measurements are recorded, repeat the cleaning process for the boxes. This is extremely important, as leaving this will prevent methylene blue from becoming permanently stuck in boxes and contaminating the experiment.
39. Immediately after the measurements are recorded, repeat the cleaning process for the boxes. This is extremely important, as leaving this will prevent salt from becoming permanently stuck in boxes and contaminating the experiment.
40. Make sure to return the gold wires to Ziploc bags and the reference electrodes to salt water holders.
Appendix C: Current measurements for 10 nm cases

10 mM 10 nm
Appendix D: Current measurements for 100 nm cases