

Coating of Nafion Membranes with Polyelectrolyte Multilayers to Achieve High Monovalent/Divalent Cation Electrodialysis Selectivities

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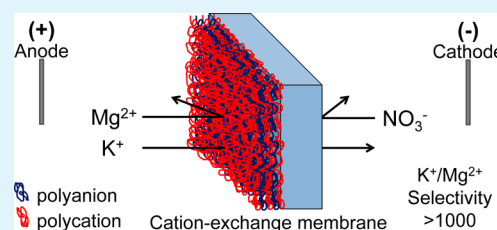
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Supporting Information

ABSTRACT: Electrodialysis (ED) membranes typically exhibit modest selectivities between monovalent and divalent ions. This paper reports a dramatic enhancement of the monovalent/divalent cation selectivities of Nafion 115 membranes through coating with multilayer poly(4-styrenesulfonate) (PSS)/protonated poly(allylamine) (PAH) films. Remarkably, K^+/Mg^{2+} ED selectivities reach values >1000 , and similar monovalent/divalent cation selectivities occur with feed solutions containing K^+ and Ca^{2+} . For comparison, the corresponding K^+/Mg^{2+} selectivity of bare Nafion 115 is only 1.8 ± 0.1 . However, with 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$ in the source phase, as the applied current density increases from 1.27 to 2.54 $mA\ cm^{-2}$, the K^+/Mg^{2+} selectivities of coated membranes decrease from >1000 to 22. Water-splitting at strongly overlimiting current densities may lead to a local pH increase close to the membrane surface and alter film permeability or allow passage of $Mg(OH)_x$ species to decrease selectivity. When the source phase contains 0.1 M KNO_3 and 0.1 M $Mg(NO_3)_2$, the K^+ transference number approaches unity and the K^+/Mg^{2+} selectivity is $>20\ 000$, presumably because the applied current is below the limiting value for K^+ and H^+ transport is negligible at this high K^+ concentration. The high selectivities of these membranes may enable electrodialysis applications such as purification of salts that contain divalent or trivalent ions.

KEYWORDS: electrodialysis, layer-by-layer, polyelectrolyte, ion-exchange membranes, selectivity



1. INTRODUCTION

Electrodialysis (ED) is a membrane-based separation technique for applications such as preconcentrating brines,¹ recovering organic acids from waste-salt solutions,² organic acid production,³ treating wastewater effluent,⁴ demineralizing milk byproducts,⁵ and desalting brackish water.^{6,7} In commercially viable configurations, alternating anion- and cation-exchange membranes in flow-cells create parallel diluate and concentrate streams to enable high throughput.⁸ Under an applied current or potential, cations leave the diluate compartment through the cation-exchange membrane, whereas anions leave in the opposite direction through the anion-exchange membrane. Thus, ED effectively removes ions from feed streams, but typical ion-exchange membranes exhibit low selectivities among ions. Such selectivities are important when employing ion-exchange membranes in some ED applications, e.g., removal of SO_4^{2-} from sea salt, or other functions such as prevention of vanadium crossover in redox flow batteries.^{9–12}

Although variation of current density and concentration polarization may provide some control over ion-transport selectivity,¹³ the development of ED for separating ions requires ion-exchange membranes with high selectivities. Sata and co-workers showed that polycation or polyanion coatings on ion-exchange membranes enhance selectivity among cations or anions, respectively.^{14–16} Deposition of protonated poly-

ethylenimine (PEI) on cation-exchange membranes increases monovalent/divalent cation selectivity, and control over the hydrophobicity and cross-linking at the membrane surface leads to Na^+/Ca^{2+} selectivities up to 7.¹⁴ Additionally, increasing the hydrophilicity of anion-exchange membranes with adsorbed ethylene glycols increases SO_4^{2-}/Cl^- selectivities from <0.1 to 0.8.^{17,18} Rakib and co-workers observed a Na^+/Cr^{3+} selectivity of 10–20 using an electrodeposited PEI film on a Nafion cation-exchange membrane.¹⁹ Nevertheless, these selectivities are relatively modest. In this study, we examine whether adsorption of polyelectrolyte multilayers on ion-exchange membranes can yield even higher selectivities.

With the development of alternating adsorption of polycations and polyanions to form ultrathin coatings,²⁰ several research groups began investigating whether polyelectrolyte multilayers (PEMs) can serve as ultrathin membrane skins that show high selectivity among cations or anions.^{21–23} In many cases, monovalent ions move through these membranes more readily than multivalent ones, presumably because of enhanced electrostatic and size-based exclusion of highly hydrated, multiply charged ions. Although Michaels formed membranes

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from polyelectrolyte complexes nearly 50 years ago,²⁴ layer-by-layer adsorption of polyelectrolytes offers much more control over the film structure to increase selectivity. For example, in diffusion dialysis, Krassemann and Tieke showed $\text{Na}^+/\text{Mg}^{2+}$ selectivities as high as 110 with 60-bilayer poly(styrenesulfonate) (PSS)/protonated poly(allylamine) (PAH) films on poly(acrylonitrile)/poly(ethylene terephthalate) supports.²⁵ Other work showed $\text{K}^+/\text{Mg}^{2+}$ diffusion dialysis selectivities of >300 with 4-bilayer films on porous alumina substrates.²⁶ ED through such membranes recently gave similarly high selectivities,²⁷ but the substrates were not ion-exchange membranes, which will limit their utility in ED applications that require transport of only cations or only anions through a membrane.

A few recent studies employed layer-by-layer polyelectrolyte deposition to enhance the selectivity of ion-exchange membranes. Abdu et al. formed polyethylenimine/PSS films on a Neosepta CMX ion-exchange membrane to generate a permselective layer while minimizing membrane resistance.²⁸ The $\text{Na}^+/\text{Ca}^{2+}$ selectivity varied with the charge and number of polyelectrolyte multilayers but was at most 1.4.²⁸ Mulyati et al. found that anion-exchange membranes modified with PSS and poly(allylamine hydrochloride) (PAH) exhibit $\text{Cl}^-/\text{SO}_4^{2-}$ selectivities of ~ 2.5 . These membranes also showed enhanced fouling resistance but required at least 15 bilayers for these effects.²⁹

This research utilizes (PAH/PSS)₅PAH films as selective barriers on commercial cation-exchange membranes (Nafion 115) to separate monovalent and multivalent cations in ED. Adsorption of these films yields $\text{K}^+/\text{Mg}^{2+}$ ED selectivities that exceed 1000. Furthermore, we investigate the effect of source-phase electrolyte concentration and current density on selectivity and current efficiency because concentration polarization strongly affects ED.³⁰ Current–potential curves and pH measurements provide additional insight into limiting currents and water splitting in this system. Membranes coated with (PAH/PSS)₅PAH films may prove useful for purifying salts containing divalent ions because these membranes remain selective when the divalent or monovalent ion is in excess.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(sodium 4-styrenesulfonate) ($M_w = 70\,000$ Da) and poly(allylamine hydrochloride) ($M_w = 15\,000$ Da) were purchased from Sigma-Aldrich. Inorganic salts were obtained from Columbus Chemical and used as received. Nafion N115 membranes were acquired from Ion Power (New Castle, DE, thickness 127 μm), and AMI-7001 anion-exchange membranes were a gift from Membranes International (Ringwood, NJ). Deionized water (Milli-Q Reference Ultrapure Water Purification System, 18 $\text{M}\Omega\cdot\text{cm}$) was used to prepare aqueous solutions. For membrane oxidation, 30% H_2O_2 (Fisher) and 98% H_2SO_4 (EMD Chemical) were separately diluted to 3% H_2O_2 and 1.0 M H_2SO_4 , respectively. The pH of polyelectrolyte solutions was adjusted with 0.1 M HCl or NaOH.

2.2. Film Formation and Characterization. Nafion membrane discs (25 mm diameter) were punched from a membrane sheet using a mechanical die. Following a literature procedure for Nafion oxidation, membranes were rinsed in deionized water prior to 30 min sequential immersions in the following solutions which were heated to 100 $^\circ\text{C}$: 3% H_2O_2 , deionized water, 1.0 M H_2SO_4 , and deionized water.^{12,31} Rinsing with room-temperature deionized water from a wash bottle also occurred for 20 s after the immersions in H_2O_2 and H_2SO_4 . This oxidation process likely exposes sulfonate groups at the Nafion surface to enhance negative surface charge. All ED experiments and current density–voltage (I – V) curves with bare Nafion employed oxidized membranes.

Layer-by-layer polyelectrolyte adsorption was performed by immersing oxidized membranes in alternating polycation (PAH in 1.0 M NaCl) and polyanion (PSS in 0.5 M NaCl) solutions for 5 min each. Polyelectrolyte solutions (pH = ~ 2.3) contained 0.02 M of the polymer repeating unit. Adsorption began with the polycation, which should adhere to the Nafion via electrostatic interactions. Membranes were rinsed with deionized water from a wash bottle for ~ 30 s after each deposition step to remove weakly adsorbed polyelectrolytes, and films contained a total of 5.5 bilayers ((PAH/PSS)₅PAH). In a few cases noted in the text, adsorption occurred using a holder to limit film formation to only one side of the membrane. X-ray photoelectron spectroscopy (XPS) using a PerkinElmer Phi 5600 ESCA instrument with a magnesium $K\alpha$ X-ray source at a 45 $^\circ$ take off angle was employed for film characterization.

2.3. Electrodialysis. Initially, coated Nafion membranes were inserted between two homemade 100 mL glass cells clamped together with an O-ring (3.1 cm^2 of exposed membrane area), and platinum wire electrodes were inserted into each compartment.²⁷ The anode and cathode were in the source and receiving phases, respectively, so that cations migrated to the receiving phase and anions toward the source phase. Using a CH Instruments model 604 potentiostat, a potential was applied across a resistor (499 Ω) to generate a constant 4.0 mA current (1.27 mA cm^{-2}). In some experiments, the voltage was increased or decreased using the same resistor to produce higher or lower current densities. (The resistor was connected between the potentiostat terminals for the working and the reference electrodes, and the reference electrode terminal was also connected to the Pt anode of the electrodialysis cell. The cathode was connected to the counter electrode terminal of the potentiostat.²⁷) Both source and receiving phases were stirred vigorously to limit concentration polarization. Sample aliquots were withdrawn periodically over 90 min from both source and receiving cells, but generally, only the receiving phase was analyzed, although the source phase was occasionally analyzed to verify concentration. Cation analysis was performed with an axial Varian 710-ES Inductively Coupled Plasma Optical Emission Spectrophotometer equipped with a Varian SPS 3 autosampler. Individual cation standards were prepared from nitrate (K^+ and Mg^{2+}) or carbonate (Ca^{2+}) salts, and serial dilutions were performed to generate a calibration curve. Concentrations in the standard solutions were verified using Specpure ICP standards obtained from Alfa Aesar. For each condition, ED was performed with three membranes, and uncertainties in fluxes, selectivities, and transference numbers represent standard deviations of values for the different membranes. Diffusion dialysis was performed with the same cell without an applied current.

ED data were plotted as total moles of cation passed through the membrane as a function of time, and fluxes were calculated by dividing the slope in these plots by the membrane area. To allow for ion exchange between the membrane and the solution, we determined the slopes only from data acquired after 30 min of dialysis. The reported $\text{K}^+/\text{Mg}^{2+}$ selectivities in these experiments are simply the ratio of K^+ and Mg^{2+} fluxes when the source phase contains equal concentrations of the two ions. Finally, transference numbers, t_i , were calculated using eq 1, where J_i is the flux of ion i in moles $\text{cm}^{-2} \text{s}^{-1}$, z_i is the ion charge, F is Faraday's constant, and I is the current density in A cm^{-2} .

$$t_i = \frac{J_i z_i F}{I} \quad (1)$$

In a few cases, current–voltage curves were obtained using the four-point method in a homemade two-compartment cell similar to the electrodialysis cell described above. Reference electrodes (Ag/AgCl, 3 M KCl, CH Instruments model 111) were brought to within ~ 4 mm of the membrane surface using homemade Haber-Luggin capillaries incorporating borosilicate glass frits (Ace glass, size E) to minimize solution leakage. The capillaries were affixed to ground-glass joints to ensure reproducible placement of the reference electrodes near the center of the membrane, and platinum wire electrodes were used for the anode and cathode. Current–voltage curves were obtained with solutions containing 0.01 M KNO_3 and 0.1 M $\text{Mg}(\text{NO}_3)_2$ on both sides of the membrane, and the current was increased stepwise at >30

s intervals to achieve steady state. The excess $\text{Mg}(\text{NO}_3)_2$ reduces solution resistance without greatly altering K^+ transport through the PEM. Over the course of these measurements, the source-phase pH decreases from 5.5 to 2.3, and the receiving-phase pH increases from 5.5 to 5.8.

Some experiments aimed to decrease proton transport employed the homemade 3-compartment ED cell illustrated in Figure 1.

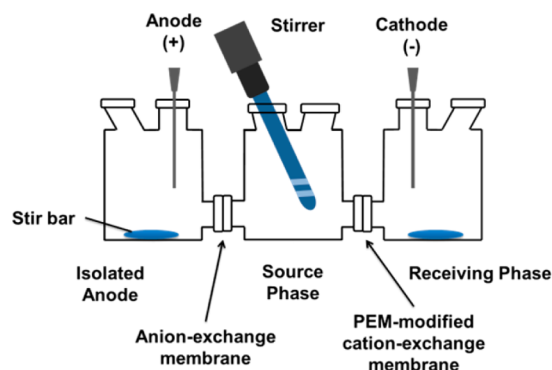


Figure 1. Home-built ED apparatus comprised of three 100 mL glass cells filled with salt or acid solutions and connected by 2.5 cm #15 flat joints with embedded tracks for O-rings to eliminate leaking. A multimeter was used to measure current that depended on the potential applied between the electrodes.

Following the manufacturer's protocol, an anion exchange membrane (AEM) was preconditioned in a 5% NaCl solution for 24 h at 40 °C. The AEM was rinsed with deionized water to remove excess salt and clamped between the left and center cells with an O-ring (3.1 cm² of exposed area). The modified cation-exchange membrane (CEM) was inserted between the center and right cells with an identical O-ring. Platinum wire electrodes were inserted in the left and right compartments, and all three compartments were stirred vigorously to minimize concentration polarization. A potential was applied between the electrodes using a DC power supply (Protek, 3006B). Voltage was adjusted periodically throughout the experiment to maintain ~4 mA of current (1.27 mA cm⁻²), as measured in series using a multimeter (TEK DMM249). The resistance between the electrodes typically increased throughout the ED as expected. Additional studies on the extent of water splitting used a similar 4-compartment electrodesorption cell to isolate the anode and cathode from the source and receiving phases, respectively. This setup is similar to that in Figure 1 but contains an additional cell for the cathode and a bare Nafion membrane that isolates the cathode compartment. Electrodesorption was performed with 0.01 M KNO_3 in the anode and source cells and 0.01 M NaNO_3 in the receiving and cathode cells. The current density was first maintained at underlimiting (0.32 mA cm⁻²) levels for 160 min before immediately switching to overlimiting (2.54 mA cm⁻²) levels for 20 min to ensure equal charge passage at each current level. The pH in the source and receiving phases was monitored periodically.

3. RESULTS AND DISCUSSION

Our previous work showed monovalent/divalent-ion selectivities of >300 in ED through porous alumina membranes coated with $(\text{PSS}/\text{PAH})_5$ films.²⁷ However, such membranes allow passage of both anions and cations, which is undesirable in some ED applications. Thus, this section initially examines layer-by-layer methods to coat ion-exchange membranes with polyelectrolyte films. Later subsections investigate whether the high selectivities of PSS/PAH multilayer films deposited on alumina membranes translate to films on commercial cation-exchange membranes. Studies of ED as a function of current density and source-phase concentration show remarkably high

selectivities, but both selectivity and current efficiency depend on the feed concentrations and current density.

3.1. Modification of Nafion Membranes. Nafion membranes are attractive for PEM adsorption because they have smooth, essentially defect-free surfaces. In contrast, other cation-exchange membranes that we obtained have large μm -sized surface voids that the thin multilayer film likely cannot bridge (see Figure S-1 in the Supporting Information). Elemental analysis with XPS confirms the adsorption of $(\text{PAH}/\text{PSS})_n$ films on oxidized Nafion (Table 1), as the

Table 1. XPS Elemental Compositions for Nafion 115 Membranes before and after Coating with $(\text{PAH}/\text{PSS})_x\text{PAH}$ Films

number of (PAH/PSS) bilayers	fluorine (%)	sulfur (%)	nitrogen (%)	carbon (%)	oxygen (%)
0	57.1	1.3	1.2	32.4	8.0
1.5, (PAH/PSS) ₁ PAH	11.5	4.7	5.1	58.0	19.7
3.5, (PAH/PSS) ₃ PAH	0.0	6.7	6.7	59.5	26.7
5.5, (PAH/PSS) ₅ PAH	0.4	7.4	6.8	55.7	28.4

elemental composition of the surface changes with successive depositions steps. The pretreated bare membrane contains a large fraction of fluorine because Nafion is a perfluorinated copolymer, but the fluorine fraction decreases after adsorption of polyelectrolytes and is essentially zero after formation of a $(\text{PAH}/\text{PSS})_3\text{PAH}$ film. Because of the limited escape depth for photoelectrons, XPS probes primarily the top ~5 nm of a surface and is most sensitive near the surface. Thus, the near-complete disappearance of fluorine signals after adsorption of 3.5 PAH/PSS bilayers suggests that the PEM is at least 5 nm thick.³² The small amount of fluorine reported after adsorption of a $(\text{PAH}/\text{PSS})_5\text{PAH}$ film stems from noise in the area of the fluorine signal. Sulfur and nitrogen signals increase as the fluorine signal decreases, confirming the adsorption of PSS (sulfur atoms) and PAH (nitrogen atoms).

3.2. Electrodialysis with Bare and Modified Cation-Exchange Membranes. Initial ED experiments employed a 2-compartment cell with 0.01 M KNO_3 and 0.01 M $\text{Mg}(\text{NO}_3)_2$ in the source phase (anode chamber) and 0.01 M HNO_3 in the receiving phase (cathode chamber). The 0.01 M HNO_3 maintains electrical conductivity and neutralizes hydroxide formed at the cathode to prevent precipitation of $\text{Mg}(\text{OH})_2$ in the receiving phase. We use nitrate rather than chloride salts to avoid generation of Cl_2 , which may damage the PEM.^{27,33} Figure 2 shows the amounts of K^+ and Mg^{2+} in the receiving phase as a function of time during constant current (1.27 mA cm⁻²) ED. The amount of K^+ in the receiving phase increases nearly linearly with ED time, and the slight decrease in flux at long times for bare Nafion membranes likely stems from an increase in the proton concentration in the source phase and a corresponding increase in the fraction of current carried by H^+ . The pH of the source phase decreased from 4.6 to ~2.3 over the course of the ED for both modified and bare membranes. (Note that pH values <4 are below the calibration range of the meter and not very accurate.)

Unmodified Nafion membranes show high passage of both K^+ and Mg^{2+} . In experiments with 3 replicate membranes, the average fluxes of K^+ ($6.4 \pm 0.3 \text{ nmol cm}^{-2} \text{ s}^{-1}$) and Mg^{2+} ($3.6 \pm 0.1 \text{ nmol cm}^{-2} \text{ s}^{-1}$) reflect an average selectivity of only 1.8 ± 0.1 at a current density of 1.27 mA cm⁻². The K^+ flux through membranes coated with $(\text{PAH}/\text{PSS})_3\text{PAH}$ films is 6.9 ± 0.2

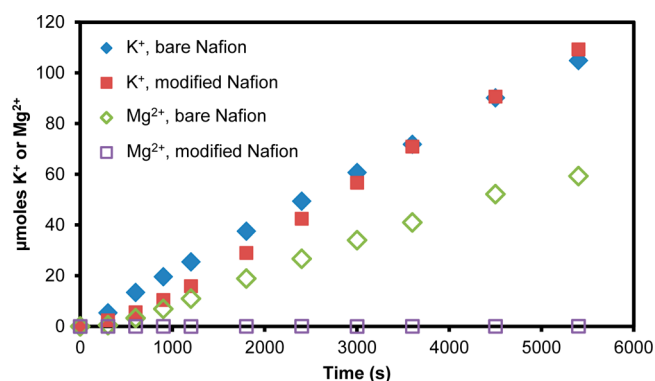


Figure 2. Moles of K^+ and Mg^{2+} in the receiving phase as a function of time during ED with initial solutions containing 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$ in the source phase and 0.01 M HNO_3 in the receiving phase. Electrolysis occurred in a 2-compartment experiment using bare (diamonds) and $(PAH/PSS)_5PAH$ -modified (squares) Nafion 115 membranes and a 1.27 mA cm^{-2} current density.

$\text{nmol cm}^{-2} \text{ s}^{-1}$ or approximately the same as that through the bare Nafion. In contrast, Mg^{2+} flux was $<5 \text{ pmol cm}^{-2} \text{ s}^{-1}$ for all three replicate membranes, which gives rise to a K^+/Mg^{2+} selectivity of >1000 for the $(PAH/PSS)_5PAH$ -coated membrane. This selectivity is similar to the value of >300 for $(PSS/PAH)_5$ films on porous alumina and is much higher than the typical selectivities of <10 for ion-exchange membranes.^{14,17–19,28,34}

In addition to selectivity, high current efficiencies are important to minimize the energy required for ED. The current efficiency (or the fraction of current carried through the membrane by a given ion, also known as the transference number, t_i) for K^+ is 0.53 for $(PAH/PSS)_5PAH$ -modified Nafion membranes at a current density of 1.27 mA cm^{-2} . In contrast, Mg^{2+} carries $\ll 1\%$ of the total current. Thus, other unwanted ions carry $\sim 50\%$ of the current through the membrane. Presuming that the Nafion is essentially 100% cation selective, protons must carry $\sim 50\%$ of the current through $(PAH/PSS)_5PAH$ -modified Nafion. In aqueous solutions, the proton electrophoretic mobility is approximately 5 times the mobility of K^+ , so proton transference numbers >0.5 are feasible at the end of the experiments when the source-phase pH is ~ 2.3 .³³ However, at the initial source-phase pH of 4.6, protons should not carry significant current. Some protons may diffuse from the acidic receiving phase to the source phase and migrate across the membrane. However, due to the cation-selectivity of Nafion, this would likely require coupled diffusion of protons to the source phase and other cations to the receiving phase. Such a process would not decrease the calculated K^+ and Mg^{2+} transference numbers, as these calculations assume all cation transport occurs through electromigration and yet measure cation transport to the receiving phase by any process (see eq 1). Diffusion dialysis experiments (no applied potential) show a K^+ flux that is only 7% of the flux in ED through $(PAH/PSS)_5PAH$ -modified Nafion. Thus, most of the K^+ transport occurs due to electromigration. In contrast, diffusive fluxes are $>50\%$ of ED fluxes through bare Nafion, and in some cases, this leads to a sum of calculated transference numbers of >1 .

Some of the non- K^+ current through modified membranes may stem from water splitting that occurs in an ion-depleted region near the polyelectrolyte/Nafion interface. At over-limiting currents, high local potential gradients in this region

may separate H^+ and OH^- ions that form due to dissociation of water (see below). Our previous measurements of transmembrane diffusion potentials suggest that PEMs are anion selective,²⁶ whereas Nafion is nearly ideally cation selective. Because cations likely carry $<50\%$ of the current in the PEM and nearly all the current in Nafion, positive currents give rise to significant cation depletion near the source-phase PEM/Nafion interface (i.e., cation electromigration through the PEM to the Nafion interface is less than that away from this interface toward the receiving phase; see Figure 3). Concurrent anion

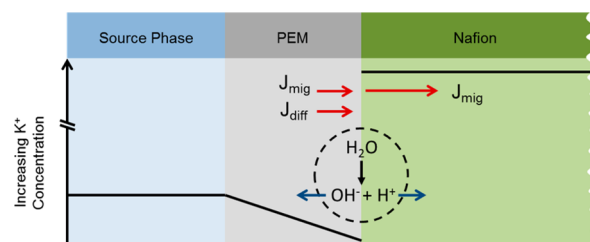


Figure 3. Schematic, qualitative diagram of the K^+ concentration profile (black lines) during ED through a PEM-coated Nafion membrane. The red arrows qualitatively represent the magnitudes of the fluxes due to electromigration, J_{mig} , and diffusion, J_{diff} , of cations in the PEM and/or Nafion. The sum of electromigration and diffusion in the PEM should equal the flux due to electromigration in Nafion, where diffusion is negligible compared to electromigration. Due to possible proton gradients, the concentration of K^+ may not be constant in the Nafion. The PEM/Nafion interface near the receiving phase (not shown) should show ion accumulation rather than depletion.

depletion occurs because few anions come to the interface through the Nafion, but anions likely carry more than 50% of the current in the PEM and thus migrate away from the PEM/Nafion interface toward the source phase. At steady state, diffusion toward the PEM/Nafion interface leads to constant ion fluxes throughout the modified membrane. The electric field in the depleted, low-conductivity region must be high to maintain a constant current, and at sufficiently high fields, water will split into OH^- and H^+ to provide current-carrying species. This should primarily occur near the PEM/Nafion interface where depletion is greatest. In this non-electrode process, water dissociates into H^+ and OH^- , and the electric field separates these ions. Moreover, Wessling's group recently showed that some PEMs act as water-splitting catalysts.^{28,35}

Water splitting should only occur at the high potentials required to drive the current density beyond the diffusion-limited value, I_{lim} . Equation 2 gives an approximate expression for the K^+ limiting current density based on the assumptions that the dominant concentration polarization occurs at the PEM/Nafion interface, that diffusive transport in Nafion is negligible, and that convection is negligible throughout the membrane (see the Supporting Information for a derivation of this equation).³⁶ In this equation,

$$I_{lim} \approx \frac{P_s \times c \times F}{\Delta t_+} \quad (2)$$

P_s is the diffusion permeance of the PEM, c is the KNO_3 concentration in the source phase, F is the Faraday constant, and Δt_+ is the difference in the K^+ transference numbers in Nafion and the PEM. Previous diffusion dialysis experiments with bare porous alumina and porous alumina coated with

(PSS/PAH)₄ films give a PEM permeance of 3.8 $\mu\text{m/s}$ for KCl.²⁶ Moreover, transmembrane potential measurements suggest that the PEM K⁺ transference number is ~ 0.3 in 0.01 M KCl.²⁶ Assuming that the (PAH/PSS)₅PAH coating on Nafion has approximately the same properties as the porous alumina-supported film, that KCl and KNO₃ transport properties are similar, and that Nafion is ideally selective (i.e., in KNO₃, the K⁺ transference number is 1), the limiting current density for a 0.01 M KNO₃ solution should be $\sim 0.5 \text{ mA cm}^{-2}$. This value is a factor of 2 lower than the $\sim 1.27 \text{ mA cm}^{-2}$ employed to obtain the data in Figure 2, which is consistent with possible water splitting at this current density. However, as mentioned above, transport of protons from the increasingly acidic anodic source phase will also decrease K⁺ transference numbers, particularly at the end of the ED.

3.3. Current–Voltage Curves and Evidence for Water Splitting. Current–voltage curves often provide insight into limiting currents and, hence, the processes occurring at membranes in ED. Typically, the I – V curve for an ion-exchange membrane exhibits three regions. At low current densities, the potential drop across the membrane is directly proportional to the current. As the current density approaches its diffusion-limited value (I_{lim}), the ion concentration near the interface decreases rapidly causing an increase in resistance and consequently a large potential drop that gives rise to a smaller slope or a plateau. Further increases in current density result in less-dramatic changes in the membrane voltage drop, presumably because electroconvection and/or water splitting bring additional ions to the interface.^{28,37,38} The intersection of the “plateau” region and the linear region serves as an estimate of I_{lim} .

As Figure 4 shows, the current density–voltage curve for a [PAH/PSS]₅PAH-modified membrane shows linear, “plateau”,

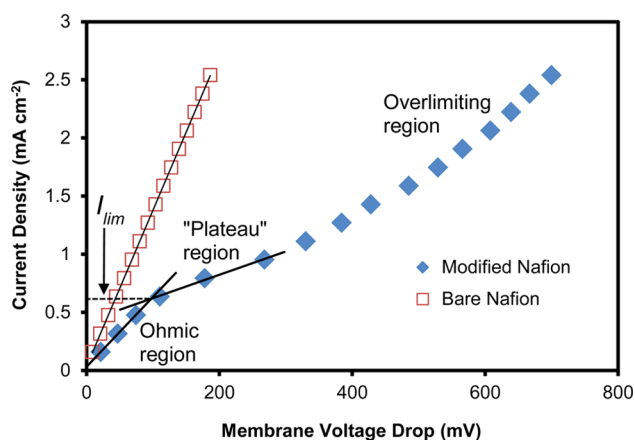


Figure 4. Current–voltage curves for bare (open squares) and [PAH/PSS]₅PAH-modified (filled diamonds) Nafion membranes. The experiments employed a two-compartment cell with solutions containing 0.01 M KNO₃ and 0.1 M Mg(NO₃)₂ on both sides of the membrane. The limiting current was determined from the intersection of the lines from the ohmic and “plateau” regions.

and overlimiting regions, with a limiting current density of around 0.6 mA cm^{-2} , which is comparable to the value calculated using eq 2. Bare, oxidized Nafion exhibits only an ohmic profile under the same conditions because its limiting current is much higher due to the absence of the restrictive film and more importantly passage of both Mg²⁺ and K⁺. These experiments employ a 10-fold excess of Mg²⁺ to minimize

solution resistance. The Mg²⁺ does not pass significantly through the PEM and thus has a negligible effect on I_{lim} for the modified membrane, but it will greatly increase I_{lim} for the bare Nafion. When we performed the same experiment without a membrane in the cell, the solution resistance was only slightly smaller than the total resistance with the bare Nafion membrane (see Figure S2 in the Supporting Information). Subtracting the solution resistance from the total resistance leads to values of 6 and 120 Ωcm^2 for the area resistances of Nafion and the [PAH/PSS]₅PAH-modified Nafion, respectively. Given that the Nafion conduction results from both 0.1 M Mg²⁺ and 0.01 M K⁺ and the modified membrane utilizes only the 0.01 M K⁺, the resistance of the modified membrane to K⁺ electromigration is likely about twice the resistance of the bare Nafion to this ion.

Water splitting should occur at high membrane potential drops and lead to changes in the pH of the source and receiving phases. However, protons and hydroxide ions generated electrolytically at the anode and cathode, respectively, also affect pH, so monitoring pH changes due to water splitting requires isolation of the anode and cathode with cation- and anion-exchange membranes, respectively. In such experiments, we employ a 4-compartment cell with 0.01 M KNO₃ solutions in the anode and source phases and 0.01 M NaNO₃ solutions in the receiving and cathode phases to allow monitoring of K⁺ flux and also avoid any pH changes due to formation of Mg(OH)₂. After passing 9.6 C of charge through the membrane using an underlimiting current density of 0.32 mA cm^{-2} (160 min of current), the pH of the source and receiving phases remained around 5.5. In contrast, during subsequent passage of 9.6 C at an overlimiting current density of 2.54 mA cm^{-2} (20 min of current), the pH of the source phase gradually increased to 7.0 and the receiving-phase pH dropped to around 4.0. Assuming that 50% of the current results in water splitting at this overlimiting current density, the pH in the receiving phase should drop to around 3.3. However, some of the protons will pass from the receiving phase into the cathode compartment, which is highly basic (pH 11 at the end of the experiment). Moreover, the anion-exchange membrane may not provide a perfect barrier to proton transport from the anode compartment to the source phase. Despite the qualitative nature of this experiment, it provides strong evidence that water splitting accounts for a substantial change in the pH of each compartment at high current densities and leads to some of the decrease in current efficiency at overlimiting current densities. As expected, extensive water splitting only occurs at relatively high transmembrane potentials.³⁹

3.4. Effect of Current Density on K⁺/Mg²⁺ Separations.

We further examined selectivity and current efficiency in ED at current densities ranging from 0.32 to 2.54 mA cm^{-2} for source-phase solutions containing 0.01 M KNO₃ and 0.01 M Mg(NO₃)₂. Figure 5 shows the K⁺ and Mg²⁺ fluxes from these experiments with coated Nafion membranes. For current densities at and below 2.22 mA cm^{-2} , the K⁺ flux increases with current density (see the Supporting Information, Table S1, for flux values). However, on going from 2.22 to 2.54 mA cm^{-2} , the K⁺ flux declines 30% and the Mg²⁺ flux increases 5-fold. Table 2 further shows that the K⁺ transference number declines at the highest current density, where the most water splitting should occur.^{28,40} The initially continuous increase in K⁺ flux and subsequent drop with increasing overlimiting current densities are difficult to explain and suggest complicated mass transport through the membrane. Wessling et al. recently found

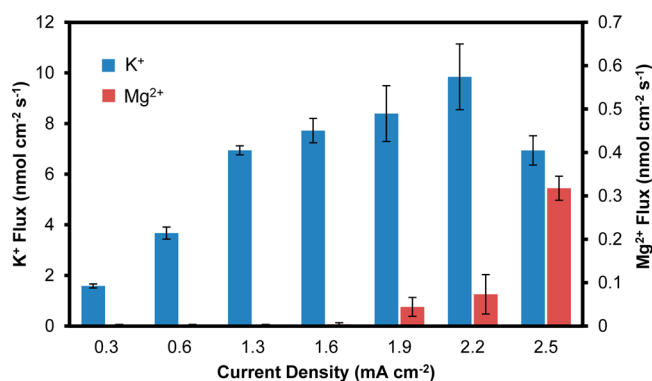


Figure 5. K^+ and Mg^{2+} fluxes as a function of applied current density in 2-cell ED experiments with 0.01 M HNO_3 in the receiving phase. The source phase initially contained 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$. Note the different scales for K^+ and Mg^{2+} flux.

Table 2. K^+/Mg^{2+} Selectivities and Cation Transference Numbers in ED through $(PAH/PSS)_3PAH$ -Modified Nafion Membranes as a Function of Current Density^a

current density ($mA\ cm^{-2}$)	K^+/Mg^{2+} selectivity	K^+ transference	Mg^{2+} transference
2.54	22.1 ± 3.5	0.26 ± 0.02	0.024 ± 0.002
2.22	176 ± 104	0.43 ± 0.06	0.006 ± 0.004
1.90	245 ± 171	0.43 ± 0.02	0.004 ± 0.002
1.59	>1000	0.47 ± 0.03	<0.0007
1.27	>1000	0.53 ± 0.01	<0.0007
0.63	>1000	0.56 ± 0.04	<0.0007
0.32	>480	0.48 ± 0.02	<0.002

^aThe source phase contained 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$.

that PEMS can cause hydrodynamic instabilities at the surface of ion-exchange membranes, which should affect transport and overlimiting currents.⁴¹

The increased Mg^{2+} transport at high current densities may result from water splitting, which produces not only protons but also stoichiometric amounts of OH^- ions that migrate toward the anode in the source phase. This should result in a locally high pH near the source phase/membrane interface where hydroxyl ions may form $Mg(OH)_x$ complexes with the incoming Mg^{2+} ions. The PEM permeability to the low concentration of neutral, soluble $Mg(OH)_2$ may be much higher than to Mg^{2+} ions, and we speculate that diffusion of this neutral species across the PEM might be the principal mechanism that enhances magnesium transfer at the higher overlimiting currents (Figure 5 and Table 2). Notably, to form a significant fraction of $Mg(OH)_x$ species, the pH value at the source-phase membrane surface must reach a threshold value of 9–11 (assuming that the Mg^{2+} concentration does not considerably increase in this region). This threshold value, which may only appear at the higher current densities, occurs locally near the PEM and is very different from the bulk solution pH. Additionally, a high local pH may alter film permeability to increase Mg^{2+} flux.

Interestingly, coating both sides of the Nafion membranes with $(PAH/PSS)_3PAH$ films yields greater selectivities than coating either side alone. Specifically, for a current density of $2.54\ mA\ cm^{-2}$, K^+/Mg^{2+} selectivities are 7.8 ± 1.6 with a $(PAH/PSS)_3PAH$ film only on the side of the membrane facing the source phase and 10.0 ± 3.8 when the films is on the side facing the receiving phase. With a $(PAH/PSS)_3PAH$ coating on

both sides of the membrane, the K^+/Mg^{2+} selectivity is 22.1 ± 3.5 (Table 2). Thus, selectivity approximately doubles when coating both sides of the membrane.

3.5. ED with Different Source-Phase Concentrations.

To further investigate the effect of current density on separations, we performed ED with different concentrations of salt in the source phase. The KNO_3 and $Mg(NO_3)_2$ source-phase concentrations were $\geq 0.01\ M$ to avoid excessive solution resistance, and the receiving phase always contained 0.01 M HNO_3 . This series of experiments used a current density of $2.54\ mA\ cm^{-2}$, which gives a detectable Mg^{2+} flux at low salt concentrations. As Figure 6 shows, although the applied current

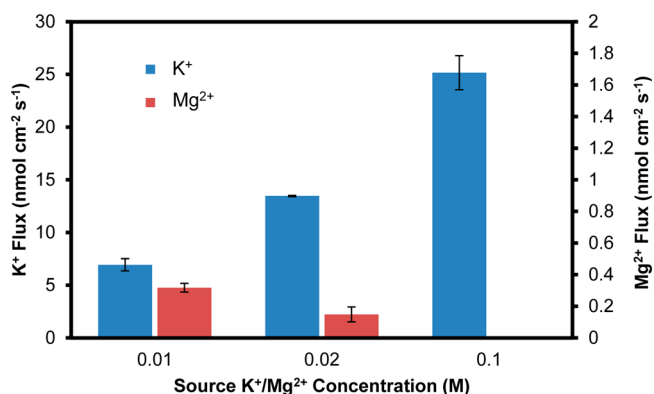


Figure 6. K^+ and Mg^{2+} fluxes as a function of the KNO_3 and $Mg(NO_3)_2$ source-phase concentrations in 2-compartment ED with 0.01 M HNO_3 in the receiving phase and a $2.54\ mA\ cm^{-2}$ current density. Note the different scales for K^+ and Mg^{2+} ; the Mg^{2+} flux was undetectable ($<1\ pmol\ cm^{-2}\ s^{-1}$) with KNO_3 and $Mg(NO_3)_2$ source-phase concentrations of 0.1 M.

is constant, K^+ flux nearly doubles from 6.94 ± 0.58 to $13.5 \pm 0.6\ nmol\ cm^{-2}\ s^{-1}$ when the source phase concentration increases from 0.01 to 0.02 M in both KNO_3 and $Mg(NO_3)_2$. This provides further evidence that in a 0.01 M KNO_3 solution this applied current density is overlimiting for K^+ . Simultaneously, Mg^{2+} flux drops from 318 ± 28 to $149 \pm 47\ pmol\ cm^{-2}\ s^{-1}$, perhaps because of less water splitting. Further increasing the source-phase KNO_3 and $Mg(NO_3)_2$ concentrations to 0.1 M increases the K^+ flux to $25.2 \pm 1.6\ nmol\ cm^{-2}\ s^{-1}$, and Mg^{2+} flux falls below its detection limit ($<1\ pmol\ cm^{-2}\ s^{-1}$).

The increase in K^+ flux and simultaneous decrease in Mg^{2+} flux on raising the source-phase concentrations from 0.01 to 0.1 M lead to a remarkable increase in selectivity from 22 to $>20\ 000$ (see Table 3). Furthermore, the transference number for K^+ approaches unity with 0.1 M KNO_3 and 0.1 M $Mg(NO_3)_2$ in the source phase. The current density is constant

Table 3. K^+/Mg^{2+} Selectivities and Cation Transference Numbers in ED through $(PAH/PSS)_3PAH$ -Modified Nafion Membranes^a

source-phase concentration (M)	K^+/Mg^{2+} selectivity	K^+ transference	Mg^{2+} transference
0.01	22.1 ± 3.5	0.26 ± 0.02	0.024 ± 0.002
0.02	96 ± 26	0.51 ± 0.01	0.011 ± 0.004
0.1	$>20\ 000$	0.96 ± 0.06	<0.0001

^aFor the feed solution with 0.1 M salts, selectivity and Mg^{2+} transference number are estimated from the minimum detectable Mg^{2+} flux. The current density was $2.54\ mA\ cm^{-2}$.

in this series of experiments and should fall below the limiting value at high source-phase concentrations. On the basis of eq 2 and the permeance value mentioned previously, the limiting current density for 0.1 M KNO_3 is $\sim 5 \text{ mA cm}^{-2}$, which is twice the applied current density. Below the limiting current, local electric fields are small and little water splitting occurs, so Mg(OH)_x species should not form and decrease $\text{K}^+/\text{Mg}^{2+}$ selectivity. Moreover, proton transport from the source to the receiving phase is negligible in the presence of 0.1 M K^+ , so the K^+ transference number is high.

We also investigated the utility of these membranes in separating K^+ and Mg^{2+} from source-phase solutions where the KNO_3 and $\text{Mg(NO}_3)_2$ concentrations are not the same. In all experiments, the receiving phase was 0.01 M HNO_3 and the current density was 2.54 mA cm^{-2} . When the source phase contained 0.1 M KNO_3 and 0.01 M $\text{Mg(NO}_3)_2$, the K^+ flux was $24.7 \pm 0.3 \text{ nmol cm}^{-2} \text{ s}^{-1}$ and the Mg^{2+} flux was not detectable. The high KNO_3 concentration in these experiments again ensures that K^+ is the dominant current carrier, and the K^+ transference number is 0.938 ± 0.010 .

In the reciprocal ED experiment, where the source phase contains 0.01 M KNO_3 and 0.1 M $\text{Mg(NO}_3)_2$, the K^+ flux is $9.9 \pm 0.6 \text{ nmol cm}^{-2} \text{ s}^{-1}$ and the Mg^{2+} flux is $272 \pm 98 \text{ pmol cm}^{-2} \text{ s}^{-1}$ giving rise to a $\text{K}^+/\text{Mg}^{2+}$ flux ratio of 40 ± 14 . However, this number does not account for the Mg^{2+} to K^+ concentration ratio of 10 in the source phase, and the true selectivity in this separation is 400 ± 140 . Because of the low KNO_3 concentration, the K^+ transference number is 0.38 ± 0.02 , and protons from water splitting probably carry much of the remainder of the current in Nafion. Interestingly, the Mg^{2+} flux remained virtually unchanged from $318 \pm 28 \text{ pmol cm}^{-2} \text{ s}^{-1}$ at a 0.01 M source-phase concentration to $272 \pm 98 \text{ pmol cm}^{-2} \text{ s}^{-1}$ at a 0.1 M concentration, even with a constant KNO_3 concentration of 0.01 M. Despite the low K^+ transference number at an overlimiting K^+ current, these membranes remain highly selective when the divalent cation is in large excess. This should prove useful in applications that require the removal of small concentrations of contaminants and would most likely be implemented using low current densities applied over larger membrane areas in flow-through cells with low solution thicknesses. Prior studies suggest that Mg^{2+} adsorption in PEMs may increase surface charge to maintain a low flux of Mg^{2+} ions, even as the Mg^{2+} concentration increases.⁴² Additionally, at the high Mg^{2+} concentration, Mg(OH)^+ rather than Mg(OH)_2 species may result from OH^- formed in water splitting. The membrane may be much more permeable to low concentrations of neutral, soluble Mg(OH)_2 than to Mg(OH)^+ .

3.6. Electrodialysis in a 3-Compartment Cell. With 0.01 M KNO_3 in the source phase, the low K^+ transference numbers even at underlimiting currents (Table 2) suggest electromigration of H^+ from the source phase, particularly as this phase becomes more acidic due to proton generation at the anode. To investigate the extent of unwanted ED proton current that is not associated with water splitting, we employed a 3-compartment cell that separates the proton-generating anode from the source phase using an anion-exchange membrane. This strategy is typical for ED applications that employ multiple compartments. Compared to the 2-compartment experiments described above, ED of 0.01 M KNO_3 and 0.01 M $\text{Mg(NO}_3)_2$ in a 3-compartment cell increases the K^+ flux from 6.9 ± 0.2 to $8.9 \pm 0.1 \text{ nmol cm}^{-2} \text{ s}^{-1}$ upon application of the same 1.27 mA cm^{-2} current density. This increases the K^+ current efficiency from 0.53 to 0.67. (Figure 7 shows data

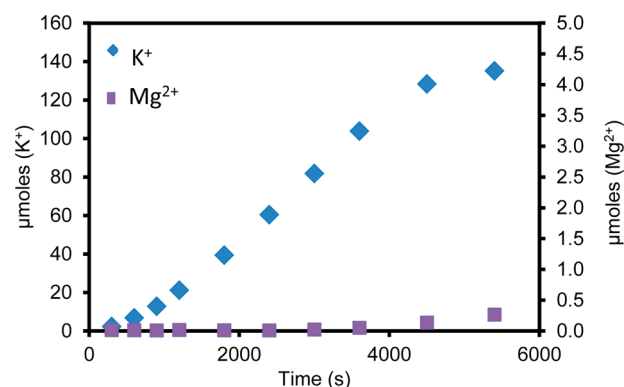


Figure 7. Moles of K^+ and Mg^{2+} in the receiving phase as a function of time in a 3-compartment ED experiment with 0.01 M KNO_3 and 0.01 M $\text{Mg(NO}_3)_2$ in the source phase and 0.01 M HNO_3 in the receiving phase. 0.01 M HNO_3 was also used in the isolated anode cell.

from a representative experiment.) Additionally, Mg^{2+} flux is still very low ($< 23 \text{ pmol cm}^{-2} \text{ s}^{-1}$) with the 3-compartment cell, and the minimum $\text{K}^+/\text{Mg}^{2+}$ selectivity with 3 different membranes was above 350.

Overall, the fraction of the current carried by K^+ increases $\sim 25\%$ on going from the 2-compartment to the 3-compartment cell (see Table 2 for the 2-compartment data). Nevertheless, other ions still carry $\sim 30\%$ of the current in this system. Similar to the 2-compartment experiments, the pH of the source phase is around 4.5 at the start of the experiment, so initially, the mobility of protons in the membrane would have to be 2 orders of magnitude higher than the mobility of K^+ to account for such large H^+ currents. By the end of the experiment, the source-phase pH decreases to 3.5 (compared to ~ 2.3 in the 2-compartment experiment, the anion-exchange membrane likely does not completely block proton transport), so a proton transference of 0.3 would still require a high proton mobility in the membrane if no water splitting occurs. Thus, these experiments suggest some water splitting under these conditions.

3.7. Selectivities among Other Cations. Experiments with other cations also show remarkable selectivity. At a current density of 1.27 mA cm^{-2} with a source phase containing 0.01 M KNO_3 and 0.01 M $\text{Ca(NO}_3)_2$, and a receiving phase of 0.01 M HNO_3 , $\text{K}^+/\text{Ca}^{2+}$ selectivities and K^+ transference numbers are similar to those in corresponding ED with 0.01 M KNO_3 and 0.01 M $\text{Mg(NO}_3)_2$ in the source phase. Specifically, K^+ flux is $5.94 \pm 0.27 \text{ nmol cm}^{-2} \text{ s}^{-1}$ and Ca^{2+} flux is $18 \pm 12 \text{ pmol cm}^{-2} \text{ s}^{-1}$, representing an average $\text{K}^+/\text{Ca}^{2+}$ selectivity of 430 ± 220 . Uncertainty in the very low Ca^{2+} flux causes the large uncertainty in selectivity. Compared to $\text{K}^+/\text{Mg}^{2+}$, slightly lower values for $\text{K}^+/\text{Ca}^{2+}$ selectivities are consistent with the larger diffusion coefficient and lower hydration energy for Ca^{2+} compared to Mg^{2+} .³³

Transference numbers in these experiments are 0.451 ± 0.021 for K^+ and 0.003 ± 0.002 for Ca^{2+} . In the corresponding control experiment, flux through unmodified Nafion membranes is $6.24 \pm 0.25 \text{ nmol cm}^{-2} \text{ s}^{-1}$ for K^+ and $3.86 \pm 0.05 \text{ nmol cm}^{-2} \text{ s}^{-1}$ for Ca^{2+} , representing an average $\text{K}^+/\text{Ca}^{2+}$ selectivity of only 1.62 ± 0.05 . Again, the multilayer film provides a relatively small resistance to K^+ transport while essentially preventing transport of the multivalent cation. These selectivities are 1–2 orders of magnitude higher than those previously reported for commercial membranes in $\text{Na}^+/\text{Ca}^{2+}$

separations with below-limiting currents.¹⁴ Such high selectivities may lead to new ED applications.

4. CONCLUSIONS

Alternating adsorption of polycations and polyanions on Nafion cation-exchange membranes leads to remarkable monovalent/divalent cation selectivities in ED. Either at high source-phase concentrations or at low current densities, the K^+/Mg^{2+} selectivity of Nafion membranes coated with $(PAH/PSS)_3PAH$ films is >1000 . Selectivities are still >350 when the concentration of one cation exceeds the other by a factor of 10. However, with low source-phase K^+ and Mg^{2+} concentrations, selectivities decline when the current greatly exceeds the K^+ diffusion-limited value, perhaps because water splitting in the membrane increases permeability to Mg^{2+} or leads to a small amount of neutral, soluble $Mg(OH)_2$ that can diffuse through the membrane. Current–voltage curves and pH monitoring confirm both the K^+ limiting current and water splitting at overlimiting currents. At 0.1 M KNO_3 source-phase concentrations, the K^+ transference number approaches 1, presumably because the current is well below the K^+ diffusion-limited value and H^+ transport is insignificant. Future work should investigate the long-term stability of these membranes and their use for recovery of more valuable cations. Additionally, modeling of the system will enhance understanding of boundary conditions and the concentration dependence of ion transport.

■ ASSOCIATED CONTENT

Supporting Information

SEM images of several ion-exchange membranes, discussion of limiting currents, additional I – V curves, and a table of ion fluxes in ED. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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