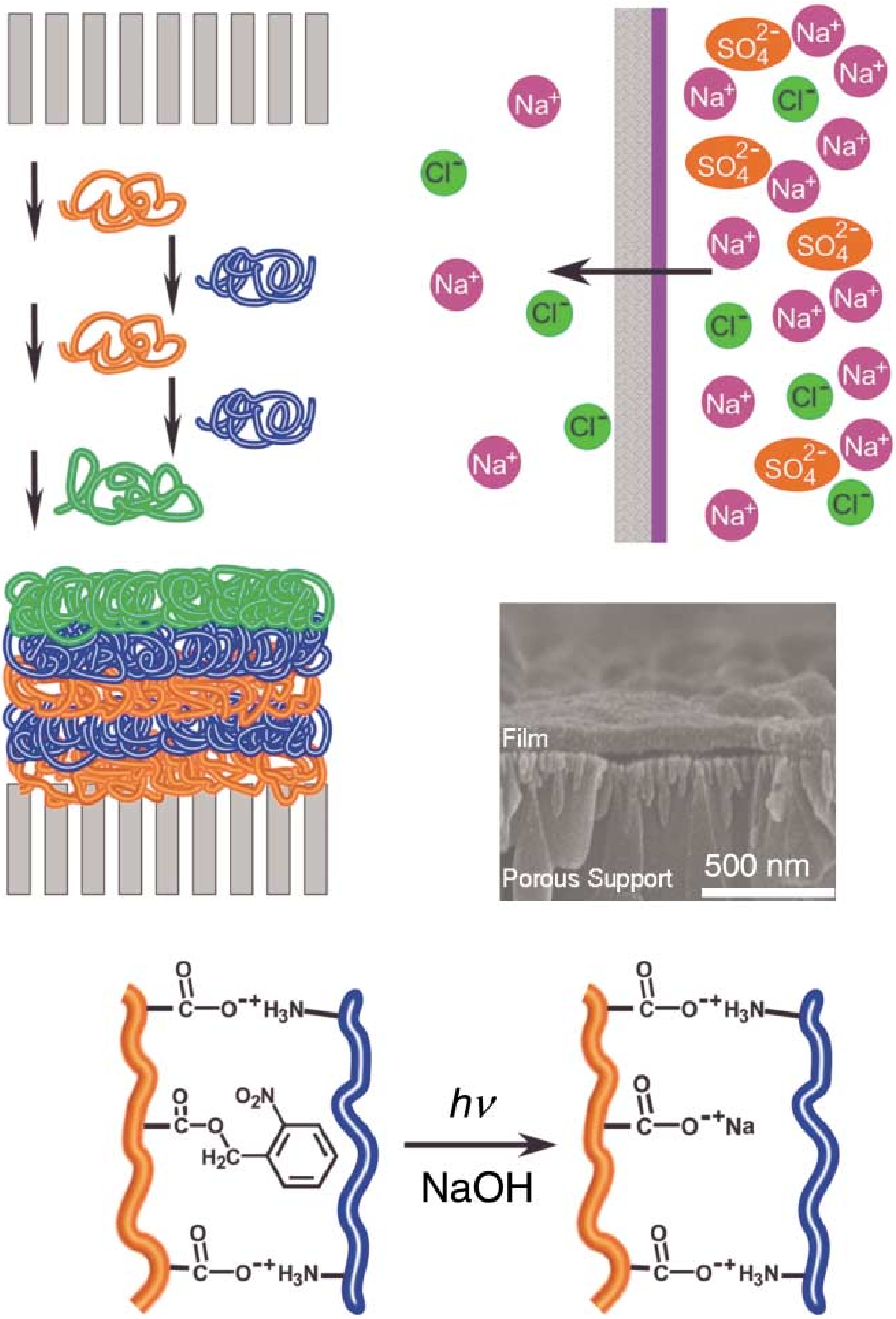
Composite Polyelectrolyte Membranes



Polyelectrolyte skins on composite membranes allow highly selective separation of ions according to charge, size, or hydration energy.

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Enhancing the Ion-Transport Selectivity of Multilayer Polyelectrolyte Membranes

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Abstract: Alternating adsorption of polycations and polyanions on permeable supports provides a convenient and versatile method for preparing composite membranes with selective, ultrathin polyelectrolyte skins. Control over charge and composition in the polyelectrolyte skin allows highly selective separation of ions according to charge, size, or hydration energy.

Keywords: layer-by-layer assembly · membranes · polyelectrolyte films · thin films

Introduction

Synthetic membrane-based separation systems are very attractive because of their convenience and low energy costs. Separation occurs by simply flowing a mixture past a membrane and collecting a permeate that contains primarily one component of the mixture. In spite of the appeal of these separations, development of highly selective membranes that allow practical fluxes is an ongoing challenge. This is particularly true because flux is often inversely proportional to selectivity.[1]

The tradeoff between flux and selectivity generally requires that practical membrane systems consist of an ultrathin skin on a highly permeable support.[2] The minimal thickness of the selective layer allows a reasonable flux, while the support provides needed mechanical strength. Such membranes are often prepared by phase-inversion processes that result in a polymeric material with a dense surface layer and a highly porous bulk.[3] Composite membranes provide an appealing alternative to phase inversion, because deposition of a thin, selective layer on an inexpensive support allows use of more expensive, and potentially more discriminating, skin materials.[2]

As one might expect, development of convenient methods for depositing ever-thinner selective skins on permeable supports is an active area of research. In spite of many successes, fabrication of selective, versatile membrane skins with thicknesses less than 50 nm is still difficult.[4, 5] The recent development of alternating polyelectrolyte deposition (APD) provides a new tool for addressing this challenge.[6, 7] In this procedure, film deposition occurs by alternating adsorption of polycations and polyanions on a charged substrate as shown in Figure 1. This "dip-and-rinse" method is extremely convenient and versatile, affording control of film thickness on the nanometer scale by simply varying the number of layers deposited. Additionally, nearly any polyelectrolyte can be a constituent of these films.

Although APD is a relatively new technique, fabrication or modification of membranes with single polyelectrolytes is already well established. Membranes prepared by casting a polyelectrolyte, such as poly(diallyldimethylammonium fluoride), often have unique separation properties due to their hydrophilicity or charge.[8] Sata and co-workers showed that adsorption of a "monolayer" of polyelectrolyte onto ion-exchange membranes can greatly enhance ion-transport selectivity.[9] Perhaps most related to this paper, complexes of polycations and polyanions formed in solution or at interfaces can form membranes that are selective for pervaporation or ion permeation.[10, 11] Compared with these methods, layer-by-layer APD provides much greater versatility for forming and modifying membrane skins, because multilayer structures can be formed and complicated archi-

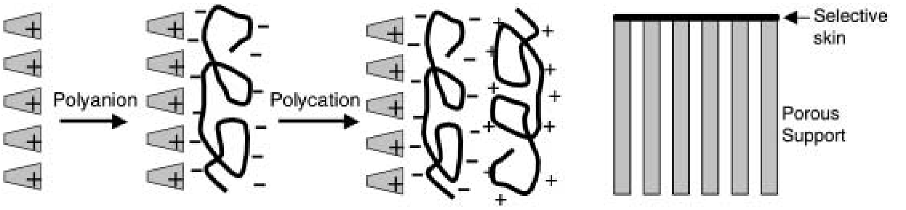

Figure 1. Schematic diagram of the deposition of a polyelectrolyte bilayer on a porous support. Repetition of this procedure yields multilayer films. For clarity, intertwining of neighboring polyelectrolytes is not shown. The cartoon on the rights shows the structure of a composite membrane.

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tectures can be prepared by depositing several different polyelectrolytes in the same film. Additionally, deposition conditions, such as pH and supporting electrolyte concentration, are easy to change, and these variables can have dramatic effects on membrane structure.[12–14]

This article focuses primarily on enhancing the ion-transport selectivity of multilayer polyelectrolyte membranes (MPMs) by controlling their composition and structure. The first section addresses the issue of whether multilayer polyelectrolyte films (MPFs) are capable of forming defect-free coatings on porous supports. Subsequent sections discuss methods to enhance transport selectivity through variation of constituent polyelectrolytes, post-deposition reactions within films, and control over net membrane charge. By using these methods, Cl^-/SO_4^{2-}-transport selectivities can reach values as high as 1000. The final section discusses future research directions with these membranes.

Formation and Structure of Composite MPMs

One of our initial questions regarding MPMs was whether polyelectrolyte films are actually capable of covering a highly permeable support without filling underlying pores. This issue is especially important for gas-separation membranes, because MPFs will not be swollen by solvents in this case, and even a few defects can negate selectivities.[15] Gas-separation studies with MPFs deposited on continuous, but relatively permeable supports, such as poly(4-methyl-1-pentene),[16] silicone,[17] and poly(ethylene terephthalate),[18] showed increased gas selectivity relative to the support. However, when deposited on highly porous supports such as Celgard™ (porous polypropylene), MPFs showed little gas-transport selectivity.[17, 19] This might be due to the inability of such films to cover large, underlying pores.

To assess the extent of coverage of porous supports by MPFs, we performed field-emission scanning electron microscopy (FESEM) studies of films deposited on porous alumina. Porous alumina is an especially attractive support for these investigations, because its high porosity and regular pore structure facilitate visualization of surface coverage.[20] Top-view images of MPFs on alumina show that four or five bilayers of poly(styrene sulfonate) (PSS)/poly(allylamine hydrochloride) (PAH) are required to cover substrate pores 0.02 μm in diameter, and cross-sectional views (Figure 2, for example) show that PSS/PAH films do not fill underlying pores.[21]

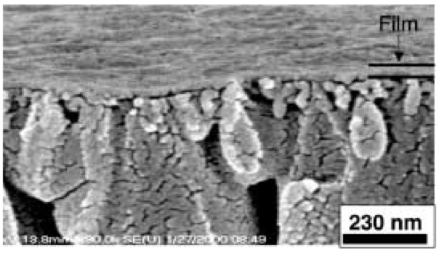

Figure 2. Cross-sectional field-emission SEM image of a porous alumina support coated with a ten-bilayer PAH/PSS film. Reproduced by permission from reference [21]. Copyright (2000) American Chemical Society.

Although SEM images suggest full coverage of porous alumina by MPFs, only transport studies can demonstrate whether films are free of small defects. In diffusion dialysis experiments with PSS/PAH, the onset of Cl^-/SO_4^{2-} selectivity occurs after deposition of four PSS/PAH bilayers on porous alumina; this is consistent with FESEM images.[21] Pervaporation studies show water/propan-2-ol transport selectivities as high as 10000 with only six bilayers of poly(ethylenimine)/alginic acid deposited on a nylon support, prepared by phase inversion to contain a dense surface layer.[22] Deposition of polyvinylamine/polyvinylsulfate films on porous supports (20–200 nm pores) yields similar selectivities when 60 bilayers are adsorbed.[23] However, as mentioned above, gas separations would be more demonstrative of defect-free coverage of a support. We recently prepared poly(amic acid)/PAH films on porous alumina, and heated them to form polyimides. With an appropriate choice of a poly(amic acid) precursor, O_2/N_2 selectivities reach values of over six for nine-bilayer films, showing that these polyimide films are indeed free of defects.[24] The high selectivity of these membranes clearly shows that MPFs are capable of forming ultrathin, defect-free films on porous substrates. We note that annealing during heat-induced imidization may help to achieve complete substrate coverage. Annealing also increases pervaporation selectivity in some cases.[25]

Ion Transport through Typical MPMs and Hybrid Structures

MPMs are attractive for separating monovalent and divalent ions because they contain a net, fixed charge at their surface. The presence of fixed charge yields unbalanced concentrations of mobile anions and cations, and a Donnan potential develops.[26] This potential results in strong exclusion of multivalent ions whose charge is of the same sign as the fixed charge. Monovalent ions are only minimally excluded, and thus selective ion transport occurs. Krasemann and Tieke first reported monovalent/divalent ion-transport selectivity through MPMs and suggested that this selectivity is due to Donnan exclusion.[27] Membranes prepared from polyelectrolytes with high charge densities exhibit especially high monovalent/divalent ion-transport selectivities as would be expected.[27] PSS/PAH films exhibit Cl^-/SO_4^{2-} selectivities that range from 4–45, depending on preparation conditions, while $Cl^-/Fe(CN)_6^{3-}$ selectivities reach values as high as 1000.[21, 27, 28] Ion-transport selectivities of poly(acrylic acid) (PAA)/PAH membranes are similar to those of PSS/PAH, although flux through these membranes is about 30% of that through PSS/PAH, presumably due to lower hydration of PAA.[21, 28] The very high $Cl^-/Fe(CN)_6^{3-}$ selectivity of MPMs is likely due to both the high charge and large size (lower diffusion coefficient) of $Fe(CN)_6^{3-}$. Farhat and Schlenoff recently showed that the rate of anion diffusion through MPFs decreases dramatically with anion charge.[29]

Because most of the net charge in MPMs resides at the surface, control over the top layer in these membranes should have a large effect on ion transport. Addition of a PAA layer to a five-bilayer PSS/PAH membrane increases selectivity by a factor of five relative to either PSS/PAH membranes terminated with PSS or pure PAA/PAH membranes terminated with PAA. Additionally, because these hybrid PSS/PAH/PAA membranes are composed primarily of PSS/PAH, flux is three times higher than for PAA/PAH membranes. Thus hybrid membrane structures offer the possibility of both high flux and high selectivity. Deposition of 2.5 bilayers of PAA/PAH on a five-bilayer PSS/PAH membrane further increases Cl^-/SO_4^{2-} selectivity to a value of 120 (a 20–30-fold increase over similar pure PSS/PAH or PAA/PAH membranes.)[28] These selectivity increases suggest that adsorption of PAA/PAH on PSS/PAH yields a more highly charged surface than does deposition of PAA on pure PAA/PAH. The role of surface charge becomes especially clear when comparing five-bilayer PSS/PAH films capped with 2.5 bilayers of PAA/PAH with similar films capped with three bilayers of PAA/PAH (changing the surface layer from a polyanion to a polycation). The selectivity for Cl^- over SO_4^{2-} decreases from 150 to 2.2 in this case.

The FESEM images in Figure 3 confirm that PAA surface layers deposited on PSS/PAH have a different structure than PAA on PAA/PAH, but as yet we are unable to give a physical interpretation of these images. We suspect that the hybrid membranes have a denser surface and, hence, a higher surface charge density. The denser surface could also result in selective diffusion of ions, but as changing the surface from a polycation to a polyanion showed, selectivity is primarily due to electrostatic exclusion of sulfate.

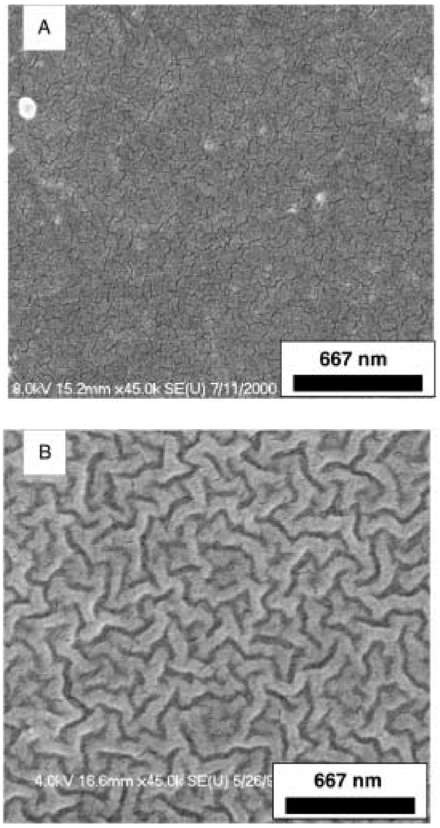

Figure 3. Top-view FESEM images of porous alumina coated with A) a five-bilayer PSS/PAH film capped with 1.5 bilayers of PAA/PAH and B) a 4.5-bilayer film of PAA/PAH. Image B reproduced by permission from reference [28]. Copyright (2000) American Chemical Society.

Control of Membrane Permeability Through Post-deposition Reactions

MPFs are reasonably hydrophilic and, thus, they swell in water. In water-saturated air, PAH/PSS films can swell by 20–40%.[12, 30] To prepare less swollen films that have higher diffusional selectivity and/or charge density, we employed cross-linking or imidization of MPMs. Cross-linking occurs by heat-induced amide formation from carboxylate–ammonium pairs in PAA/PAH films, and reflectance FTIR spectra show that heating in a N_2 atmosphere at temperatures above 180 °C results in virtually quantitative amide formation.[31] However, after complete amide formation, flux through PAA/PAH membranes is unacceptably low. Therefore, we heated films at lower temperatures to partially cross-link films, and found that the optimal cross-linking temperature for Cl^-/SO_4^{2-} transport selectivity is around 115 °C. The limited amidation at this temperature increases selectivity by a factor of four and still allows flux that is 50% of that through an unheated PAA/PAH film.[28] When combined with templating of films with Cu^{2+}, cross-linking has an even more beneficial effect on selectivity (see below).

For MPMs containing poly(amic acids), imidization results in extremely selective membranes. Figure 4 shows the chemical structure of the poly(pyromellitic dianhydride-phenylenediamine) (PMDA-PDA)/PAH films that we employed for ion separations. Heating PMDA-PDA/PAH at temperatures

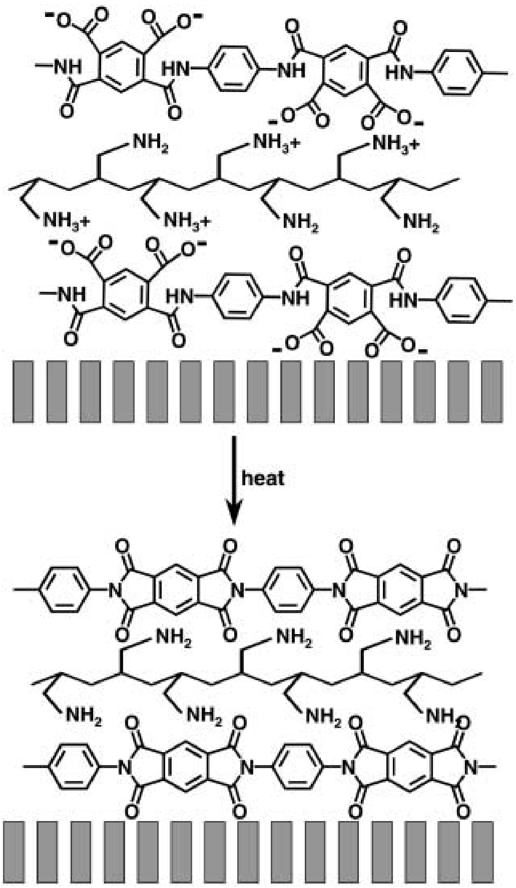

Figure 4. Imidization of a poly(pyromellitic dianhydride-phenylenediamine)/PAH membrane.

ranging from 130 to 180 °C results in partial imidization, and diffusion dialysis studies show that imidization at these temperatures yields Cl^-/SO_4^{2-} selectivities as high as 1000. (Heating of these films was done under N_2 to avoid burning of the polyelectrolytes. Under N_2, PAH and poly(amic acids) are stable at temperatures up to 300 °C.) As might be expected, fluxes through these films decrease with respect to unheated films, but even at a selectivity of 800, Cl^- flux is only 20% lower than that through an unheated membrane and 50% lower than that through a bare alumina support.[32] To achieve these high fluxes, we employ hybrid membranes consisting of a PSS/PAH base and a few bilayers of PMDA-PDA/PAH.

As imidization should reduce the negative charge density in these membranes, we think that selectivity in these systems is based on differences in ion hydration energies and/or selective diffusion.[33] The hydration energy of SO_4^{2-} is 700 $kJ\,mol^{-1}$ higher than that of Cl^-, and both the ionic and hydrated radii of SO_4^{2-} are 50 – 60 pm higher than the corresponding Cl^- radii.[34] Thus both selective partitioning and selective diffusion may be responsible for discrimination between Cl^- and SO_4^{2-}. Further work is needed to better understand the factors behind selective transport in imidized MPMs.

Control of Fixed Charge Density in the Bulk of MPFs

Because Donnan exclusion due to fixed charge in the membrane is one of the most important factors in separating monovalent and divalent ions,[35] we pursued methods to introduce fixed charge into the bulk of MPFs. In the structure of many MPFs, charges on polycations are compensated by charges on polyanions and vise versa; thus, net charge resides only at the surface of the membrane.[36] To overcome this limitation, we began forming charged groups after film deposition. Figure 5 shows one method of inserting charge into MPMs. Photolysis of nitrobenzyl ester groups on derivatized PAA through an intramolecular reaction[37] yields −COOH groups and nitrosobenzaldehyde; the nitrosobenzaldehyde is presumably later rinsed from the film. Subsequent deprotonation of −COOH groups by immersion in a basic solution results in fixed negative charge in the film. Similarly, photolysis of PAH that is partially derivatized with nitrobenzylcarbamate groups results in amines which can be protonated to yield a net positive charge in the membrane. We synthesized polymers that are only partially derivatized, because some $-COO^-$ and $-NH_3^+$ groups are necessary for film formation.

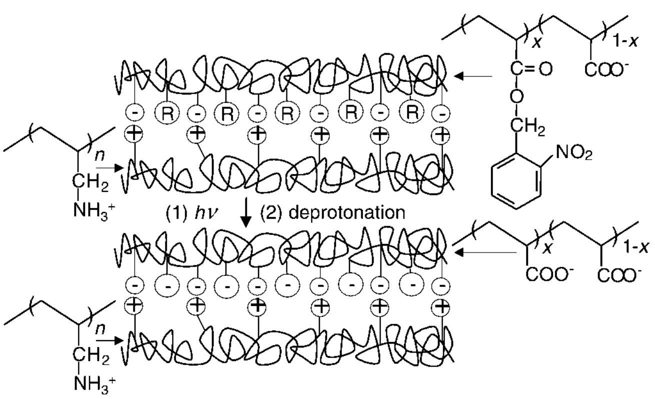

Figure 5. Introduction of net negative charge into multilayer polyelectrolyte membranes through photolysis of nitrobenzyl esters.

Transport selectivities vary with both the sign and the concentration of fixed charge in the membrane. After photolysis, PAA/PAH membranes prepared with 0%, 33%, 50%, and 63% nitrobenzylesterified PAA show Cl^-/SO_4^{2-} selectivities of 9, 100, 150, and 170, respectively. These results demonstrate that a greater negative fixed-charge density due to derivatization and hydrolysis increases monovalent/divalent anion-transport selectivity. Films prepared with PAA and 50%-derivatized PAH showed a Cl^-/SO_4^{2-} selectivity of 1, but a Na^+/Mg^{2+} selectivity of 40, reflective of the net positive charge in these films. Thus derivatization affords wide-ranging control over selectivity. Additionally, Cl^- transport through these films is within 20% of that through similar PAA/PAH membranes, showing that selectivity can be achieved without a significant diminution of flux.[38]

A simpler, but perhaps less controlled, method for inserting charges into MPMs is to use metal-ion complexes as templates for ion-exchange sites. We partially complexed the carboxylate groups of PAA with Cu^{2+}, and then formed PAA-Cu^{2+}/PAH films. Because PAA is only partially complexed with the metal ion, it can still be deposited as a polyanion. Post-deposition removal of Cu^{2+} from the membrane results in a net, fixed negative charge, and, hence, a fourfold increase in Cl^-/SO_4^{2-} selectivity (to a value of 55) relative to pure PAA/PAH membranes prepared under similar conditions.[39]

Cross-linking of PAA-Cu^{2+}/PAH membranes yields further increases in selectivity. Heating these films at 130 °C (under N_2) for two hours prior to removal of Cu^{2+} increases selectivity from 55 to 610.[39] Again this remarkable selectivity is achieved with little diminution in flux relative to similar pure PAA/PAH films. The increase in selectivity could result from decreased swelling of the film after cross-linking, which would yield both higher charge densities and more selective diffusion.

Future Directions

Although MPMs show highly selective transport in diffusion dialysis experiments, they have not yet been demonstrated in more practical nanofiltration, reverse osmosis, or electrodialysis applications. Future work will likely concentrate on these areas and examine how selectivity and water flux through MPMs vary with membrane composition and structure. Additionally, formation of selective membranes by APD on practical, porous polymeric substrates needs to be demonstrated. Hollow fiber supports may be particularly interesting in this regard.

On a more fundamental level, the factors that govern transport selectivity in MPMs need to be examined. Efforts focused on experimentally separating selectivity into diffusivity and partitioning contributions would be especially useful for understanding transport. Such experiments are difficult, however, due to the minimal thickness of MPFs. Future studies with a wider range of analytes, polyelectrolytes, and film structures will also help to better elucidate the factors that govern ion transport, and MPMs that exhibit high selectivities among ions of the same charge would be especially interesting for both applications and fundamental understanding. As the use of MPMs for ion separations began only a few years ago, new discoveries and understanding should greatly expand possible applications of these materials.

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