

High Selectivities among Monovalent Cations in Dialysis through Cation-Exchange Membranes Coated with Polyelectrolyte Multilayers

Liu Yang^a, Chao Tang^b, Muhammad Ahmad^a, Andriy Yaroshchuk^{c,d} and Merlin L. Bruening^{a,b,*}

^aDepartment of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

^bDepartment of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana 46556, United States

^cICREA, pg.L.Companys 23, 08010 Barcelona, Spain

^dDepartment of Chemical Engineering, Polytechnic University of Catalonia, av. Diagonal 647, 08028 Barcelona, Spain

*Corresponding author: Merlin L. Bruening E-mail: mbruenin@nd.edu

ABSTRACT

Cation-exchange membranes allow preferential passage of cations over anions, but they show minimal selectivity among cations, which limits their use in ion separations. Recent studies show that modification of cation-exchange membranes with polyelectrolyte multilayers leads to exceptional monovalent/divalent cation electro dialysis selectivities, but no studies report high selectivity among monovalent ions. This work demonstrates that adsorption of protonated poly(allylamine) (PAH)/poly(4-styrenesulfonate) (PSS) multilayers on Nafion membranes leads to high K^+/Li^+ selectivities in Donnan dialysis, where K^+ and Li^+ ions in a source phase pass through the membrane and exchange with Na^+ ions in a receiving phase. Addition of 0.01 M HNO_3 to a source phase containing 0.01 M KNO_3 and 0.01 M $LiNO_3$ increases the K^+/Li^+ selectivity from 8 to ~60 through (PAH/PSS)₅PAH-coated Nafion membranes, primarily because of a ≥ 5 -fold increase in K^+ flux. These selectivities are much larger than the ratio of 1.9 for the aqueous diffusion coefficients of K^+ and Li^+ , and uncoated Nafion membranes give a K^+/Li^+ selectivity < 3 . Bi-ionic transmembrane potential measurements at neutral pH confirm that the membrane is more permeable to K^+ than Li^+ , but this selectivity is less than in Donnan dialysis with acidic solutions.

In-situ ellipsometry data indicate that PAH/PSS multilayers (assembled at pH 2.3, 7.5 or 9.3) swell at pH 2.0, and this swelling may open cation-exchange sites that preferentially bind K^+ to enable highly selective transport. The coated membranes also exhibit modest selectivity for K^+ over H^+ , suggesting selective transport based on preferential partitioning of K^+ into the coatings. Selectivity declines when increasing the source-phase KNO_3 concentration to 0.1 M, perhaps because the discriminating transport pathway saturates. Moreover, selectivities are lower in electro dialysis than in Donnan dialysis, presumably because electro dialysis engages other transport mechanisms, such as electroosmosis and strong electromigration.

KEYWORDS:

Ion-exchange membranes, Donnan dialysis, monovalent cations, layer-by-layer, selectivity

1. Introduction

Ion-exchange membranes allow preferential passage of cations or anions¹ to enable applications such as desalination of brackish waters,² deacidification of fruit juices,³ energy storage in redox flow batteries,⁴ and wastewater treatment.⁵ However, most ion-exchange membranes exhibit modest selectivities among various cations or anions,⁶⁻⁷ which limits their application in salt separations such as water softening, NaCl purification, and isolation of Li^+ from other alkali metals. Through variation of membrane cross-linking,⁸⁻⁹ hydrophobicity,¹⁰⁻¹¹ and surface charge,¹² many studies focused on creating ion-exchange membranes with selectivities among cations or anions. Recently several papers reported remarkable selectivities between monovalent and divalent cations or anions when coating ion-exchange membranes with polyelectrolyte multilayers (PEMs).¹³⁻¹⁵ For example, White and coworkers demonstrated K^+/Mg^{2+} electro dialysis selectivities >1000 ,¹⁶ and Zhao et al. found Cl^-/SO_4^{2-} selectivities as high

as 47.¹⁷ PEM coatings also enhance ion separations with nanofiltration membranes.¹⁸⁻²⁰ However, no studies reported high selectivities among monovalent ions. Recent crown ether-containing membranes show K^+/Li^+ and Cs^+/Na^+ selectivities around 4,²¹⁻²² and metal-organic framework membranes exhibit a Li^+/K^+ selectivity of 2.2.²³

We focus on separating Li^+ from various monovalent cations because the hydrated radius and hydration energy of Li^+ are larger than the corresponding values for other alkali metal ions,²⁴⁻²⁷ which may enable high selectivity. If the Li^+ ions retain their waters of hydration while passing through the membrane, the large hydrated radius should lead to a low diffusion coefficient.²⁵ On the other hand, if they must lose some of the waters of hydration this should lead to a low partition coefficient in the membrane.²⁸

Membrane-based separation of Li^+ from other metal ions is also significant because of the importance of Li-containing refrigerants and batteries.²⁹ Methods for isolating Li^+ include solvent extraction,³⁰ nanofiltration,³¹ low-pressure reverse osmosis,³² and electrodialysis.³³ However, prior work mainly investigated the separation of cations with different valences. Selective ion-exchange membranes may provide a platform that can efficiently isolate Li^+ from other monovalent cations.

Separations through ion-exchange membranes can, in principle, occur through either electrodialysis (ED) or Donnan dialysis (DD). ED employs an electric current to drive cations through cation-exchange membranes and anions through anion-exchange membranes, thus moving salts from diluate to concentrate compartments. In contrast, with a perfectly cation-selective ion-exchange membrane, in DD cations in the source phase must exchange with different cations in the receiving phase (**Figure 1**).³⁴ In potential applications, DD using a thin flow cell with an acid receiving phase could extract contaminating ions away from Li^+ if the cation-exchange membrane were highly permeable and selective for the contaminating ions. Previous

reports examined DD for separations such as the isolation of Au^{3+} from Ni^{2+} and Cu^{2+} ,³⁵ removal of Mg^{2+} and Ca^{2+} from lime softening sludge,³⁶ capture of Cu^{2+} ,³⁷ nitrate,³⁸ or borate³⁹ from aqueous solutions, and the exchange of Mg^{2+} in river water with Na^+ in seawater prior to reverse electrodialysis.⁴⁰ However, low selectivity limits DD applications, most of which focus on separating ions with different valences.

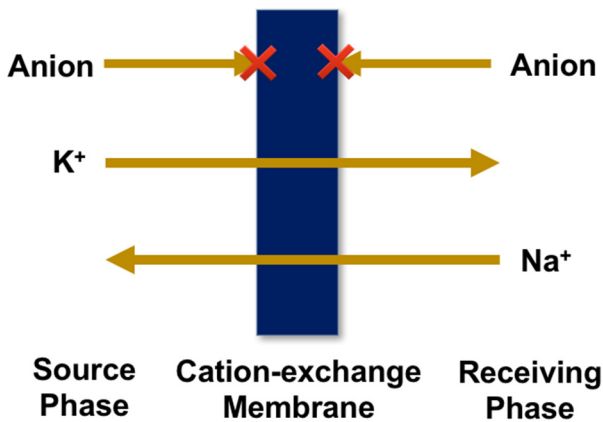


Figure 1. Scheme of K^+/Na^+ exchange in DD through a cation-exchange membrane.

This study examines the selectivities among K^+ , H^+ , and Li^+ in ED and DD through Nafion 115 membranes coated with films prepared using alternating adsorption of protonated poly(allylamine) (PAH) and poly(4-styrenesulfonate) (PSS). These polyelectrolytes have a high charge density and form relatively smooth, dense, stable ionically cross-linked films that do not swell greatly in water,⁴¹⁻⁴⁴ and they previously showed high selectivities in separating monovalent and divalent cations.^{16, 45} We investigate selectivities as a function of source-phase compositions and concentrations. Additionally, ellipsometric studies of PEM swelling aim to help explain why K^+ flux increases in acidic conditions. Remarkably, DD K^+/Li^+ selectivities reach values of ~ 60

when the source phase is acidic. To our surprise, the membranes also show modest K^+ over H^+ selectivities in DD.

2. Experimental

2.1 Materials

Poly(sodium 4-styrenesulfonate) ($M_w = 70\ 000$ Da) and poly(allylamine hydrochloride) ($M_w = 17\ 500$ Da) were purchased from Sigma-Aldrich, and the pH of polyelectrolyte solutions was adjusted using 0.1 M HCl or 0.1 M NaOH. All inorganic salts: sodium chloride (Sigma-Aldrich), potassium nitrate (Sigma-Aldrich), sodium nitrate (J.T. Baker), and lithium nitrate (Spectrum), were used as received. Nafion 115 membranes were acquired from Ion Power (New Castle, DE, thickness 127 μm), and aqueous solutions were prepared using deionized water (Milli-Q Reference Ultra-Pure Water Purification System, 18 $M\Omega$ cm). 3-Mercaptopropionic acid (MPA, 99%) (Aldrich) was used as received.

2.2 Film deposition and characterization

Membrane discs (25 mm diameter) were punched from a Nafion membrane sheet and pretreated according to literature procedures.⁴⁶⁻⁴⁷ Specifically, membranes were rinsed with deionized water and sequentially immersed in 100 °C solutions of 3% H_2O_2 , deionized water, 1.0 M H_2SO_4 , and deionized water for 30 min each. Membranes were rinsed with room-temperature deionized water from a wash bottle for 30 s after every immersion.

Film adsorption (assembly pH of 2.3) started with immersion of pretreated membranes in 0.02 M PAH (dissolved in 1.0 M NaCl, pH 2.3) for 5 min, and rinsing with deionized water to remove weakly adhered polyelectrolytes. This was followed by immersion in 0.02 M PSS (dissolved in 0.5 M NaCl, pH 2.3) for 5 min, and rinsing with deionized water again. (Polymer concentrations are those of the repeat unit.) This process was repeated to give a (PAH/PSS)₅PAH

film (this terminology denotes adsorption of 5 PAH/PSS layer pairs and an additional PAH layer) on the surface. To make (PAH/PSS)₅PAH films with assembly pH values of 7.5 or 9.3, PAH and PSS solutions were adjusted to the desired pH values and the same protocol was followed.

Ellipsometry studies employed (PAH/PSS)₅PAH films on Au-coated Si wafers. The wafers (200 nm of Au sputtered on 20 nm of Cr on Si(100) wafers, coating was performed by LGA Thin Films, Santa Clara, CA) were initially cleaned in a UV/O₃ chamber for 15 min prior to their immersion in a solution of 0.005 M MPA in ethanol for 24 h. After rinsing with ethanol and water and drying with N₂, these modified wafers served as substrates for (PAH/PSS)₅PAH adsorption, which occurred using the procedure described above for coating pretreated Nafion. The “dry” thicknesses of the PEMs were determined in air using a spectroscopic ellipsometer (alpha-SE, J.A. Woollam) at an incident angle of 70°. The coated wafers were soaked in different salt- or acid-containing solutions for 1.5 h prior to the performance of in-situ ellipsometry using a 500 µL liquidCell (J.A. Woollam). In all experiments, film refractive indices were fit using a Cauchy model. For films in solution, the model specified high purity water as the ambient medium (20 °C), and the gold substrate n and k values were determined in a prior experiment in air. (The low salt concentrations in the water do not significantly change the water refractive index.) Ellipsometric measurements were performed on two or three spots for each wafer on at least three replicate films. The fitted refractive indices for the swollen films ranged from 1.450 to 1.505.

2.3 Donnan dialysis

The DD apparatus was described previously.⁴⁸ A membrane disc and an O-ring were clamped between two homemade glass cells to expose a membrane area of 3.1 cm². Initially, the source-phase compartment contained 90 mL of an inorganic salt solution, and the receiving-phase compartment was filled with 90 mL of 0.02 M or 0.03 M NaNO₃. Both source and receiving

compartments were stirred vigorously to limit concentration polarization. During 90 min of DD, 1-mL aliquots were collected periodically from the receiving and source phases to determine the concentrations of target monovalent cations. The total number of moles that passed to the receiving phase was calculated taking into account changes in volume due to the removed aliquots and the salt removed in the aliquot.

Cation concentrations (Li^+ , K^+ , Na^+) were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 8000) with standard calibration curves. The calibration standards were prepared by dilution of commercial ICP-OES standard solutions (GFS chemicals) with 2% nitric acid. Subsequent calibration curves with Na^+ added to the standards (to mimic the receiving phase conditions) were used to correct for the effect of the excess Na^+ , which tends to increase K^+ and Li^+ emissions $\sim 40\%$ and $\sim 20\%$, respectively. Similarly, the relatively high concentrations of K^+ and Li^+ increase the emission from Na^+ in the source phase by $\sim 30\%$, which was corrected for using subsequent calibration curves with added K^+ and Li^+ . H^+ concentrations were determined with a pH meter calibrated with reference standard buffers (pH = 4.00 or 7.00, BDH Chemicals) and two buffers with lower pH values (pH = 2.00 or 3.00, GFS Chemicals). The total amounts of monovalent cations passed through the membrane were plotted as a function of time. To determine ion fluxes, the slope in each plot (for data in the linear region) was divided by the exposed membrane area. Selectivities are simply the ratios of ion fluxes when the concentrations of different cations are the same in the source phase. (The activity coefficients for K^+ and Li^+ differ by $<4\%$ under the conditions of this study, and the activity coefficient for H^+ is within 7% of the values for alkali metal ions.⁴⁹)

2.4 Electrodialysis

ED was performed as described previously,^{16, 50} and the apparatus is the same as that used for DD except for an externally applied current. A CH Instruments (Model 660E) potentiostat/galvanostat was used to generate a 2.0 mA constant current, which carries cations from the source phase to the receiving phase. Pt wire electrodes served as the anode in the source phase and the cathode in the receiving phase. The reference electrode terminal was attached to the Pt cathode.

The transference number (fraction of current carried by a specific ion) was calculated using equation 1, where J_i is the flux of ion i , z_i is the ion charge, F is Faraday's constant, and I is the total current density.

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

This equation assumes no diffusive ion transport. If significant ion diffusion occurs (either coupled diffusion of different cations in the source and receiving phases⁵¹ or coupled diffusion of a cation and an anion from the source to the receiving phase),³⁴ equation (1) will overestimate the transference number.

2.5 Bi-ionic transmembrane potential and impedance spectroscopy measurements

Bi-ionic transmembrane potentials (receiving-phase potential minus source-phase potential) were measured using KNO_3 (source phase) and LiNO_3 (receiving phase) solutions at various equal concentrations (0.01 M, 0.02 M, 0.1 M and 0.5 M). The apparatus for determining the potentials is a homemade two-compartment cell with capillaries on each side that approach the membrane to within ~4 mm. Ag/AgCl reference electrodes (1 M KCl, CH Instruments) were immersed into the capillaries (filled by 3 M KCl) to measure potentials. Initially, the two capillaries were both placed in the receiving solution to determine the correction for the small potential difference between the reference electrodes. Subsequently, with the capillaries on two sides of the membrane, a

multimeter determined the potential difference between the two reference electrodes, which includes the membrane potential and the potentials at the junctions between the solutions and the capillaries. The junction potentials were estimated using the Henderson equation.⁴⁵ Thus, the transmembrane potential is equal to the total potential difference minus the junction potentials at the two capillaries and the small correction for the difference between the reference electrodes. The net corrections for junction potentials were <2.3 mV. All solutions were stirred vigorously to minimize the effect of boundary layers. The activity of KNO₃ or LiNO₃ is the product of its concentration and activity coefficient obtained from the literature.⁴⁹ The standard deviations of experimental data are from experiments with 3 replicate membranes.

Electrical impedance measurements were performed using the same homemade two-compartment cell as above described. The membrane separated two phases with 0.01 M KNO₃ or 0.01 M LiNO₃. Impedance measurements employed a CH Instruments (Model 660E) potentiostat/galvanostat at 21 ± 2 °C. In this 4-electrode configuration, platinum wire electrodes were used for the working and counter electrodes, and two reference electrodes (Ag/AgCl, 1 M KCl, CH Instruments model 111) served as a sensing electrodes to measure the ac potential difference across the membrane.

2.6 Modeling of ion transport and bi-ionic potentials across (PAH/PSS)₅PAH-coated membranes

Equation (2) describes the fluxes, j_i , of specific ions passing through coatings. In this

$$-\frac{j_i}{P_i^*} = \frac{dc_i^*}{dx^*} + z_i c_i^* \frac{d\varphi^*}{dx^*} \quad (2)$$

equation, P_i^* is the ion permeability in the coating, φ^* is the dimensionless (in F/RT units) electrostatic potential in a virtual solution, c_i^* is the concentration of ion i in this solution, x^* is the coordinate scaled on the coating thickness, and z_i is the ion charge. The virtual (or reference)

solution is a bulk electrolyte solution that could be in thermodynamic equilibrium with a given plane inside the coating.

Similarly, equations (3) and (4) describe ion fluxes, j_i , through Nafion and solution

$$-\frac{j_i}{D_i} = \frac{d\bar{c}_i}{d\bar{x}} + z_i \bar{c}_i \frac{d\bar{\varphi}}{d\bar{x}} \quad (3)$$

$$-\frac{j_i}{D_i} = \frac{dc_i}{dx} + z_i c_i \frac{d\varphi}{dx} \quad (4)$$

boundary layers, respectively. The overbars denote properties in Nafion, and D_i is the diffusion coefficient of ion i . Instead of a virtual solution, we use the real ion concentrations and potentials in Nafion and an ideal Donnan model (equation (5)) to describe partitioning at the coating/Nafion interfaces, assuming electroneutrality inside Nafion (equation (6)).

$$\Delta\phi^D = \frac{RT}{z_i F} \ln \frac{c_i^*}{\bar{c}_i} \quad (5)$$

$$\sum_i z_i \bar{c}_i = -z_{ix} c_x \quad (6)$$

In these equations, $\Delta\phi^D$ is the Donnan potential at the coating/Nafion interfaces and c_x is the fixed-charge concentration in Nafion.

For two salts with a bi-ionic potential system, equations (2), (3), and (4) are systems of three equations (one equation for each ion). We assume boundary layers with a thickness of 100 μm in the solution next to the PAH/PSS films, and that Nafion is a homogenous membrane ($\frac{dc_x}{d\bar{x}} = 0$). Under zero-current condition ($\sum_i z_i j_i = 0$), one can rewrite equations (2-4) as:

$$\frac{dc_i^*}{dx^*} = -\frac{j_i}{P_i} + z_i c_i^* \frac{\sum_i z_i \frac{j_i}{P_i}}{\sum_i z_i^2 c_i^*} \quad (7)$$

$$\frac{d\bar{c}_i}{d\bar{x}} = -\frac{j_i}{D_i} + z_i \bar{c}_i \frac{\sum_i z_i \frac{j_i}{D_i}}{\sum_i z_i^2 \bar{c}_i} \quad (8)$$

$$\frac{dc_i}{dx} = -\frac{j_i}{D_i} + z_i c_i \frac{\sum_i z_i \frac{j_i}{D_i}}{\sum_i z_i^2 c_i} \quad (9)$$

We solved equations (7-9) using an iterative procedure based on a 4th order Runge-Kutta method programmed to match target receiving-phase concentrations by varying two ion fluxes (the third flux is specified by the zero-current condition) and specifying source-phase concentrations. Potential differences inside each boundary layer, coating, and Nafion, along with the Donnan potentials at the Nafion/coating interfaces were calculated along with the concentration profile. The sum of all potentials is the bi-ionic potential. **Table S1** (table and figure numbers beginning with “S” refer to the supporting information) lists the simulation parameters.

3. Results and discussion

Previous work indicates that adsorption of (PAH/PSS)₅PAH films yields defect-free coatings on Nafion membranes to enable highly selective separation of monovalent and divalent cations.^{16, 50, 52} Thus, for monovalent ion separations, we also examined Nafion membranes coated with 5.5-bilayer PAH/PSS films. Coatings that terminate in PAH show less swelling than films ending in PSS, and PAH-capped films also exhibit higher monovalent/divalent cation selectivities.⁵³⁻⁵⁴ Electrostatic effects due to the positive surface charge should not affect discrimination among monovalent ions, but the lower swelling should influence selectivity. This research explores whether such membranes show selectivities among K⁺, H⁺ and Li⁺. We examine monovalent ion transport in both DD and ED through bare and (PAH/PSS)₅PAH-coated membranes. The sections below first describe DD, bi-ionic potential measurements, and ED using a neutral-pH source phase for PEMs assembled at pH 2.3. Subsequently, we examine the acid-induced swelling of films assembled at acidic, neutral and basic conditions. For all of these films, the K⁺/Li⁺ selectivities in DD increase remarkably with the addition of H⁺ to the source phase. We also study transport as a function of salt concentrations. Finally, the last section speculates on possible mechanisms behind the unusual selectivities.

3.1 Donnan dialysis, impedance measurements and bi-ionic potentials with neutral source-phase solutions

Initial DD experiments employed 0.01 M KNO_3 and 0.01 M LiNO_3 in the source phase and 0.02 M NaNO_3 in the receiving phase. The equal concentrations of NO_3^- in each cell avoid NO_3^- transport that results from concentration differences, whereas chemical potential gradients drive K^+ and Li^+ from the source to the receiving phase and Na^+ from the receiving to the source phase. Moreover, if NO_3^- transport is negligible, the combined transfer of K^+ and Li^+ to the receiving phase should equal the transfer of Na^+ to the source phase to maintain zero electric current. **Figure 2** shows the cumulative amounts of K^+ and Li^+ that transferred to the receiving phase during DD through a $(\text{PAH/PSS})_5\text{PAH}$ -coated Nafion membrane. After an initial induction time of ~ 900 s, the amounts of both K^+ and Li^+ in the receiving phase increase linearly with time. However, the K^+ flux is greater than that of Li^+ , and replicate experiments give an average K^+/Li^+ selectivity of 8.3 ± 1.8 , which is ~ 5 times the K^+/Li^+ selectivity of 1.7 ± 0.3 for bare Nafion (**Table 1**). This selectivity in bare Nafion is close to the ratio of the aqueous diffusion coefficients of these two ions (1.9).⁵⁵ However, compared to the coated Nafion, the bare membrane shows an order of magnitude higher K^+ flux (**Table 1**). Thus, the $(\text{PAH/PSS})_5\text{PAH}$ film decreases the fluxes of both K^+ and Li^+ , but the decrease is much larger for Li^+ . Consistent with these results, in electrical impedance spectroscopy, the difference between the magnitude of the impedance at low and high frequencies in a LiNO_3 solution is twice that in a KNO_3 solution. The low coating permeability to Li^+ likely gives rise to high concentration polarization at the coating/membrane interfaces. Unfortunately, quantitative interpretation of the impedance data requires a number of parameters that we do not yet know (see the supporting information).

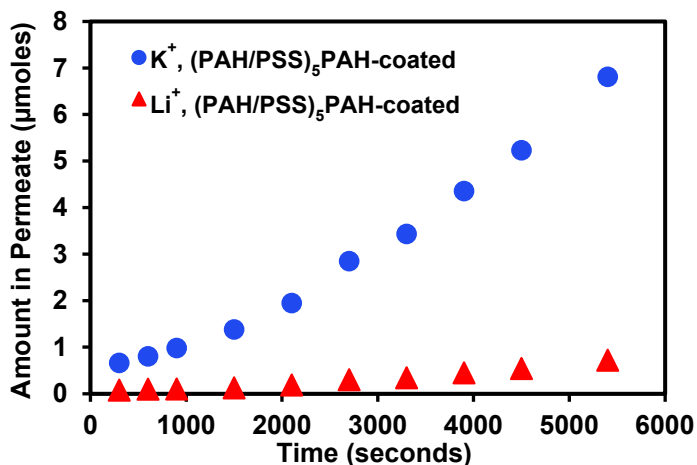


Figure 2. Moles of K⁺ (blue circles) and Li⁺ (red triangles) transferred to the receiving phase as a function of time during DD through (PAH/PSS)₅PAH-coated (assembly pH of 2.3) Nafion. The source phase initially contained 0.01 M KNO₃ and 0.01 M LiNO₃, and the receiving phase initially contained 0.02 M NaNO₃.

Table 1. K⁺, Li⁺ and Na⁺ fluxes and K⁺/Li⁺ selectivities in DD and ED through bare and (PAH/PSS)₅PAH-coated (assembly pH of 2.3) Nafion membranes. The source phase initially contained 0.01 M KNO₃ and 0.01 M LiNO₃, and the receiving phase was initially 0.02 M NaNO₃. The current density in ED was 0.64 mA cm⁻².

Membrane	Experiment	K ⁺ flux ^a (nmol cm ⁻² s ⁻¹)	Li ⁺ flux ^a (nmol cm ⁻² s ⁻¹)	Na ⁺ flux ^b (nmol cm ⁻² s ⁻¹)	K ⁺ /Li ⁺ selectivity
(PAH/PSS) ₅ PAH-Nafion	DD	0.35 ± 0.06	0.047 ± 0.010	1.22 ± 0.16	8.3 ± 1.8
Bare Nafion	DD	4.97 ± 0.44	3.03 ± 0.36	7.8 ± 0.6	1.7 ± 0.3
(PAH/PSS) ₅ PAH-Nafion	ED	2.99 ± 0.13	1.33 ± 0.03	< 0.01	2.3 ± 0.1
Bare Nafion	ED	5.56 ± 0.81	4.19 ± 0.38	6.2 ± 1.2	1.3 ± 0.1

^aFlux from source to receiving phase.

^bFlux from receiving to source phase.

In DD through bare Nafion, the Na⁺ flux to the source phase is approximately equal to the sum of the K⁺ and Li⁺ fluxes to the receiving phase (**Table 1**). In contrast, DD through the coated membranes shows Na⁺ concentrations in the source phase that are more than twice the sum of K⁺ and Li⁺ concentrations in the receiving phase. During coating of the membrane using

polyelectrolyte solutions containing 1.0 M or 0.5 M NaCl, we load the Nafion with Na⁺ ions prior to the experiment. We think that exchange of these “loaded” ions with K⁺ and Li⁺ in the membrane contributes some of the excess Na⁺ in the source phase and gives rise to the induction time for Li⁺ and K⁺ fluxes in **Figure 2**.

For coated membranes, DD experiments with either 0.01 M KNO₃ or 0.01 M LiNO₃ in the source-phase (see **Tables S2** and **S3**) give a K⁺ flux similar to that in **Table 1**, but the Li⁺ flux increases 60% in the absence of K⁺. Thus, the K⁺/Li⁺ selectivity is only 4.2 when using single-salt solutions in the source phase. Moreover, there is no significant K⁺/Li⁺ selectivity in bare Nafion with single-salt source phases. Competition for sorption sites likely increases K⁺/Li⁺ selectivity when both K⁺ and Li⁺ are present in the source phase.

Bi-ionic transmembrane potential measurements are consistent with the selectivities in DD. These experiments determine the transmembrane potentials with solutions of KNO₃ in the source phase and LiNO₃ in the receiving phase. **Figure 3** shows measured and simulated potentials as a function of salt concentrations, where the simulation assumes the PEM permeability to K⁺ is 5 times that to Li⁺. We chose this permeability ratio to approximately match the selectivity obtained in DD experiments with either KNO₃ or LiNO₃ in the source phase. Simulated potentials as a function of salt concentrations agree well with experimental data, providing further evidence for a higher film permeability to K⁺ than Li⁺. The supporting information discusses bi-ionic transmembrane potentials in more detail, including experiments with bare Nafion (see **Figure S4**).

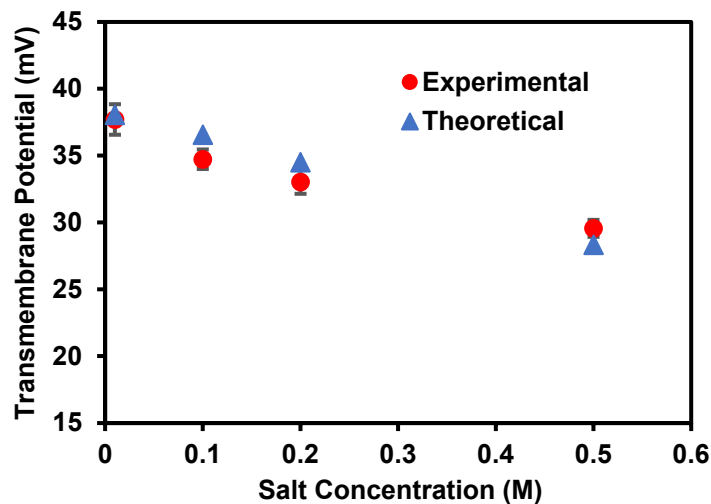


Figure 3. Experimental (red circles) and simulated (blue triangles) transmembrane electrical potential drops (receiving-source phase) across (PAH/PSS)₅PAH-coated (assembled at pH 2.3) Nafion membranes as a function of salt concentrations. The source phase contained KNO₃ and the receiving phase contained an equal concentration of LiNO₃. The error bars represent standard deviations from at least 3 replicate membranes.

3.2 Electrodialysis

In ED across a cation-exchange membrane, the applied current should increase cation flux compared to DD. **Table 1** shows the ion fluxes during ED with 0.01 M KNO₃, 0.01 M LiNO₃ as the source phase and 0.02 M NaNO₃ as the receiving phase. With (PAH/PSS)₅PAH-coated Nafion, when going from DD to ED, the K⁺ flux increases ~8.5-fold. However, ED increases the Li⁺ flux 28-fold so the K⁺/Li⁺ selectivity in ED is only 2.3 ± 0.1 . This is still significantly higher than the corresponding selectivity of 1.3 ± 0.1 in ED through bare Nafion, but much less than the DD selectivity of the coated membrane.

The relatively low ED K⁺/Li⁺ selectivity with (PAH/PSS)₅PAH-coated Nafion membranes suggests that the transport pathways in DD and ED are different. ED may emphasize ion passage through small but less selective areas (defects or porous regions) in the film, particularly if electroosmosis plays a role in transport. Additionally, electrically driven dialysis complicates transport due to the generation of H⁺ and OH⁻ from electrode reactions. The pH in the source phase

decreases from 6.9 to ~2.8 after 1.5 h of ED with both bare and modified membranes, and the receiving phase pH increases from 7.1 to 10.9.

In ED through the coated membranes, the transference numbers for K^+ and Li^+ are 0.45 and 0.20, respectively, so the total current efficiency is 65% at this current density. Protons generated in the source phase may carry a significant fraction of the current. The Na^+ flux to the source phase was undetectable ($<0.01 \text{ nmol cm}^{-2} \text{ s}^{-1}$) during ED through three different coated Nafion membranes, suggesting that ions generated at the electrodes maintain electrical neutrality rather than diffusion of Na^+ to the source phase. These results also suggest that diffusive transport does not inflate calculated transference numbers for the coated membrane. In contrast, with ED through bare Nafion the Na^+ flux to the source phase is $6.2 \pm 1.2 \text{ nmol cm}^{-2} \text{ s}^{-1}$, which is about 64% of the sum of the fluxes of K^+ and Li^+ to the receiving phase. Thus, during ED through bare membranes, DD likely accounts for much of the transport.

3.3 Film swelling at pH 2.0

Coating of Nafion with (PAH/PSS)₅PAH films (assembled at pH 2.3) gives K^+/Li^+ DD selectivities around 8, but the K^+ flux is low. Swelling of these films in acidic solutions might increase flux without sacrificing selectivity. Miller et al. found a positive correlation between the swelling of polyelectrolyte films and diffusion dialysis fluxes.⁵⁶ In addition, cations may move more freely among sulfonate groups when the water content is high.⁵⁷ Rubner and coworkers showed that PAH/PSS multilayers swell at low pH when these films are assembled at pH 9.3, but PAH/PSS multilayers assembled at pH 7.5 swelled minimally at pH 2.0.⁵⁸ However, those studies did not add salt to polyelectrolyte adsorption solutions, and the supporting electrolyte increases the thickness and changes the structure of the film.⁵⁹⁻⁶⁰ We add 0.5 or 1.0 M NaCl to polyelectrolyte solutions to obtain relatively thick films and high selectivities.^{16, 50} Thus, this work uses in-situ

ellipsometry to test the low-pH swelling of PAH/PSS films assembled at several pH values from salt-containing solutions. In the next subsection, we examine whether swelling increases K^+ flux at pH 2.0, perhaps without greatly decreasing K^+/Li^+ selectivity.

Figure 4 shows the percent swelling of (PAH/PSS)₅PAH films (assembled at pH 2.3, 7.5 or 9.3 on gold-coated Si wafers) immersed in different solutions. The “dry” thicknesses of the (PAH/PSS)₅PAH films assembled at pH 2.3, 7.5 and 9.3 are $207 \pm 19 \text{ \AA}$, $225 \pm 5 \text{ \AA}$ and $320 \pm 3 \text{ \AA}$, respectively. The film thickness likely increases with assembly pH because of decreased protonation of PAH.⁶¹ For films assembled at pH 2.3, immersion in 0.01 M HNO₃ or 0.01 M HNO₃ with 0.01 M KNO₃ increases film thickness around 46% or 53%, respectively, compared to the dry films. However, when immersed in solutions containing just alkali metal salts (0.01 M KNO₃ or 0.02 M NaNO₃, pH~6.0), films swelled only ~34%. At low pH, a small increase in the fraction of protonated amine groups in PAH should lead to incorporation of counterions along with water in the coating. We also investigated the swelling of (PAH/PSS)₅PAH films (assembled at pH 2.3) with salt solutions containing LiNO₃ (see **Figure S5** of the supporting information). Interestingly, a solution containing 0.01 M LiNO₃ and HNO₃ gave less film swelling than a solution containing 0.01 M KNO₃, LiNO₃ and HNO₃, although the difference was significant only at the 90% confidence level.

As **Figure 4** shows, films assembled at pH 7.5 and 9.3 also swell more in acidic solutions than in salt solutions at pH 6.0. The assembly pH has only a small effect on the swelling. For films assembled at pH 9.3, we do not see the previously reported more than 380% swelling in acid,⁵⁸ presumably because the supporting electrolyte in the deposition solution changes the dry film structure compared to the prior study, which employed no supporting electrolyte. However, in 0.01 M KNO₃ or 0.01 M HNO₃, films deposited at pH 7.5 show lower swelling than films

deposited at either pH 2.3 or 9.3 (at >90% confidence). Films deposited at pH 2.3 also show the highest swelling in solutions containing 0.01 M KNO₃ and 0.01 M HNO₃. The trends in swelling do not directly correlate with the fraction of deprotonated amine groups present during film deposition.

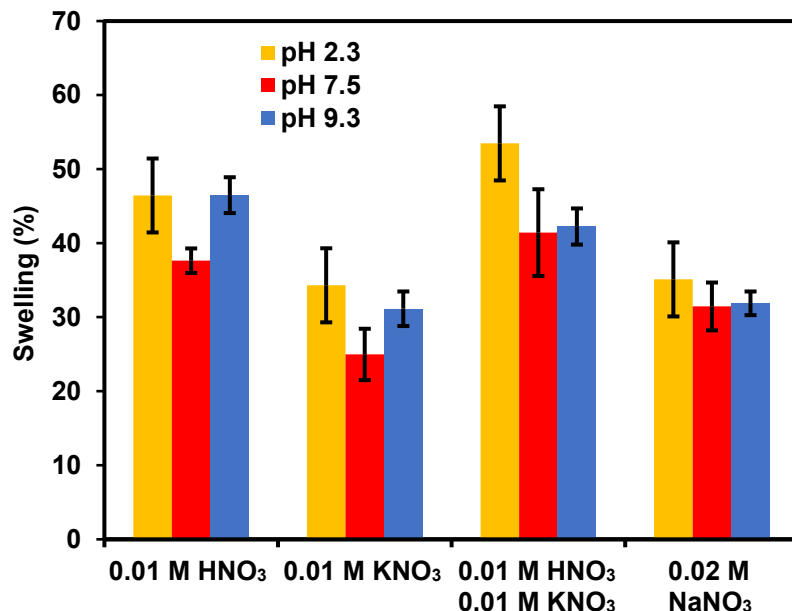


Figure 4. Percent swelling of (PAH/PSS)₅PAH films assembled at pH 2.3 (yellow bars), 7.5 (red bars) and 9.3 (blue bars) on gold wafers and immersed in the following solutions: 0.01 M HNO₃; 0.01 M KNO₃; 0.01 M HNO₃ and 0.01 M KNO₃; and 0.02 M NaNO₃. The percent swelling is the difference between the swollen and “dry” (in ambient air) film thicknesses divided by the “dry” film thickness. The error bars represent standard deviations from at least 3 replicate films. For each specific assembly pH value, the differences between swelling in 0.01 M HNO₃ and in 0.01 M KNO₃ solutions is significant at >95% confidence. The difference in swelling in 0.01 M HNO₃, KNO₃ solutions and 0.02 M NaNO₃ solutions is significant at >95% confidence for assembly at pH 2.3 and 9.3, but only >90% for pH 7.5.

3.4 Donnan dialysis and electro dialysis with the source phase at pH 2.0

3.4.1 (PAH/PSS)₅PAH films assembled at pH 2.3

Decreasing the source-phase pH from neutral to 2.0 has a dramatic effect on K⁺ transport. In DD through (PAH/PSS)₅PAH-coated (assembly pH of 2.3) membranes with 0.01 M KNO₃ as the source phase (pH ~6.0) and 0.02 M NaNO₃ as the receiving phase, the K⁺ flux is only 0.32 nmol cm⁻² s⁻¹ (**Figure 5**), or 4% of the flux through a bare Nafion membrane with the same source and receiving phases (see **Table S2**). However, with 0.01 M KNO₃ and 0.01 M HNO₃ in the source phase (pH 2.0), the K⁺ flux through coated membranes increases 8-fold to ~2.7 nmol cm⁻² s⁻¹ (**Figure 5**). This occurs despite H⁺ transport that could decrease the electrical coupling of K⁺ transport with Na⁺ movement to the source phase. Surprisingly, with 0.01 M KNO₃ and 0.01 M HNO₃ in the source phase, the K⁺ flux through the coated membranes is ~2 times the H⁺ flux, although the proton diffusion coefficient in water is 5-fold higher than the K⁺ diffusion coefficient.⁵⁵ Even in bare Nafion, the ratio of the H⁺ and K⁺ diffusion coefficients is ~5.⁶² We

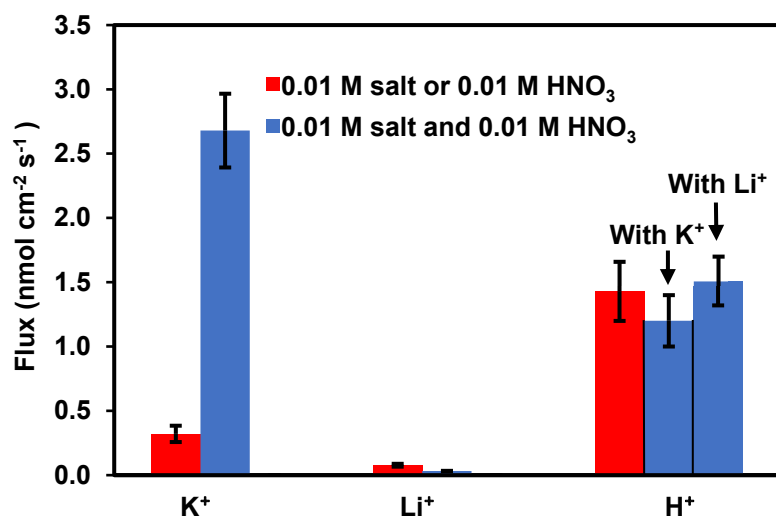


Figure 5. K⁺, Li⁺ and H⁺ fluxes (nmol cm⁻² s⁻¹) in DD through (PAH/PSS)₅PAH-coated (assembly pH of 2.3) Nafion membranes. The experiments employed several source phases: red bars represent source phases of 0.01 M KNO₃ or 0.01 M LiNO₃ or 0.01 M HNO₃, and blue bars represent source phases of 0.01 M KNO₃ and 0.01 M HNO₃ or 0.01 M LiNO₃ and 0.01 M HNO₃. The receiving phase initially contained 0.02 M NaNO₃.

surmise that the relative dominance of K^+ transport reflects selective K^+ ion-exchange into (PAH/PSS)₅PAH films (see below) and Nafion. With bare membranes, H^+ fluxes are only 43% higher than K^+ fluxes, and pH has no significant effect on K^+ transport (see **Table S2**). In contrast, Li^+ fluxes through both bare and coated Nafion membranes decrease with the addition of H^+ , and H^+ fluxes are much higher than Li^+ fluxes (**Figure 5** and **Table S3**). The similarity in K^+ and H^+ transport rates in bare membranes, despite the higher H^+ diffusion coefficient, suggests extensive partitioning of mobile K^+ ions into Nafion.

In addition to increasing the K^+ flux, adding 0.01 M HNO_3 to the source phase greatly increases the K^+/Li^+ selectivity. **Figure 6** shows the amounts of K^+ , Li^+ , and H^+ in the receiving phase during DD through a coated membrane (assembly pH of 2.3) when the source-phase solution contains 0.01 M KNO_3 , 0.01 M $LiNO_3$, and 0.01 M HNO_3 . The figure illustrates the high K^+/Li^+ and H^+/Li^+ selectivities of the system. As described above (see **Table 1**), with 0.01 M KNO_3 and 0.01 M $LiNO_3$ (pH 6.9) in the source phase and 0.02 M $NaNO_3$ in the receiving phase, the K^+/Li^+ selectivity is ~ 8 . With addition of 0.01 M HNO_3 to this source phase, the K^+/Li^+ selectivity increases to ~ 60 . This selectivity is ~ 30 times the ratio of ~ 2 for the aqueous diffusion coefficients of these ions.⁵⁵ The increase in K^+/Li^+ selectivity at low pH results from both an increase in K^+ flux and a decrease in Li^+ flux (see **Tables 1 and S4**).

DD with 0.01 M KNO_3 , 0.01 M $LiNO_3$ and 0.01 M HNO_3 in the source phase also shows an H^+/Li^+ selectivity of 39 and a K^+/H^+ selectivity of 1.6 ± 0.3 (see **Table S4** of the supporting information). For uncoated Nafion membranes with a source phase containing 0.01 M KNO_3 , 0.01 M $LiNO_3$, and 0.01 M HNO_3 , the DD K^+/Li^+ and H^+/Li^+ selectivities are about 2.1 and 3.5, respectively, and the K^+/H^+ selectivity is 0.6 (**Table S4**). Clearly, the polyelectrolyte-coated membranes show much higher selectivity than the bare Nafion.

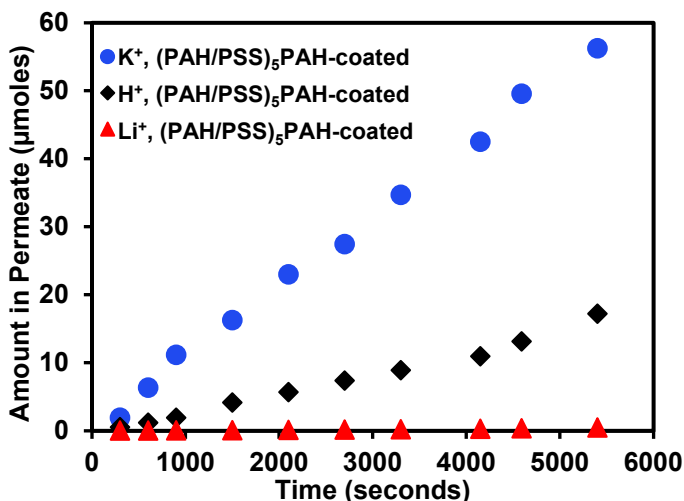


Figure 6. Moles of K^+ (blue circles), H^+ (black diamonds), and Li^+ (red triangles) in the receiving phase as a function of time during DD through $(PAH/PSS)_5PAH$ -coated Nafion. The source phase initially contained 0.01 M KNO_3 , 0.01 M $LiNO_3$ and 0.01 M HNO_3 , and the receiving phase was initially 0.02 M $NaNO_3$. The film was assembled at pH 2.3.

Longer DD experiments verify that the measured fluxes represent a steady state and that membranes are stable for at least 6 hours. **Figure S6** shows the fluxes of K^+ and Li^+ during four 1.5-h periods of DD through same membrane. The cell was rinsed with deionized water after each 1.5 h before adding fresh source- and receiving-phase solutions. Both K^+ and Li^+ fluxes were essentially constant during the 6 h of DD, and K^+/Li^+ selectivities were around 50 over the entire experiment with this membrane.

We also examined ED with an acidic source phase. Compared to the DD results, in ED through $(PAH/PSS)_5PAH$ -coated (assembly pH of 2.3) membranes both the K^+ flux and the K^+/Li^+ selectivity are smaller (**Table S4**). Nevertheless, the K^+/Li^+ ED selectivity of 7 is still nearly 4 times the ratio of aqueous K^+ and Li^+ diffusion coefficients or the selectivity of bare Nafion in control ED experiments.⁵⁵ The supporting information gives additional discussion of ED below **Table S4**.

3.4.2 Transport through $(PAH/PSS)_5PAH$ films assembled at pH 7.5 and 9.3

Like films assembled at pH 2.3, (PAH/PSS)₅PAH films assembled at pH 7.5 and pH 9.3 both show increased swelling in acidic solutions. If the swelling contributes to the increased DD K⁺ flux, assembly at pH 2.3 may not be a unique condition for creating PEMs that give a high K⁺/Li⁺ selectivity. Thus, we conducted DD experiments with membranes coated with (PAH/PSS)₅PAH films adsorbed at pH 7.5 and 9.3.

For membranes with coatings assembled at pH 7.5, the K⁺ flux increases 6-fold while Li⁺ flux decreases ~50% when adding 0.01 M HNO₃ to a source phase containing 0.01 M KNO₃ and 0.01 M LiNO₃. Accordingly, the K⁺/Li⁺ selectivity jumps from 4.2 ± 0.3 to 59 ± 13 (**Table S5**) with addition of the acid. These coated Nafion membranes also show a H⁺/Li⁺ selectivity of 19 ± 6 . Although K⁺ and Li⁺ fluxes are similar to those for membranes with films adsorbed at pH 2.3, H⁺ fluxes are ~50% lower through films deposited at pH 7.5.

Membranes modified with coatings assembled at pH 9.3 show the highest K⁺/Li⁺ selectivities. In DD through (PAH/PSS)₅PAH-coated (assembly pH of 9.3) Nafion membranes, upon adding 0.01 M HNO₃ to a source phase containing 0.01 M KNO₃ and 0.01 M LiNO₃, K⁺ flux increases ~12-fold from 0.21 ± 0.02 to 2.46 ± 0.12 nmol cm⁻² s⁻¹ and Li⁺ flux decreases ~50%. This leads to K⁺/Li⁺ selectivities of 92, 185 and 202 from three replicate membranes (see **Table S6** of the supporting information). Nafion membranes coated with PEMs at pH 9.3 also show a H⁺/Li⁺ selectivity of 38 ± 8 , which is the same as that for films assembled at pH 2.3. Most importantly, PEMs assembled at all three pH values (2.3, 7.5 and 9.3) show much higher K⁺ fluxes and K⁺/Li⁺ selectivities when the source phase is acidic.

3.5 The effect of source-phase concentrations on DD

Higher source-phase concentrations should increase flux due to a larger chemical potential gradient across the membrane. Thus, we performed DD through (PAH/PSS)₅PAH-coated

(assembly pH of 2.3) Nafion membranes using KNO_3 and LiNO_3 concentrations of 0.01 M, 0.02 M and 0.1 M in the source phase. The receiving phase was always initially 0.02 M NaNO_3 . **Figure 7** shows the K^+ and Li^+ fluxes in these experiments. At pH 6.9 (no added HNO_3), both K^+ and Li^+ fluxes increase ~10-fold when the source-phase concentration increases from 0.01 M to 0.1 M, so the K^+/Li^+ selectivity is 8-11 at all concentrations (**Table S7**). Without the addition of acid, the fluxes of K^+ and Li^+ increase approximately linearly with their source-phase concentrations. At low concentrations, the Na^+ flux to the source phase is higher than the sum of K^+ and Li^+ fluxes to the receiving phase, but this is not the case when the source phase contains 0.1 M salt (**Table S7**). At high source-phase concentrations, NO_3^- flux to the receiving phase likely becomes significant.

For bare membranes at neutral pH, the K^+/Li^+ selectivities are between 1 and 2 for all concentrations, and the fluxes increase sublinearly with concentration (**Table S8**). The sublinear increases suggest that in this case, the Na^+ flux to the source phase may limit the ion fluxes to the receiving phase. The fluxes through the bare membrane are always higher than those through coated membranes.

When adding 0.01 M HNO_3 to the source phase, the K^+ fluxes through coated membranes significantly increase for source-phase salt concentrations of either 0.01 and 0.02 M (**Figure 7**, pH=2.0). With these acidic source phases, the K^+/Li^+ selectivity in DD through coated membranes is 60-80 (**Table S9**). Comparing 0.1 M and 0.01 M source-phase salt concentrations, however, in the presence of 0.01 M HNO_3 the flux through coated membranes increases only 2.6-fold for K^+ and 6.5-fold for Li^+ , so the K^+/Li^+ selectivity with 0.1 M source-phase alkali metal cation concentrations drops to 21 (**Figure 7** and **Table S9**). Nevertheless, for monovalent ions this is still a remarkable selectivity. We also performed DD with 0.01 M KNO_3 , LiNO_3 , and HNO_3 in the source phase, but we increased the concentration of NaNO_3 in the receiving phase from 0.02 to

0.03 M. The increase in the NaNO_3 receiving-phase concentration decreased the K^+/Li^+ selectivity from 57 to 22 (see **Table S10**). This might suggest that selective K^+ transport includes some codiffusion of K^+ and NO_3^- , and this codiffusion declines when the source- and receiving-phase NO_3^- concentrations are equal. **Table S11** shows the fluxes and selectivities for DD through bare membranes as a function of K^+ and Li^+ source-phase concentrations when the source phase contains 0.01 M HNO_3 . At all of the source-phase concentrations, bare Nafion membranes exhibit K^+/Li^+ selectivities between 1.8 and 2.5.

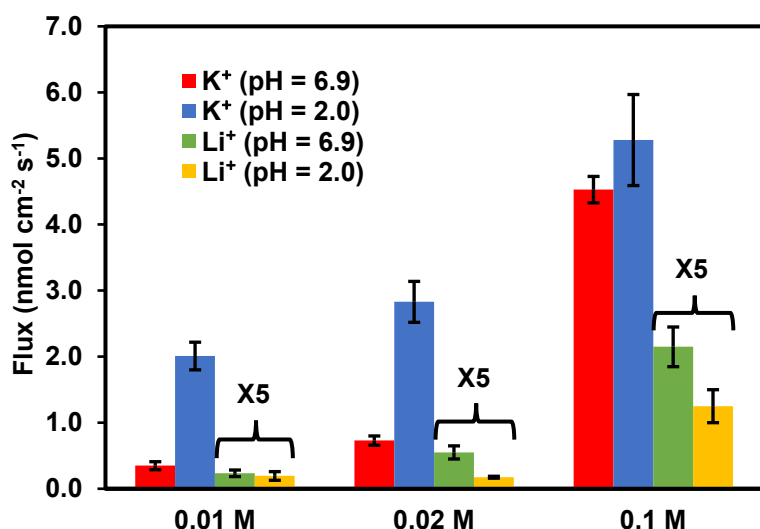


Figure 7. K^+ and Li^+ fluxes ($\text{nmol cm}^{-2} \text{s}^{-1}$) in DD through $(\text{PAH/PSS})_5\text{PAH}$ -coated (assembled at pH 2.3) Nafion membranes. The experiments employed source phases containing 0.01 M, 0.02 M or 0.10 M KNO_3 and LiNO_3 with (pH=2.0, blue and yellow bars) or without (pH=6.9, red and green bars) 0.01 M HNO_3 . The receiving phase initially contained 0.02 M NaNO_3 . Li^+ fluxes are multiplied by 5 to make them more visible.

3.6 Possible mechanisms of selective ion transport through PEM-coated Nafion

Previous studies of bare Nafion show that both partitioning into the membrane and mobility vary among monovalent ions.⁶³ Of the alkali metal cations, Li^+ shows the lowest partitioning from acidic solutions into Nafion membranes.⁶² In addition, Li^+ also shows the lowest electrical

mobility of the alkali metal cations in solution.⁶⁴ Similar factors should control transport rates in PEMs, but these films are denser than cation-exchange membranes and thus may show more discrimination in terms of both partitioning and diffusion coefficients.

With K^+ and Li^+ in the source phase, K^+/Li^+ selectivity through bare Nafion is ~ 1.7 . A coating of $(PAH/PSS)_5PAH$ on Nafion significantly improves K^+/Li^+ selectivity to ~ 8 with the sacrifice of K^+ and Li^+ fluxes, primarily due to a deeper drop of Li^+ flux than K^+ flux. This high K^+/Li^+ selectivity agrees with the higher PEM permeability to K^+ than Li^+ indicated by bi-ionic transmembrane potential measurements. Because selectivities are higher in mixed-salt than single-salt source-phase experiments, partitioning likely plays a key role in the selectivity. For sulfonated ion exchange materials, the counter-ion affinity to K^+ is 2.9-fold higher than that to Li^+ .^{26, 65} The K^+/Li^+ selectivity remains 8-11 with source-phase salt concentrations ranging from 0.01-1.0 M. In ED, other transport pathways such as electroosmosis likely decrease the overall selectivity. Moreover, the generation of H^+ and OH^- from electrode reactions as well as current-polarized coating/membrane interfaces complicate ED.

In acidic solutions, PEMs swell, which likely opens new partitioning sites. These sites evidently favor K^+ transport but not Li^+ transport, perhaps due to a mechanism that includes binding to ion-exchange sites, albeit weakly to enable mobility. A literature study suggests a selectivity of around 7.5 for partitioning of K^+ over Li^+ in bare Nafion in acidic solutions,⁶³ and the partitioning selectivity may increase significantly in the confined environment of a PEM. Studies of partitioning in cation-exchange resins show that the resin volume is greater when Li^+ is the counterion rather than K^+ .^{26, 65} This highly selective H^+ -induced pathway likely saturates at high K^+ concentrations where selectivity declines.

4. Conclusions

This research developed modified Nafion membranes that show remarkable selectivities among monovalent cations in DD. Adsorption of (PAH/PSS)₅PAH films on Nafion membranes increases the K⁺/Li⁺ DD selectivity from 1.7 to 8.3. Impedance spectroscopy suggests that with single-salt solutions the Li⁺ transference number is lower than the K⁺ transference number, and bi-ionic transmembrane potentials confirm that membranes are more permeable to K⁺ than Li⁺. With source phases containing 0.01 M HNO₃, the K⁺/Li⁺ selectivity jumps to ~60. In ED at pH 2.0, the same membranes show respectable K⁺/Li⁺ selectivities around 7, but discrimination clearly declines in ED, probably because of different transport pathways. In situ ellipsometry shows that for films assembled at a pH of 2.3, 7.5, or 9.3, swelling increases at low pH, and changes in film structure at pH 2.0 likely lead to new transport pathways that rely on selective K⁺ binding to charged sites. At high salt concentrations, these binding sites may saturate so the K⁺/Li⁺ selectivity declines. In the absence of H⁺, the DD K⁺/Li⁺ selectivity is ~10 even with source-phase salt concentrations of 0.1 M.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: ????. This information includes: impedance spectroscopy data, bi-ionic potentials for bare Nafion, swelling of films in LiNO₃ solutions, examination of flux over extended times, and tables of fluxes through bare and coated Nafion membranes.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mbruenin@nd.edu Tel: +1 574 631-3024 Fax: +1 574 631-0315

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

We gratefully acknowledge funding of this work by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-SC0017618. We also thank the Center for Environmental Science & Technology, University of Notre Dame for help with the cation analysis. AY acknowledges funding from the Spanish Ministry of Economy and Competitiveness through project CTM2017-85346-R.

References

- (1) Varcoe, J. R.; Atanassov, P.; Dekel, D. R.; Herring, A. M.; Hickner, M. A.; Kohl, P. A.; Kucernak, A. R.; Mustain, W. E.; Nijmeijer, K.; Scott, K.; Xu, T. W.; Zhuang, L. Anion-Exchange Membranes in Electrochemical Energy Systems. *Energ. Environ. Sci.* **2014**, *7*, 3135-3191.
- (2) Kim, D. H. A Review of Desalting Process Techniques and Economic Analysis of the Recovery of Salts from Retentates. *Desalination* **2011**, *270*, 1-8.
- (3) Serre, E.; Rozoy, E.; Pedneault, K.; Lacour, S.; Bazinet, L. Deacidification of Cranberry Juice by Electrodialysis: Impact of Membrane Types and Configurations on Acid Migration and Juice Physicochemical Characteristics. *Sep. Purif. Technol.* **2016**, *163*, 228-237.
- (4) Chen, D. Y.; Hickner, M. A.; Agar, E.; Kumbur, E. C. Optimized Anion Exchange Membranes for Vanadium Redox Flow Batteries. *ACS Appl. Mater. Inter.* **2013**, *5*, 7559-7566.
- (5) Luo, T.; Abdu, S.; Wessling, M. Selectivity of Ion Exchange Membranes: A Review. *J. Membr. Sci.* **2018**, *555*, 429-454.
- (6) Sata, T. Studies on Anion Exchange Membranes Having Permselectivity for Specific Anions in Electrodialysis - Effect of Hydrophilicity of Anion Exchange Membranes on Permselectivity of Anions. *J. Membr. Sci.* **2000**, *167*, 1-31.
- (7) Lambert, J.; Avila-Rodriguez, M.; Durand, G.; Rakib, M. Separation of Sodium Ions from Trivalent Chromium by Electrodialysis Using Monovalent Cation Selective Membranes. *J. Membr. Sci.* **2006**, *280*, 219-225.

- (8) Xiong, Y.; Fang, J.; Zeng, Q. H.; Liu, Q. L. Preparation and Characterization of Cross-Linked Quaternized Poly(vinyl alcohol) Membranes for Anion Exchange Membrane Fuel Cells. *J. Membr. Sci.* **2008**, *311*, 319-325.
- (9) Pan, J. F.; Ding, J. C.; Tan, R. Q.; Chen, G. Y.; Zhao, Y.; Gao, C. J.; Van der Bruggen, B.; Shen, J. N. Preparation of a Monovalent Selective Anion Exchange Membrane through Constructing a Covalently Crosslinked Interface by Electro-Deposition of Polyethyleneimine. *J. Membr. Sci.* **2017**, *539*, 263-272.
- (10) Vasselbehagh, M.; Karkhanechi, H.; Takagi, R.; Matsuyama, H. Effect of Polydopamine Coating and Direct Electric Current Application on Anti-Biofouling Properties of Anion Exchange Membranes in Electrodialysis. *J. Membr. Sci.* **2016**, *515*, 98-108.
- (11) Sodaye, S.; Suresh, G.; Pandey, A. K.; Goswami, A. Determination and Theoretical Evaluation of Selectivity Coefficients of Monovalent Anions in Anion-Exchange Polymer Inclusion Membrane. *J. Membr. Sci.* **2007**, *295*, 108-113.
- (12) Vasselbehagh, M.; Karkhanechi, H.; Takagi, R.; Matsuyama, H. Surface Modification of an Anion Exchange Membrane to Improve the Selectivity for Monovalent Anions in Electrodialysis - Experimental Verification of Theoretical Predictions. *J. Membr. Sci.* **2015**, *490*, 301-310.
- (13) Zhao, Y.; Tang, K. N.; Liu, H. M.; Van der Bruggen, B.; Diaz, A. S.; Shen, J. N.; Gao, C. J. An Anion Exchange Membrane Modified by Alternate Electro-Deposition Layers with Enhanced Monovalent Selectivity. *J. Membr. Sci.* **2016**, *520*, 262-271.
- (14) Abdu, S.; Marti-Calatayud, M. C.; Wong, J. E.; Garcia-Gabaldon, M.; Wessling, M. Layer-by-Layer Modification of Cation Exchange Membranes Controls Ion Selectivity and Water Splitting. *ACS Appl. Mater. Inter.* **2014**, *6*, 1843-1854.
- (15) Mulyati, S.; Takagi, R.; Fujii, A.; Ohmukai, Y.; Matsuyama, H. Simultaneous Improvement of the Monovalent Anion Selectivity and Antifouling Properties of an Anion Exchange Membrane in an Electrodialysis Process, Using Polyelectrolyte Multilayer Deposition. *J. Membr. Sci.* **2013**, *431*, 113-120.
- (16) White, N.; Misovich, M.; Yaroshchuk, A.; Bruening, M. L. Coating of Nafion Membranes with Polyelectrolyte Multilayers to Achieve High Monovalent/Divalent Cation Electrodialysis Selectivities. *ACS Appl. Mater. Inter.* **2015**, *7*, 6620-6628.
- (17) Zhao, Y.; Zhu, J. J.; Ding, J. C.; Van der Bruggen, B.; Shen, J. N.; Gao, C. J. Electric-Pulse Layer-by-Layer Assembled of Anion Exchange Membrane with Enhanced Monovalent Selectivity. *J. Membr. Sci.* **2018**, *548*, 81-90.
- (18) Ilyas, S.; de Grooth, J.; Nijmeijer, K.; de Vos, W. M. Multifunctional Polyelectrolyte Multilayers as Nanofiltration Membranes and as Sacrificial Layers for Easy Membrane Cleaning. *J. Colloid. Interf. Sci.* **2015**, *446*, 386-393.
- (19) Ilyas, S.; English, R.; Aimar, P.; Lahitte, J. F.; de Vos, W. M. Preparation of Multifunctional Hollow Fiber Nanofiltration Membranes by Dynamic Assembly of Weak Polyelectrolyte Multilayers. *Colloids Surf. A* **2017**, *533*, 286-295.
- (20) de Grooth, J.; Oborny, R.; Potreck, J.; Nijmeijer, K.; de Vos, W. M. The Role of Ionic Strength and Odd-Even Effects on the Properties of Polyelectrolyte Multilayer Nanofiltration Membranes. *J. Membr. Sci.* **2015**, *475*, 311-319.
- (21) Chaudhury, S.; Bhattacharyya, A.; Goswami, A. Electrodriven Ion Transport through Crown Ether-Nafion Composite Membrane: Enhanced Selectivity of Cs⁺ over Na⁺ by Ion Gating at the Surface. *Ind. Eng. Chem. Res.* **2014**, *53*, 8804-8809.

- (22) Tas, S.; Zoetebier, B.; Hempenius, M. A.; Vancso, G. J.; Nijmeijer, K. Monovalent Cation Selective Crown Ether Containing Poly(arylene ether ketone)/SPEEK Blend Membranes. *RSC Adv.* **2016**, *6*, 55635-55642.
- (23) Zhang, H. C.; Hou, J.; Hu, Y. X.; Wang, P. Y.; Ou, R. W.; Jiang, L.; Liu, J. Z.; Freeman, B. D.; Hill, A. J.; Wang, H. T. Ultrafast Selective Transport of Alkali Metal Ions in Metal Organic Frameworks with Subnanometer Pores. *Sci. Adv.* **2018**, *4*, eaaq0066.
- (24) Xie, G.; Okada, T. Pumping Effects in Water Movement Accompanying Cation Transport across Nafion 117 Membranes. *Electrochim. Acta.* **1996**, *41*, 1569-1571.
- (25) Izquierdo-Gil, M. A.; Barragan, V. M.; Villaluenga, J. P. G.; Godino, M. P. Water Uptake and Salt Transport through Nafion Cation-Exchange Membranes with Different Thicknesses. *Chem. Eng. Sci.* **2012**, *72*, 1-9.
- (26) Geise, G. M.; Paul, D. R.; Freeman, B. D. Fundamental Water and Salt Transport Properties of Polymeric Materials. *Prog. Polym. Sci.* **2014**, *39*, 1-42.
- (27) Smith, D. W. Ionic Hydration Enthalpies. *J. Chem. Educ.* **1977**, *54*, 540-542.
- (28) Volkov, A. G.; Paula, S.; Deamer, D. W. Two Mechanisms of Permeation of Small Neutral Molecules and Hydrated Ions across Phospholipid Bilayers. *Bioelectrochem. Bioenerg.* **1997**, *42*, 153-160.
- (29) Li, L.; Deshmane, V. G.; Paranthaman, M. P.; Bhave, R.; Moyer, B. A.; Harrison, S. Lithium Recovery from Aqueous Resources and Batteries: A Brief Review. *Johnson Matthey Tech.* **2018**, *62*, 161-176.
- (30) Pranolo, Y.; Zhang, W.; Cheng, C. Y. Recovery of Metals from Spent Lithium-Ion Battery Leach Solutions with a Mixed Solvent Extractant System. *Hydrometallurgy* **2010**, *102*, 37-42.
- (31) Wen, X.; Ma, P.; Chaoliang, Z.; He, Q.; Deng, X. Preliminary Study on Recovering Lithium Chloride from Lithium-Containing Waters by Nanofiltration. *Sep. Purif. Technol.* **2006**, *49*, 230-236.
- (32) Somrani, A.; Hamzaoui, A. H.; Pontie, M. Study on Lithium Separation from Salt Lake Brines by Nanofiltration (NF) and Low Pressure Reverse Osmosis (LPRO). *Desalination* **2013**, *317*, 184-192.
- (33) Nie, X. Y.; Sun, S. Y.; Song, X. F.; Yu, J. G. Further Investigation into Lithium Recovery from Salt Lake Brines with Different Feed Characteristics by Electrodialysis. *J. Membr. Sci.* **2017**, *530*, 185-191.
- (34) Geise, G. M.; Cassady, H. J.; Paul, D. R.; Logan, B. E.; Hickner, M. A. Specific Ion Effects on Membrane Potential and the Permselectivity of Ion Exchange Membranes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 21673-21681.
- (35) Agarwal, C.; Cattrall, R. W.; Kolev, S. D. Donnan Dialysis Based Separation of Gold(III) from Electronic Waste Solutions Using an Anion Exchange Pore-Filled Membrane. *J. Membr. Sci.* **2016**, *514*, 210-216.
- (36) Wang, Q. H.; Lenhart, J. J.; Walker, H. W. Recovery of Metal Cations from Lime Softening Sludge Using Donnan Dialysis. *J. Membr. Sci.* **2010**, *360*, 469-475.
- (37) Wan, D. J.; Xiao, S. H.; Cui, X. Y.; Zhang, Q. H.; Song, Y. H. Removal of Cu²⁺ from Aqueous Solution Using Proton Exchange Membrane by Donnan Dialysis Process. *Environ. Earth Sci.* **2015**, *73*, 4923-4929.
- (38) Turki, T.; Ben Amor, M. Nitrate Removal from Natural Water by Coupling Adsorption and Donnan Dialysis. *Water Sci. Tech-W. Sup.* **2017**, *17*, 771-779.
- (39) Bryjak, M.; Duraj, I. Anion-Exchange Membranes for Separation of Borates by Donnan Dialysis. *Desalination* **2013**, *310*, 39-42.

- (40) Rijnaarts, T.; Shenkute, N. T.; Wood, J. A.; de Vos, W. M.; Nijmeijer, K. Divalent Cation Removal by Donnan Dialysis for Improved Reverse Electrodialysis. *ACS Sustain. Chem. Eng.* **2018**, *6*, 7035-7041.
- (41) Dubas, S. T.; Schlenoff, J. B. Swelling and Smoothing of Polyelectrolyte Multilayers by Salt. *Langmuir* **2001**, *17*, 7725-7727.
- (42) Krasemann, L.; Tieke, B. Selective Ion Transport across Self-Assembled Alternating Multilayers of Cationic and Anionic Polyelectrolytes. *Langmuir* **2000**, *16*, 287-290.
- (43) Lavalle, P.; Gergely, C.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C.; Picart, C. Comparison of the Structure of Polyelectrolyte Multilayer Films Exhibiting a Linear and an Exponential Growth Regime: An in Situ Atomic Force Microscopy Study. *Macromolecules* **2002**, *35*, 4458-4465.
- (44) Feldötö, Z.; Varga, I.; Blomberg, E. Influence of Salt and Rinsing Protocol on the Structure of PAH/PSS Polyelectrolyte Multilayers. *Langmuir* **2010**, *26*, 17048-17057.
- (45) Cheng, C.; Yaroshchuk, A.; Bruening, M. L. Fundamentals of Selective Ion Transport through Multilayer Polyelectrolyte Membranes. *Langmuir* **2013**, *29*, 1885-1892.
- (46) Xi, J. Y.; Wu, Z. H.; Teng, X. G.; Zhao, Y. T.; Chen, L. Q.; Qiu, X. P. Self-Assembled Polyelectrolyte Multilayer Modified Nafion Membrane with Suppressed Vanadium Ion Crossover for Vanadium Redox Flow Batteries. *J. Mater. Chem.* **2008**, *18*, 1232-1238.
- (47) Jiang, S. P.; Tang, H. L. Methanol Crossover Reduction by Nafion Modification Via Layer-by-Layer Self-Assembly Techniques. *Colloids Surf. A* **2012**, *407*, 49-57.
- (48) Liu, X. Y.; Bruening, M. L. Size-Selective Transport of Uncharged Solutes through Multilayer Polyelectrolyte Membranes. *Chem. Mater.* **2004**, *16*, 351-357.
- (49) Kielland, J. Individual Activity Coefficients of Ions in Aqueous Solutions. *J. Am. Chem. Soc.* **1937**, *59*, 1675-1678.
- (50) White, N.; Misovich, M.; Alemayehu, E.; Yaroshchuk, A.; Bruening, M. L. Highly Selective Separations of Multivalent and Monovalent Cations in Electrodialysis through Nafion Membranes Coated with Polyelectrolyte Multilayers. *Polymer* **2016**, *103*, 478-485.
- (51) Wallace, R. M. Concentration and Separation of Ions by Donnan Membrane Equilibrium. *Ind. Eng. Chem. Proc. Des. Dev.* **1967**, *6*, 423-431.
- (52) Zhu, Y.; Ahmad, M.; Yang, L.; Misovich, M.; Yaroshchuk, A.; Bruening, M. L. Adsorption of Polyelectrolyte Multilayers Imparts High Monovalent/Divalent Cation Selectivity to Aliphatic Polyamide Cation-Exchange Membranes. *J. Membr. Sci.* **2017**, *537*, 177-185.
- (53) Wong, J. E.; Rehfeldt, F.; Hanni, P.; Tanaka, M.; Klitzing, R. V. Swelling Behavior of Polyelectrolyte Multilayers in Saturated Water Vapor. *Macromolecules* **2004**, *37*, 7285-7289.
- (54) Carrière, D.; Krastev, R.; Schönhoff, M. Oscillations in Solvent Fraction of Polyelectrolyte Multilayers Driven by the Charge of the Terminating Layer. *Langmuir* **2004**, *20*, 11465-11472.
- (55) Vanýsek, P. *Ionic Conductivity and Diffusion at Infinite Dilution*. In CRC Handbook of Chemistry and Physics, 94th ed, CRC Press: Boca Roton: FL, 2014.
- (56) Miller, M. D.; Bruening, M. L. Correlation of the Swelling and Permeability of Polyelectrolyte Multilayer Films. *Chem. Mater.* **2005**, *17*, 5375-5381.
- (57) Saito, M.; Arimura, N.; Hayamizu, K.; Okada, T. Mechanisms of Ion and Water Transport in Perfluorosulfonated Ionomer Membranes for Fuel Cells. *J. Phys. Chem. B* **2004**, *108*, 16064-16070.
- (58) Itano, K.; Choi, J. Y.; Rubner, M. F. Mechanism of the pH-Induced Discontinuous Swelling/Deswelling Transitions of Poly(allylamine hydrochloride)-Containing Polyelectrolyte Multilayer Films. *Macromolecules* **2005**, *38*, 3450-3460.

- (59) Schwarz, B.; Schönhoff, M. A ^1H NMR Relaxation Study of Hydration Water in Polyelectrolyte Mono and Multilayers Adsorbed to Colloidal Particles. *Colloids Surf. A* **2002**, *198*, 293-304.
- (60) Boddohi, S.; Killingsworth, C. E.; Kipper, M. J. Polyelectrolyte Multilayer Assembly as a Function of pH and Ionic Strength Using the Polysaccharides Chitosan and Heparin. *Biomacromolecules* **2008**, *9*, 2021-2028.
- (61) Choi, J.; Rubner, M. F. Influence of the Degree of Ionization on Weak Polyelectrolyte Multilayer Assembly. *Macromolecules* **2005**, *38*, 116-124.
- (62) Samec, Z.; Trojanek, A.; Langmaier, J.; Samcova, E. Diffusion Coefficients of Alkali Metal Cations in Nafion[®] from Ion-Exchange Measurements - An Advanced Kinetic Model. *J. Electrochem. Soc.* **1997**, *144*, 4236-4242.
- (63) Okada, T.; Satou, H.; Okuno, M.; Yuasa, M. Ion and Water Transport Characteristics of Perfluorosulfonated Ionomer Membranes with H^+ and Alkali Metal Cations. *J. Phys. Chem. B* **2002**, *106*, 1267-1273.
- (64) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. Solvent Structure, Dynamics, and Ion Mobility in Aqueous Solutions at 25 °C. *J. Phys. Chem. B* **1998**, *102*, 4193-4204.
- (65) Bonner, O. D.; Smith, L. L. A Selectivity Scale for Some Divalent Cations on Dowex 50. *J. Phys. Chem.* **1957**, *61*, 326-329.

Table of Contents Graphic

