

NDnano Undergraduate Research Fellowship (NURF) 2018 Project Summary

1. Student name & home university: Nishtha Gupta, Indian Institute of Technology Delhi

2. ND faculty name & department: Dr William Phillip, Chemical and Biomolecular Engineering

3. Summer project title: Elucidating fundamental processing property relationships for chemically patterned membranes

4. Briefly describe new skills you acquired during your summer research:

I learned to handle different kinds of equipment in the laboratory like micropipettes, weight balance, stirred cells, reengineered inkjet printers and perform solute transport experiments at different pressure conditions. I was trained on the Fourier-transform infrared spectroscopy (FTIR) instrument and I learned to analyze the spectra of the membrane samples to determine their chemical structure. I also compared the intensity of the peaks of the reference and reacted sample membranes to calculate the reaction conversion. I honed my public speaking skills by giving presentations in the group meetings as well as the final poster presentation. I explored many features of Microsoft Excel and Power Point while making presentations, poster presentations and graphs.

5. Briefly share a practical application/end use of your research:

Charge mosaic membranes are emerging as a new class of membranes that aim to transport ionic species (e.g., KCl) more rapidly than that of neutral solutes with comparable size (e.g., water molecules). As a result, development of such a membrane with enhanced solute-membrane interactions can benefit its application in field of cell patterned sensors, textured surfaces for antifouling applications and pharmaceutical applications.

6. 50- to 75-word abstract of your project:

The Phillip lab has developed chemically-patterned membranes like charge mosaic membranes which have patterns of positively and negatively charged domains that traverses the membrane thickness. The membrane with these oppositely charge-functionalized domains are able to separate charged species from neutral molecules of comparable sizes. Pressure driven transport experiments performed using these membranes showed that the concentration of ions was enhanced in the permeate as compared to the retentate. In order to improve the selectivity and increase the density of specific ion interactions on the pore walls of a nanoporous copolymer membrane, the pore wall chemistry was modified. The successful functionalization of pore chemistry using polyethyleneimine and 4-imidazolecarboxylic acid was characterized using FTIR and single solute rejection experiments.

7. References for papers, posters, or presentations of your research:

- Qu, Siyi, et al. "Copolymer Nanofilters with Charge-Patterned Domains for Enhanced Electrolyte Transport." *Chemistry of Materials* 29.2 (2017), pp 762-772.

- Qu, Siyi, et al. "Preparation of Chemically-Tailored Copolymer Membranes with Tunable Ion Transport Properties." *ACS Applied Materials and Interfaces* (2015), 7 (35), pp 19746-19754
- Park, Ho Bum, et al. "Maximizing the right stuff: the Trade-off between membrane permeability and selectivity." *Science* 356 (2017), Issue 6343
- Scheiner, et al. "Proton Transfer Properties of Imidazole." *J. Phys. Chem.* (1996), 100, pp 9235-9241

One-page project summary that describes problem, project goal and your activities / results:

Charge mosaic membranes are a class of membranes with patterns of alternating positively-charged and negatively-charged domains that traverse the membrane thickness. The arrangement of these domains allows dissolved cations and anions to permeate through the counter charged domains faster than neutral molecules of a comparable size which results in separation of charged species from neutral molecules. The patterns on the membranes can be designed and printed as alternating stripes, squares (cubically-patterned), or triangles (hexagonally-patterned). The feature size of a charge mosaics corresponds to the height of a stripe in a stripe patterned membrane; the edge length of a unit square in a cubically patterned membrane; or the height of a unit triangle in a hexagonally patterned membrane. The pressure driven transport experiments performed using these membranes showed that the concentration of ions was enhanced in the permeate as compared to the filtrate. Additionally, it has been identified that the enhanced transport of electrolyte is effective only near interfacial regions between oppositely charged domains where the characteristic size of these regions is governed by the electrical double layer (EDL). The Debye length, which characterizes the thickness of EDL, is on the scale of nanometer for a dilute electrolyte. Although it is desired to pattern geometries with feature size comparable to the Debye length to achieve a higher selectivity, the development of charge mosaics with high permselectivity is lagging as the minimum feature size of a unit charge-functionalized domain is around one hundred microns which is determined by the inkjet printing technology. Hence, this project takes a scope of modifying pore wall chemistry of a nanoporous membrane in order to improve the permselectivity of a charge mosaic membrane.

In order to improve the selectivity and increase the density of specific ion interactions with the pore walls, membranes fabricated from a poly(acrylonitrile-co-oligo(ethylene glycol) methyl ether methacrylate-co-glycidyl methacrylate) (P(AN-co-OEGMA-co-GMA)) copolymer were used since the PGMA units are amenable to reaction with specific molecules that allow the pore walls to be decorated for targeted ion interactions. The modification of pore chemistry is completed in two steps of reaction (Figure 1). First, the pore walls having epoxide group were reacted with polyethylenimine (PEI) based on a nucleophilic oxirane ring-opening reaction mechanism. The second step of the reaction was the carbodiimide coupling reaction of 4-imidazole carboxylic acid to the primary amine that has been attached to pore walls in step 1.

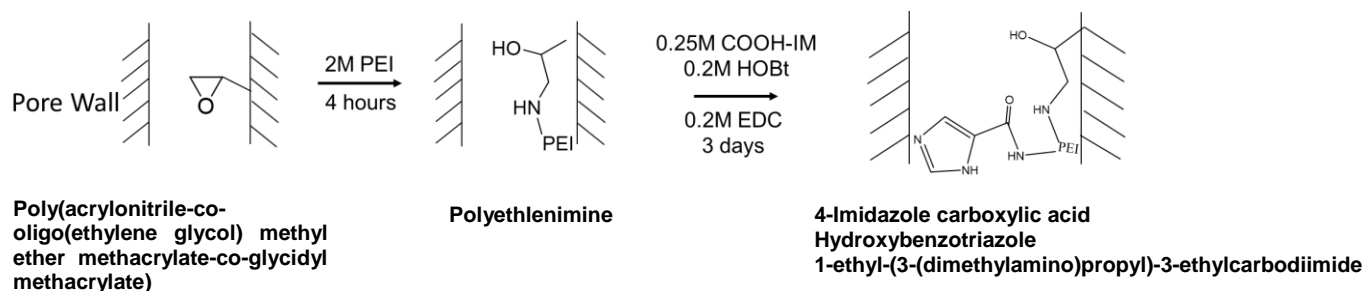


Figure 1: Reaction scheme showing the two steps. Step 1: PEI functionalization and Step 2: Carbodiimide reaction

For the first step of reaction, the membranes were reacted in an aqueous solution of PEI (molecular weight 600 g/mol and 2000 g/mol); the influence of PEI concentration and reaction time were studied using Fourier Transform Infrared Spectroscopy (FTIR). On analysing a series of FTIR spectra between unreacted and reacted membranes, it was concluded that complete

conversion occurred with 2M PEI (MW=600 g/mol and MW=2000 g/mol) in 4 hours (Figure 2). The pressure driven transport experiments were performed using 1 mM $MgCl_2$. The rejection values confirmed that the PEI functionalized membranes show higher surface charge densities than the parent PGMA membranes. The rejection values of PEI (MW=2000 g/mol) are slightly higher than PEI (MW=600 g/mol) which suggests that almost equal density of ion interactions are present. (Figure 3)

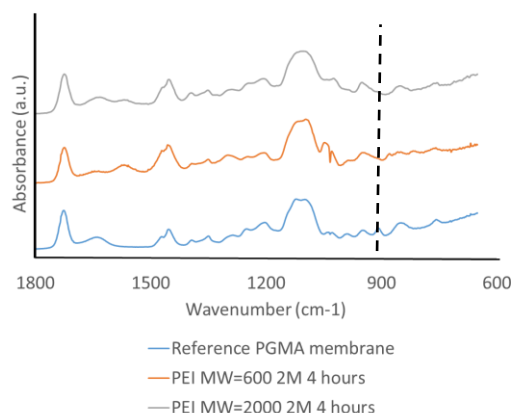


Figure 2: FTIR Spectra showing that complete conversion occurred in the reaction of P(AN-r-OEGMA-r-GMA) copolymer with 2M PEI (MW=600) and (MW = 2000) in 4 hours as the peak at 908 cm⁻¹ indicating epoxide group disappears.

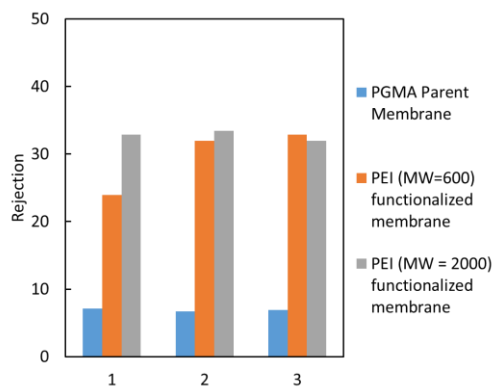


Figure 3: Average rejection of magnesium chloride ($MgCl_2$) is around 7% for the PGMA membrane, 30% for the PEI (MW=600) functionalized membrane and 32.7% for the PEI (MW=2000) functionalized membrane

The carbodiimide coupling reaction between carboxylic acid and primary amine (from PEI) resulted in the formation of amide bond which was characterized using FTIR spectra. (Figure 4)

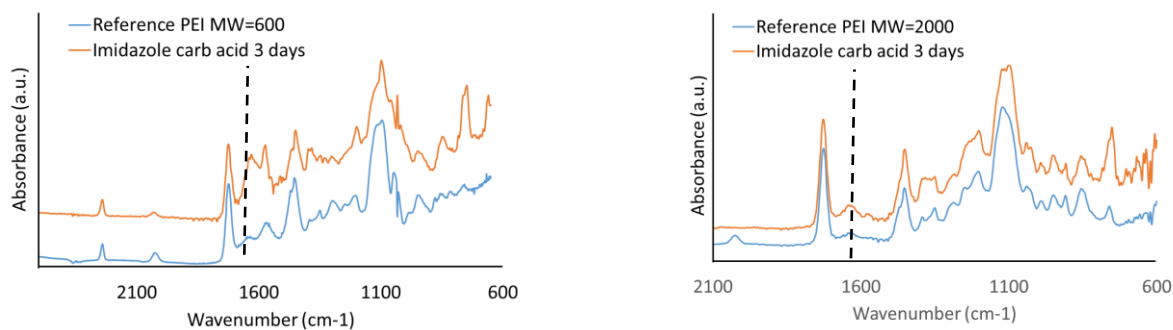


Figure 4: In both the FTIR spectra for PEI MW=600 and MW=2000, the intensity of the peak at 1630 cm⁻¹ indicating the amide bond has increased showing that some amount of reaction has progressed.

The imidazole functionalized membranes were characterized using single solute rejection experiments. (Figure 5) The rejection values of 1 mM $MgCl_2$ for the imidazole functionalised membranes of PEI (MW=2000 g/mol) were higher than the PEI (MW=600 g/mol) indicating that higher electrostatic interactions are obtained in the former case.

The rejection values of 1 mM $MgCl_2$ were also compared for the parent PGMA membrane, PEI (MW=2000 g/mol) functionalised membrane and the imidazole functionalised membrane. These are in ascending order as can be seen from Figure 6, indicating that each step of functionalization increases the density of electrostatic interactions.

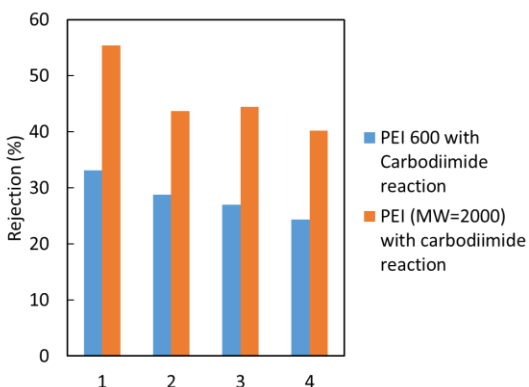


Figure 5: Average rejection of magnesium chloride ($MgCl_2$) is around 28% for PEI MW=600 with carbodiimide reaction and 45% for PEI MW=2000 with carbodiimide reaction.

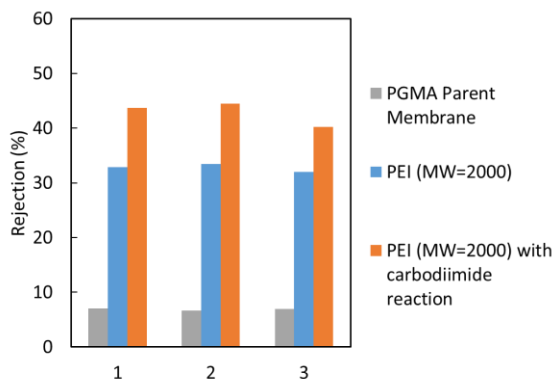


Figure 6: Average rejection of magnesium chloride ($MgCl_2$) increases from 7% for PGMA parent membrane to 30% for PEI (MW=2000) and 43% for PEI (MW=2000) with carbodiimide reaction

The results show that the surface chemistry of the membranes can be modified to create membranes that allow higher throughput of charged species. The successful functionalization of pore chemistry using PEI and Imidazole carboxylic acid was characterized using FTIR and single solute rejection tests. The experimental results are consistent with the initial hypothesis. Knowledge generated in this study will be utilized to generate charge mosaic membranes with higher selectivity.