# EILERS GRADUATE STUDENT FELLOWSHIP
## FINAL REPORT

**EILERS FELLOW:** John Hoffman  
**FACULTY ADVISOR:** William Phillip (Chemical and Biomolecular Engineering)  
**REPORT PERIOD:** 2021  
**PROJECT TITLE:** Spatially-Controlled Functionalization of Nanofiltration Membranes  
**CONNECTION TO ND ENERGY’S RESEARCH AREAS:** (x) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear  
( ) Smart Storage and Distribution ( ) Transformation Solar  
( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind  

## MAJOR GOALS AND ACCOMPLISHMENTS:
List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

<table>
<thead>
<tr>
<th>MAJOR RESEARCH GOALS</th>
<th>ACTUAL PERFORMANCE AND ACCOMPLISHMENTS</th>
<th>% OF GOAL COMPLETED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabricate charge patterned mosaic membranes using patterned, UV initiated thiol-ene reactions</td>
<td>A process for fabricating surface patterned membranes was established using the controlled exposure of UV light via laser-etched photomasks. This created domains on ~200 µm. Future work aims to reduce this to ~30 µm.</td>
<td>75</td>
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<td>Characterize membrane surface to assess confinement of patterned domains</td>
<td>The ability to isolate multiple domains was established through a sequence of reactions with controlled exposure of UV light. Experimental techniques such as FTIR, heavy metal uptake, and fluorescent microscopy highlighted the ability to form distinct patterned domains.</td>
<td>100</td>
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<td>Assess ion transport performance of membranes</td>
<td>Unfortunately, ion transport was unable to be assessed due to a larger than expected membrane pore size. Thus, multiple heavy metal binding functionalities were introduced onto the membrane to create a multi-functional surface patterned membrane. Future work will build upon initial findings.</td>
<td>50</td>
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</tbody>
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## RESEARCH OUTPUT:
Please provide detailed information below regarding any output resulting from your research project.

**CATEGORY** | **INFORMATION**
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**EXTERNAL PROPOSALS** | NSF, Elucidating Molecular Design Principles for Copolymer Membranes with Solute-Tailored Selectivity for the Separations of Rare Earth Elements, William A Phillip and Alex Dowling, 08/2021, $450,000  
ARO, Unifying Principles for the Design of Multifunctional Polymer-based Membrane Sorbents, William A Phillip and Ruilan Guo, in preparation, $570,000  
NAWI, Multiscale Optimization of 3D-Printed Sorbents w/ Hierarchical Structures, William A Phillip, Ruilan Guo, Kyle Doudrick and Alex Dowling, 08/2021, $1,490,000 |

**EXTERNAL AWARDS** | Oak Ridge National Lab, CNMS User Research Proposal, Detailed Chemical Mapping of Charge-Patterned Mosaic Membranes, William A Phillip, 02/2021, use of instrumentation within CNMS facility. |

**JOURNAL ARTICLES** | |

**BOOKS AND CHAPTERS** | |

**PUBLIC PRESENTATIONS, SEMINARS, LECTURES** | |

**AWARDS, PRIZES, RECOGNITIONS** |
INTERNAL COLLABORATIONS FOSTERED
Collaborated with Tao Wang, a graduate student in Prof. Ruilan Guo’s (Chemical and Biomolecular Engineering) group who synthesized the polymer used in this study.

EXTERNAL COLLABORATIONS FOSTERED
Collaborated with Anton Ievlev from Oak Ridge National Lab. This work required analysis using a time-of-flight secondary-ion mass spectrometer (ToF-SIMS) to detect the presence of each patterned functional domain.

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)

MAJOR GOALS AND ACCOMPLISHMENTS

Goal 1 was to develop a platform for the surface patterning of functional domains of a polymer membrane. This was done through a collaboration with the Guo group in the chemical and biomolecular engineering department. Tao Wang was able to synthesize a phenolphthalein-based cardo poly(arylene ether sulfone) with pendant carboxylic acid groups (PPAES-COOH) copolymer. This is shown in Figure 1. Initial attempts were made using an alkene functionalized polymer but the -ene group was unable to be exposed upon the pore surface through multiple variations of the membrane casting procedure. To overcome this, the -COOH functional polymer was used and was able to be cast into a membrane which possessed a high surface area of exposed -COOH brushes. These brushes lend themselves for additional, post-fabrication functionalization reactions.

![Figure 1: Phenolphthalein-Based Cardo Poly(Arylene Ether Sulfone) with Pendant Carboxylic Acid Groups (PPAES-COOH) Copolymer and Cross-Sectional Image Showing High Surface Area.](image)

In order to control the distribution of functional groups along the membrane surface, a protocol for a series of post-fabrication functionalization reactions was developed. This process converted the -COOH groups into alkyne groups through a carbodiimide coupling reaction with propargylamine. This now exposed -yne group was capable of being modified through the thiol-yne reaction, which was performed with mercaptopropionic acid. This reintroduced a carboxylic acid group onto the pore wall, but in this case, it was only done in locations where UV was exposed. Large scale patterns were used to visually demonstrate the patterning, in which a surface color change also occurred during this process. In Figure 2, the color of the membrane changes from brown to white when it is exposed to UV light. This membrane was then soaked in a copper chloride solution, in which the affinity between Cu$^{2+}$ and the -COOH groups resulted in the binding and uptake of this heavy metal. This resulted in a visible color change, as shown in the far-right image of Figure 2.
Figure 2: Large-scale photomask patterning of UV initiated thiol-yne membranes. When exposed to a copper chloride solution, the -COOH domains adsorb copper, changing the membrane color to blue.

Using the knowledge that large-scale patterns could be made, smaller patterns were attempted using a laser-etched photomask. This formed stripes along the membrane surface with feature sizes of ~200 micrometer. This pattern was demonstrated experimentally by soaking the membrane in a copper chloride solution and performing scanning-electron microscopy with energy-dispersive x-ray spectrometry (SEM-EDX). This detected the presence of copper, which was shown to only occur where the -COOH stripes were patterned. This is shown in Figure 3.

The ability to incorporate multiple functionalities onto the membrane surface was done through a series of thiol-yne reactions. A protocol was developed in which the first reaction was performed with mercaptopropionic acid using the photomask. The membrane was then rinsed and exposed to a solution of another thiol, 2-(Boc-amino)ethanethiol, without the photomask. This is possible because all the reactive sites exposed to UV light in the first reaction have been fully reacted. Exposure to additional UV light did not result in the coupling of the second reactive group in the unwanted surface areas. This multistep reaction process formed distinct domains of separate functionality. This was confirmed by coupling a fluorescent isothiocyanate with the amine functionalized domains. When viewed under a fluorescent microscope, only the areas reacted with the amine group were shown to fluoresce.

Finally, the goal of this project was to create charge-patterned membranes for the applications of controlled ion transport. These membranes were unable to be tested using ionic solutions because the pore size was too big for the charge pattern to impact transport. To demonstrate the impact these patterns have though, multiple heavy-metal binding functionalities were investigated. The -COOH group was shown to have a high capacity for copper binding and initial work using a thiol group from binding gold was unable to be distinguished between the two domains due to interactions with the background polymer. Future work will use a terpyridine group to bind iron and the -COOH group to bind copper. This type of multi-functional patterning has the potential impact of improving sensors used for the removal of toxic heavy metals from drinking water.