Cu²⁺-SELECTIVE FACILITATED ION TRANSPORT THROUGH PDCMAA/PAH MULTILAYER FILMS

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ABSTRACT

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Layer-by-layer adsorption of poly[(N,N'-dicarboxymethyl) allylamine] (PDCMAA)/poly(allylamine hydrochloride) (PAH) films at low pH yields a thin film with abundant Cu^{2+} -binding sites. When deposited on a porous alumina substrate, $(PDCMAA/PAH)_n$ films show average Cu^{2+}/Mg^{2+} diffusion dialysis selectivities of 50 and 80 for PAH-capped and PDCMAA-capped films, respectively. PDCMAA/PAH membranes also exhibit Cu^{2+}/Ni^{2+} and Cu^{2+}/Ca^{2+} selectivities. The high Cu^{2+}/Mg^{2+} selectivity despite similar aqueous diffusion coefficients and equal charge for the two ions suggests a facilitated transport mechanism. In contrast, PAA/PAH and PSS/PAH films show Cu²⁺/Mg²⁺ selectivities <10. With PDCMAA/PAH films, Cu²⁺ flux increases nonlinearly with increasing CuCl₂ concentration in the feed. Sorption isotherms show that PDCMAA/PAH films contain both strong and weak binding sites, and the nonlinear increases in flux with increasing feed concentration likely represent hopping between weak binding sites, probably the amine groups of PAH. Strong binding of Cu^{2+} to PDCMAA binding sites may displace ionic cross-links in the film and free amine groups for facilitated transport. Additionally, Cu^{2+} binding to the film suppresses Mg^{2+} transport, either through electrostatic exclusion or removal of hopping sites.

To my family, for all the love and support

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KEY TO ABBREVIATIONS

PEM	polyelectrolyte multilayer
LBL	layer by layer
РАН	poly(allylamine hydrochloride)
PAA	poly(acrylic acid)
FESEM	field-emission scanning electron microscopy
PSS	poly(sodium 4-styrenesulfonate)
PVS	poly(vinylammonium)
PVA	poly(vinylsulphate)
NF	nanofiltration
RO	reverse osmosis
PDCMAA	poly[(N,N'-dicarboxymethyl) allylamine]
IDA	iminodiacetic acid
MPA	3-mercaptopropionic acid
ICP-OES	inductively coupled plasma optical emission spectroscopy
AAS	atomic absorption spectroscopy
EDTA	ethylenediaminetetraacetate acid
UV-Vis	ultraviolet-visible
FT-IR	fourier transform infrared spectroscopy
en	ethylenediamine

Chapter 1

Introduction and Background

This thesis describes a metal-binding membrane prepared by layer-by-layer deposition of polyelectrolytes on a porous substrate and demonstrates facilitated ion transport through this membrane using Cu²⁺ and other divalent cations as probes. These studies build on a large body of research on polyelectrolyte multilayer films and facilitated transport membranes. To put this work in perspective, this introduction describes layer-by-layer film formation and the factors influencing film growth and permeability, and then reviews the applications of such films in various fields, especially ion separations. A subsequent section contains an overview of facilitated transport membranes. Finally, I present an outline of the thesis.

1.1 Layer by layer assembly of polyelectrolyte multilayer films

Decher et al. introduced layer by layer (LBL) deposition of complementary polymers in the early 1990's,^{1,2} and this technique has become one of the most attractive strategies for synthesizing functional thin films. In one of its simplest forms, the deposition procedure features a dip-and-rinse process, during which the selected substrate undergoes alternating immersions in polycation or polyanion solutions, with solvent rinsing to remove excessive polymer after each immersion (Figure 1.1). The substrates suitable for film deposition include planar supports,³⁻⁵ porous membranes,⁶⁻⁸ and nanoparticles.⁹⁻¹¹ Moreover, the constituents of the multilayers can range from the most

common polyelectrolytes to other charged species such as proteins, ¹²⁻¹⁴ colloidal nanoparticles, ¹⁵⁻¹⁸ and dyes. ¹⁹⁻²¹ In addition to electrostatic interactions between polycations and polyanions, other interactions that may facilitate LBL film formation include hydrophobic interactions, ^{8,22,23} hydrogen bonding, ²⁴⁻²⁶ π - π interactions^{27,28} and covalent bonding²⁹⁻³⁷. Importantly, the thickness and permeability of LBL films depend on the film constituents, number of layers, and deposition conditions. ³⁸⁻⁴¹



Figure 1.1 Schematic illustration of layer-by-layer deposition of oppositely charged polyelectrolytes on a planar substrate. A) Experimental procedure for layer-by-layer deposition, B) cartoon of polyelectrolyte film growth. (Used by permission of American Association for the Advancement of Science from Science, 1997, 277, 1232-1237). For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis.

1.1.1 Factors influencing polyelectrolyte multilayer growth

The growth of polyelectrolyte multilayer films relies in many cases on charge overcompensation that reverses the substrate's surface charge after each adsorption step.⁴²⁻⁴⁴ The extent of charge overcompensation depends on deposition conditions such as the type and molecular weight of polyelectrolyte,⁴⁵⁻⁴⁸ polyelectrolyte charge density,⁴⁹ supporting electrolyte species and concentration,^{50,51} dipping solution pH^{41,52} and adsorption time. Adjustment of deposition conditions can tailor film properties such as swelling,⁵⁰ thickness,⁵² and permeability⁴⁸ for different applications.

Supporting electrolytes affect the conformations of polyelectrolytes in both the dipping solution and the film to alter film structure.^{45,53,54} In the absence of salt polyelectrolytes extend to minimize the electrostatic repulsion between the charged groups. In contrast, high salt concentrations screen charges on the polyelectrolyte, such that the polymer adopts conformations with loops and tails.^{43,45} The variations in conformations of polyelectrolytes lead to a difference in the degree of surface-charge overcompensation and the interdiffusion of polymers, and finally result in dramatic differences in PEM film thicknesses.⁵⁵⁻⁵⁷ The choice of salt for the supporting electrolyte also affects the film thickness and permeability.^{45,58}

Even with similar concentrations of supporting electrolyte, the morphology, thickness, and permeability of PEMs vary dramatically with the composition of the constituent polyelectrolytes. For example, high charge density on a given polyelectrolyte leads to extended polymers and high densities of ionic cross-links to give thin films with low permeabilities.⁵⁹⁻⁶¹ Polyelectrolyte molecular weight also contributes to film growth patterns. Sun et al.⁶² demonstrated an exponential growth (thickness increases

exponentially with the number of adsorption of poly(allylamine steps) hydrochloride)/poly(acrylic acid) (PAH/PAA) films with low molecular weight PAA (7, 15 or 50 kDa) in contrast to linear film growth with high molecular weight PAA (90 kDa). Confocal microscopy combined with fluorescently labeled PAA showed that low molecular weight polyelectrolyte penetrates or diffuses into the film over large distances. However, low molecular weights can also lead to film instability. Whereas high molecular weight polyelectrolytes (100 kDa) may exhibit kinetic irreversibility, ⁴² low molecular weight polyelectrolytes can leach from films when exposed to oppositely charged polyelectrolytes during deposition.⁶³ Polyelectrolyte concentrations^{64,65} generally have a relatively small effect on film growth.

For weak polyelectrolytes such as PAA, film growth strongly depends on the dipping solution pH. In the early 1990's Rubner et al.⁶⁶ found a 2-fold decrease in the thickness of $(PAH/PAA)_{30}$ films when the deposition pH was 4.5 rather than 2.5. The decrease in film thickness stems from the increased ionization of PAA at pH 4.5. The higher charge density at the higher deposition pH results in more extended polymer chains and thinner films. More recent studies confirm these results.^{41,52,67-69}

Adsorption times less than those required for equilibration should also alter film properties. A few studies show that 95% of the adsorption typically occurs during the first 1 or 2 min of exposure to the polyelectrolyte solutions.^{70,71} Thus the immersion time in this thesis is typically 5 min to minimize variations from incomplete equilibration.

1.1.2 Factors influencing polyelectrolyte multilayer film permeability

Membrane-based separations are attractive because of their operational convenience and low energy cost, but efficient separations of molecules or ions require membranes with both high selectivity and high permeability. Unfortunately, membranes that exhibit high selectivity usually have low permeability, and vice versa. To some extent, composite membranes overcome this tradeoff by employing ultrathin, selective layers that allow high flux due to their minimal thickness. A highly permeable support layer provides mechanical stability for the composite membrane.⁷²

Polyelectrolyte multilayer films can cover the surface of a highly permeable membrane support without filling the underlying pores to create the ultrathin skin of a composite membrane. The field-emission scanning electron microscopy (FESEM) images in Figure 1.2 clearly show the formation of a complete polyelectrolyte skin on a porous support.⁶⁰ Layer-by-layer deposition of polyelectrolytes can take place on a variety of supports with a number of different polyelectrolytes and deposition conditions to create a wide range of membrane properties. Additionally, changing the film growth conditions (see the previous section) can tailor membrane permeabilities and selectivities.



330 nm

Figure 1.2 Cross-sectional FESEM image of porous alumina substrates before (A) and after (B) deposition of 10 (PAH/poly (sodium 4-styrenesulfonate) (PSS)) bilayers. (Used by permission of the American Chemical Society from *Chem. Mater.* **2000**, *12*, 1941-1946).

As a result of the charge overcompensation during film growth, PEMs usually contain a highly charged surface layer in addition to a neutral bulk film covering the porous support (see Figure 1.3).⁷³ With their immobile surface charge that varies with polyelectrolyte type and deposition conditions, PEM films are particularly attractive for the separation of ions with different valences. Ion transport through the PEM depends not only on size exclusion from the film structure but also on the electrostatic potential due to the fixed surface charge.⁶¹ Variations in the polyelectrolyte type and number of bilayers deposited dramatically change the ion permeability by changing the surface charge density, film thickness and swelling, and consequently the selectivity among different ions.^{57,60,61,74} For example, changing the capping layer of a (PSS/PAH)_n film from PSS to PAH gives significantly different salt rejections in nanofiltration, from 86 to 96% for Ca²⁺ and from 56 to 35% for SO4²⁻, mainly because of the change in film surface

charge. Similarly, PAA-capped and PSS-capped films exhibit distinct SO_4^{2-} rejections of 56% and 92% due to the different surface charge density. ⁷⁵



Figure 1.3 Illustration of a simplified model of ion transport through a PEM. The film consists of two layers, a highly charged surface layer and a mostly charge compensated film bulk layer. The line represents a hypothetical concentration profile for the excluded ion. (Reproduced with permission of the American Chemical Society from *Macromolecules* **2002**, *35*, 3171-3178).

In addition to the optimization of ion separations by changing the polyelectrolyte type and number of bilayers in a PEM, post-deposition crosslinking and variation of fixed charge density can also control ion transport. Toutianoush et al.⁷⁶ improved the Na⁺/Mg²⁺ transport selectivity through a poly(vinylammonium)/poly(vinylsulphate) (PVS/PVA)₆₀ film by adsorbing Cu²⁺ ions in the film, allegedly increasing the crosslink density in the membrane. Capping of a (PAH/PSS)₅ film with (PAA/PAH) layers and subsequent heat-induced crosslinking enhanced the Cl⁻/SO₄²⁻ transport selectivity from 7

for a (PAH/PSS)₅ film⁶⁰ to as high as 360 for a (PAH/PSS)₅(PAA/PAH)_{2.5} hybrid film crosslinked at 115 °C.⁷⁴ Balachandra et al.^{73,77} improved the Cl⁻/SO₄²⁻ selectivity of PAA/PAH films by increasing the film charge density through templating with Cu²⁺ during deposition and subsequent removing the Cu²⁺ in pH 3 water to create a negatively charged film. Similarly, Dai et al. partially modified polyelectrolytes with photolabile groups, and postdeposition removal of the protecting groups from PEMs led to charged films with increased selectivities.

1.1.3 Applications of polyelectrolyte multilayer films

With their notable advantages of simple deposition, versatile functionality, and tunable thickness and permeability, PEMs have found a broad spectrum of potential applications in fields such as drug delivery,⁷⁸⁻⁸⁰ enzyme^{81,82} or catalyst⁸³ immobilization, membrane reactors,^{84,85} fuel cells,⁸⁶⁻⁸⁸ and liquid,⁸⁹⁻⁹¹ molecule⁹¹⁻⁹³ and ion separations.^{59,74,94,95} PEMs are especially attractive in nanofiltration (NF) because of their nanometer-scale thickness and selective permeabilities for monovalent over multivalent ions. Nanofiltration is a pressure-driven process similar to reverse osmosis (RO), but it requires a lower operating pressure than RO and thus consumes less energy. For applications such as water softening that do not require high rejections of monovalent ions, NF is preferable to RO. Previous studies showed high transport selectivities for monovalent ions over multivalent ions with PEMs deposited on porous supports. Selectivity can occur with both anions (Cl⁷/SO4²⁻ selectivity as high as 310^{60} in diffusion dialysis) or cations (Na⁺/Mg²⁺ NF

selectivity of 22⁵⁹). The selective removal of divalent ions from monovalent ions effectively reduces the osmotic pressure required in water softening process and thus decreases energy costs.

1.2 Facilitated transport in membrane-based separations

Conventional methods for the removal and recovery of heavy metals from waste streams include chemical precipitation,⁹⁶ adsorption,⁹⁷ solvent extraction,⁹⁸ and ion exchange.⁹⁹ Unfortunately, these methods often suffer from low efficiency, high capital costs and sensitive operating conditions.^{100,101} Membrane-based processes such as reverse osmosis, nanofiltration, and electrodialysis can potentially provide much simpler remediation methods.^{102,103} However, most membrane separations depend on size exclusion or electrostatic exclusion to achieve selectivity and are thus not particularly selective among similarly charged ions. Facilitated transport membranes have emerged as a promising technique for the highly selective separation of some specific ions such as copper, zinc, cobalt, nickel, gold, silver and lanthanides.^{104,105}

1.2.1 Facilitated transport mechanisms

Facilitated transport membranes contain mobile or fixed carriers that selectively and reversibly interact with one ion, the facilitated species, in a mixture. The carriers facilitate transport of the binding species through the membrane to provide high selectivity if other transport mechanisms such as solution-diffusion are slow.¹⁰⁶ A variety of carriers can facilitate different separation processes, e.g. quaternary or tertiary amines, pyridine and derivatives, hydroxyquinoline, carboxylic acids, phosphoric acid esters, crown ethers and calix arenes.¹⁰⁷

Figure 1.4 illustrates facilitated transport with both fixed and mobile carriers. The flux of the facilitated species depends on both the concentration gradient across the membrane and the carrier concentration. Flux increases with increasing feed concentration until the facilitated species saturate the carriers and facilitated transport reaches a maximum rate. In fixed-carrier membranes with different carrier concentrations, a percolation threshold in terms of carrier concentration may appear if the transport occurs only when two carriers are close enough to transfer the facilitated species.¹⁰⁸⁻¹¹⁰



Figure 1.4 Cartoon of facilitated transport through a (left) mobile-carrier liquid membrane and (right) fixed-carrier polymer membrane. The orange smiley faces stand for facilitated species selected by the carriers, and green circles stand for nonbinding species. (Adapted with permission of Elsevier from *J. Membr. Sci.* **2001**, *181*, 97-110).

^{1.2.2} Facilitated transport membranes

Li et al.¹¹¹ first reported the use of a liquid surfactant membrane for the separation of different hydrocarbons via facilitated transport. A liquid membrane contains a thin organic liquid film that separates aqueous feed and receiving phases. Carriers dissolved in the liquid-phase membrane control the permeation of different ions from the feed to the receiving side, enabling higher carrier diffusivity than in solid membranes.¹⁰⁶ The carrier interacts with specific ions and shuttles them through the membrane, as Figure 1.4A illustrates. Several types of liquid membranes, including emulsion liquid membranes, bulk liquid membranes, and supported liquid membranes, can facilitate the separation of metal ions.¹¹² In supported liquid membranes immobilization of the organic phase in the microporous structure of a supporting material through capillary forces increases stability,¹¹³ however the loss of carriers and the organic phase remains the main obstacle in the technical implementation of liquid membranes.^{106,113}

Casting of carriers along with plasticizers in polymer films yields polymer inclusion membranes that may eliminate the challenges of carrier and organic phase loss in liquid membranes. Several studies reported extraction and recovery of ions such as zinc, cadmium, lead and copper using polymer inclusion membranes containing carriers such as crown ethers, and phosphoric acids.^{107,114-116} However these membranes are usually much less permeable than liquid membranes because of the high viscosity and hydrophobicity of the membrane. Another approach to create stable, carrier-containing membranes employs covalent attachment of the carriers to the backbones of the matrix polymer. In these fixed-carrier membranes, transporting species hop through the membrane from site to site as a result of the thermal motions of the polymer chains (see Figure 1.4B).¹⁰⁶ Yoshikawa et al. studied halogen ion transport through synthetic polymeric membranes containing pyridine carriers in the 1980s.¹¹⁷ Other studies examined fixed-carrier transport of ions such as europium, iron, zinc, potassium and sodium with carriers such as phosphonate esters, phosphoric acids, phosphonate esters and pseudo crown ethers.¹¹⁸⁻¹²⁰ However the limited selectivity (<5) among different ions plagued the separation process.

Molecular imprinting has emerged as an attractive strategy to form membranes with well-defined morphologies and pore structures tailored for highly specific separations.¹²¹ An ultrathin, imprinted layer on a highly porous support should lead to increased fluxes with imprinted films. Deng et al.¹²² prepared an ion-selective membrane by cross-linking a polyelectrolyte film (on an ultrafiltration support) in the presence of a template ion. The minimal thickness of the imprinted film afforded improved ion flux, however the selectivity for Cu^{2+}/Zn^{2+} through a Cu^{2+} -imprinted membrane was below 5 and decreased with increasing feed concentration.

Layer by layer deposition also provides a promising method for including specific metal-binding ligands in ultrathin membrane skins. Carrier incorporation can occur through electrostatic adsorption (in the case of charged carriers) or covalently bonding carriers to the polyelectrolyte backbone before deposition. Tieke et al.^{40,123-126} studied selective ion transport through layer-by-layer assembled calixarene/polyelectrolyte membranes, as well as through similar membranes with other macrocyclic compounds such as azacrowns and cyclodextrins (see figure 1.5). Interestingly, they found retarded transport for ions that interact with the complexing agent. Ions that specifically interact

with different calixarenes showed as much as a 2.9-fold lower permeation rate through the calixarene/polyelectrolyte membrane compared to the all-electrolyte PSS/PVA membrane. Examples of ions that experienced retarded transport include Li⁺ through calix4/PVA, Mg²⁺ through calix6/PVA, and transition metal and lanthanide ions through calix8/PVA.⁴⁰ However the displacement of calixarene polyanions by divalent sulfate ions occured, which could cause a loss in ion selectivity or film desorption over time. And the ions with same charge, either monovalent or divalent, exhibited selectivities limited to below 5.



A: anionic polyelectrolyte B: cationic polyazacronw ether or aminocyclodextrin

Figure 1.5 Schematic drawing of layer-by-layer assembly of anionic macrocycles with cationic polyelectrolyte (top) and cationic macrocycles with anionic polyeletrolytes (bottom) on a porous support. (Reproduced with permission of Elsevier from *Thin Solid Films* **2008**, *516* (24), 8814-8820).

1.3 Thesis outline

This thesis examines whether selective, facilitated transport can occur though polyelectrolyte multilayer that contain metal-binding functionalities such as nitrilotriacetate and amines. The minimal thickness (<50 nm) of PEMs on porous support should lead to high fluxes even with fixed carrier transport. Specifically, I first

describe the layer-by-layer deposition of poly[(N,N'-dicarboxymethyl) allylamine] (PDCMAA)/poly(allylamine hydrochloride) (PAH) films at low pH to give a thin film with abundant Cu^{2+} -binding sites. Subsequent diffusion dialysis studies show that when deposited on a porous alumina substrate, (PDCMAA/PAH)_n polyelectrolyte multilayer (PEM) films have average Cu^{2+}/Mg^{2+} selectivities of 50 and 80 for PAH-capped and PDCMAA-capped films, respectively. PDCMAA/PAH membranes also exhibit Cu^{2+}/Ni^{2+} and Cu^{2+}/Ca^{2+} selectivities. The high Cu^{2+}/Mg^{2+} selectivity despite similar aqueous diffusion coefficients and equal charge for the two ions suggests a facilitated transport mechanism. In contrast, PAA/PAH and PSS/PAH films show Cu^{2+}/Mg^{2+} selectivities <10. With PDCMAA/PAH films, Cu²⁺ flux increases nonlinearly with increasing CuCl₂ concentrations in the feed. In typical facilitated transport flux initially increases with feed ion concentration and then reaches a maximum value upon carrier saturation. To investigate the reasons behind the nonlinear relationship between flux and feed ion concentration, I present sorption isotherms for Cu^{2+} . These isotherms show that PDCMAA/PAH films contain both strong and weak binding sites, and the nonlinear increases in flux with increasing feed concentration likely represents hopping between weak binding sites, probably the amine groups of PAH. Strong binding of Cu^{2+} to PDCMAA binding sites may displace ionic cross-links in the film and free amine groups for facilitated transport. Additionally, Cu^{2+} binding to the film suppresses Mg^{2+} transport, either through electrostatic exclusion or removal of hopping sites.

REFERENCES

REFERENCES

(1) Decher, G. Science **1997**, 277, 1232-1237.

(2) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210–211*, *Part* 2, 831-835.

(3) Cheng, C.; Yaroshchuk, A.; Bruening, M. L. *Langmuir* **2013**, *29*, 1885-1892.

(4) Duong, P. H. H.; Zuo, J.; Chung, T. S. J. Membr. Sci. 2013, 427, 411-421.

(5) Vinzenz, X.; Huger, E.; Himmerlich, M.; Krischok, S.; Busch, S.; Wollenstein, J.; Hoffmann, C. J. Colloid Interface Sci. **2012**, *386*, 252-259.

(6) Lazzara, T. D.; Lau, K. H. A.; Abou-Kandil, A. I.; Caminade, A. M.; Majoral, J. P.; Knoll, W. *ACS Nano* **2010**, *4*, 3909-3920.

(7) Carrillo, J. M. Y.; Dobrynin, A. V. *Langmuir* **2012**, *28*, 1531-1538.

(8) Muppalla, R.; Rana, H. H.; Devi, S.; Jewrajka, S. K. Appl. Surf. Sci. 2013, 268, 355-367.

(9) Toth, I. Y.; Illes, E.; Bauer, R. A.; Nesztor, D.; Szekeres, M.; Zupko, I.; Tombacz, E. *Langmuir* **2012**, *28*, 16638-16646.

(10) Shchukina, E. M.; Shchukin, D. G. Curr. Opin. Colloid Interface Sci. 2012, 17, 281-289.

(11) Xu, F.; Geiger, J. H.; Baker, G. L.; Bruening, M. L. *Langmuir* **2011**, *27*, 3106-3112.

(12) Su, X. F.; Kim, B. S.; Kim, S. R.; Hammond, P. T.; Irvine, D. J. *ACS Nano* **2009**, *3*, 3719-3729.

(13) Balabushevich, N. G.; Izumrudov, V. A.; Larionova, N. I. *Polymer Science Series* A **2012**, *54*, 540-551.

(14) Takahashi, S.; Sato, K.; Anzai, J. Anal. Bioanal. Chem. 2012, 402, 1749-1758.

(15) Han, S. T.; Zhou, Y.; Wang, C. D.; He, L. F.; Zhang, W. J.; Roy, V. A. L. Adv. *Mater.* **2013**, *25*, 872-877.

(16) Jiao, Y. H.; Li, Y.; Wang, S.; Zhang, K.; Jia, Y. G.; Fu, Y. *Langmuir* **2010**, *26*, 8270-8273.

(17) Dotzauer, D. M.; Abusaloua, A.; Miachon, S.; Dalmon, J. A.; Bruening, M. L. *Appl. Catal.*, *B* **2009**, *91*, 180-188.

(18) Bhattacharjee, S.; Dotzauer, D. M.; Bruening, M. L. J. Am. Chem. Soc. **2009**, 131, 3601-3610.

- (19) Chen, X. D.; Lang, J.; Liu, M. H. Thin Solid Films 2002, 409, 227-232.
- (20) Ariga, K.; Lvov, Y.; Kunitake, T. J. Am. Chem. Soc. 1997, 119, 2224-2231.

(21) Tedeschi, C.; Caruso, F.; Mohwald, H.; Kirstein, S. J. Am. Chem. Soc. 2000, 122, 5841-5848.

(22) Kotov, N. A. Nanostruct. Mater. 1999, 12, 789-796.

(23) Zhao, Y. P.; Lu, P.; Li, C. T.; Fan, X. P.; Wen, Q. B.; Zhan, Q.; Shu, X.; Xu, T. L.; Zeng, G. M. *Environ. Technol.* **2013**, *34*, 201-207.

(24) Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717-2725.

(25) Wang, L. Y.; Wang, Z. Q.; Zhang, X.; Shen, J. C.; Chi, L. F.; Fuchs, H. *Macromol. Rapid Commun.* **1997**, *18*, 509-514.

- (26) Cao, Y.; He, W. Acta Biomater. 2013, 9, 4558-4568.
- (27) Shen, X. F.; Cui, Y.; Pang, Y. H.; Qian, H. *Electrochim. Acta* **2012**, *59*, 91-99.
- (28) Tang, T. J.; Qu, J. Q.; Mullen, K.; Webber, S. E. *Langmuir* **2006**, *22*, 26-28.
- (29) Broderick, A. H.; Manna, U.; Lynn, D. M. Chem. Mater. **2012**, 24, 1786-1795.

(30) Yang, W. J.; Pranantyo, D.; Neoh, K. G.; Kang, E. T.; Teo, S. L. M.; Rittschof, D. *Biomacromolecules* **2012**, *13*, 2769-2780.

(31) Islam, M. R.; Bach, L. G.; Park, J. M.; Hong, S. S.; Lim, K. T. J. Appl. Polym. Sci. **2013**, *127*, 1569-1577.

(32) Liu, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. Angew. Chem. Int. Ed. Engl. **1997**, *36*, 2114-2116.

(33) Liu, Y. L.; Zhao, M. Q.; Bergbreiter, D. E.; Crooks, R. M. J. Am. Chem. Soc. **1997**, *119*, 8720-8721.

(34) Kohli, P.; Blanchard, G. J. Langmuir 2000, 16, 8518-8524.

(35) Kohli, P.; Blanchard, G. J. *Langmuir* **2000**, *16*, 4655-4661.

(36) Such, G. K.; Quinn, J. F.; Quinn, A.; Tjipto, E.; Caruso, F. J. Am. Chem. Soc. **2006**, *128*, 9318-9319.

(37) Such, G. K.; Tjipto, E.; Postma, A.; Johnston, A. P. R.; Caruso, F. *Nano Lett.* **2007**, *7*, 1706-1710.

(38) Bruening, M. L.; Dotzauer, D. M.; Jain, P.; Ouyang, L.; Baker, G. L. *Langmuir* **2008**, *24*, 7663-7673.

(39) Adusumilli, M.; Bruening, M. L. Langmuir 2009, 25, 7478-7485.

(40) Toutianoush, A.; Schnepf, J.; El Hashani, A.; Tieke, B. Adv. Funct. Mater. 2005, 15, 700-708.

(41) Ma, Y.; Dong, J.; Bhattacharjee, S.; Wijeratne, S.; Bruening, M. L.; Baker, G. L. *Langmuir* **2013**, *29*, 2946-2954.

(42) Schlenoff, J. B.; Ly, H.; Li, M. J. Am. Chem. Soc. 1998, 120, 7626-7634.

(43) Schlenoff, J. B.; Dubas, S. T. *Macromolecules* **2001**, *34*, 592-598.

(44) Wu, B.; Li, C. L.; Yang, H. Y.; Liu, G. M.; Zhang, G. Z. J. Phys. Chem. B 2012, 116, 3106-3114.

(45) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **2001**, *34*, 3736-3740.

(46) Song, S. L.; Liu, H. Y.; Guo, X. H.; Hu, N. F. *Electrochim. Acta* **2009**, *54*, 5851-5857.

(47) Garvey, M. J.; Tadros, T. F.; Vincent, B. J. Colloid Interface Sci. **1976**, 55, 440-453.

(48) Miller, M. D.; Bruening, M. L. Langmuir 2004, 20, 11545-11551.

(49) Schöler, B.; Sharpe, S.; Hatton, T. A.; Caruso, F. *Langmuir* **2004**, *20*, 2730-2738.

(50) Wong, J. E.; Diez-Pascual, A. M.; Richtering, W. *Macromolecules* **2009**, *42*, 1229-1238.

(51) Apaydin, K.; Laachachi, A.; Bour, J.; Toniazzo, V.; Ruch, D.; Ball, V. Colloids Surf. Physicochem. Eng. Aspects **2012**, 415, 274-280.

(52) Bhattacharjee, S.; Dong, J.; Ma, Y.; Hovde, S.; Geiger, J. H.; Baker, G. L.; Bruening, M. L. *Langmuir* **2012**, *28*, 6885-6892.

(53) Guzman, E.; Ritacco, H.; Rubio, J. E. F.; Rubio, R. G.; Ortega, F. Soft Matter **2009**, *5*, 2130-2142.

- (54) Lundstrom-Hamala, L.; Johansson, E.; Wagberg, L. *Starch/Stärke* **2010**, *62*, 102-114.
- (55) Blomberg, E.; Poptoshev, E.; Caruso, F. *Langmuir* **2006**, *22*, 4153-4157.
- (56) Schöler, B.; Kumaraswamy, G.; Caruso, F. Macromolecules 2002, 35, 889-897.
- (57) Farhat, T. R.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 1184-1192.

(58) El Haitami, A. E.; Martel, D.; Ball, V.; Nguyen, H. C.; Gonthier, E.; Labbe, P.; Voegel, J. C.; Schaaf, P.; Senger, B.; Boulmedais, F. *Langmuir* **2009**, *25*, 2282-2289.

- (59) Ouyang, L.; Malaisamy, R.; Bruening, M. L. J. Membr. Sci. 2008, 310, 76-84.
- (60) Harris, J. J.; Stair, J. L.; Bruening, M. L. Chem. Mater. 2000, 12, 1941-1946.
- (61) Krasemann, L.; Tieke, B. *Langmuir* **2000**, *16*, 287-290.
- (62) Sun, B.; Jewell, C. M.; Fredin, N. J.; Lynn, D. M. Langmuir 2007, 23, 8452-8459.
- (63) Sui, Z. J.; Salloum, D.; Schlenoff, J. B. *Langmuir* **2003**, *19*, 2491-2495.
- (64) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153-8160.
- (65) Khopade, A. J.; Caruso, F. Langmuir 2002, 18, 7669-7676.
- (66) Yoo, D.; Shiratori, S. S.; Rubner, M. F. *Macromolecules* **1998**, *31*, 4309-4318.
- (67) Aulin, C.; Varga, I.; Claessont, P. M.; Wagberg, L.; Lindstrom, T. *Langmuir* **2008**, *24*, 2509-2518.
- (68) Schöler, B.; Poptoschev, E.; Caruso, F. *Macromolecules* **2003**, *36*, 5258-5264.

(69) Moussallem, M. D.; Olenych, S. G.; Scott, S. L.; Keller, T. C. S.; Schlenoff, J. B. *Biomacromolecules* **2009**, *10*, 3062-3068.

(70) Lvov, Y.; Yamada, S.; Kunitake, T. *Thin Solid Films* **1997**, *300*, 107-112.

(71) Garg, A.; Heflin, J. R.; Gibson, H. W.; Davis, R. M. *Langmuir* **2008**, *24*, 10887-10894.

(72) Bruening, M. L.; Sullivan, D. M. Chem. Eur. J. 2002, 8, 3832-3837.

(73) Balachandra, A. M.; Dai, J. H.; Bruening, M. L. *Macromolecules* **2002**, *35*, 3171-3178.

(74) Stair, J. L.; Harris, J. J.; Bruening, M. L. Chem. Mater. 2001, 13, 2641-2648.

(75) Stanton, B. W.; Harris, J. J.; Miller, M. D.; Bruening, M. L. *Langmuir* **2003**, *19*, 7038-7042.

(76) Toutianoush, A.; Tieke, B. Mater. Sci. Eng., C 2002, 22, 135-139.

(77) Dai, J. H.; Balachandra, A. M.; Lee, J. I.; Bruening, M. L. *Macromolecules* **2002**, *35*, 3164-3170.

(78) Johnston, A. P. R.; Cortez, C.; Angelatos, A. S.; Caruso, F. Curr. Opin. Colloid Interface Sci. 2006, 11, 203-209.

(79) Ai, H.; Jones, S. A.; Lvov, Y. M. Cell Biochem. Biophys. 2003, 39, 23-43.

(80) Liu, X. Y.; Gao, C. Y.; Shen, J. C.; Mohwald, H. *Macromol. Biosci.* **2005**, *5*, 1209-1219.

(81) Balabushevich, N. G.; Sukhorukov, G. B.; Larionova, N. I. Macromol. Rapid Commun. 2005, 26, 1168-1172.

(82) Smuleac, V.; Butterfield, D. A.; Bhattacharyya, D. *Langmuir* **2006**, *22*, 10118-10124.

(83) Dotzauer, D. M.; Dai, J. H.; Sun, L.; Bruening, M. L. Nano Lett. **2006**, *6*, 2268-2272.

(84) Priya, D. N.; Modak, J. M.; Raichur, A. M. ACS Appl. Mater. Interfaces. 2009, 1, 2684-2693.

(85) Wiemann, L. O.; Buthe, A.; Klein, M.; van den Wittenboer, A.; Dahne, L.; Ansorge-Schumacher, M. B. *Langmuir* **2009**, *25*, 618-623.

(86) Farhat, T. R.; Hammond, P. T. Adv. Funct. Mater. 2005, 15, 945-954.

(87) Jiang, S. P.; Liu, Z. C.; Tian, Z. Q. Adv. Mater. 2006, 18, 1068-+.

(88) Argun, A. A.; Ashcraft, J. N.; Hammond, P. T. Adv. Mater. 2008, 20, 1539-+.

(89) Lenk, W.; Meier-Haack, J. Desalination 2002, 148, 11-16.

(90) Meier-Haack, J.; Lenk, W.; Lehmann, D.; Lunkwitz, K. J. Membr. Sci. 2001, 184, 233-243.

- (91) van Ackern, F.; Krasemann, L.; Tieke, B. Thin Solid Films 1998, 327, 762-766.
- (92) Rmaile, H. H.; Schlenoff, J. B. J. Am. Chem. Soc. 2003, 125, 6602-6603.
- (93) Hong, S. U.; Bruening, M. L. J. Membr. Sci. 2006, 280, 1-5.
- (94) Hong, S. U.; Malaisamy, R.; Bruening, M. L. J. Membr. Sci. 2006, 283, 366-372.
- (95) Hollman, A. M.; Bhattacharyya, D. Langmuir 2004, 20, 5418-5424.
- (96) Geoffroy, N.; Demopoulos, G. P. J. Hazard. Mater. 2011, 185, 148-154.
- (97) Liang, S.; Guo, X. Y.; Tian, Q. H. Desalination 2011, 275, 212-216.
- (98) Parhi, P. K.; Park, K. H.; Kim, H. I.; Park, J. T. *Hydrometallurgy* **2011**, *105*, 195-200.
- (99) Leao, V. A.; Ciminelli, V. S. T. Solvent Extr. Ion Exch. 2000, 18, 567-582.
- (100) Kurniawan, T. A.; Chan, G. Y. S.; Lo, W. H.; Babel, S. *Chem. Eng. J.* **2006**, *118*, 83-98.
- (101) Ahluwalia, S. S.; Goyal, D. Eng. Life Sci. 2005, 5, 158-162.
- (102) Cussler, E. L.; Dutta, B. K. AlChE J. 2012, 58, 3825-3831.
- (103) Drioli, E.; Stankiewicz, A. I.; Macedonio, F. J. Membr. Sci. 2011, 380, 1-8.
- (104) Arous, O.; Gherrou, A.; Kerdjoudj, H. Desalination 2004, 161, 295-303.
- (105) Arous, O.; Kerdjoudj, H.; Seta, P. J. Membr. Sci. 2004, 241, 177-185.

(106) Ferraz, H. C.; Duarte, L. T.; Di Luccio, M.; Alves, T. L. M.; Habert, A. C.; Borges, C. P. *Braz. J. Chem. Eng.* **2007**, *24*, 101-118.

(107) Nghiem, L. D.; Mornane, P.; Potter, I. D.; Perera, J. M.; Cattrall, R. W.; Kolev, S. D. J. Membr. Sci. **2006**, 281, 7-41.

- (108) Cussler, E. L.; Aris, R.; Bhown, A. J. Membr. Sci. 1989, 43, 149-164.
- (109) Noble, R. D. J. Membr. Sci. 1991, 56, 229-234.
- (110) Noble, R. D. J. Membr. Sci. 1992, 75, 121-129.

- (111) Li, N. N. AlChE J. 1971, 17, 459-463.
- (112) Parhi, P. K. Journal of Chemistry 2013.

(113) Kemperman, A. J. B.; Bargeman, D.; van den Boomgaard, T.; Strathmann, H. Sep. Sci. Technol. **1996**, *31*, 2733-2762.

(114) Gherasim, C.-V. I.; Bourceanu, G.; Olariu, R.-I.; Arsene, C. J. Membr. Sci. 2011, 377, 167-174.

(115) Kavitha, N.; Palanivelu, K. J. Membr. Sci. 2012, 415-416, 663-669.

(116) Ulewicz, M.; Sadowska, K.; Biernat, J. F. Desalination 2007, 214, 352-364.

(117) Yoshikawa, M.; Yatsuzuka, Y.; Sanui, K.; Ogata, N. *Macromolecules* **1986**, *19*, 995-998.

(118) Vasudevan, T.; Das, S.; Debnath, A. K.; Pandey, A. K. J. Membr. Sci. 2009, 342, 113-120.

(119) Thunhorst, K. L.; Noble, R. D.; Bowman, C. N. J. Membr. Sci. 1997, 128, 183-193.

(120) Elliott, B. J.; Willis, W. B.; Bowman, C. N. J. Membr. Sci. 2000, 168, 109-119.

(121) Ulbricht, M. J. Chromatogr. B 2004, 804, 113-125.

(122) Deng, H.; Gao, L.; Zhang, S.; Yuan, J. Ind. Eng. Chem. Res 2012, 51, 14018-14025.

(123) El-Hashani, A.; Tieke, B. J. Nanosci. Nanotechnol. 2006, 6, 1710-1717.

(124) Tieke, B.; El-Hashani, A.; Toutianoush, A.; Fendt, A. *Thin Solid Films* **2008**, *516*, 8814-8820.

(125) Tieke, B.; Toutianoush, A.; Jin, W. Q. Adv. Colloid Interface Sci. 2005, 116, 121-131.

(126) Toutianoush, A.; El-Hashani, A.; Schnepf, J.; Tieke, B. Appl. Surf. Sci. 2005, 246, 430-436.

Chapter 2

Facilitated Ion Transport through Polyelectrolyte Multilayer Films Containing Metal-binding Ligands

2.1 Introduction

Layer-by-layer adsorption of oppositely charged polyelectrolytes^{1,2} offers a simple and versatile way to form functional thin films on porous membrane supports. Moreover, variation of the multilayer composition, 3,4 deposition conditions $^{5-7}$ and post-deposition treatment $^{8-10}$ affords control over the thickness, permeability and charge density of the polyelectrolyte multilayers (PEMs). Previous studies investigated the transport properties of PEM-coated membranes in pervaporation,¹¹⁻¹⁶ gas separation,¹⁶⁻¹⁸ and various separations with dissolved ions.¹⁹⁻²² In particular, in nanofiltration²³⁻²⁵ PEMs allow selective transport of monovalent ions over multivalent ions, which is important in water softening.^{18,25} The monovalent/divalent ion selectivity may stem from differences in ion hydration or electrostatic exclusion.²⁶ However, for ions with the same charge and similar hydrated radii, e.g. Cu^{2+} and Mg^{2+} , PEMs will likely show minimal selectivity. Nevertheless with appropriate selectivity and permeability, membrane-based processes should be attractive for such separations due to their high efficiency and low energy cost^{27,28} compared to the conventional methods such like precipitation,^{29,30} flotation,³¹ evaporation,³² ion exchange,³³ adsorption^{34,35} or solvent extraction.^{36,37}

Facilitated transport through membranes can address the challenge of obtaining selectivity when separating ions with the same charge and similar hydrated radii. This type of transport relies on ion complexation in the membrane and subsequent transport

either by ligand diffusion across the membrane or ion hopping between immobile binding sites.³⁸⁻⁴¹ The development of facilitated transport membranes has progressed from liquid membranes⁴² to supported liquid membranes,^{43,44} to polymer inclusion membranes⁴⁵ and molecularly imprinted membranes.⁴⁶ However, most membranes still suffer from limited stability, selectivity or permeability. PEM membranes may overcome some of the stability issues that plague liquid membranes, and the minimal thickness of these films will enhance permeance relative to thicker solid membranes.

Development of facilitated transport through PEMs will require polyelectrolytes that bind metal ions and allow hopping between binding sites. Additionally, the rate of simple diffusion through these films must be much lower than the rate of facilitated transport. Tieke et al.^{4,19,47-49} reported the formation of membranes through alternating adsorption of charged macrocyclic compounds, e.g. calixarenes, azacrowns and cyclodextrins, and oppositely charged polyelectrolytes. However, ions that specifically interacted with the macrocycles passed through these membranes more slowly than ions that did not interact with the macrocycles. Additionally, the selectivities among ions with the same charge, either monovalent or divalent, were <5.

This paper reports the formation of membranes through layer-by-layer adsorption of poly[(N,N'-dicarboxymethyl) allylamine] (PDCMAA) and poly(allylamine hydrochloride) (PAH). PDCMAA contains many iminodiacetic acid (IDA) groups that should strongly bind Cu^{2+} , and at suitably high concentrations, Cu^{2+} may also interact with the amine groups of PAH. Remarkably, these membranes show Cu^{2+}/Mg^{2+} diffusion dialysis selectivities 50. We compare through around transport

(PDCMAA/PAH)₄, (poly (acrylic acid) (PAA)/PAH)₄, and (poly (sodium 4-styrenesulfonate) (PSS)/PAH)₄ films, and only films containing PDCMAA show selectivities >10. Measurements of transport rates as a function of feed concentration and Cu^{2+} sorption isotherms suggest that facilitated transport occurs via the amine sites in (PDCMAA/PAH)₄ films.

2.2 Experimental

2.2.1 Materials

Poly(allylamine hydrochloride) (PAH, M_w =120,000~200,000 Da) and poly(acrylic acid) (PAA, M_w =100,000 Da) were purchased from Polysciences. Poly(sodium 4-styrenesulfonate) (PSS, M_w =70,000 Da), 3-mercaptopropionic acid (MPA) and were obtained from Sigma-Aldrich. Ethylenediaminetetraacetate acid disodium salt (EDTA-Na2) was purchased from Jade Scientific. All reagents were used without further purification. Deionized water (18 M Ω cm, Milli-Q) was used to prepare all the aqueous solutions. Alumina membrane supports (Anodisc, pore diameter = 0.02 μ m) were purchased from Whatman. Colloidal silica nanoparticles (70-100 nm, SNOWTEX-ZL) were purchased from Nissan Chemical Industries, Japan.

2.2.2 Film preparation and characterization

PEM films were first deposited on Au-coated (200 nm of Au sputtered on 20 nm of Cr on Si(100)) wafers. The Au-coated wafer was cleaned with UV/ozone for 15 min before a

30-min immersion in MPA solution (5mM), followed by rinsing with ethanol and then water for 1 min each, and drying under a N_2 stream. The MPA-modified wafer was immersed in a PAH solution for 5 min, rinsed with water from a squirt bottle for 1 min, immersed in a polyanion solution (PSS or PAA or PDCMAA) for 5 min, and rinsed again. The dip-and-rinse process was continued to deposit the desired number of polyelectrolyte bilayers. Adsorption of PEMs on porous alumina membranes followed essentially the same procedure starting with the polyanion. The alumina membrane was placed in a holder that exposed only the top of the membrane to the solutions. All polyelectrolyte solutions contained 0.01 M polymer repeating unit and 0.5 M NaCl. The pH of these solutions was adjusted to the desired pH of 3 with 0.1 M HCl or 0.1 M NaOH.

In modification of silica nanoparticles, 500 mL of a 0.02 M PAH solution (pH=3) was added to 1 g of silica colloid suspension. The samples were sonicated for 15 min, and the adsorption solution was left to stand for a minimum time of 30 min with continuous stirring. The solution was then centrifuged for 30 min at 6000 rpm. After the supernatant was removed, 500 mL of water was added to the sample, and the solution was sonicated for 5 min. The supernatant was removed again to rinse the unabsorbed polyelectrolyte from the colloids. 500 mL of a 0.01 M PDCMAA solution (pH=3) was then added to the remaining colloidal solution. Similar adsorption and washing steps were performed until films of ten PAH-PDCMAA bilayers had been prepared.

Thicknesses of films deposition on Au-coated wafers were determined using a rotating analyzer ellipsometer (J.A. Woollam model M-44), assuming a 1.5 refractive

index for the dry films. Films in water have a smaller refractive index ranging from 1.3 to 1.5. Fourier transform infrared spectroscopy (FT-IR) spectra of these films were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer (80 °incident angle in a Pike grazing angle holder) with a MCT detector. A UV/ozone cleaned Au-coated wafer served as a background. Ultraviolet-visible (UV-Vis) spectra were acquired with a PerkinElmer UV/VIS spectrophotometer (Lambda 25).

2.2.3 Diffusion dialysis

Diffusion dialysis studies were carried out in a home-made apparatus that consists of feed and permeate chambers separated by a membrane with the PEM facing the feed solution.⁸ Initially, 90 mL of salt solution and 90 ml of deionized water were added to the feed and permeate chambers, and the two solutions were stirred vigorously. For analyses, one-mL aliquots were removed from the permeate approximately every 5 min for 40~60 min. To balance the water level in the two chambers, one mL of feed solution was simultaneously removed from the feed. The permeate aliquots were diluted 10-fold with 2% nitric acid and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (Axial ICP-OES, Varian 710-ES). Over the course of the experiment, the salt concentration in the permeate is always small compared to that in the feed so the slope in a plot of permeate ion concentration versus time can be used to calculate the ion flux, taking into account the permeate volume and membrane area (2.1 cm²).

2.2.4 Sorption studies

Sorption studies were carried out with (PDCMAA/PAH)₁₀-modified nanoparticles. The high surface area of the nanoparticles and large number of bilayers gives the high number of binding sites needed for these studies. The modified nanoparticles were dried and ground into a fine powder with a mortar and pestle (dried, modified nanoparticles tend to aggregate). Weighed amounts of nanoparticles (0.1 g to 0.4 g) were then mixed with fixed volumes (1 mL or 5 mL) of source solutions with varied Cu²⁺ concentrations, and incubated overnight at room temperature. The mass of the nanoparticles and solution volume were chosen to achieve sorption of at least 20% of the Cu²⁺ in the loading solution. Sorption of Cu²⁺ on bare nanoparticles was 10-20% of that on the modified particles. The total sorption was determined from ICP-OES analysis of the Cu²⁺ concentration in the source solution before and after sorption.

After sorption, the residual solution was decanted and the nanoparticles were rinsed with 1.5 ml of deionized water three times to remove the remaining solution and the weakly adsorbed ions. These particles were dried under vacuum and subsequently mixed with 1 mL of 0.1 M EDTA (pH=6.4) and incubated overnight. The resulting eluate was diluted and analyzed by atomic absorption spectroscopy (AAS, Varian AA240) because EDTA may precipitate in acid and clog the ICP sampling system which typically employs 2% nitric acid as a solvent. The Cu²⁺ adsorption calculated from either the loading or eluate solutions was normalized by the initial mass of nanoparticles and then plotted against the equilibrium (residual loading solution) concentration to give the sorption isotherm.

2.3 Results and discussion

2.3.1 Preparation and characterization of Cu²⁺-binding PDCMAA/PAH films



Figure 2.1 Structures of the polymers employed to prepare PEMs.

Figure 2.1 shows the structure of the polymers we employed to create thin polyelectolyte films on porous alumina supports. Partial deprotonation of PAA and PDCMAA allows their adsorption as polyanions. Prior studies²⁶ demonstrated adsorption of PEMs using PAH as a polycation and PSS, PAA, or PDCMAA as the polyanion. For both PAA and PDCMAA, film thickness varies with adsorption pH, and we chose to deposit these films at pH 3 both to achieve a relatively high thickness and to create free – COOH groups for subsequent metal-ion complexation. At this deposition pH, (PAH/PAA)₄ and (PAH/PDCMAA)₄ films adorbed on MPA-modified gold-coated wafers have dry thicknesses of 26 and 42 nm, respectively. The corresponding (PAH/PSS)₄ films are only 11 nm thick.

In-solution UV-Vis spectra (Figure 2.2) demonstrate that PSS, PAH, PAA, and PDCMAA have very different affinities for Cu^{2+} in solutions at pH 3.6. (This is the approximate pH of a 0.1 M CuCl₂ solution.) Although for the spectra in Figure 2.2 the polymer repeat unit is in a 10-fold excess with respect to the 1 mM CuCl₂, the presence

of PAH or PSS does not significantly alter the UV-vis spectrum of the solution, showing that complexes between PAH or PSS and Cu^{2+} do not form at this pH. In contrast, the formation of PAA- Cu^{2+} and PDCMAA- Cu^{2+} complexes gives rise to dramatic changes in the Cu^{2+} UV-Vis spectrum.



Figure 2.2 UV-VIS spectra of 1 mM Cu^{2+} in water or aqueous solutions containing various polyelectrolytes. The concentration of the polyelectrolyte repeat units was 10 mM, and the solution pH was 3.6.

Reflectance FT-IR spectra of (PAH/PDCMAA) films on gold (Figure 2.3) provide evidence for Cu^{2+} sorption in these films. After Cu^{2+} sorption, the split COO⁻ peak at around 1589 cm⁻¹ and 1645 cm⁻¹ shifts and merges into the peak observed around 1600 cm⁻¹. The shoulder due to the -COOH carbonyl stretch (~ 1720 cm⁻¹) also decreases in intensity after Cu²⁺ sorption. Elution of Cu²⁺ from the film using an EDTA solution and subsequent equilibration in pH 3 water returns the spectrum to essentially its initial intensities.



Figure 2.3 Reflectance FT-IR spectra of a $(PAH/PDCMAA)_{3.5}$ film on Au wafter before and after immersion in 0.1 M CuCl₂ solution (pH=3.6), and after subsequent immersion in 0.1 M EDTA solution (pH=6.4).

2.3.2 Selective Cu^{2+} transport through (PDCMAA/PAH)_n films adsorbed on porous alumina

As Table 2.1 shows, the equilibrium constant for formation of Cu^{2+} -iminodiacetic acid (IDA) complexes is >7 orders of magnitude higher than the corresponding constant for Mg²⁺-IDA. Similarly, binding constants for formation of Cu²⁺-ethylenediamine (en) complexes are also many orders of magnitude higher than for Mg²⁺. Thus if ion transport through (PDCMAA/PAH)_n films involves hopping between ion-binding sites, Cu²⁺ should move through the film with the exclusion of Mg²⁺.

Table 2.1 Ion diffusion coefficients⁵⁰ and equilibrium constants for formation* of ligand-metal ion complexes.⁵¹

Ions	Cu ²⁺	Ni ²⁺	Ca ²⁺	${\rm Mg}^{2+}$
Diffusion Coefficient $(10^{-5} \text{ cm}^2/\text{s})$	0.714	0.661	0.792	0.706
Formation Constant (IDA-M ²⁺ , log K)	10.63	8.19	2.59	2.94
Formation Constant (en-M ²⁺ , log K)	10.71	7.47	-	0.37

*Temperature (T) and ionic strength (I) are 20 °C and 0.1 for IDA-M²⁺, 25 °C and 0.5 for en-M²⁺.

Figure 2.4 presents permeate ion concentrations as a function of time during diffusion dialysis through porous alumina membranes coated with (PDCMAA/PAH)₄ and (PDCMAA/PAH)₃PDCMAA films. The feed solution contained 0.1 M CuCl₂ and 0.1 M MgCl₂, and the receiving phase was initially deionized water. Based on the slopes of linear fits to the data in Figure 2.4, Cu²⁺ diffuses through these membranes 43-fold and 64-fold faster than Mg²⁺ for (PDCMAA/PAH)₄ and (PDCMAA/PAH)₃PDCMAA, respectively. The aqueous diffusion coefficients of Cu²⁺ and Mg²⁺ differ by only 1%, so this high Cu²⁺/Mg²⁺ selectivity most likely reflects selective Cu²⁺ binding to functional groups in the film and not size-based selectivity. Regardless of whether films terminate with PDCMAA or PAH, they show high Cu²⁺/Mg²⁺ selectivities. Hence, if facilitated transport is responsible for the high selectivity, it does not require a large excess of PDCMAA at the membrane surface.



Figure 2.4 Evolution of permeate concentrations with time during diffusion dialysis of 0.1 M CuCl₂, 0.1 M MgCl₂ solutions through (PDCMAA/PAH)_n-modified porous alumina membranes. The permeate initially contained deionized water. Filled and open symbols represent dialysis through (PDCMAA/PAH)₄- and (PDCMAA/PAH)₃PDCMAA-modified membranes, respectively.

The formation constants for IDA- and en-metal ion complexes also suggest that PDCMAA/PAH films should exhibit Cu^{2+}/Ni^{2+} and Cu^{2+}/Ca^{2+} selectivity in diffusion dialysis. As Figure 2.5 shows, a (PDCMAA/PAH)₄-coated membrane with a Cu^{2+}/Mg^{2+} selectivity of 20 also shows Cu^{2+}/Ca^{2+} and Cu^{2+}/Ni^{2+} selectivities >5. Because replicate membranes show some variation in flux and selectivity, which may result from the variability of the alumina substrates, in Figure 2.5 we compared selectivities with a single membrane. Given that both the Cu^{2+} -IDA and Cu^{2+} -en formation constants are at least 250-fold greater than the formations constants of other ions, we think that passage of the other ions may include diffusion through imperfect regions of the film. The Ca^{2+} flux is higher than the Mg^{2+} and Ni^{2+} fluxes, perhaps because of the higher aqueous diffusion coefficient (smaller hydrated ion size) for Ca^{2+} . Among Cu^{2+} , Ni^{2+} , Ca^{2+} , and Mg^{2+} ,

 Ni^{2+} has the second highest affinity for IDA and amines, but its low rate of transport likely reflects a non-facilitated pathway. However, the Cu^{2+} flux is lowest with the solution containing Ni²⁺, suggesting some competition for binding sites between Ni²⁺ and Cu²⁺.



Figure 2.5 Evolution of permeate concentrations with time during diffusion dialysis of 0.1 M CuCl₂, 0.1 M MCl₂ (M=Mg, Ca or Ni) solutions through (PDCMAA/PAH)₄-modified porous alumina membranes. The permeate initially contained deionized water. This membrane was the least selective (Cu²⁺/Mg²⁺ = 20) of those we examined.

2.3.3 Comparison of fluxes and selectivities in mixed and single-salt diffusion through several types of polyelectrolyte multilayer films

If Cu^{2+} binding to coordination sites limits the transport of other ions through polyelectrolyte films, ion fluxes and selectivities based on diffusion dialysis with single and mixed salts should differ greatly. Table 2.2 compares single- and mixed-salt selectivities in diffusion dialysis through bare alumina membranes and alumina coated with (PDCMAA/PAH)₄, (PDCMAA/PAH)₃PDCMAA, (PAA/PAH)₄ and (PSS/PAH)₄ films. In the control experiment with bare porous alumina, the Cu²⁺ and Mg²⁺ fluxes are the same within experimental uncertainty, regardless of whether the feed solutions contain single or mixed salts. Thus the transport selectivity through the PEM-modified membranes results exclusively from the PEMs. Membranes coated with any of the polyelectrolyte films show significant Cu²⁺/Mg²⁺ selectivities in mixed-salt solutions. Nevertheless, selectivities are much higher for the (PDCMAA/PAH)₄ and (PDCMAA/PAH)₃PDCMAA films relative to the other PEMs.

Comparison of ion fluxes in single- and mixed-salt solutions provides further evidence for Cu^{2+} complexation in (PDCMAA/PAH)₄, (PDCMAA/PAH)₃PDCMAA, and (PAA/PAH)₄ films. For membranes coated with these films, Cu^{2+} fluxes with mixed and single-salt feed solutions differ by a factor less than 2, but the Mg²⁺ fluxes decrease more than an order of magnitude in the presence of CuCl₂. Binding of Cu²⁺ may remove Mg²⁺ hopping transport pathways in the film, but it could also introduce positive charge that contributes to electrostatic exclusion of divalent cations from the membrane. In contrast to PDCMAA/PAH and PAA/PAH systems, ion transport through (PSS/PAH)₄ films shows little difference between single- and mixed salt solutions. Presumably this reflects minimal Cu²⁺ complexation by PSS.

Table 2.2 Cu^{2+} and Mg^{2+} fluxes (10⁻¹⁰ mol cm⁻² s⁻¹) and Cu^{2+}/Mg^{2+} selectivities in diffusion dialysis through bare and PEM-modified alumina membranes. Dialysis employed either single- or mixed-salt solutions^a in the feed.

Film Composition	Mg ²⁺ (single)	Cu ²⁺ (single)	Mg ²⁺ (mixed)	Cu ²⁺ (mixed)	Cu ²⁺ /Mg ²⁺ Selectivity ^b
Bare Substrate	302±46	273±44	275±21	264±19	1.04±0.02
(PDCMAA/PAH) ₄	8.8±3.0	3.6±0.9	0.16±0.10	6.1±0.7	51±32
(PDCMAA/PAH) _{3.5}	20.4±4.9	3.1±1.1	0.075 ± 0.0022	5.9±1.9	82±35
(PAA/PAH) ₄	164±43	5.6±3.0	1.0±1.2	3.8±1.8	6.9±4.8
(PSS/PAH) ₄	9.3±8.0	22.9±2.4	6.6±4.2	24.0±8.5	4.2±1.6

^aThe pH values of the feed solutions were 6.4, 3.6, and 3.6 for 0.1 M MgCl₂, 0.1 M CuCl₂, and a mixture containing 0.1 M MgCl₂ and 0.1 M CuCl₂, respectively. ^bSelectivity was calculated based on mixed-salt fluxes, and the uncertainty is the standard deviation of selectivities for 3 different membranes.

In addition to the formation of Cu^{2+} complexes, decreases in the feed solution pH from 6.4 to 3.6 upon addition of 0.1 M CuCl₂ might alter Mg^{2+} fluxes. To test this possibility, we adjusted the pH of 0.1 M MgCl₂ feed solutions with HCl and performed shows, diffusion dialysis. 2.3 for (PDCMAA/PAH)₄ As Table and $(PDCMAA/PAH)_3PDCMAA$ films, the feed pH does not significantly change the Mg²⁺ flux. This insensitivity of Mg^{2+} permeability to pH may reflect the pKa values of PDCMAA. The pKa values for the -COOH groups of IDA are 2.6 and 1.8. Presuming that in PDCMAA/PAH films the -COOH pKa values are similar, they lie out of the range of the feed solution pH change (from 6.4 to 3.6). The FTIR spectra in Figure 2.3

confirm that –COOH groups in PDCMAA/PAH films are nearly all deprotonated. Thus, for PDCMAA/PAH films the primary effect of $CuCl_2$ on the Mg^{2+} flux should stem from complexation.

In contrast, PAA/PAH films show a 20- to 30-fold decrease in Mg^{2+} flux after changing the feed solution pH from 6.4 to 3.6 (Table 2.3). A second exposure to 0.1 M MgCl₂ at pH 6.4 restores nearly all of the flux. The decrease in flux at low pH likely reflects a structural change⁵² induced by the protonation of PAA side chains (the pKa of PAA in solution is around 6.5 and is shifted to around 2.0 in PAA/PAH film^{52,53}). Unfortunately the large variation in fluxes through PSS/PAH membranes prevents a conclusion on the effect of pH (Table 2.3), but Table 2.2 shows that the Mg²⁺ flux did not change significantly in the presence of Cu²⁺. The degree of protonation of either PAH (pKa in the range of 8-9^{52,54}) or PSS (pKa of protonated PSS around 1.0⁵⁵) will not change greatly on going from pH 6.4 to pH 3.6.

	Feed solution pH				
Film Composition	6.4	3.6	6.4 ^b		
(PDCMAA/PAH) ₄	8.8±3.0	12.0±4.2	7.1±2.6		
(PDCMAA/PAH) _{3.5}	20.4±4.9	24.4±4.2	43.2±9.7		
(PAA/PAH) ₄	164±43	5.4±4.9	116±56		
(PSS/PAH) ₄	9.3±8.0	8.1±7.2	8.9±7.9		

Table 2.3 Mg^{2+} fluxes $(10^{-10} \text{ mol cm}^{-2} \text{s}^{-1})$ as a function of feed^a pH during diffusion dialysis through PEM-modified porous alumina membranes.

^aThe feed solution contained 0.1 M MgCl₂.

^bAfter exposure of the film to pH 3.6 feed solution.

The effect of CuCl₂ on the Mg²⁺ flux through (PDCMAA/PAH)₄, (PDCMAA/PAH)₃PDCMAA, and (PAA/PAH)₄ films is reversible, but only fully reversible after eluting Cu²⁺ from the film. As Table 2.4 shows, after experiments with feed solutions containing 0.1 M CuCl₂ and 0.1 M MgCl₂, diffusion dialysis of just 0.1 M MgCl₂ yields Mg²⁺ fluxes lower than in the same experiment with a fresh membrane. Subsequent exposure of membranes to EDTA (pH=6.4) restores Mg²⁺ fluxes in diffusion dialysis, further suggesting that Cu²⁺ adsorption inhibits Mg²⁺ flux. This kind of gate effect accompanying facilitated transport also occurs in molecularly imprinted facilitated transport membranes.⁴⁶ For PAA/PAH films, the Mg²⁺ flux reduction with CuCl₂ in the feed solution is on the same level as flux reduction at pH 3.6 (compare Tables 2.3 and 2.4). However, the effects of the CuCl₂ solution did not dissipate until after EDTA elution of adsorbed Cu²⁺ from the film. Complexation of Cu²⁺ may stabilize changes in film structure at low pH. **Table 2.4** Mg²⁺ fluxes $(10^{-10} \text{ mol cm}^{-2} \text{s}^{-1})$ in sequential diffusion dialysis with single and mixed salts.

Film Composition	Before Cu ²⁺ exposure ^a	Mixed with Cu ^{2+b}	After Cu ²⁺ exposure ^c	After EDTA elution ^d
(PDCMAA/PAH) ₄	8.8±3.0	0.16±0.10	0.73±0.27	12.5±1.2
(PDCMAA/PAH) _{3.5}	20.4±4.9	0.075 ± 0.0022	2.4±1.6	14.0±9.0
(PAA/PAH) ₄	164±43	1.0±1.2	9.6±2.1	145±35
(PSS/PAH) ₄	9.3±8.0	6.6±4.2	7.0±5.0	11.1±9.7

^aDiffusion dialysis of 0.1 M MgCl₂ with a freshly prepared membrane. ^bSubsequent diffusion dialysis of 0.1 M MgCl₂, 0.1 M CuCl₂.

^cDiffusion dialysis of 0.1 M MgCl₂ after dialysis of the mixed salt solution.

^dDiffusion dialysis of 0.1 M MgCl₂ after immersion the same membrane in 0.1 M EDTA (pH=6.4) for 30 min and rinsing with deionized water.

2.3.4 PEM thickness and swelling

Assuming a constant diffusion coefficient through a polyelectrolyte film and minimal mass transport resistance in the alumina support, the diffusive flux through a PEM-coated membrane is inversely proportional to the PEM thickness. Figure 2.6 shows the ellipsometric thicknesses of PEMs after a series of different treatment. The PEMs were adsorbed on a modified gold-coated substrate to facilitate ellipsometric studies. Soaking the film in water for 1 hour and determination of the film thicknesses in water leads to an increase of ~40% in thickness compared to dry films for PSS/PAH and PDCMAA/PAH, and ~20% for PAA/PAH. Immersion of PEMs in 0.1 M CuCl₂ and subsequent determination of the film thickness in deionized water leads to a small but not statistically

significant increase in film thickness. Thus the inhibition of Mg^{2+} flux after Cu^{2+} adsorption for PDCMAA/PAH and PAA/PAH likely does not stem from a change in film swelling.

However, the thickness of PAA/PAH films in deionized water decreases about 50% after immersion in 0.1 M EDTA solution. The shrinkage may stem from deprotonation of carboxylic acid groups, which leads to film reconstruction and possible deswelling⁵⁶ as the charge density on the PAA chain increases. The swollen thickness of PAA/PAH films after exposure to EDTA was recoverable after prolonged soaking in pH 3 water. The dry thickness of the film and FT-IR peak intensity remained relatively constant after exposure to EDTA, which precludes the loss of PEM film upon elution. For the PDCMAA/PAH film, the pH of the EDTA solution was not high enough to trigger a large scale deprotonation on the PDCMAA chain (pKa of both COOH groups < 3), so that the film structure remained stable in the process.



Figure 2.6 Ellipsometric thicknesses (Å) of PEMs adsorbed on Au wafers modified with MPA monolayers. The columns in each series stand for (from left to right): dry thickness in air, thickness under deionized water after a 1-h or a 2.5-h immersion (pH=6.4), thickness under deionized water after a 1-h immersion in 0.1 M CuCl₂ (pH=3.6) followed by rinsing with deionized water, and finally the thickness under deionized water after a subsequent 1-h immersion in 0.1 M EDTA (pH=6.4) followed by rinsing with water.

2.3.5 Flux as a function of feed concentration

For ions undergoing facilitated transport, as their feed concentration increases, eventually their flux should plateau due to saturation of binding sites in the membrane.^{38,39} However, Figure 2.7 shows that Cu^{2+} flux through (PDCMAA/PAH)₄ films increases nonlinearly with increasing CuCl₂ feed concentration. Moreover, the flux continues to increase at feed concentrations as high as 0.5 M (see Figure 2.7). The nonlinear increase suggests unsaturated binding sites and an increasing hopping rate or increasing number of sites at high Cu²⁺ concentrations. Isotherms of Cu²⁺ sorption in similar films confirm the presence of weak binding sites that fill only at high Cu²⁺

concentrations (see below for further discussion). For $(PAA/PAH)_4$ and $(PSS/PAH)_4$ membranes, plots of Cu²⁺ flux versus feed concentration show at most small deviations from linearity (Figure 2.8).

Whereas the Cu²⁺-imprinted polyelectrolyte membrane reported by Deng et al.⁵⁷ exhibited decreasing selectivity with increasing feed concentration, PDCMAA/PAH films maintain their selectivity at a high feed concentration. The use of high feed concentrations should enable high ion fluxes in separations.



Figure 2.7 (Left) Cu^{2+} fluxes through a (PDCMAA/PAH)₄ film deposited on porous alumina. (Right) Cu^{2+} and Mg^{2+} fluxes for 3 (PDCMAA/PAH)₄ films deposited on porous alumina. A fourth membrane showed much lower fluxes for both Cu^{2+} and Mg^{2+} , but the flux trends remained the same.



Figure 2.8 Cu²⁺ and Mg²⁺ diffusion dialysis fluxes through porous alumina coated with $(PAA/PAH)_4$ (Left) and $(PSS/PAH)_4$ (Right) films. Large error bars in the flux arise from the defects in manufactured skin layer of commercial alumina membranes which may lead to variation in fluxes through the PEM film.⁵⁸ However, each individual membrane exhibited similar evolution of flux with feed concentration.

2.3.6 Isotherm for Sorption of Cu^{2+} in (PDCMAA/PAH)₁₀-modified nanoparticles

Sorption isotherms may help explain trends in diffusion dialysis fluxes as a function of feed concentration. We chose to examine sorption on PEM-modified nanoparticles because their large surface area enables quantitation of binding even with high (0.4 M) Cu^{2+} concentrations in solution. The use of 10 rather than 4 polyelectrolyte bilayers also increases the total sorption. In these experiments, the decrease in the Cu^{2+} concentration in a loading solution after equilibration with (PDCMAA/PAH)₁₀-modified nanoparticles allows an estimate of the amount of Cu^{2+} adsorption per mass of particles. We also rinsed the loaded particles with deionized water and eluted the Cu^{2+} with EDTA. The amount of eluted Cu^{2+} may be less than the bound Cu^{2+} if rinsing removes some of the Cu^{2+} from the beads.

Figure 2.9 shows the Cu^{2+} sorption isotherms as calculated from both the decrease in

 Cu^{2+} concentration in the loading solution and the amount of Cu^{2+} eluted after rinsing. The isotherm based on eluted Cu^{2+} already approaches saturation at a 19 mM equilibrium concentration in the loading solution, and the maximum sorption is ~ 130 µmol/g. However, for total sorption (determined from the loading solution), Cu^{2+} binding approximately doubles on increasing the equilibrium concentration from 19 mM to 376 mM. These data and the shape of the total sorption isotherm suggest two types of sorption sites, with different affinities for Cu^{2+} . We speculate that the strong binding sites, which saturate at Cu^{2+} concentrations around 20 mM, are the IDA functionalities of PDCMAA and the weak binding sites are amine groups of PAH. At sufficiently high concentrations, the Cu^{2+} ions may effectively compete with protons and bind to the amines of PAH. If facilitated transport involves hopping between weak binding sites (amines), increased binding to these sites at high Cu^{2+} concentrations should enhance flux. Moreover the flux should increase nonlinearly with the number of binding sites as more percolation pathways become available.

However, if transport occurs via the amine sites, why do $(PAA/PAH)_4$ and $(PSS/PAH)_4$ films not show similarly high Cu^{2+}/Mg^{2+} selectivities. In fact, Table 2.2 shows that the Cu^{2+} fluxes through $(PSS/PAH)_4$ films are higher than those through $(PDCMAA/PAH)_4$ films. Even when normalized to film thickness, the Cu^{2+} permeability through $(PSS/PAH)_4$ is higher than that through $(PDCMAA/PAH)_4$ and $(PAA/PAH)_4$. Nevertheless, fluxes of both Cu^{2+} and Mg^{2+} increase linearly with concentration for $(PSS/PAH)_4$ films. Most likely, the sulfonate-ammonium groups in PSS/PAH remain ionically cross-linked even at Cu^{2+} concentrations of 0.1 M. Because Cu^{2+} binds weakly

to amines and negligibly to sulfonates, the presence of 0.1 M CuCl₂ does not affect Mg²⁺ or Cu²⁺ transport though these films and ion permeabilities are essentially independent of the feed concentration. With (PDCMAA/PAH)₄, Cu²⁺ binding to PDCMAA should break ionic cross-links and create free ammonium groups that may bind Cu²⁺. A similar effect may occur with (PAA/PAH)₄, but these films are much more permeable to Mg²⁺ than (PDCMAA/PAH)₄ in the absence of Cu²⁺, and diffusional transport even after Cu²⁺ binding may at least partially mask facilitated transport.



Figure 2.9 Adsorption isotherm for Cu^{2+} binding to (PDCMAA/PAH)₁₀-modified nanoparticles. The inset is an expansion of the lower concentration range. Adsorption incubation time was 14 hours at each concentration, and each point represents a fresh set of modified nanoparticles.

2.4 Conclusions

PDCMAA/PAH films adsorbed on porous alumina allow selective diffusive transport of Cu^{2+} over Mg^{2+} , Ni^{2+} , and Ca^{2+} in mixed salt solutions, with Cu^{2+}/Mg^{2+} selectivities reaching values as high as 80. These high Cu^{2+}/Mg^{2+} selectivities do not occur with PSS/PAH and PAA/PAH films or in single-salt experiments with PDCMAA/PAH films. Binding of Cu^{2+} to PDCMAA/PAH membranes greatly decreases the Mg²⁺ flux, either by saturating hopping sites or inducing electrostatic exclusion. The high Cu^{2+}/Mg^{2+} selectivity of these films in mixed salt solutions suggests facilitated transport, as the aqueous diffusing coefficients of the two ions differ by only 1%. Unlike most facilitated transport membranes the Cu^{2+} flux through PDCMAA/PAH membranes increases nonlinearly with the concentration of Cu^{2+} in the feed solution. Sorption isotherms suggest that facilitated transport may occur through binding to weak sorption sites, perhaps amine groups. Binding of Cu^{2+} to PDCMAA may disrupt ionic crosslinks and create free amine groups that serve as hopping sites for Cu^{2+} transport. REFERENCES

REFERENCES

(1) Decher, G. Science 1997, 277, 1232-1237.

(2) Decher, G.; Hong, J. D.; Schmitt, J. Thin Solid Films 1992, 210-211, Part 2, 831-835.

(3) Miller, M. D.; Bruening, M. L. Langmuir 2004, 20, 11545-11551.

(4) Toutianoush, A.; Schnepf, J.; El Hashani, A.; Tieke, B. Adv. Funct. Mater. 2005, 15, 700-708.

(5) Adusumilli, M.; Bruening, M. L. Langmuir 2009, 25, 7478-7485.

(6) Ma, Y.; Dong, J.; Bhattacharjee, S.; Wijeratne, S.; Bruening, M. L.; Baker, G. L. *Langmuir* **2013**, *29*, 2946-2954.

(7) Bhattacharjee, S.; Dong, J.; Ma, Y.; Hovde, S.; Geiger, J. H.; Baker, G. L.; Bruening, M. L. *Langmuir* **2012**, *28*, 6885-6892.

(8) Dai, J. H.; Balachandra, A. M.; Lee, J. I.; Bruening, M. L. *Macromolecules* **2002**, *35*, 3164-3170.

(9) Balachandra, A. M.; Dai, J. H.; Bruening, M. L. *Macromolecules* **2002**, *35*, 3171-3178.

(10) Stair, J. L.; Harris, J. J.; Bruening, M. L. Chem. Mater. 2001, 13, 2641-2648.

(11) El-Hashani, A.; Toutianoush, A.; Tieke, B. J. Membr. Sci. 2008, 318, 65-70.

(12) Krasemann, L.; Toutianoush, A.; Tieke, B. J. Membr. Sci. 2001, 181, 221-228.

(13) Li, J.; Zhang, G. J.; Ji, S. L.; Wang, N. X.; An, W. J. Membr. Sci. 2012, 415, 745-757.

(14) Krasemann, L.; Tieke, B. Mater. Sci. Eng., C 1999, 8–9, 513-518.

(15) Krasemann, L.; Tieke, B. J. Membr. Sci. 1998, 150, 23-30.

(16) Ji, Q.; Yoon, S. B.; Hill, J. P.; Vinu, A.; Yu, J.-S.; Ariga, K. J. Am. Chem. Soc. 2009,

131, 4220-4221.

(17) Sullivan, D. M.; Bruening, M. L. Chem. Mater. 2002, 15, 281-287.

(18) Bruening, M. L.; Dotzauer, D. M.; Jain, P.; Ouyang, L.; Baker, G. L. *Langmuir* **2008**, 24, 7663-7673.

(19) Tieke, B.; Toutianoush, A.; Jin, W. Q. Adv. Colloid Interface Sci. 2005, 116, 121-131.

(20) Stanton, B. W.; Harris, J. J.; Miller, M. D.; Bruening, M. L. Langmuir 2003, 19, 7038-7042.

(21) Malaisamy, R.; Bruening, M. L. Langmuir 2005, 21, 10587-10592.

(22) Tieke, B.; Krasemann, L.; Toutianoush, A. Macromol. Symp. 2001, 163, 97-111.

(23) Hoffmann, K.; Friedrich, T.; Tieke, B. Polym. Eng. Sci. 2011, 51, 1497-1506.

(24) Hoffmann, K.; Tieke, B. J. Membr. Sci. 2009, 341, 261-267.

(25) Ouyang, L.; Malaisamy, R.; Bruening, M. L. J. Membr. Sci. 2008, 310, 76-84.

(26) Bruening, M. L.; Sullivan, D. M. Chem. Eur. J. 2002, 8, 3832-3837.

(27) Kurniawan, T. A.; Chan, G. Y. S.; Lo, W. H.; Babel, S. Chem. Eng. J. 2006, 118, 83-98.

(28) Ahluwalia, S. S.; Goyal, D. Eng. Life Sci. 2005, 5, 158-162.

(29) Burkhart, L. E. Journal of Metals 1985, 37, A111-A111.

(30) Chmielewski, A. G.; Urbański, T. S.; Migdał, W. Hydrometallurgy **1997**, 45, 333-344.

(31)Luo, C.-S.; Huang, S.-D. Sep. Sci. Technol. 1993, 28, 1395-1408.

(32) Kekesi, T.; Mimura, K.; Isshiki, M. Materials Transactions Jim 1995, 36, 649-658.

(33) CerjanStefanovic, S.; Grubisa, D.; Smid, V. Plat. Surf. Finish. 1996, 83, 74-79.

(34) Liang, S.; Guo, X. Y.; Tian, Q. H. Desalination 2011, 275, 212-216.

(35) Juang, R. S.; Wu, F. C.; Tseng, R. L. Water Res. 1999, 33, 2403-2409.

(36) Parhi, P. K.; Park, K. H.; Kim, H. I.; Park, J. T. Hydrometallurgy 2011, 105, 195-200.

(37) Agrawal, A.; Manoj, M. K.; Kumari, S.; Bagchi, D.; Kumar, V.; Pandey, B. D. *Miner*. *Eng.* **2008**, *21*, 1126-1130.

(38) Cussler, E. L.; Aris, R.; Bhown, A. J. Membr. Sci. 1989, 43, 149-164.

(39) Noble, R. D. J. Membr. Sci. 1991, 56, 229-234.

(40) Noble, R. D. J. Membr. Sci. 1991, 60, 297-306.

(41) Noble, R. D. J. Membr. Sci. 1992, 75, 121-129.

(42) Visser, H. C.; Reinhoudt, D. N.; de Jong, F. Chem. Soc. Rev. 1994, 23, 75-81.

(43) Kemperman, A. J. B.; Bargeman, D.; van den Boomgaard, T.; Strathmann, H. Sep. Sci. Technol. **1996**, *31*, 2733-2762.

(44) de Agreda, D.; Garcia-Diaz, I.; Lopez, F. A.; Alguacil, F. J. *Rev. Metal. Madrid.* **2011**, 47, 146-168.

(45) Nghiem, L. D.; Mornane, P.; Potter, I. D.; Perera, J. M.; Cattrall, R. W.; Kolev, S. D. *J. Membr. Sci.* **2006**, *281*, 7-41.

(46) Ulbricht, M. J. Chromatogr. B 2004, 804, 113-125.

(47) El-Hashani, A.; Tieke, B. J. Nanosci. Nanotechnol. 2006, 6, 1710-1717.

(48) Tieke, B.; El-Hashani, A.; Toutianoush, A.; Fendt, A. *Thin Solid Films* **2008**, *516*, 8814-8820.

(49) Toutianoush, A.; El-Hashani, A.; Schnepf, J.; Tieke, B. Appl. Surf. Sci. 2005, 246, 430-436.

(50) In *CRC Handbook of Chemistry and Physics Online*; 93rd ed.; Chemical Rubber Company; pp Section 5, 77-79.

(51) Martell, A. E.; Smith, R. M. Critical stability constants; Plenum Press: New York,,

1974.

(52) Choi, J.; Rubner, M. F. Macromolecules 2005, 38, 116-124.

(53)Petrov, A. I.; Antipov, A. A.; Sukhorukov, G. B. *Macromolecules* **2003**, *36*, 10079-10086.

(54) Itano, K.; Choi, J. Y.; Rubner, M. F. Macromolecules 2005, 38, 3450-3460.

(55)Lewis, S. R.; Datta, S.; Gui, M.; Coker, E. L.; Huggins, F. E.; Daunert, S.; Bachas, L.; Bhattacharyya, D. *Proc. Natl. Acad. Sci.* **2011**, *108*, 8577-8582.

(56) Jaber, J. A.; Schlenoff, J. B. Langmuir 2006, 23, 896-901.

(57) Deng, H.; Gao, L.; Zhang, S.; Yuan, J. Ind. Eng. Chem. Res 2012, 51, 14018-14025.

(58) Cheng, C.; Yaroshchuk, A.; Bruening, M. L. Langmuir 2013, 29, 1885-1892.

Chapter 3

Summary and Future Work

3.1 Summary

This thesis describes a simple and convenient method for preparing an ultrathin facilitated transport membrane with metal ion-binding groups. Chapter 1 discusses the versatility of the layer by layer (LBL) technique for synthesizing functional polymeric films with tunable thickness and permeability. These polyelectrolyte multilayers (PEMs) are especially attractive for a variety of ion-separation processes such as water softening and metal ion removal/recovery. Chapter 2 demonstrates the preparation of a facilitated transport membrane by LBL deposition of poly[(N,N'-dicarboxymethyl) allylamine] (PDCMAA)/poly(allylamine hydrochloride) (PAH) films at low pH. The abundant Cu²⁺binding sites in the film, either iminodiacetic acid groups from PDCMAA or amine groups from PAH, afford selective facilitated transport of Cu²⁺ through the membrane. The rejections of other ions with identical charge and similar hydrated radii but much lower ligand binding constants (e.g. Mg²⁺, Ni²⁺, Ca²⁺) are high compared to Cu²⁺ rejection due to the preferential Cu^{2+} -sorption in the film. Diffusion dialysis studies show average Cu^{2+}/Mg^{2+} selectivities of 50 and 80 with PAH-capped and PDCMAA-capped films, respectively.

3.2 Future Work

This thesis shows the feasibility of synthesizing facilitated transport membranes using LBL deposition of functional polyelectrolyte. These membranes allow selective Cu²⁺ transport. Separation of other ions such as alkali metal ions, lanthanides and transition metals will require ion-binding groups tailored for different ions. Tieke et al.^{1,2} incorporated various ion-binding compounds (e.g. calixarenes, cyclodextrins, and azacrowns) into the PEMs by electrostatic adsorption, but these films suffered from instability. Covalent bonding between the ion-binding groups and the polyelectrolyte backbone could potentially solve the problem. One method to prepare such films would employ polyelectrolytes partially modified with ion-binding groups prior to deposition. The unmodified ionic groups would ensure the PEM buildup and stability. For example, poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) can both be partially modified with ion-binding.

Postdeposition modification of the PEM provides another way to covalently incorporate ion-binding groups. For example, PAA/PAH films deposited at low pH have an abundance of free carboxylic acid groups, which may serve as attachment sites for ion-binding groups.^{3,4} The modification process could utilize reactions such as 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide/N-hydroxysuccinimide (EDC/NHS) amine coupling⁵ or copper(I)-catalyzed alkyne-azide cycloaddition (click chemistry)^{6,7} for polyelectrolytes with different functionalities (see Figure 3.2.1 and 3.2.2).



Figure 3.1 EDC-NHS amine coupling for modification of carboxylic acid-containing polyelectrolytes.



Figure 3.2 Cu(I) catalyzed alkyne-azide cycloaddition. Use of the chemistry for PEM modification will require polyelectrolyte with azide or alkyne groups.

Separations of rare earth metal ions, lanthanides along with scandium and yttrium, through tailor-made facilitated transport membranes is especially attractive due to the similar radii of these ions and labor costs in conventional separation techniques such as cascading, fractional crystallization and solvent extraction. Suitable ion-binding groups for lanthanide separations vary from the iminodiacetic acid group used in the present study, to calixarenes, crown ethers, diazamacrocyles, cryptands, and also amines (see Figure 3.2.3).⁸ Efficient separation will also require optimization of the PEM thickness, permeability and charge density to achieve high flux for the selected ion as well as high rejection for the other ions.



Figure 3.3 Structures of lanthanide-binding compounds

REFERENCES

REFERENCES

(1) Tieke, B.; El-Hashani, A.; Toutianoush, A.; Fendt, A. *Thin Solid Films* **2008**, *516*, 8814-8820.

(2) Tieke, B.; Toutianoush, A.; Jin, W. Q. *Adv. Colloid Interface Sci.* **2005**, *116*, 121-131.

(3) Bhattacharjee, S.; Dong, J.; Ma, Y.; Hovde, S.; Geiger, J. H.; Baker, G. L.; Bruening, M. L. *Langmuir* **2012**, *28*, 6885-6892.

(4) Ma, Y.; Dong, J.; Bhattacharjee, S.; Wijeratne, S.; Bruening, M. L.; Baker, G. L. *Langmuir* **2013**, *29*, 2946-2954.

(5) Saeki, D.; Nagao, S.; Sawada, I.; Ohmukai, Y.; Maruyama, T.; Matsuyama, H. J. *Membr. Sci.* **2013**, *428*, 403-409.

(6) Zolotarskaya, O. Y.; Yuan, Q.; Wynne, K. J.; Yang, H. *Macromolecules* **2013**, *46*, 63-71.

(7) Liang, L.; Astruc, D. Coord. Chem. Rev. 2011, 255, 2933-2945.

(8) Di Bernardo, P.; Melchior, A.; Tolazzi, M.; Zanonato, P. L. *Coord. Chem. Rev.* **2012**, *256*, 328-351.