Electrically Driven Ion Separations in Permeable Membranes

Final Report

submitted to the
Office of Basic Energy Sciences
Chemical Sciences, Geosciences, and Biosciences Division
Separations and Analysis Program
United States Department of Energy

Technical Program Manager: Dr. Philip Wilk

DOE Award Number DE-FG02-98ER14907

By

Merlin Bruening

Professor

Department of Chemistry
578 S. Shaw Lane
Michigan State University
East Lansing, MI 48824-1322

Departments of Chemical and
Biomolecular Engineering and Chemistry
University of Notre Dame
South Bend, IN 46556-5637

e-mail: bruening@chemistry.msu.edu and mbruenin@nd.edu

phone: 574-631-3024

administrative contact

Stacy Salisbury
Hannah Administration Building
426 Auditorium Road, Room 2
East Lansing, MI 48824
(517) 884-4252
salisbury@cga.msu.edu

April 21, 2017

Summary

Membranes are attractive for a wide range of separations due to their low energy costs and continuous operation. To achieve practical fluxes, most membranes consist of a thin, selective skin on a highly permeable substrate that provides mechanical strength. Thus, this project focused on creating new methods for forming highly selective ultrathin skins as well as modeling transport through these coatings to better understand their unprecedented selectivities. The research explored both gas and ion separations, and the latter included transport due to concentration, pressure and electrical potential gradients. This report describes a series of highlights of the research and then provides a complete list of publications supported by the grant. These publications have been cited more than 4000 times. Perhaps the most stunning finding is the recent discovery of monovalent/divalent cation and anion selectivities around 1000 when modifying cation- and anion-exchange membranes with polyelectrolyte multilayers (PEMs). This discovery builds on many years of exciting research. (Citation numbers refer to the journal articles in the bibliography.)

Highlights

Formation of Ultrathin Skins. This research first demonstrated that layer-by-layer adsorption of PEMs or growth of hyperbranched polymer films yields coatings that fully cover nanoporous membranes to form selective, ultrathin skins.[40,42] Films as thin as 20 nm span alumina pores with diameters of 20 nm without filling the underlying substrate (Figure 1), and ion-transport studies show that coatings are essentially free of defects after deposition of 4-5 polyanion/polycation bilayers.[42] These findings spawned numerous subsequent studies (by us and many others) of transport through PEMs or hyperbranched polymers. Later papers showed full coverage of polymeric supports.[24]

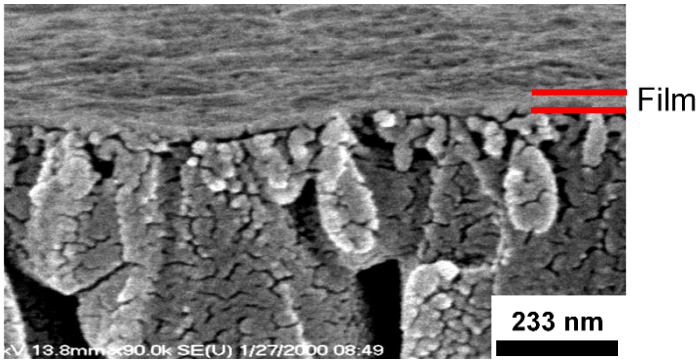

Figure 1. Scanning electron microscope image of a poly-electrolyte multilayer film on a porous alumina support.

Heat-induced Formation of Polyamides and Polyimides from Polyelectrolyte Multilayers. Polyamides and polyimides are some of the most attractive membrane materials due to their high selectivities and permeabilities. This research developed simple

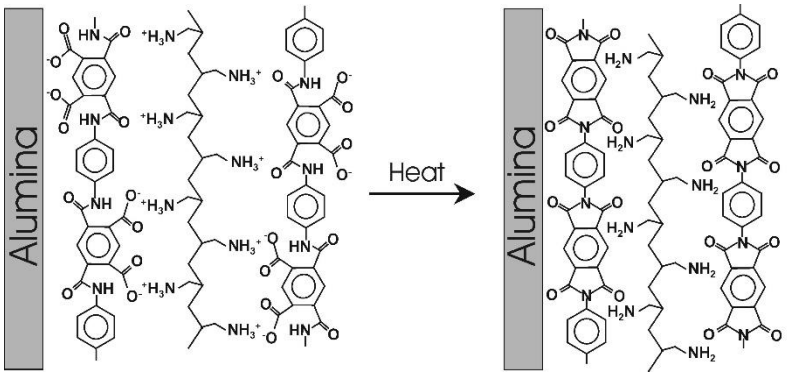

Figure 2. Imidization of a poly(*p*-phenylenepyromellitamic acid)/protonated poly(allylamine) film.

heating of PEMs to dehydrate them and form either polyimides or polyamides, depending on the composition of the PEM (see Figure 2 for an example).[26,31,37,41] Ultrathin aromatic polyimide films created in this way show the same high gas-transport selectivities as much thicker cast films,[31] and Cl^-/SO_4^{2-} diffusion dialysis selectivities as high as 1000.[37] Moreover, formation of polyamides leads to films that resist corrosion.[41] Thus, these findings yield methods for creating unusually thin films for membranes and anticorrosion coatings.

Templating PEMs to Enhance Selectivity. This project hypothesized that introducing charge into PEMs would greatly increase monovalent/divalent ion-transport selectivities. New methods to insert charge into PEMs include templating films with either metal-ion complexes or photolabile groups.[35-36] Subsequent removal of metal ions (Figure 3) or photolysis leads to excess anionic groups in the films and enhances Cl^-/SO_4^{2-} diffusion dialysis selectivities to values as high as 600 when including cross-linking to avoid film swelling in water. Without templating, films show selectivities <30. Models of transport suggest that both electrostatic and diffusive factors contribute to discrimination among ions.

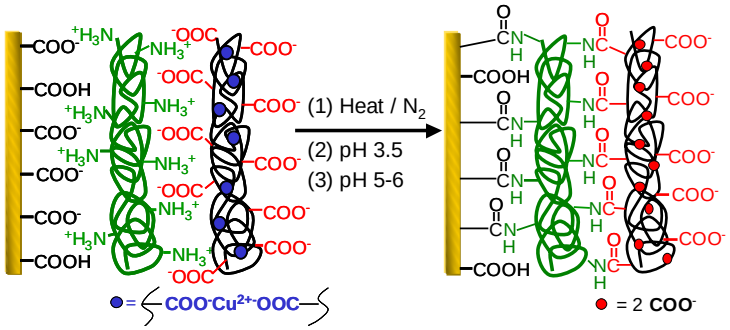

Figure 3. Schematic diagram showing Cu^{2+} imprinting of a cross-linked PAA/PAH film.

Nanofiltration through Ultrathin Polyelectrolyte Multilayers. Initial transport studies employed diffusion dialysis.[35-38,42] While such experiments provide insight into membrane selectivity, diffusion dialysis is not a high-flux separation method. Subsequent cross-flow nanofiltration (NF) studies (Figure 4 depicts the experimental apparatus) showed that water flux through PEMs can exceed that through commercial NF membranes, although flux varies with the number of polyelectrolyte layers and their composition.[17,21,30] Polyelectrolyte multilayer membranes show NF selectivities of 20-30 between monovalent and divalent anions or cations,[17,30] but this selectivity is sometimes less than in diffusion dialysis, presumably because of convective ion transport.[10] Highly selective NF occurs with films deposited on both porous alumina and polymeric ultrafiltration membranes.[24,30]

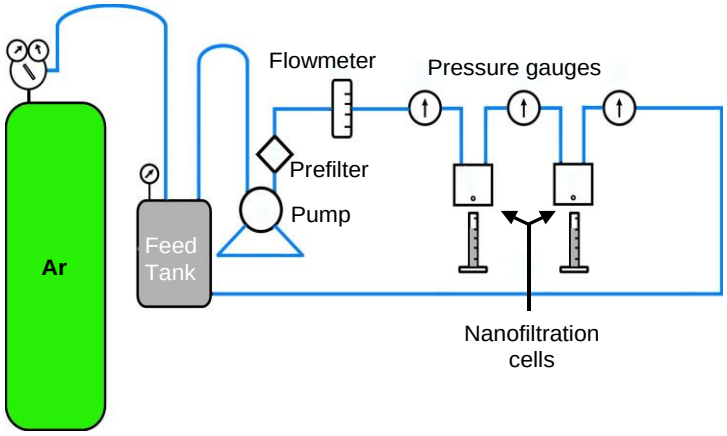

Figure 4. Cross-flow nanofiltration apparatus.

Formation of Metal Nanoparticles in PEMs. PEMs are also excellent templates for forming metal nanoparticles.[34] Layer-by-layer adsorption using films containing metal-ion complexes followed by reduction (Figure 5) gives nanoparticles whose sizes depend on the ratio of metal ion to polyethyleneimine in the polycation deposition solution. These nanoparticle-containing films exhibit anti-bacterial properties and also catalyze the selective hydrogenation of alkenes. Using the same principles as in the membrane studies, selective transport of alkenes to the nanoparticles results in selective catalysis,[16] which could potentially allow synthetic chemists to proceed to a subsequent reaction without performing a purification step. The rate of hydrogenation of allyl alcohol by films containing Pd nanoparticles is as much as 24-fold greater than the rate of hydrogenation of 3-methyl-1-penten-3-ol. Additionally, nanoparticles in polyelectrolyte multilayers may allow membrane catalysis,[20] which can combine separation and reaction in a single operation.

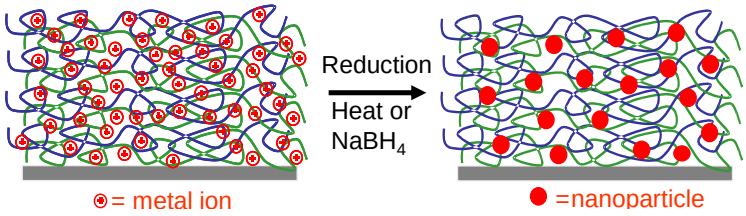

Figure 5. Formation of nanoparticles in a polyelectrolyte multilayer film.

Correlation of PEM Swelling and Permeability. Diffusion dialysis and NF with sugars and small alcohols give an indication of the size-based selectivity of PEMs because charge has minimal effect on the transport of these molecules. Based on modelling of the transport of a series of small molecules, the effective pores size in protonated poly(allylamine) (PAH)/poly(styrene sulfonate) (PSS) films is about 0.8 nm, and the porosity is 2.8%.[29] Equally important, permeability varies with film swelling (determined from in situ ellipsometry), which is a function of the polyelectrolytes employed to form membranes.[25,27] Coatings that show a 400% increase in thickness upon immersion in water minimally reject sugars, whereas films that swell ~100% show >99.5% rejection of sucrose. By varying the composition of polyelectrolytes, one can optimize membranes to pass salt and reject sucrose.[22,27]

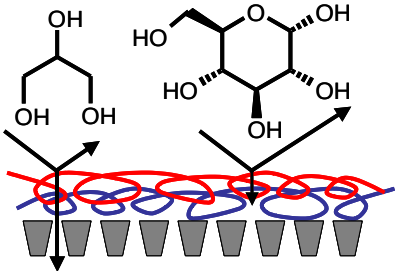

Figure 6. Scheme of selective permeation of glycerol over glucose in a PEM-coated membrane.

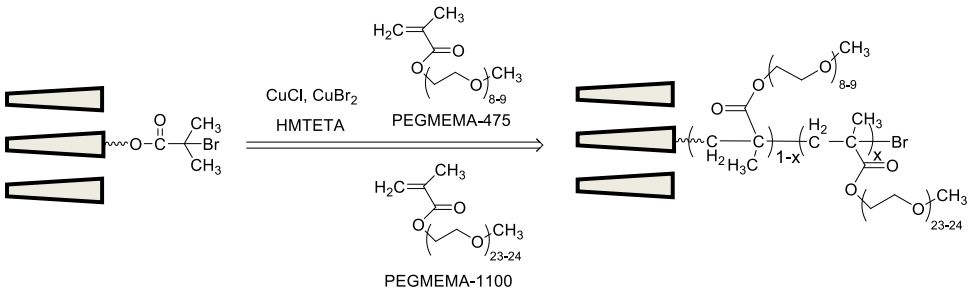

Figure 7. Surface-initiated copolymerization of PEGMEMA-475 and PEGMEMA-1100 to provide a membrane skin that remains amorphous at room temperature.

CO_2-Selective Polymer Brush Membranes. Selective removal of CO_2 from gas streams is becoming increasingly important for applications such as CO_2 sequestration, fuel

cell operation, and H_2 synthesis. Poly(ethylene glycol) (PEG) exhibits a particularly high selectivity for CO_2 over H_2. To develop thin PEG-containing skins, this work employed atom-transfer radical polymerization (ATRP) from porous supports (Figure 7).[12] However, for monomers with long PEG chains crystallization limits permeability, and with short PEG side chains CO_2/H_2 selectivity is not as high as with longer side chains. This research showed that the use of copolymer films (poly(PEGMEMA-475-*co*-PEGMEMA-1100, see Figure 7 for structures) prevents crystallization while maintaining the selectivity of PEGMEMA-1100 films, and films cover underlying pores without filling them. The ATRP method is vital for controlling film thickness because it minimizes polymerization in solution and affords controlled film growth. Importantly, the room-temperature CO_2/H_2 selectivity of 12 achieved with these membranes is equivalent to the selectivities of the best membranes in the literature.

Separation of Fluoride from Other Monovalent Anions Using PEM Nanofiltration Membranes. Separation of different monovalent ions is much more difficult than our prior monovalent/divalent ion (e.g. Cl^-/SO_4^{2-}) separations because charge-based selectivity is precluded. Nevertheless, development of NF for F^- removal will require the synthesis of highly permeable membranes that reject F^- while passing other monovalent anions such as Cl^- and Br^- (Figure 8) to both reduce osmotic pressures and avoid the need for remineralization. Remarkably, deposition of 4.5-bilayer PSS/poly(diallyl dimethylammonium chloride) (PDADMAC) films on porous alumina supports yields membranes that exhibit Cl^-/F^- and Br^-/F^- selectivities >3 with low Cl^- and Br^- rejections and a solution flux of 3.5 m^3/m^2-day at 4.8 bar.[19] In contrast, the selectivities of commercial NF membranes (NF 90 and NF 270 from DOW) and PSS/PAH-coated membranes were about 1 under the same experimental conditions, and the highest flux through the commercial membranes was 1.1 m^3/m^2-day at 4.8 bar.

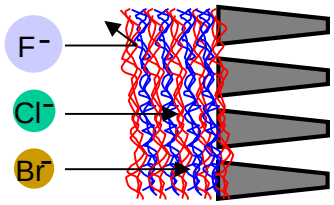

Figure 8. Selective permeation of fluoride salts relative to chloride and bromide salts is important for water purification.

Understanding the Variation of Selectivity with the number of layers in a PEM. In a number of anion separations, the selectivity of PSS/PDADMAC films shows a maximum after deposition of around 4.5 bilayers. For example, the Cl^-/SO_4^{2-} selectivities of PSS/PDADMAC-coated membranes are >30 with 4.5 bilayers but only 3 with 6.5-bilayer films.[13] The Cl^-/F^- selectivities of 4.5-, 5.5-, and 6.5-bilayer films were 3.4, 1.9, and 1.1, respectively.[19] Attenuated total reflectance infrared spectroscopy (Figure 7) showed a dramatic increase in the concentration of adsorbed SCN^- in PSS/PDADMAC films on going from 6 to 7 bilayers, and a similar trend occurred in the adsorption of $Ni(CN)_4^{2-}$. Zeta potentials of films also began decreasing after formation of about 6 bilayers. This suggests that after deposition of about

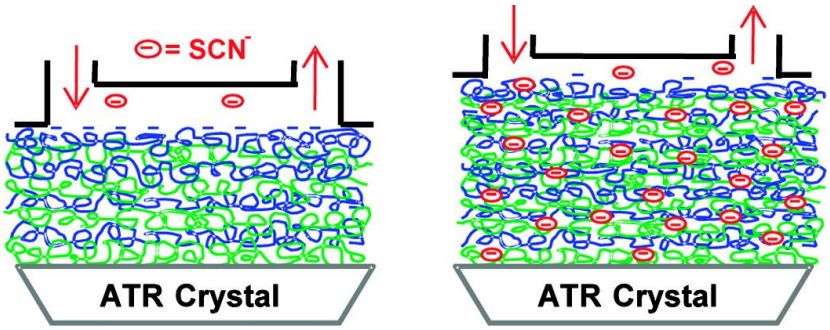

Figure 9. Schematic drawing of increased anion partitioning into thicker PSS/PDADMAC films. Attenuated total reflectance IR spectroscopy enabled studies of ion partitioning.

4-6 bilayers, film growth involves deposition of large excesses of PDADMAC during polycation adsorption, which results in a large number of ion-exchange sites. This is consistent with much larger growth rates after deposition of the first 4-6 layers. During PSS adsorption, the excess PDADMAC in the film likely diffuses to the surface and forms the PSS/PDADMAC complex. This process should yield a highly hydrated material, so only with <6 layers is film hydration low enough to give Cl^-/F^- selectivity.

Facilitated Transport through PEMs. Facilitated transport in PEMs may enhance discrimination among cations with the same valence. The minimal thickness of the films should lead to reasonable fluxes even with fixed-carrier facilitated transport (Figure 10) where hopping between ion-binding sites may be slow. To prepare ultrathin membrane skins that selectively bind Cu^{2+}, we deposited poly[(N,N'-dicarboxymethyl)allylamine] (PDCMAA, Figure 10)/PAH films on porous alumina supports.[6] In diffusion dialysis, these membranes show Cu^{2+}/Mg^{2+} transport selectivities of 50 and 80 for PAH-capped and PDCMAA-capped films, respectively. Although Cu^{2+} and Mg^{2+} have similar aqueous diffusion coefficients, the equilibrium constant for metal-ion binding to iminodiacetic acid functionalities is 7 orders of magnitude higher for Cu^{2+} than for Mg^{2+}. Amines also bind Cu^{2+} more strongly than Mg^{2+}. In the presence of Cu^{2+}, the Mg^{2+} flux through the membrane decreases several orders of magnitude to generate the selectivity, so presumably the Cu^{2+} binding excludes the Mg^{2+} from the membrane. These membranes also exhibit high Cu^{2+}/Ca^{2+} and Cu^{2+}/Ni^{2+} selectivities, again, likely because of specific sorption of Cu^{2+}.

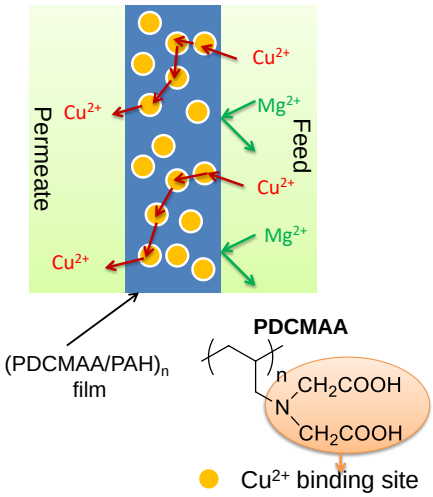

Figure 10. Cartoon of Cu^{2+}-selective fixed carrier facilitated transport through a $(PDCMAA/PAH)_n$ film.

Selective Transport in Charged Nanopores. Charged nanochannels offer unique opportunities for ion separations because at small enough dimensions, the electrical double layer in such channels selectively excludes cations or anions. This research employed adsorption of polyelectrolyte multilayers in the pores of track-etched membranes to control nanopore size and charge and enable separations based on ion exclusion from a nanopore double layer.[8] In the simplest case, selective exclusion of a divalent cation, e.g. Mg^{2+}, from a $(PSS/PAH)_1$-coated (positively charged) nanopore leads to K^+/Mg^{2+} transport selectivities >20. Negatively charged pores show Br^-/SO_4^{2-} selectivity. Because the selectivity relies on exclusion from the nanopore, however, it decreases with ionic strength.

Charged capillaries will exclude all monovalent cations to approximately the same extent, so selectivity among different monovalent cations is not feasible through electrostatic exclusion. However, when the pore surface charge is opposite in sign to the ions of interest, streaming potentials can separate ions according to their mobilities as Figure 11 shows. When Cs^+ and Li^+ are the more and less mobile cations, respectively, the negatively charged capillary excludes anions and attracts Li^+ and Cs^+ equally. Application of a transmembrane pressure creates a streaming potential that decreases cation transport and enhances anion transport to achieve zero current. However, because they have different mobilities, the Cs^+ and Li^+ traverse the membrane at different rates. The higher rate of electrical migration (in the negative direction) of Cs^+

compared to Li^+ yields selective transport of Li^+ over Cs^+. For PSS-modified track-etched membranes (nominal 30 nm pores prior to modification), Li^+/Cs^+ selectivities are around 3.4. Similarly, pores modified with a PSS/PAH film have a positive charge that leads to acetate/Br^- selectivities around 5.7.

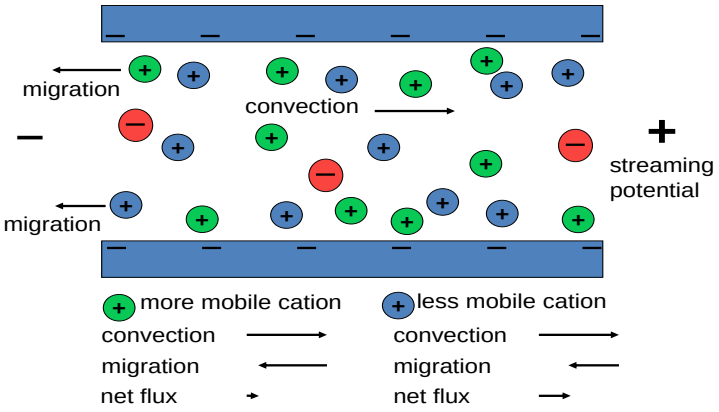

Figure 11. Schematic mechanism of selective permeation of a less mobile cation during convective flow through a charged nanopore. Partial exclusion of anions from the pore results in a streaming potential that retards transport of cations, but especially the more mobile cation. This image assumes diffusive transport is negligible.

Adsorption of Polyelectrolyte Multilayers to Create Highly Selective ED Membranes. Electrodialysis (ED) is similar to diffusion dialysis, but as Figure 12 shows an electrical potential, rather than a concentrations gradient, drives ions across the membrane. ED is an established membrane-based technique for applications such as preconcentrating brines and treating wastewater. Nevertheless, although ED ion-exchange membranes allow highly specific passage of either anions or cations, they show minimal selectivities among anions or among cations. Such discrimination among cations or anions could open new applications such as acid recovery and salt purification or production. Common cation-exchange membranes show monovalent/divalent cation selectivities <2. *Remarkably, adsorption of PAH/PSS multilayers on Nafion cation-exchange membranes yields unprecedented K^+/Mg^{2+} selectivities >1000.* Such selectivities also occur for Li^+/Co^{2+} and K^+/La^{3+}.[3,5,7] Very recent studies show that similar discrimination also occurs with polyelectrolyte films on inexpensive poly(amide) cation-exchange membranes, and high selectivities are also possible with anions in transport through coated anion-exchange membranes.[1]

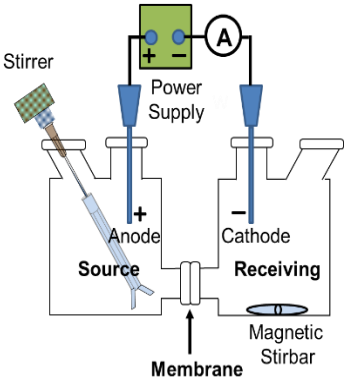

Figure 12. Diagram of the ED apparatus. Diffusion dialysis occurs in the same cell without an applied potential. Cations move from the source to the receiving phase in ED across a cation-exchange membrane.

Modelling of Ion Transport. Commercial reverse osmosis (RO) and NF membranes contain ultrathin barrier layers on porous supports. Although solution-diffusion models of salt transport through barriers assume electroneutrality,[2] with ultrathin skins and low ion partition coefficients, space-charge regions may occupy most of the layer. Thus, this research examined theoretically the implications of nonelectroneutrality on salt transport.[4] Both immobile external surface charge and unequal cation and anion solvation energies in the barrier layer can give regions with excess mobile charge, and the size of these regions increases with decreasing feed concentrations and ion partition coefficients. Figure 13 shows the ion concentration profile in a membrane skin where the intrinsic partition coefficient (the partition coefficient with no electrical potential difference between the solution and the membrane) is much lower for the cation. The low cation solubility in the barrier

gives a negatively charged region with a low cation concentration. This space charge creates a gradient of electrical potential between the solution and the membrane interior, and for this case the potential difference leads to nearly equal cation and anion concentrations only in the center of the membrane. The low cation concentrations control transport and may increase the resistance to ion passage by an order of magnitude compared to the assumption of a neutral membrane, depending on the values of intrinsic partition coefficients. This is a new paradigm for explaining selective ion transport in NF and RO membranes.[4]

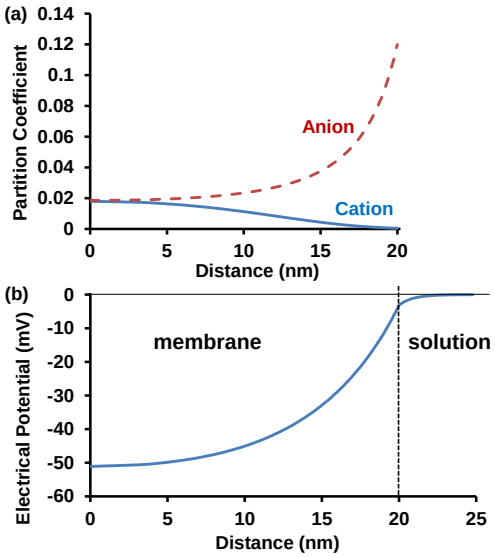

Figure 13. Simulated (a) ion-concentration profiles and (b) electrical potential for a membrane equilibrated on both sides with a solution containing 31 mM MA_2. In figure (a), the partition coefficient is the ratio of the concentration at the location in the membrane to the feed concentration. The X-axis is the distance from the center of the membrane barrier, which has a total thickness of 40 nm. The concentration profile is symmetric about zero due to the assumption of a low concentration difference across the membrane. The simulation assumes intrinsic partition coefficients (in the absence of electrical potential) of 0.14 for the anion A^- and 3.4 x 10^{-4} for the cation M^{2+}.

Publications Supported by this Grant (total number of citations-4100 from Google Scholar) (Noted DOE support comes only from this grant.)

Peer-reviewed Journal Articles

1. Y. Zhu, "Adsorption of Polyelectrolyte Multilayers Imparts High Monovalent/Divalent Cation Selectivity to Aromatic Polyamide Cation-exchange Membranes" submitted to *J. Membr. Sci.* March 13, 2017. DOE- only federal sponsor.

2. A. Yaroshchuk and M.L. Bruening, "An Analytical Solution of the Solution-Diffusion-Electromigration Equations Reproduces Trends in Ion Rejections During Nanofiltration of Mixed Electrolytes" *J. Membr. Sci.* **523**, 361-372 (2017). DOE- only federal sponsor, not yet cited.

3. N. White, M. Misovich, E. Alemayehu, A. Yaroshchuk, and M.L. Bruening "Highly Selective Separations of Multivalent and Monovalent Cations in Electrodialysis Through Nafion Membranes Coated with Polyelectrolyte Multilayers" *Polymer* **103**, 478-485 (2016). DOE- only federal sponsor, 2 citations.

4. A. Yaroshchuk, Y. Zhu, M. Bondarenko, and M.L. Bruening "Deviations from Electroneutrality in Membrane Barrier Layers: A Possible Mechanism Underlying High Salt Rejections" *Langmuir* **32**, 2644–2658 (2016). DOE- only federal sponsor, 3 citations.

5. N. White, M. Misovich, A. Yaroshchuk, and M.L. Bruening, "Coating of Nafion Membranes with Polyelectrolyte Multilayers to Achieve High Monovalent/Divalent Cation Electrodialysis Selectivities" *ACS Appl. Mater. Interfaces* **7**, 6620–6628 (2015). DOE- only federal sponsor, 17 citations.

6. C. Sheng, S. Wijeratne, C. Cheng, G.L. Baker, and M.L. Bruening, "Facilitated Ion Transport Through Polyelectrolyte Multilayer Films Containing Metal-Binding Ligands" *J. Membrane Sci.* **459**, 169-176 (2014). DOE- only federal sponsor, 8 citations.

7. C. Cheng, N. White, H. Shi, M. Robson, and M.L. Bruening, "Cation Separations in Electrodialysis Through Membranes Coated with Polyelectrolyte Multilayers" *Polymer* **55**, 1397-1403 (2014). DOE- only federal sponsor, 18 citations.

8. J.A. Armstrong, E.E.L. Bernal, A. Yaroshchuk, and M.L. Bruening, "Separation of Ions Using Polyelectrolyte-Modified Nanoporous Track-Etched Membranes" *Langmuir* **29**, 10287-10296 (2013). DOE- only federal sponsor, 12 citations.

9. A. Yaroshchuk, M.L Bruening, and E.E.L. Bernal, "Solution-Diffusion-Migration Model and its Uses for Analysis of Nanofiltration, Pressure-Retarded Osmosis and Forward Osmosis in Multi-ionic Solutions" *J. Membrane Sci.***447**, 463-476 (2013). DOE- only federal sponsor, 29 citations.

10. C. Cheng, A. Yaroshchuk, and M.L. Bruening, "Fundamentals of Selective Ion Transport Through Multilayer Polyelectrolyte Membranes" *Langmuir*, **29**, 1885-1892 (2013). DOE- only federal sponsor, 35 citations.

11. Y. Zheng, M.L. Bruening, and G.L. Baker, "Crystallization Kinetics of Polymer Brushes with Poly(ethylene oxide) Side Chains" *J. Polymer Sci. B. Polymer Phys.* **48**, 1955-1959 (2010). DOE- <50% federal support, 9 citations.

12. S.T. Grajales, X. Dong, Y. Zheng, G.L. Baker, and M.L. Bruening, "Effects of Monomer Composition on CO_2-Selective Polymer Brush Membranes" *Chem. Mater.* **22**, 4026–4033 (2010). DOE- only federal sponsor, 16 citations.

13. M. Adusumilli and M.L. Bruening, "Variation of Ion-exchange Capacity, Zeta Potential, and Ion-transport Selectivities with the Number of Layers in a Multilayer Polyelectrolyte Film" *Langmuir* **25**, 7478-7485 (2009). DOE- only federal sponsor, 49 citations.

14. S. U. Hong, L. Ouyang, and M.L. Bruening, "Recovery of Phosphate Using Multilayer Polyelectrolyte Nanofiltration Membranes" *J. Membr. Sci.* **327**, 2-5 (2009). DOE- 50 % federal sponsor, 60 citations.

15. M.L. Bruening, D.M. Dotzauer, P. Jain, L. Ouyang, and G.L. Baker, "Creation of Functional Membranes Using Polyelectrolyte Multilayers and Polymer Brushes" *Langmuir* **24**, 7663-7673 (2008). DOE- 50% federal sponsor, 171 citations.

16. S. Bhattacharjee, and M.L. Bruening, "Selective Hydrogenation of Monosubstituted Alkenes by Pd Nanoparticles Embedded in Polyelectrolyte Films" *Langmuir* **24**, 2916-2920 (2008). DOE- only federal sponsor, 54 citations.

17. L. Ouyang, R. Malaisamy, and M.L. Bruening, "Multilayer Polyelectrolyte Films as Nanofiltration Membranes for Separating Monovalent and Divalent Cations" *J. Membrane Sci.* **310**, 76-84 (2008). DOE- 50% federal sponsor, 170 citations.

18. Y. Zheng, M.L. Bruening, and G.L. Baker, "Crystallization of Polymer Brushes with Poly(ethylene oxide) Side Chains" *Macromolecules* **40**, 8212-8219 (2007). DOE- <50% federal sponsor, 41 citations.

19. S.U. Hong, R. Malaisamy, and M.L. Bruening, "Separation of Fluoride from Other Monovalent Anions Using Multilayer Polyelectrolyte Nanofiltration Membranes" *Langmuir* **23**, 1716-1722 (2007). DOE- only federal sponsor, 83 citations.

20. D.M. Dotzauer, J. Dai, L. Sun, and M.L. Bruening, "Catalytic Membranes Prepared Using Layer-by-Layer Adsorption of Polyelectrolytes and Metal Nanoparticles in Porous Supports" *Nano Letters* **6**, 2268-2272 (2006). DOE- only federal sponsor, 275 citations.

21. S.U. Hong, R. Malaisamy, and M.L. Bruening, "Optimization of Flux and Selectivity in Cl^-/SO_4^{2-} Separations with Multilayer Polyelectrolyte Membranes" *J. Membr. Sci.* **283**, 366-372 (2006). DOE- only federal sponsor, 66 citations.

22. S.U. Hong, M.D. Miller, and M.L. Bruening, "Removal of Dyes, Sugars, and Amino Acids from NaCl Solutions Using Multilayer Polyelectrolyte Nanofiltration Membranes" *Ind. Eng. Chem. Res.* **45**, 6284-6288 (2006). DOE- only federal sponsor, 54 citations.

23. S.U. Hong and M.L. Bruening, "Separation of Amino Acid Mixtures using Multilayer Polyelectrolyte Nanofiltration Membranes" *J. Membr. Sci.* **280**, 1-5 (2006). DOE- only federal sponsor, 81 citations.

24. R. Malaisaimy and M.L. Bruening, "High-Flux Nanofiltration Membranes Prepared by Adsorption of Multilayer Polyelectrolyte Membranes on Polymeric Supports", *Langmuir*, **21**, 10587-10592 (2005). DOE- only federal sponsor, 148 citations.

25. M.D. Miller and M.L. Bruening, "Correlation of the Swelling and Permeability of Polyelectrolyte Multilayer Films", *Chem. Mater.* **17**, 5375-5381 (2005). DOE- only federal sponsor, 125 citations.

26. D.M. Sullivan and M.L. Bruening, "Ultrathin, Cross-linked Polyimide Pervaporation Membranes Prepared from Polyelectrolyte Multilayers", *J. Membrane Sci.*, **248**, 161-170 (2005). DOE- 50% federal sponsor, 59 citations.

27. M.D. Miller and M.L. Bruening, "Controlling the Nanofiltration Properties of Multilayer Polyelectrolyte Membranes Through Variation of Film Composition", *Langmuir*, **20**, 11545-11551 (2004). DOE- only federal sponsor, 125 citations.

28. S. Kidambi, J. Dai, J. Li, and M.L. Bruening, "Selective Hydrogenation by Pd Nanoparticles Embedded in Polyelectrolyte Multilayers", *J. Am. Chem. Soc.*, **126**, 2658-2659 (2004). DOE- only federal sponsor, 300 citations.

29. X. Liu and M.L. Bruening, "Size-Selective Transport of Uncharged Solutes Through Multilayer Polyelectrolyte Membranes", *Chem. Mater.*, **16**; 351-357 (2004). DOE- only federal sponsor, 166 citations.

30. B.W. Stanton, J.J. Harris, M.D. Miller, and M.L. Bruening, "Ultrathin, Multilayered Polyelectrolyte Films as Nanofiltration Membranes", *Langmuir*, **19**, 7038-7042 (2003). DOE- only federal sponsor, 211 citations.

31. D.M. Sullivan and M.L. Bruening, "Ultrathin, Gas-selective Polyimide Membranes Prepared from Multilayer Polyelectrolyte Films", *Chem. Mater.*, **15**, 281-287 (2003). DOE- 50% federal support, 88 citations.

32. B.Y. Kim and M.L. Bruening, "pH-Dependent Growth and Morphology of Multilayer Dendrimer/Poly(acrylic acid) Films", *Langmuir*, **19**, 94-99 (2003). Correction published *Langmuir*, **20**, 6074 (2004). DOE- 50% federal support, 75 citations.

33. M.L. Bruening and D.M. Sullivan, “Enhancing the Ion-Transport Selectivity of Multilayer Polyelectrolyte Membranes”, *Chem. Eur. J.*, **8**, 3832-3837 (2002). DOE- 50% federal sponsor, 69 citations.

34. J. Dai, J.I. Lee, and M. L. Bruening, “Catalytic Nanoparticles Formed by Reduction of Metal Ions in Multilayered Polyelectrolyte Films”, *Nano Letters*, **2**, 47-51 (2002). DOE- only federal sponsor, 350 citations.

35. A.M. Balachandra, J. Dai, and M.L. Bruening, “Enhancing the Anion-Transport Selectivity of Polyelectrolyte Multilayer Membranes by Templating with Cu^{2+}”, *Macromolecules*, **35**, 3171-3178 (2002). DOE- 50% federal sponsor, 102 citations.

36. J. Dai, A.M. Balachandra, and M.L. Bruening, “Controlling Ion Transport Through Multilayer Polyelectrolyte Membranes by Derivatization with Photolabile Functional Groups”, *Macromolecules*, **35**, 3164-3170 (2002). DOE- only federal sponsor, 68 citations.

37. D.M. Sullivan and M.L. Bruening, “Ultrathin, Ion-selective Polyimide Membranes Prepared from Layered Polyelectrolytes”, *J. Am. Chem. Soc.*, **123**, 11805-11806 (2001). DOE- 50% federal sponsor, 65 citations.

38. J.L. Stair, J.J. Harris, and M.L. Bruening, “Enhancement of the Ion-Transport Selectivity of Layered Polyelectrolyte Membranes Through Cross-Linking and Hybridization”, *Chem. Mater.*, **13**, 2641-2648 (2001). DOE- only federal sponsor, 83 citations.

39. J. Dai, A.W. Jensen, D.K. Mohanty, J. Erndt, and M.L. Bruening, "Controlling the Permeability of Multilayer Polyelectrolyte Films Through Derivatization, Cross-linking, and Hydrolysis", *Langmuir*, **17**, 931-937 (2001). DOE- only federal sponsor, 146 citations

40. M. Nagale, B.Y. Kim, and M.L. Bruening, "Ultrathin, Hyperbranched Polymer Membranes", *J. Am. Chem. Soc.*, **122**, 11670-11678 (2000). DOE- 50% federal sponsor, 61 citations.

41. J. Dai, D.M Sullivan, and M.L. Bruening, "Ultrathin, Layered Polyamide and Polyimide Films as Protective Coatings for Aluminum", *Ind. & Eng. Chem.*, **39**, 3528-3535 (2000). DOE- only federal sponsor, 67 citations.

42. J.J. Harris, J. Stair, and M.L. Bruening, "Layered Polyelectrolyte Films as Selective, Ultrathin Barriers to Anion Transport", *Chem. Mater.*, **12**, 1941-1946 (2000). DOE- only federal sponsor, 196 citations.

43. J.J. Harris and M.L. Bruening, "Electrochemical and In Situ Ellipsometric Investigation of the Permeability and Stability of Layered Polyelectrolyte Films", *Langmuir*, **16**, 2006-2013 (2000). DOE- only federal sponsor, 343 citations.

Book Chapters

1. M.L. Bruening and A.Y. Yaroshchuk, "Modelling of Ion Transport in Nanofiltration" invited chapter for publication in **Nanofiltration**, A.I. Schäfer & A.G.Fane Eds, Elsevier, New York, NY. DOE- only federal sponsor.

2. M.L. Bruening, "Analytical Applications of Membranes" in **Encyclopedia of Membrane Science and Technology**, V. Tarabara and E.M. Hoek, Eds., Wiley, Hoboken, NJ, Vol. 3, 1915-1926 (2013). DOE- primary federal sponsor.

3. M.L. Bruening, "Creating Functional Membranes Through Polyelectrolyte Adsorption" in **Multilayer Thin Films, Sequential Assembly of Nanocomposite Materials**, G. Decher and J.B. Schlenoff, Eds., Wiley-VCH, Weinheim, Germany, Vol. 2, 907-924 (2012). DOE- 50% federal sponsor.

4. M.L. Bruening, "Formation of Composite Membranes with Ultrathin Skins Using New Methods of Organic Film Formation: Gas Selective Membranes" in **Advanced Materials for Membrane Separations**, I. Pinnau and B.D. Freeman, Eds., American Chemical Society, Washington, DC, pp. 269-280 (2004). DOE- 50% federal sponsor.

5. M.L. Bruening, "Controlling the Ion-Permeability of Layered Polyelectrolyte Films and Membranes", in **Multilayer Thin Films, Sequential Assembly of Nanocomposite Materials**, G. Decher and J.B. Schlenoff, Eds., Wiley-VCH, Weinheim, Germany, pp. 487-510 (2003). DOE- 50% federal sponsor.

PhD Dissertations and MS Theses

1. J.J. Harris, " Fundamental Study of the Ion Permeability of Ultrathin, Layered Polyelectrolyte Films" PhD dissertation, Michigan State University, East Lansing, MI (2001). DOE- primary federal sponsor.

2. B.Y. Kim, "Hyperbranched Polymer Films as Ultrathin Membrane Skins and Adhesives" PhD dissertation, Michigan State University, East Lansing, MI (2002). DOE- 50% federal sponsor.

3. J. Dai, "Applications of Multilayer Polyelectrolyte Films in Corrosion Inhibition, Ion Separation, and Catalysis" PhD dissertation, Michigan State University, East Lansing, MI (2002). DOE- primary federal sponsor.

4. D.M. Sullivan, "Ultrathin, Selective Polyimide Membranes Prepared from Layered Polyelectrolytes" PhD dissertation, Michigan State University, East Lansing, MI (2002). DOE- 50% federal sponsor.

5. A.M. Balachandra, "Selective, Ultrathin Membrane Skins Prepared by Deposition of Novel Polymer Films on Porous Alumina Supports" PhD dissertation, Michigan State University, East Lansing, MI (2003). DOE- 50% federal sponsor.

6. B.W. Stanton, “Ultrathin, Multilayered Polyelectrolyte Films as Nanofiltration Membranes” MS thesis, Michigan State University, East Lansing, MI (2003). DOE- primary federal sponsor.

7. X. Liu, “Size-selective Transport of Uncharged Solutes Through Multilayer Polyelectrolyte Membranes” MS thesis, Michigan State University, East Lansing, MI (2003). DOE- primary federal sponsor.

8. M.D. Miller, “Novel Polymer Films for Separations in Nanofiltration” PhD dissertation, Michigan State University, East Lansing, MI (2005). DOE- primary federal sponsor.

9. S. Kidambi, “Investigation of Metal Nanoparticles Encapsulated in Polyelectrolyte Multilayers for Catalytic and Antibacterial Applications” PhD dissertation, Michigan State University, East Lansing, MI (2007). DOE- <50% federal sponsor.

10. S. Bhattacharjee, “Regio and Chemo Selective Hydrogenation by Palladium Nanoparticles Embedded in Polyelectrolyte Films” PhD dissertation, Michigan State University, East Lansing, MI (2007). DOE- <50% federal sponsor.

11. D.M. Dotzauer, “Catalytic Membranes Prepared by Adsorption of Polyelectrolyte/Metal Nanoparticle Films in Porous Supports” PhD dissertation, Michigan State University, East Lansing, MI (2009). DOE- <50% federal sponsor.

12. L. Ouyang, “Layer-by-layer Modification of Membranes for Ion Separations and Catalysis” PhD dissertation, Michigan State University, East Lansing, MI (2009). DOE- 50% federal sponsor.

13. M. Adusumilli, “Polyelectrolyte Multilayer Films for Ion Separation and Water Purification” PhD dissertation, Michigan State University, East Lansing, MI (2010). DOE- primary federal sponsor.

14. X. Dong, “Reverse-selective Gas-separation Membranes Prepared by Atom Transfer Radical Polymerization” PhD dissertation, Michigan State University, East Lansing, MI (2012). DOE- primary federal sponsor.

15. C. Cheng, “Ion Transport Through Multilayer Polyelectrolyte Membranes and Conductive Membranes” PhD dissertation, Michigan State University, East Lansing, MI (2013). DOE- primary federal sponsor.

16. S.T. Grajales, “CO_2-selective Polymer Brush Membranes and Antibacterial Polyelectrolyte Multilayer Membranes: Synthesis, Characterization, and Application” PhD dissertation, Michigan State University, East Lansing, MI (2014). DOE- 50% federal sponsor.

17. J. Armstrong, “Ion Separations Based on Electrical Potentials- Nanoporous and Microporous Membranes” PhD dissertation, Michigan State University, East Lansing, MI (2015). DOE- primary federal sponsor.

18. N. White, “Electrically Driven Ion Separations and Nanofiltration Through Membranes Coated with Polyelectrolyte Multialyers” PhD dissertation, Michigan State University, East Lansing, MI (2015). DOE- primary federal sponsor.

19. Y. Zhu, “Electrically Driven Ion Separations Using Membranes Coated with Polyelectrolyte Multilayers or Conductive Films” PhD dissertation, Michigan State University, East Lansing, MI (2016). DOE- primary federal sponsor.