

Developing Selective Carbon-Based Membranes for Ionic and Gas Separations

by

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ABSTRACT

Membrane-based separations hold significant promise for transforming industrial separations by reducing both energy and material intensity of legacy separations. Carbon-based membranes with rigid, well-defined pores, such as atom-thin graphene membranes and carbon molecular sieves (CMS), are particularly attractive because they have the potential for high permeance and selectivity and can operate at extreme conditions, including high temperatures and extremely acidic environments. However, realizing their full potential depends on the ability to precisely tune pore structure and thereby control transport and drive selectivity in these membranes. This thesis develops strategies to modulate ionic and gas transport through carbon-based membranes by engineering their porous architecture.

The first two chapters focus on nanoporous atom-thin graphene membranes that offer minimal transport resistance due to their sub-nanometer thickness. Pore size distributions in these membranes are altered using atomic layer deposition (ALD) and polyelectrolyte assembly (PEA), resulting in improved ion-ion separation. The underlying principles of pore modification and its impact on ionic transport are examined for both approaches. ALD enables precise reduction in pore sizes, leading to size-sieving dominated transport. Deposition of a small amount of hafnium oxide achieves K^+/Dy^{3+} selectivity of 50 while retaining 45% of the support permeance for monovalent ions, consistent with preferential blockage of the tail of the pore size distribution. Polyelectrolyte assembly on larger pores in these membranes additionally introduces ion binding interactions, enabling selective ion transport that mimics solvent extraction mechanisms and leads to selectivity between rare earth ions. The optimized membranes exhibit K^+/La^{3+} selectivity of 126 and Dy^{3+}/La^{3+} selectivity of 7.5. Together, these studies establish complementary pathways for tailoring selectivity in atom-thin membranes.

The next two chapters investigate carbon molecular sieve (CMS) membranes derived from polymers of intrinsic microporosity (PIM-1) and its derivatives. The effects of modification of the polymeric precursor, specifically through hydrogen bonding and urea crosslinking, on the evolution of CMS structure and performance are evaluated. Urea-based crosslinking is shown increase nitrogen incorporation in the carbon matrix at low carbonization temperatures (600 °C). At higher temperatures (750 °C), the resulting CMS shows a simultaneous increase in permeability and selectivity, for instance, a 91% increase in the permeability of O_2 and a 185%

increase in O₂/N₂ selectivity, attributed to a selective porogen effect during pyrolysis. To further elucidate structural evolution of PIM-1 derived CMS, *in situ* XRD is employed during carbonization, providing experimental verification of previously hypothesized mechanisms in literature governing CMS structure development.

The final chapter examines membrane materials for an emerging gas separation need. The deblending of hydrogen from natural gas pipelines is evaluated as a pathway to transport hydrogen while leveraging existing infrastructure. The performance of 224 membrane materials, including commercial and emerging materials, is assessed. We demonstrate recovery of fuel-grade A hydrogen (98% purity) at \$0.320 kg⁻¹ H₂. This system-level analysis links intrinsic material properties to practical deployment conditions.

Overall, this thesis develops techniques and uncovers mechanistic insights into the design of carbon-based membranes including atom-thin graphene membranes and carbon molecular sieve membranes for critical separations across ionic and gaseous systems.

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