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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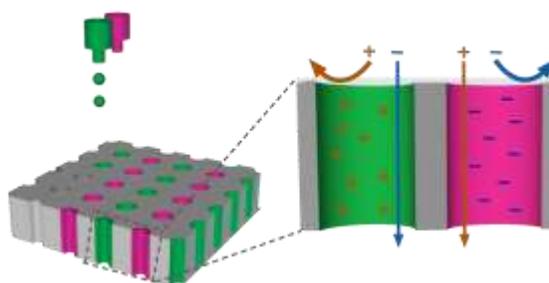
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Introduction

Desalination by reverse osmosis is an effective method of producing potable water, but the process is energy intensive due to fundamental thermodynamic restrictions.[1] Therefore, in addition to desalination, water reuse will be 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 is forced through a size-selective membrane that rejects 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 template.[2] 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

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

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 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, which has previously been lacking.

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. This simple and rapid method of producing CMMs will provide an avenue for exploring the fundamental ion transport mechanism driving this enrichment behavior.

To understand the ion transport mechanism, we examine our flux equation below:

$$\boldsymbol{j_i} = \boldsymbol{j_i}^{\text{conv}} + \boldsymbol{j_i}^{\text{diff}} + j_i^{\text{em}} = \vec{\boldsymbol{u}}C_i - D_i\nabla C_i - \mu_i\mathcal{F}C_i\nabla\varphi$$

where j_i^{conv}, j_i^{diff}, j_i^{em} are the convective, diffusive, and electromigratory flux components, respectively, which correspond each to a different driving force, namely a pressure drop, concentration gradient, and

electrostatic potential gradient, respectively, as shown in the right-hand side of the equation. Initially these experiments were executed in a dead-end filtration set-up, where the convection of the solvent tends to dominate over the other terms.

To isolate the diffusion and electromigration terms, the membranes were loaded into a diffusion cell, where the membrane is placed between two reservoirs. One reservoir contained a salt solution of known concentration, and the other contained DI water. The concentration and electrostatic potential gradients drive the transport of ions across the membrane. Plotting the downstream concentration as a function of time yields a diffusion curve of which the slope is proportional to DH, the diffusion coefficient multiplied by the partition coefficient, which is representative of the flux of ions across the membrane. Using these diffusion cell experiments, we will investigate the ion transport mechanisms of different salts across different types of membranes (*i.e.* anionic, cationic, and CMM) by comparing the DH values across these salts and membranes.

Progress to Date

The current design of the CMMs used poly(diallyldimethylammonium chloride) (PDADMAC) as the polycation and poly(styrene sulfonate) (PSS) as the polyanion. We examined the performance of two symmetric salts (*i.e.* KCl and $MgSO_4$) and two asymmetric salts (*i.e.* K_2SO_4 and $MgCl_2$) at different concentrations and through membranes monofunctionalized with PDADMAC (positively-charged) and PSS (negatively-charged) each and a CMM.

For the monofunctionalized membranes, the asymmetric salts dominated the flux, with the divalent counterion (*e.g.* Mg^{2+} for PSS) had the highest flux, and the divalent coion (*e.g.* SO_4^{2-}) had the lowest flux. This seems to indicate that the electrostatic interactions are dominating. The strong electrostatic attraction between the charges on the membrane and the divalent counterion drives the ions to the boundary layer and across the membrane. Conversely, the strong electrostatic repulion between the membrane and its coion restrict passage of the ion. The need to maintain electroneutrality controls the co-transport of salt's corresponding monovalent ion.

However, in the case of the CMM, it is the symmetric salts that have the highest and lowest transport. In particular, the symmetric monovalent salt, KCl, has the highest DH value. This is attributed to the ability of the membrane to electrostatically attract the ions at even rates, transporting them rapidly across the membrane and maintaining electroneutrality. By comparing this to a membrane with no surface charge, which removes and electrostatic contribution, we found that the KCl DH is much higher through a CMM than an uncharged membrane. This indicates that there is some additional interaction beyond diffusion at play to increase the KCl transport, namely electrostatic attraction.

Conclusions

We have identified that electrostatic attraction plays a significant factor in driving salt ions across charged membranes. For the CMM, the symmetric monovalent salt has the highest permeability. This is because both ions from the salt are transported evenly. There is an uneven electrostatic attraction/repulsion for the asymmetric salts through a CMM. This differs from the monofunctionalized membrane where the asymmetric salts have the highest and lowest transport due to strong electrostatic attraction and repulsion for the divalent counterion and coion, respectively.

Next Steps

We will continue to explore the effects of different salts on the transport through a charge mosaic membrane, particularly by investigating the effect of different monovalent anions and cations. Furthermore, we will look at the effect of concentration on the transport of salts.

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