

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Evan Wood
FACULTY ADVISOR:	Dr. William Phillip
PROJECT PERIOD:	Summer 2023
PROJECT TITLE:	Selective Ion Transport Through Copolymer Membranes Functionalized with Imidazole Ligands
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Functionalize copolymer membrane with Imidazole	CuAAC reaction procedure was used with around 100% conversion. Additional procedures were developed to clean off excess reaction solution using acid.	100
Analyze the strength of interaction between imidazole and different metals	Ultraviolet-visible light spectroscopy of imidazole-metal complexes characterized the binding ratio of imidazole to metal and can be used to obtain an equilibrium coefficient for the complex.	75
Characterize the ligand selectivity for different metals	XRF was used to determine the ratio of different metals bound to the membrane ligands. Imidazole selectively complexes with copper over cobalt and the selectivity for other relevant metals such as Manganese and Nickel can be characterized.	90
Quantify transport phenomena of single-salt and dual-salt systems	Diffusion cell experiments revealed that the functionalized membranes led to 2x faster diffusion of copper through the membrane compared the unfunctionalized membranes. Additional experiments must be done to demonstrate separation between two salts and to gain estimates for the diffusion coefficient and partitioning coefficient of the membrane.	50

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Summer Undergraduate Research Symposium Poster, <i>Selective Ion Transport Through Copolymer Membranes Functionalized with Imidazole Ligands</i> , 7/26/23, Jordan Hall of Science, Notre Dame
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	1 st Place at Shaheen 3MT Competition, Better Lithium-Ion Battery Recycling, 7/26/23
INTERNAL COLLABORATIONS FOSTERED	

EXTERNAL COLLABORATIONS FOSTERED	
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

I greatly enjoyed being able to work with the graduate students in the lab. They were a model for work ethic, patience, and professionalism. I was very pleased that I could get a glimpse into the graduate students' lives and routines—which ultimately helped me discern my next steps after graduation. There was lots of work to do in the lab, but I found it intellectually engaging and I am very grateful for the valuable skills and insights I gained from this work.

FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

Nearly 500,000 tons of lithium-ion battery waste is produced per year. Held within these batteries is a substantial amount of cobalt, nickel, manganese, and lithium. Furthermore, these batteries pose a large environmental hazard to the environment if they are not properly disposed of. Lithium-battery recycling is clearly needed, but must be further developed.

A critical step in the traditional recycling of lithium batteries involves a complicated liquid-extraction process to separate the similar metals from each other. This process generates a large volume of environmentally-hazardous waste, and is resource-intensive, which both serve to make lithium battery recycling prohibitively expensive and complicated. Membranes could be used to separate these metals from each other and reduce waste, energy-consumption, and cost.

The goal of my research project is to modify P(TFEMA)OEGMA-GMA (GMA) copolymer membranes by attaching an imidazole ligand. The separation of such similarly-sized, and similarly-charged metals as cobalt, nickel, and manganese, presents a challenging separation that has not been achieved with current nanofiltration membranes.

Imidazole was selected as a suitable membrane ligand to carry out this separation due to its ability to complex with different metals. Ultraviolet-visible light spectroscopy was performed on solutions with the free imidazole ligand and various metals.

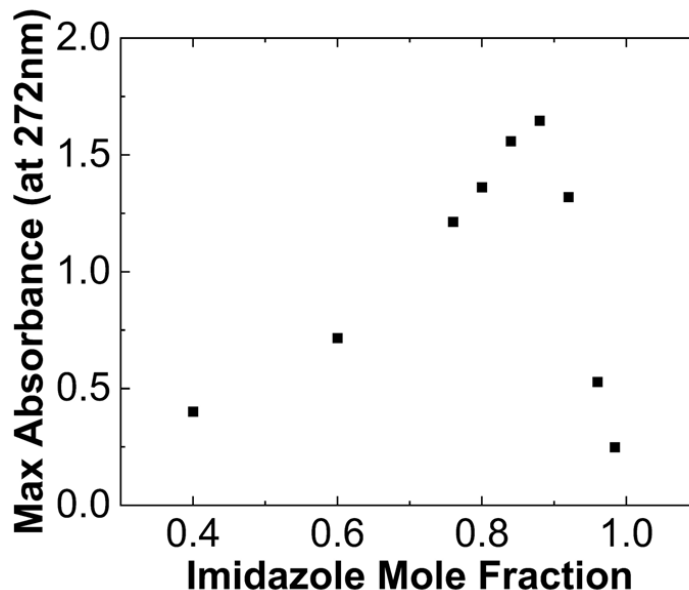
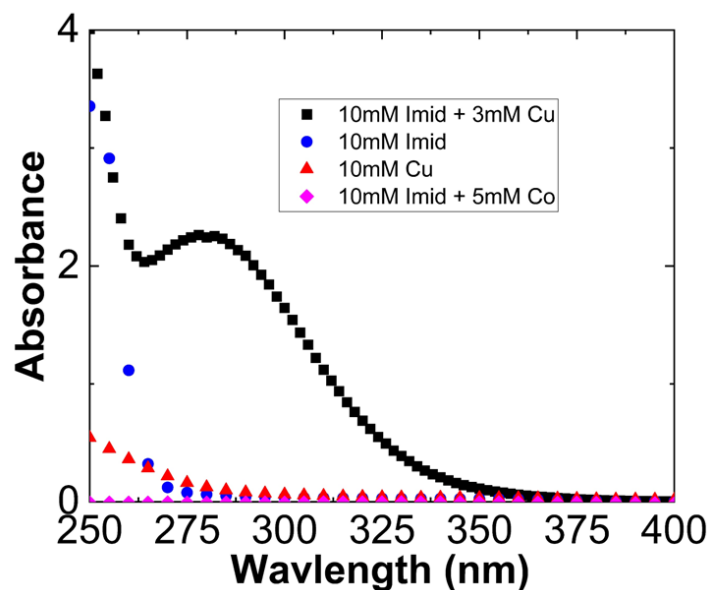


Figure 1. Pure propargyl 1H-imidazole-1-carboxylate is transparent in these wavelengths—as is pure copper (II) chloride. A shoulder forms around 275 nm and is due to imidazole-copper complexes. No equivalent shoulder peak appeared in the investigated wavelengths for imidazole-cobalt complexes, which indicates its higher energy state. **(B)** A Jobs plot was used to determine the stoichiometric ratio of the imidazole to copper complex as being around 4:1.

Notably, the imidazole-copper complex results in a Ligand to Metal Charge Transfer with maximum wavelength absorbance around 275 nm. The ligand to metal charge transfer for imidazole-cobalt complexes does not form in this range of wavelengths which indicates that the complex must be of a higher energy state than imidazole-copper complexes. This difference between the two complexes indicates the selectivity of the imidazole ligand for copper over cobalt.

Furthermore, as seen in Figure 1, the maximum absorbance at 275 nm changes based on the ratio of imidazole to copper. A Jobs plot was then created to determine a stoichiometric ratio of 4:1 imidazoles to copper in complexes. Future work could use the changes in the peak at 275 nm to determine an equilibrium coefficient for the imidazole-copper complexes.

The imidazole ligand was attached through an epoxide ring-opening reaction of the GMA block on the membrane to convert it to an azide moiety. This azide moiety then participates in a Copper-Catalyzed Azide Alkyne Coupling reaction (CuAAC) with propargyl 1H-imidazole-1-carboxylate to attach the imidazole ligand to the membrane. From Fourier Transform Infrared Spectroscopy (FTIR) results, the azide moiety peak at 2100 nm was completely eliminated which indicates total conversion of the moiety to an imidazole.

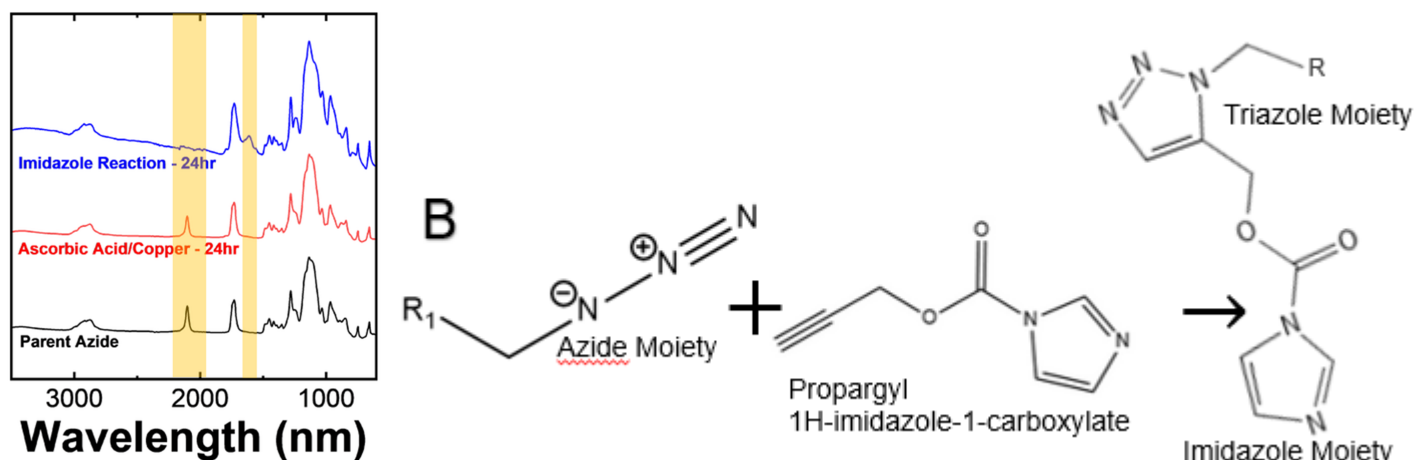


Figure 2. (A) CuAAC reaction procedure: 50 mM of propargyl 1H-imidazole-1-carboxylate was reacted with excess $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and ascorbic acid in water for at least 15 minutes. Fourier Transform Infrared Spectroscopy results confirmed the elimination of the Azide peak at 2100nm as well as the appearance of a shoulder at 1600nm to confirm attachment of the ligand. **(B)** Schematic of the CuAAC reaction which forms a triazole ring as well as attaches the imidazole ligand to the membrane. R represents the membrane wall.

The selectivity of the imidazole-metal complexes was further investigated using X-ray Fluorescence spectroscopy which can indicate the presence of bound copper or cobalt on the membrane. Membranes were submerged in solutions with aqueous copper or cobalt present and then were washed with water to remove unbound metal from the membrane.

Trial	Ion Introduced	Copper Present	Cobalt Present
1	Cu + Co	X	
2	Co		X
3	Cu (24hr Water Bath)	X	

Table 1. X-Ray Fluorescence Spectroscopy was performed on GMA membranes that had undergone the Imidazole CuAAC reaction. All membranes were then washed three times with 1M HCl solutions to clean excess reaction solution from the membrane. Membranes were then treated with either 10mM CuCl_2 , 10mM CoCl_2 , or 10mM equimolar mixture of the two metals for 24 hours before being washed with water for 60s, or for 24hr if otherwise noted.

When both copper and cobalt are introduced into the membrane, the imidazole ligand selectively complexes with copper as seen in Trial 1. Furthermore, imidazole-metal complexes seem to not be readily reversible in water as seen in Trial 3.

Diffusion cell experiments were used to test if our current system setup would result in a separation. An equimolar mixture of copper and cobalt was placed in the donating side, which was exposed to one side of the membrane. The other side of the membrane—the receiving side—started off as distilled water. As time progressed, aliquots were taken from the receiving side to measure the concentration of copper and cobalt that diffused through the membrane.

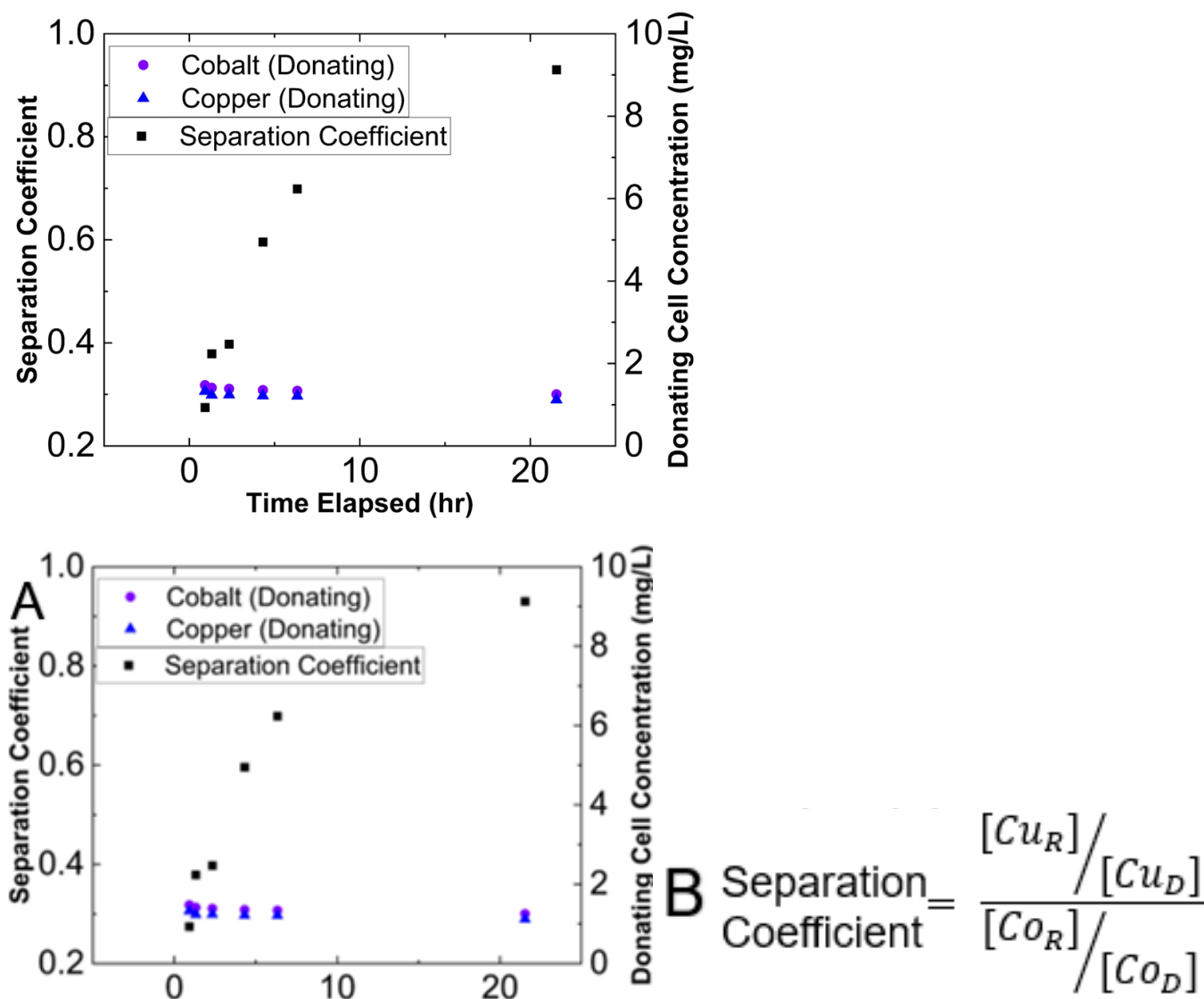


Figure 4. (A) Diffusion cell experiments were conducted using the Imidazole membranes. An equimolar mixture of 1mM solution of copper and cobalt were put in the donating cell while water was put in the receiving cell. Aliquots were drawn from the cell for 20 hours. The concentration of cobalt and copper in these samples were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). **(B)** The separation coefficient was calculated by dividing the normalized concentration of copper in the receiving cell by that of cobalt.

Initial diffusion cell experiments of dual-salt (cobalt and copper) systems yielded a separation coefficient on smaller time-scales which ultimately trend towards no separation. This indicates that the membrane ligands are initially acting as a absorbents that hinder the diffusion of copper initially. However, as time progresses, this hindrance could be negated as more free ligands become bound to copper, and other metal ions are able to freely diffuse through the pore unaffected by any interaction with the membrane ligands. Future work must be done to achieve smaller membrane pore sizes such that every ion that diffuses through the membrane must interact with the membrane ligand.

In order to characterize our current membrane pore sizes and to have a baseline from which to quantify future changes in pore size, Neutral Solute Rejection experiments were performed. These experiments involve passing different molecular weights of Poly(ethylene glycol) molecules through the membrane. Once around 90% of the molecules are rejected, then a conversion factor is used from prior literature to estimate the membrane pore size. Membranes with azide moieties and membranes with imidazole moieties were characterized to have pore sizes around 5 nm.

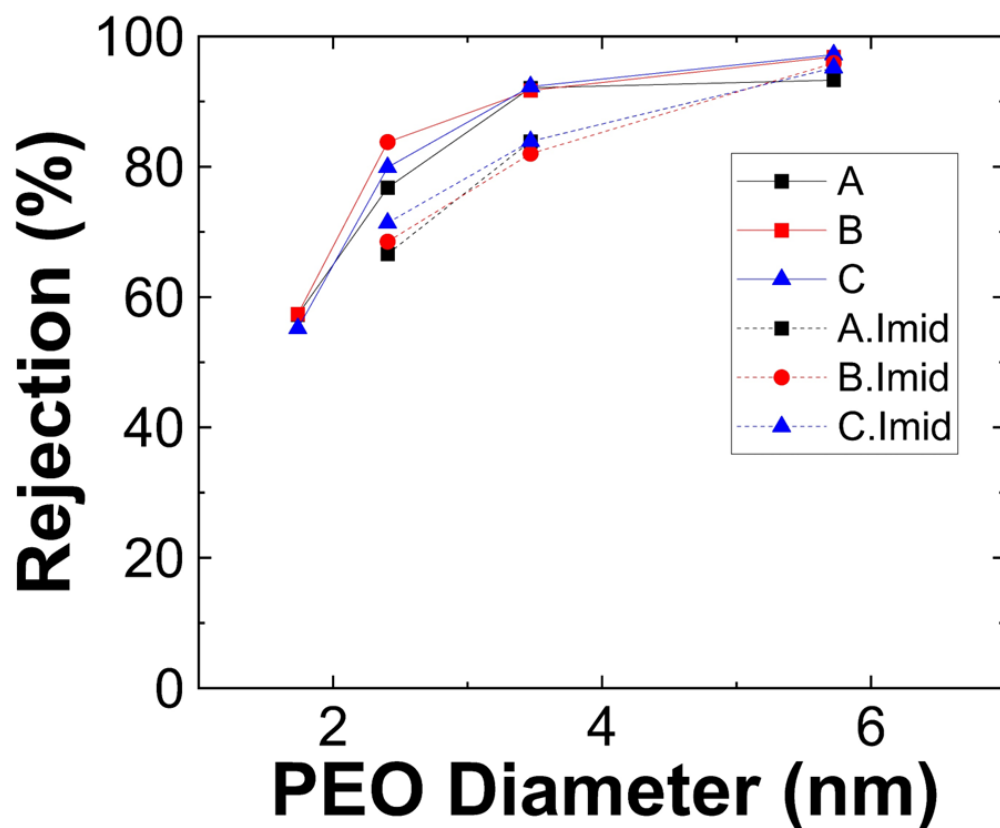


Figure 5. Neutral solute rejections were conducted using filtration cells with 10mL initial feed solution of differing molecular weight polyethylene glycol solutions. Membranes were subjected to 60psi for around 20mins and the retentate and permeate samples were analyzed using the Total Organic Carbon Analyzer. Percent rejection was calculated by $(C_r - C_p)/C_r$ where C_r is the concentration of carbon in the retentate and C_p is the concentration of carbon in the permeate.

My future work will be focused on synthesizing membranes with smaller pore sizes and altering the strength of the interaction between the membrane ligand and metals. Pore sizes can be altered by altering the weight ratio of the molecular blocks used when synthesizing GMA copolymer. Once a smaller pore size is achieved, then a greater and prolonged separation is hypothesized. Additionally, I wish to investigate a different form of imidazole that can complex with metals but also has a pH sensitive nitrogen in the moiety. Thus, we could potentially tune the strength of the interaction between the ligand and metal just by altering the pH.