

NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Charge Mosaic Membranes from Ink-Jet Printing for Improved Water Reuse and Treatment

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Introduction

Desalination by reverse osmosis is an effective method of producing potable water, but the process is energy intensive due to fundamental thermodynamic restrictions.¹ Water reuse, which is less energy intensive than desalination, is also an important component of the water supply portfolio. Water reuse attempts to use non-traditional sources for a beneficial purpose, (e.g., reclaimed wastewater for irrigation). This process will be another source for potable water and requires a fraction of the energy required by desalination.

The presence of dilute ionic contaminants such as nitrate, perchlorate, and heavy metals are a notable concern that hinder the advancement of water reuse due to their well-documented effects on human health.¹ This proposal seeks to develop an innovative technology to remove dilute ionic species from aqueous feed streams for improved water reuse. Specifically, charge mosaic membranes (CMMs) that allow charged solutes to permeate more rapidly than water will be designed and fabricated. Previously, to remove contaminants from wastewater, water was forced through a size-selective membrane that rejected contaminants too large to flow through the membrane pores. Alternatively, the use of CMMs will make it possible to remove only that small percent of contaminant rather than forcing 99.9% of solution through a size-selective membrane.

Due to past difficulty in producing charge mosaics with well-defined and controlled nanostructures, their development has lagged severely. To overcome these difficulties, our research group recently developed a promising avenue to CMM design by ink-jet printing polymeric materials onto a structural template² which is versatile, fast, and consistent, and does not require harsh chemical treatments. Figure 1 illustrates the fabrication process of these mosaic membranes. Polyelectrolytes are printed on a polycarbonate track etched membrane into discrete regions. Using the striped pattern, positively charged and negatively charged polyelectrolytes are alternatively printed to form the mosaic. Selecting certain polyelectrolytes and printing conditions offers a wide array of functionalities and nanostructures for this system.³ This ability will enable a fundamental understanding of how the performance of

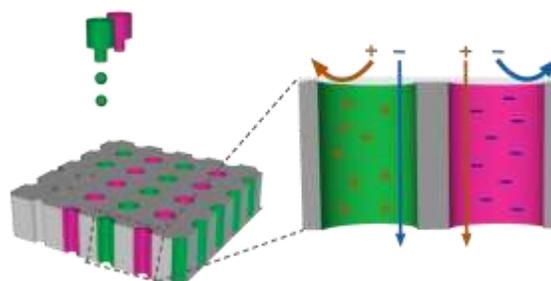


Figure 1 Schematic of the fabrication process for printing the mosaic structure.

these membranes relates to their basic physio-chemical features—something that is lacking in prior studies and prevents the systematic design of more effective charge mosaics.

Research Plan

Using the control over the nanostructure and chemical functionality of mosaic membranes provided by these new fabrications methods, I will generate rigorous structure-property-performance relationships for these membranes to enable a novel design for CMMs for removal of dilute hazardous contaminants from reclaimed wastewater. By studying the effect different modifications to the structure has on the physical and chemical properties of the membrane, we will elucidate a fundamental understanding of the transport phenomena that dictates the performance of these membranes.

CMMs facilitate the transport of dissolved salts because the charged ions are drawn electrostatically to the oppositely charged nanopores. This produces an enrichment of salt, which is a greater concentration of salt in the permeate. This results from salt being preferentially transported over water. Membranes of a single charge reject salt because the coions (i.e. ions of the same charge as the membrane) are electrostatically repelled, and the counterions (i.e. ions of opposite charge) are bound to the coions because of electroneutrality. The constraint of electroneutrality dictates that the overall charge of a solution must be neutral, meaning that there must be an equal concentration of anions and cations. This condition is maintained in a CMM, which allows both ions to flow through oppositely charged regions of the membrane.⁴

Three conditions are necessary for the mosaic to achieve enrichment:

- 1) Charged domains must traverse the entire membrane thickness and be closely packed;
- 2) Charged densities of charged regions should be equal in magnitude and opposite in charge;
- 3) Overall surface charge should be neutral.

Harsh chemical treatments and difficulty in orienting domains perpendicular to the surface have caused development of CMMs to lag severely.

Our lab group has already published two articles on printing membranes using an inkjet printer.^{2,5} In the second paper, we described how we produced the CMM structure using poly(vinyl alcohol) (PVA) blended with either a polycation or polyanion to produce positively-charged or negatively-charged regions, respectively. Our membranes demonstrate the characteristic salt enrichment of CMMs with significantly easier processing conditions and shorter processing times than typical CMMs. Our next hypothesis is that by using a pH-responsive polyelectrolyte, such as poly(acrylic acid) (PAA), we should be able to alternate between positive rejection and negative rejection, (i.e., enrichment). Stimuli-responsive membranes that alter their physical properties in response to an external stimulus (e.g., pH, temperature), have been widely used for applications in drug delivery, biointerfaces, and sensors.

Progress to Date

We have begun to print mosaics with poly(diallyldimethylammonium chloride) (PDADMAC) as the polycation and PAA as the polyanion. At high pH values, the acid groups are deprotonated and charged. In the mosaic, this means that roughly 50% of the surface will be positively charged and 50% negatively charged. This membrane would have an overall neutral surface charge. This is the typical CMM that would produce an enrichment. When the pH is lowered, the acid chains are protonated and become uncharged, producing a membrane with 50% of the surface positively-charged and 50% uncharged, for an overall positive membrane surface charge. As discussed earlier, this singly-charged membrane would result in rejection of ions

Work on this project has been in formulating the correct concentrations and printing conditions to produce the mosaic.

We have been focused on fabricating membranes with PAA and PDADMAC that fulfill all of these requirements.

We tested different membranes printed with PAA blended with PVA by two means.

First, rejection measurements were carried out in an Amicon® stirred cell using 1 mM KCl solutions. Percent rejection (%R) and enrichment (%E) were calculated by the following equation:

$$\%R = -\%E = 1 - \frac{C_p}{C_f}$$

where C_p and C_f are the concentrations in the permeate and feed, respectively, measured by ion chromatography. KCl rejection at various pH ranges of membranes printed only with PAA/PVA did exhibit a pH-responsive salt rejection, alternating between ~0% at low pH values where there is no surface charge and ~50% rejection at high pH values where PAA acid chains are deprotonated to give the membrane surface a negative charge. Thus far, mosaics using the PDADMAC/PVA and PAA/PVA blends show a pH-responsive rejection, but we are working to optimize this effect. We want to increase the range of salt transport as much as possible. This means a high enrichment (i.e. high salt transport) at one pH and as high as 100% rejection (i.e. no salt transport) at another pH.

Second, surface charge measurements were made by pressurizing a 1 mM KCl solution across the membrane in a homebuilt apparatus and measuring current across electrodes immersed in feed and draw. Surface charge measurements of membranes printed with just the PAA/PVA blend are underway to find the correct parameters to produce a surface charge equal in magnitude to the PDADMAC/PVA blend.

Conclusions

We already produced a pH-responsive membrane using the PVA/PAA blend that alternates between a 0 and 50 percent rejection at pH 2.0 and 9.0, respectively, without affecting the water flux, or the amount of material that flows across the membrane of given area. This indicates that PAA is a suitable polyelectrolyte to create a pH-responsive membrane. The surface charge measurements are leading us to the correct design parameters to produce a mosaic that, when PAA is charged, will have an overall neutral surface charge.

Understanding how the structure of different membranes produced with different polyelectrolytes, concentrations, and pore sizes will lead to a greater understanding of the fundamental of how CMMs operate, which is currently not well understood. This will lead to higher-performance membranes, which could potentially be further functionalize for applications beyond wastewater reuse and membrane separations to drug deliver and biomaterials.

Next Steps

We will continue to focus on optimizing concentrations of polyelectrolytes in the PVA blends and printing parameters to ensure a membrane that oscillates between enrichment and rejection. Finding the correct set of conditions for printing these membranes will present the largest challenge, but it should also teach us some fundamentals of how each parameter affects performance. These parameters include polyelectrolyte

concentration, number of overcoats (*i.e.* the number of times the print head passes over a single point), and template pore diameter. Performance will be characterized by both surface charge measurements and rejection.

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