

Introduction

The goal of this project is to develop a **scalable, energy-efficient separation process for recovery of copper** from mining process waters. To achieve this goal, we will develop cation exchange membranes that are strongly permselective towards copper over other dissolved ions. This will be achieved by incorporating the strongly copper-chelating functional group iminodiacetic acid into an ion exchange membrane and testing these materials through diffusion dialysis and pressure-driven separations.

PEG/IDA Membranes

1. Overview:

Membranes were fabricated through UV-induced free radical polymerization of a mixture of reactive molecules, including polyethylene glycol diacrylate (PEGMA) with $Mn=575$ and $Mn=700$, polyethylene glycol methacrylate (PEGMEA), and glycerol methacrylate-iminodiacetic acid (GMA-IDA). This enables the preparation of a series of water-swollen membranes varying in water content and iminodiacetic acid functional group concentration. We characterized ion sorption, ion diffusivity, and ion permeability with respect to three divalent cations with similar size, specifically, Cu^{2+} , Ni^{2+} , and Mg^{2+} .

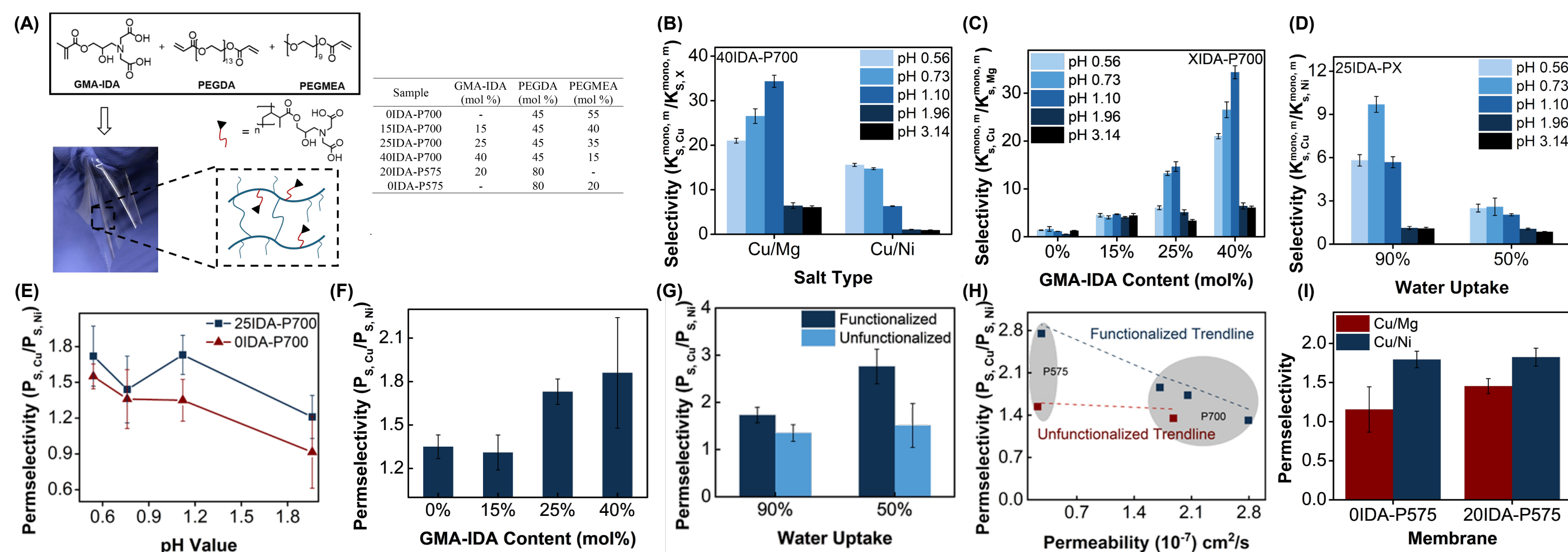
2. Results:

Robust, clear, homogeneous membranes with water uptake of 50% and 90% and varying IDA content were

synthesized following the procedure and recipe shown below. (A)

Universal strong pH dependence for both single and mixed salt sorption selectivity was observed, yielding up to 35 for Cu^{2+}/Mg^{2+} and 15 for Cu^{2+}/Ni^{2+} for membranes with 90% water uptake. (B) Sorption was also found to increase substantially as IDA concentration increased and as water uptake increased. (C, D)

In addition, pH was found to have slight effect on single salt Cu^{2+}/Ni^{2+} permselectivity. (E) On the other hand, permselectivity was shown to increase from 1.3 to 1.8 as GMA-IDA content increased from 0 to 40 mol%. (F) Moreover, permselectivity also increased from 1.4 to 2.7 for 50% water uptake membranes with 0 and 20 mol% IDA content, and 1.7 to 2.7 for membranes with same IDA concentration but decreased water uptake. (G, H) Mixed salt solution yields lower permselectivity. (I)



Schematic for fabricating PEG membranes, single salt sorption selectivity and perm-selectivity for Cu^{2+} over Mg^{2+} or Ni^{2+}

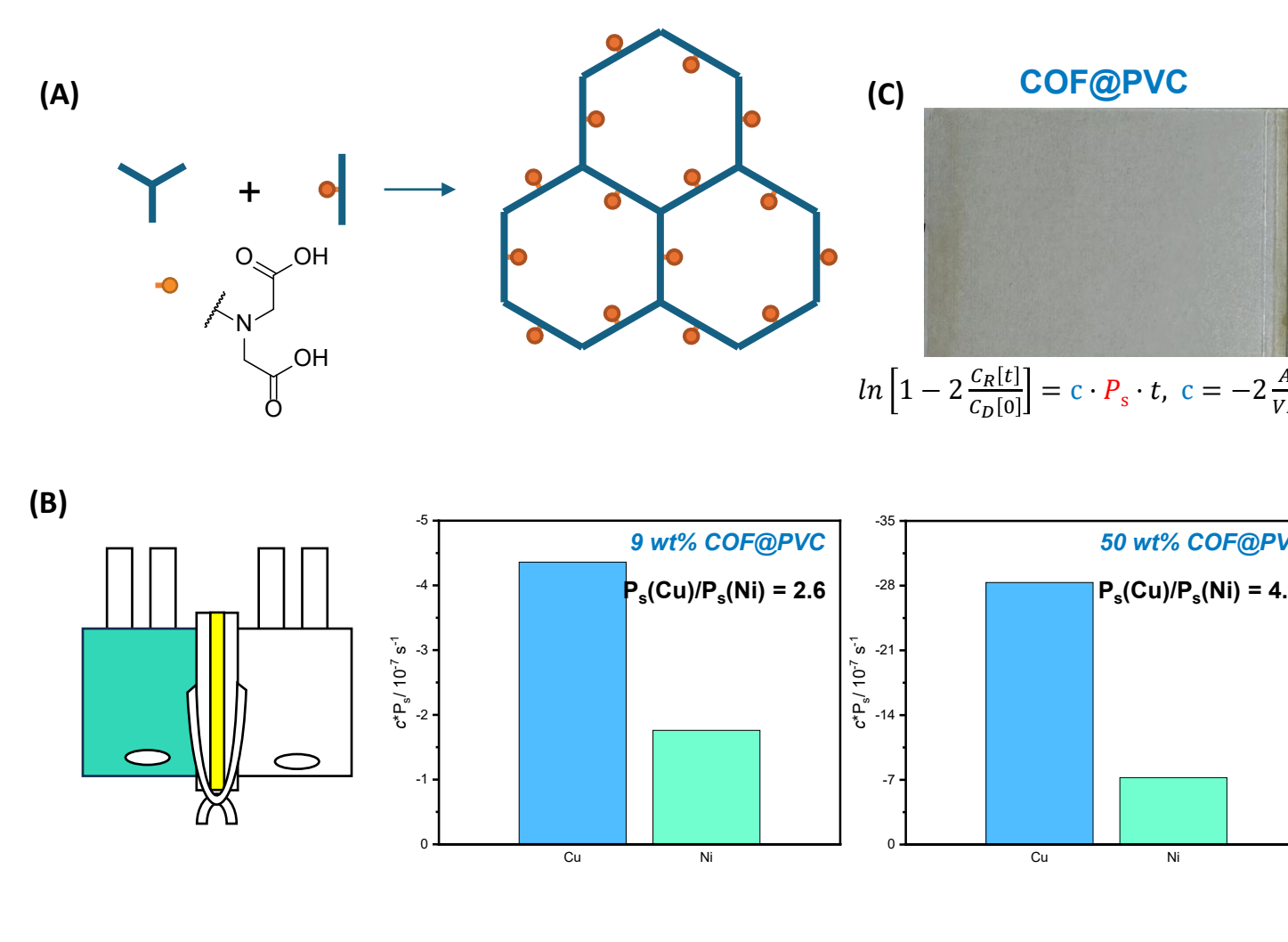
COF-based Membrane

1. Overview:

As a potential route to highly selective membranes, we investigated membranes based on covalent organic framework (COFs). These materials have well-defined nanoscale pores that can be molecularly tuned to incorporate desired functionalities and pore sizes. They can be incorporated in membranes by blending with a polymeric binder such as poly(vinyl chloride) (PVC).

2. Results:

Composite COF@PVC membranes with COF content ranging from 9 – 50 wt % were produced by solution blending and casting. We observed Cu^{2+}/Ni^{2+} single salt permselectivity as high as 4:1, but the selectivity was only 1.1:1 under multi-salt conditions. Optimizing membrane chemistry may further improve selectivity.



Schematic for fabricating COF@PVC membranes and single salt diffusion testing

NAWI CONNECTIONS

Period of Performance: October 2022 - Present

Challenge Area/Topic Area: This project will advance the development of ion-selective charged membranes for use in electric-field driven separations.
NAWI Leverage

We have leveraged the expertise of a diverse group of academic, national lab, and industrial collaborators to develop new materials, perform testing, and produce application-relevant advances.

KEY FINDINGS AND CONCLUSIONS

1. Ion exchange membranes can be surface-modified using thin polymeric coatings to produce strong selectivities towards Cu^{2+}
2. New IDA functionalized COF was designed and synthesis to use as a fillers of intrinsic nanopores added to polymer membrane to realized selectivities towards Cu^{2+} .

REFERENCES

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