Electrodialysis through Nafion Membranes Coated with Polyelectrolyte Multilayers Yields >99% Pure Monovalent Ions at High Recoveries

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Abstract

Separation of monovalent and multivalent ions is important in processes ranging from water softening to recycling of Li. Previous studies show that cation-exchange membranes coated with multilayer polyelectrolyte films exhibit monovalent/divalent ion selectivities as high as 1000 in electrodialysis (ED) under ideal conditions with low ion recoveries. This work shows that even at 60-80% monovalent-ion recoveries, ED through Nafion membranes coated with protonated poly(allylamine)/poly(4-styrenesulfonate) multilayers can separate equimolar K^+ and Mg^{2+} or Li^+ and Mg^{2+} to give 99.5% pure monovalent ion. Moreover, the use of a low-volume receiving phase allows ED to concentrate the monovalent ion. Typical current efficiencies are around 70% for these separations. Selectivities appear to increase when the membrane-coating procedure uses a higher polyelectrolyte concentration in the deposition solution. Because the limiting current declines with ED time due to depletion of the monovalent ion in the source phase, use of a gradually decreasing applied current enhances current efficiency compared to ED at a constant high current. The membranes also show Li^+/Mg^{2+} selectivities around 100 when Mg^{2+} is in a 20-fold excess in the source phase at an ionic strength of 0.6 M, but selectivity decreases at even higher ionic strengths.

Keywords: electrodialysis, layer-by-layer films, monovalent/multivalent selectivity, Li^+/Mg^{2+} separations, ion-exchange membranes

1. Introduction

Ion separations are crucial for providing the materials needed for devices ranging from batteries [1,2] to high-performance magnets [3]. Conventional ion-separation techniques such as precipitation and solvent extraction are effective, but they can require long evaporation times or toxic solvents [4]. Membrane-based ion separations complement traditional salt-purification techniques, and they can operate continuously often without the need for additional reagents. In particular, specific membranes allow passage of monovalent ions while rejecting divalent species [5]. Applications that exploit selective rejection of divalent ions include removal of sulfate from salt solutions [6] and water-softening [7]. Typical membrane selectivities are around 10-20 between monovalent and divalent ions [8]. This work employs electrodialysis (ED) through ion-exchange membranes coated with multilayer polyelectrolyte films (MPFs) to separate monovalent and divalent cations with monovalent/divalent selectivities >100. With further improvements and study, such a process might prove useful in the recovery of pure salts from recycling streams or perhaps natural resources.

ED is attractive for ion separations because the use of a highly perm-selective ion-exchange membrane (IEM) can, in principle, lead to energy-efficient separations [9–11]. For example, because cation-exchange membranes (CEMs) highly reject anions, passage of current through these membranes occurs almost completely via cations. If the CEM also allows selective passage of only one cation, the current efficiency for recovery of this cation will approach 100%. However, typical cation-exchange membranes show relatively low selectivities among cations [12], and anion-exchange membranes (AEMs) exhibit low selectivities among anions [13].

To increase selectivities among counterions (ions whose charge sign is opposite to that of the fixed charge in the IEM), many studies focused on modifying ED membranes with highly selective coatings [14,15]. Frequently the selective coating contains fixed charge whose sign is the same as that of the IEM counterions. Thus, the coating electrostatically excludes counterions for the IEM, and importantly the exclusion is particularly high for multivalent ions. The coating may also selectively exclude multivalent ions due to their large hydrated size and hydration energy [16]. A recent paper showed exceptionally high monovalent ion purities in nanofiltration combined with an applied current [17]. The authors suggest that the high selectivity stems from changes in surface charge upon application of current.

Several groups examined salt purification using IEMs specifically designed to give high monovalent/divalent counterion selectivities [18–20]. This manuscript examines K^+/Mg^{2+} and Li^+/Mg^{2+} separations using IEMs coated with MPFs. Many studies showed that layer-by-layer polyelectrolyte films can serves as thin, highly selective skins for separation membranes [21–31]. The gain in entropy due to release of counterions along with hydrophobic interactions create multilayer films that are stable for ions separations [31].

Especially relevant to this work, adsorption of polyelectrolyte films on ion-exchange membranes can lead to electrodialysis (ED) selectivities >1000 between monovalent and multivalent ions [32,33]. High selectivity can occur when coating either Nafion or less-expensive Fujifilm membranes [34], although selectivities may vary with source- and receiving-phase concentrations and compositions [22]. Nevertheless, our prior work on polyelectrolyte-coated membranes with high selectivities did not examine ED separations with high recoveries. At high recoveries the concentration of the desired ion is low in the source-phase solution. At such low concentrations, the separation is more difficult [35].

This work demonstrates that remarkable monovalent-ion purities (99.5%) are possible at high salt recoveries (60-80%) and current efficiencies around 75%, but the magnitude of the applied current is an important variable in these separations. Although coatings may greatly increase the selectivity of IEMs, they also decrease the magnitude of limiting currents [33]. In ED, limiting currents arise because a specific ion, e.g. K^+, carries a different fraction of the total current in the membrane than in the neighboring coating (MPF) or solution boundary layer. If the IEM is highly selective for a given counterion, e.g. K^+, this ion carries nearly 100% of the current through the membrane. In a solution boundary layer or MPF coating, however, both counterions and coions carry current. (Coions are ions whose charge sign is the same as that of the fixed charge in the underlying IEM.) Thus, the current moves more counterions away from the coating-IEM interface than arrive at this interface via electromigration (see Figure 1). To achieve the same K^+ flux in the MPF and IEM (steady state), a K^+ concentration gradient arises in the MPF and induces K^+ diffusion in this region. At steady state the sum of diffusion and electromigration of K^+ in the MPF is equal to the K^+ electromigration away from the MPF/membrane interface. Because diffusion in the IEM is often negligible compared to electromigration, the concentration of cations in the cation-exchange membrane in Figure 1 is essentially constant. Moreover, the concentration of counterions in the IEM is high to compensate the fixed charge.

The limiting current appears when the concentration of the desired ion, e.g. K^+, approaches zero near the MPF-IEM interface (Figure 1). Selective coatings on IEMs are often less permeable than boundary layers in solution, and they may also be selective for coions of the IEM [36]. Thus, limiting currents can be especially low in IEMs with selective coatings. Moreover, because the limiting current is proportional to the ion concentration in the source-phase solution, it will decrease over the course of selective electrodialysis.

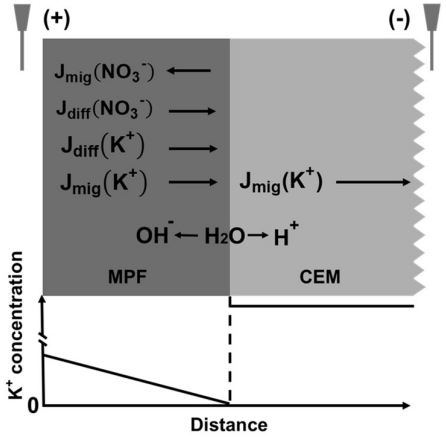

Fig. 1. Scheme of ion fluxes and the K^+ concentration profile at a multilayer polyelectrolyte film (MPF)/cation-exchange membrane (CEM) interface during ED with a KNO_3 solution. The arrows show fluxes due to electromigration, J_{mig}, or diffusion, J_{diff}, for ions in the MPF or CEM. Water splitting will occur at highly overlimiting currents.

Energy-efficient separations employ currents below the limiting value to avoid unwanted energy-consuming processes such as water splitting [37,38]. Moreover, at overlimiting currents selectivities often decrease [33,39]. Unfortunately, low limiting currents in coated membranes will require relatively large membrane areas to achieve a given amount of product. This is particularly important when considering high ion recoveries because the limiting current decreases as the concentration of the target ion in the source phase declines over the course of the separation. Thus, achieving high selectivities and energy efficiencies will likely require a separation where the applied current decreases with time, so this work examines ED with different current programs to optimize selectivity.

2. Experimental

2.1. Materials

Poly(sodium 4-styrenesulfonate) (PSS, Mw = 70000 Da), poly(allylamine hydrochloride) (PAH, Mw = 17500 Da), sodium chloride, potassium chloride, and potassium nitrate were obtained from Sigma-Aldrich. Magnesium nitrate was acquired from Jade Scientific, and lithium nitrate was purchased from Spectrum Chemical. All salts were used as received. Deionized water (Milli-Q reference Ultra-pure Water Purification System, 18MΩ cm) was used to prepare all solutions, and the pH values of polyelectrolyte solutions were adjusted with 1.0 M solutions of HCl and NaOH. Nafion N115 membranes were purchased from Ion Power (New Castle, DE, thickness 127 μm). Fujifilm type-1 anion exchange membranes were gifts from Fujifilm, Netherlands. For the pretreatment of Nafion membranes, 30% H_2O_2 (Fisher) and 98% H_2SO_4 (Sigma-Aldrich) were diluted to 3% H_2O_2 and 1.0 M H_2SO_4, respectively. Commercial ICP-OES standard solutions of K^+, Li^+ and Mg^{2+} were purchased from Sigma-Aldrich.

2.2. Membrane preparation and MPF formation

Nafion membrane disks were cut from a membrane sheet and immersed sequentially for 30 minutes in the following 4 boiling aqueous solutions: 3% v:v H_2O_2, deionized water, 1.0 M H_2SO_4, and deionized water [40]. Using a squirt bottle, the membrane disks were also washed with room-temperature deionized water for 30 seconds between every immersion. These oxidized Nafion membranes were used for subsequent modification. Fujifilm type-1 anion exchange membranes were soaked in 0.1 M NaCl overnight before use.

MPFs were formed by immersing oxidized Nafion membranes in alternating polycation (PAH in 1.0 M NaCl) and polyanion (PSS in 0.5 M NaCl) solutions for 5 minutes each to obtain 5.5-bilayer films, $(PAH/PSS)_5PAH$. After each polyelectrolyte adsorption step, the film was rinsed with deionized water from a squirt bottle for 30 sec to remove loosely bound polyelectrolyte. Polyelectrolyte solutions (pH ~2.3) contained 0.02 M of the polymer repeating unit. For some cases with Li^+ separations, the concentration of the polymer repeating units was 0.04 M during film deposition.

2.3. Electrodialysis

Figure 2 depicts the 4-cell electrodialysis apparatus for the recovery of monovalent cations from a mixture of monovalent and multivalent cations. The system contains an anode cell, source-phase compartment, receiving-phase compartment, and cathode cell. The AEMs next to the anode and cathode cells isolate the electrodes from the source and receiving phases. These membranes largely prevent cations from entering the source phase or exiting the receiving phase via the electrode compartments. The cathode cell contained 3% v:v aqueous HNO_3 to avoid high pH values due to generation of OH^- at the cathode. The anode solution contained 0.1 M NaOAc, which prevents large drops in pH due to protons formed at the anode. In cases with high current densities and high source-phase concentrations, the concentration of NaOAc was 0.5 M. The source phase contained both KNO_3 and $Mg(NO_3)_2$ or $LiNO_3$ and $Mg(NO_3)_2$, and the receiving cell contained 0.03 M HNO_3. The acid in the receiving phase provides conductivity and facilitates high-sensitivity analysis of cations moving into this phase. The coated Nafion membrane was clamped between the source and receiving phases. A CH Instruments potentiostat/galvanostat (model 660E) generated the current using platinum wire electrodes as the anode and cathode, and the current density is reported as the current divided by the exposed area of the Nafion membrane. The working electrode terminal was connected to the platinum anode, and the counter and reference electrode terminals were connected to the platinum cathode. All compartments were stirred vigorously during experiments to limit concentration polarization in solution. Membranes were soaked in the source-phase solution overnight prior to ED and rinsed quickly with water prior to transport experiments. The 4-cell system in Figure 2 operates in batch mode, which is similar to electrodialysis stacks that employ recirculating solutions. Nevertheless, stacks could, in principle, operate continuously without recirculation. Additionally, because of

extensive stirring the system in Figure 2 likely has less concentration polarization in solution than a stack. Prior current-voltage experiments with bare Nafion membranes showed no limiting current over the range of interest, so solution boundary layers likely do not play a major role in these experiments, particularly because of the high resistance of the MPF [33,36,39].

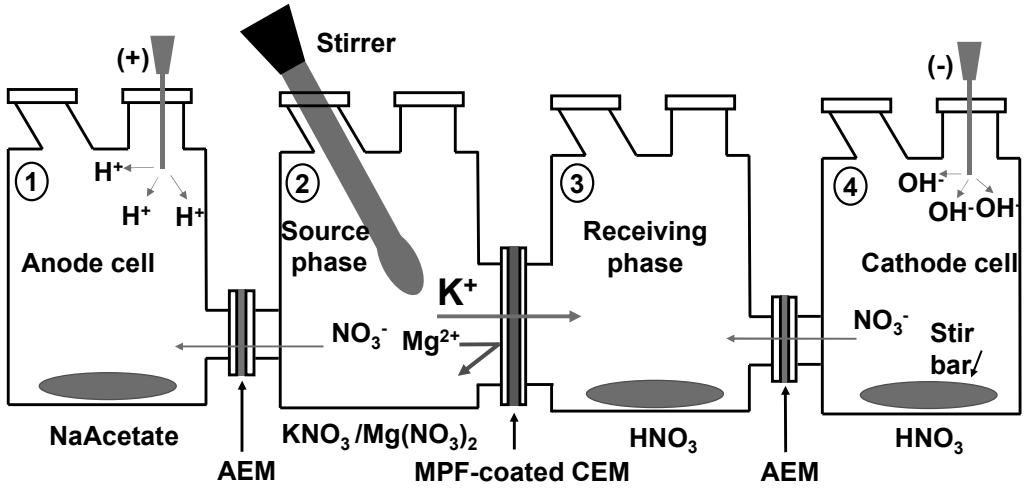

Fig. 2. The 4-cell electrodialysis system for extracting monovalent ions from a source phase.

In most studies, the source and receiving phases contained the same initial volume of 45 mL, and the cell exposed a membrane area of 5 cm^2. However, some experiments used a much larger source-phase cell that holds a volume of 450 mL, along with a smaller receiving-phase cell that holds 30 mL. These experiments aimed to concentrate the ion of interest in the receiving cell and employed a larger exposed membrane area of 7.5 cm^2.

During ED, 1-mL aliquots were typically collected periodically from the source and receiving phases to determine the concentrations of K^+ or Li^+ and Mg^{2+}. In some experiments, however, the source and receiving phases were sampled only at the beginning and the end of the experiment. Cation concentrations were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES PerkinElmer Optima 8000) with calibration curves. Standards were prepared by diluting commercial ICP-OES standard solutions with 3% (v:v) aqueous nitric acid.

We define the K^+ recovery using equation (1).

$$Recovery = \left(1 - \frac{c_{K+}^{source}}{c_{K+}^{source,i}}\right) * 100\% \quad (1)$$

where c_{K+}^{source} is the source-phase K^+ concentration at a given time, and $c_{K+}^{source,i}$ is the initial K^+ source-phase concentration. With equal source- and receiving-phase volumes throughout the experiment and assuming minimal K^+ in the membrane, using a mass balance one can also write

$$Recovery\ \ (\%) = \frac{c_{K^+}^{receiving}}{c_{K^+}^{source,i}} * 100\% \quad (2)$$

The supplementary information (section S-4) discusses the definition of recovery in more detail and small discrepancies in the mass balance.

We calculated the transference number (t_i, fraction of current carried by a specific ion) using equation (3), where N_i is the number of moles of ion *i* that passed to the receiving phase, Z_i is the charge number of cation *i*, *F* is Faraday's constant and *Q* is the total amount of charge passed through the electrodes during the experiment.

$$t_i = \frac{N_i \times Z_i \times F}{Q} \quad (3)$$

The transference number is an overestimation because some ions may move to the receiving phase due to exchange of cations between the source and receiving phases or between the receiving phase and the membrane. However, a control experiment with no applied potential gave a flux that is ~5% of the initial flux during the corresponding ED with a current density of 0.8 mA/cm^2. In most cases, ED was performed with at least three replicate membranes. Uncertainties in purities, selectivities, recoveries and transference numbers are standard deviations of calculated values for the three different membranes.

3. Results and discussion

This work examines ED with MPF-coated membranes to achieve recoveries up to 80% with >99% pure monovalent ions, and such separations require relatively long ED times (2 to as many as 12 h). These studies include separations with different current programs and source-phase volumes to determine if decreases in current efficiency at recoveries >60% occur partially due to overlimiting currents. Based on knowledge acquired from separating K^+ and Mg^{2+}, we also examine the separation of Li^+ and Mg^{2+} at high recoveries as well as with an excess of Mg^{2+}, which decreases selectivity.

3.1. Highly selective K^+ transport with high recovery in electrodialysis of solutions containing K^+ and Mg^{2+}

Initial experiments aimed to determine if the high K^+/Mg^{2+} selectivities observed previously during ED [32,33] are also possible at high recovery. K^+ and Mg^{2+} have very different hydrodynamic sizes, so this pair of ions should provide high monovalent/divalent selectivity. Moreover, the use of K^+ rather than Na^+ avoids challenges with ubiquitous Na^+ contamination. These studies employed a 4-compartment cell (Figure 2) that uses anion-exchange membranes to isolate electrode compartments and limit transport of cations between these compartments and other phases. The use of a receiving phase that does not contain K^+ and Mg^{2+} (0.03 M HNO_3) facilitates determination of high selectivities and purities as a function of recovery.

Table 1 shows the purities in the receiving phase along with selectivities after ED for several hours at different current densities. In a single 3.5-h ED at a current density of 0.8 mA/cm^2 (case 2, Table 1), the K^+ purity (relative to K^+ and Mg^{2+}) goes from 50% in the initial source phase to above 99.5% in the final receiving phase. This occurs at a K^+ recovery around 80%. In contrast, bare Nafion membranes (case 1, Table 1) give a K^+/Mg^{2+} selectivity of just 1.5 and a K^+ purity of only 59% at 85 % K^+ recovery.

Table 1. Selectivities and K^+ recoveries, transference numbers, and purity during ED through bare Nafion membranes (Case 1)[a] and through Nafion membranes coated with $(PAH/PSS)_5PAH$ films (Cases 2-4).[a]

Case	Current density (mA/cm^2)	Time (hours)	K^+/Mg^{2+} selectivity	K^+ Transference number (%)	K^+ recovery (%)	K^+ purity (%)
1[b]	0.8	3.5	1.5±0.1	-	85±1	59.2±0.1
2[b]	0.8	3.5	1050±850	74±8	80±8	99.7±0.3
3[c]	0.8	4	400±240	-	-	99.6±0.4
4[b]	1.6	2	110±30	63±3	78±7	99.0±0.3

[a] The source phase initially contained 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$, and the receiving phase was 0.03 M HNO_3. The membrane area was 5 cm^2, and the source- and receiving-phase volumes were 45 mL. Uncertainties are standard deviations from experiments with 3 or more membranes.

[b]In these experiments, source and receiving phases were analyzed only at the beginning and end of the experiment. The recovery is based on measurements of the source-phase concentrations.

[c]Several aliquots were periodically removed from the source and receiving phases during the experiment to monitor concentrations over time.

We use equation (4) to define selectivity, $\alpha_{K^+/Mg^{2+}}$, where $n_{K^+}^{rec}$ and $n_{Mg^{2+}}^{rec}$ are the total moles of K^+ and Mg^{2+}, respectively, transported to the receiving phase. The variables $c_{K^+}^{source,i}$ and $c_{Mg^{2+}}^{source,i}$ are the initial concentrations of these ions in the source-phase solution.

$$\alpha_{K^+/Mg^{2+}} = \frac{n_{K^+}^{rec}/c_{K^+}^{source,i}}{n_{Mg^{2+}}^{rec}/c_{Mg^{2+}}^{source,i}} \quad (4)$$

Even at 80% recovery, the K^+/Mg^{2+} selectivity is at least several hundred at a current density of 0.8 mA/cm^2. Unfortunately, the uncertainty in purities and selectivities is relatively large because the low concentration of Mg^{2+} is hard to detect precisely and varies significantly among replicates. Using 3.5 h of ED (Table 1, case 2), the ratio of K^+ to Mg^{2+} in the receiving phase ranged from 200 to 2000 in experiments with 3 different membranes. Taking into account the decreasing concentration of K^+ in the feed solution over time would give an even

higher selectivity value (sometimes termed the separation factor [41]). In addition to high selectivity, these separations offer overall current efficiencies of around 70% for K^+ transport (see Table 1). The pH values in the receiving and source phases were ~1.9 and 5.6, respectively, and hardly changed throughout the experiment.

Ion passage through the membrane occurs primarily via electromigration, and the MPF controls the ion flux. The flux of a given ion depends on its concentration and mobility in the film. The MPF significantly excludes divalent Mg^{2+} in part due to its large hydrodynamic radius and high hydration energy [14]. Moreover, the positively charged MPF electrostatically excludes the divalent ion as shown in prior studies [39]. Finally, the large hydration shell and hydration energy also likely lead to a low Mg^{2+} mobility in the film.

3.2. Selectivities and limiting currents

Figure 3 shows the time-dependent percent recoveries of K^+ and Mg^{2+} during ED with a source phase that initially contained 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$. The rate of increase in K^+ recovery (proportional to the slope in Figure 3) declines sharply at recoveries >60%, even though the current density is constant. Additionally, the Mg^{2+} flux slowly rises at high K^+ recovery. One might expect such trends due to the declining ratio of K^+ to Mg^{2+} in the source phase over time. However, section S-1 of the supplementary information shows that with a high and constant selectivity of 100 (with selectivity defined based on the instantaneous fluxes and instantaneous source-phase concentrations [41]), decreases in the K^+ flux should be small until the K^+ recovery approaches 100%. Thus, depletion of the source-phase concentration alone probably does not explain the trends in Figure 3.

The most likely reason for the decline in the K^+ flux and the K^+/Mg^{2+} selectivities at K^+ recoveries >60% is that the applied current significantly exceeds the limiting current when the K^+ concentration in the source phase decreases. When this occurs the K^+ transference number should decrease. Water splitting could lead to local pH changes that increase the film permeability to Mg species [39]. In Table 1 case 4, we applied a higher current density (1.6 mA/cm^2) for 2 hours. The average selectivity and purity in case 4 are lower than in case 3, even though these experiments employ the same amount of total charge passed. This suggests that exceeding the limiting current to a larger extent may impair selectivity, even though the difference in selectivities for case 3 and case 4 is significant only at the 90% confidence level.

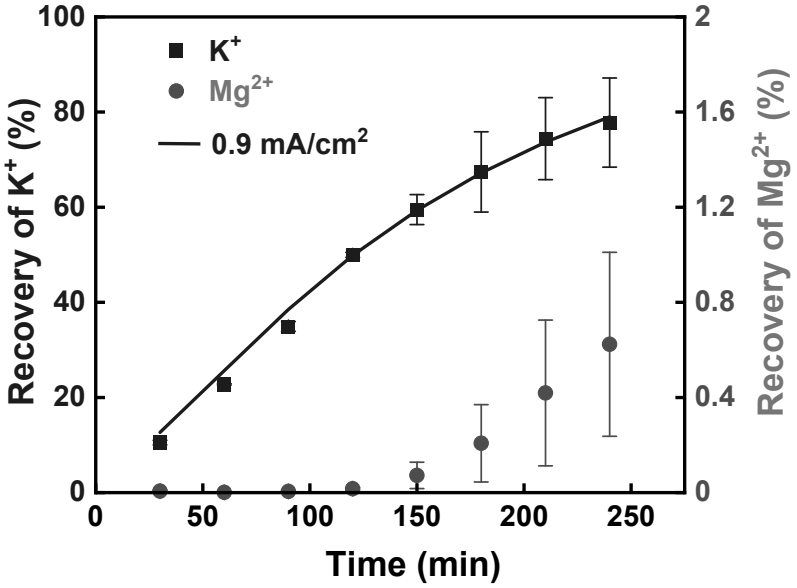

Fig. 3. K^+ and Mg^{2+} percent recoveries during ED through Nafion membranes coated with $(PAH/PSS)_5PAH$ films. The initial source phase contained 0.01 M KNO_3 and 0.01M $Mg(NO_3)_2$, and the receiving phase was 0.03 M HNO_3. Recovery was calculated using equation (2). The blue curve models the K^+ recovery using equations (5) and (6), with an initial limiting current density of 0.9 mA/cm^2. The applied current density was 0.8 mA/cm^2, the membrane area was 5 cm^2, and the source- and receiving-phase volumes were initially 45 mL. Error bars are the range of 2 measurements.

We modelled the K^+ recovery in Figure 3 using different equations for currents above and below the limiting value. When $I * t_{K^+} < I_{lim}^{K^+}$, we employed equation (5).

$$c_{K^+}^{rec} = c_{K^+}^{rec,o} + \frac{I * t_{K^+} * A}{FV} \quad \tau \qquad (5)$$

In this equation $c_{K^+}^{rec}$ is the concentration of K^+ in the receiving phase, $c_{K^+}^{rec,o}$ is the initial concentration of K^+ in the receiving phase at the beginning of a given time interval, I is the applied current density, F is Faraday's constant, V is the receiving-phase volume during the time interval, A is the exposed membrane area, and τ is the elapsed time. Based on the first four data points in Figure 3, we assumed a constant t_{K^+} value of 0.76 for underlimiting conditions. Note that V changes slightly between sampling intervals due to removal of solution for analysis, so we model concentrations interval by interval.

The limiting current decreases with time because the concentration of K^+ in the source phase declines during ED. When $I * t_{K^+} > I_{lim}^{K^+}$, we model the receiving phase concentration as

$$c_{K^+}^{rec} = c_{K^+}^{rec,o} + c_{K^+}^{source,o}\left(1 - exp\left(-\frac{kA\tau}{FV}\right)\right) \quad (6)$$

where

$$I_{lim}^{K^+} = I_{lim} = kc_{K^+}^{source} \quad (7)$$

In these equations, k is the proportionality constant between the source-phase K^+ concentration and the limiting current density, and $c_{K^+}^{source,o}$ is the initial concentration in the source phase at the beginning of a typical time interval that corresponds to the volume V. Equations (6) and (7) assume that the flux of K^+ is proportional to the limiting current, which is proportional to the K^+ source-phase concentration. Thus, the flux of K^+ across the membrane decreases exponentially with time. Section S-2 of the supplementary information derives these equations and gives more details of the model.

Figure 3 shows modelling data for $c_{K^+}^{rec}$ with a limiting current of 0.9 mA/cm^2. This value is close to the limiting current of 0.6 mA/cm^2 that we determined previously from current-voltage curves [33,39]. Given the uncertainties in the experimental data, the simulated limiting current in Figure 3 could fall within a range of 0.7 to 1.8 mA/cm^2.

Lower applied currents should increase the efficiency of the separation by avoiding overlimiting currents. Thus, we also performed ED with a lower initial applied current density (0.5 mA/cm^2) and decreased the current density in a stepwise fashion (Figure 4a) to avoid approaching the limiting current upon K^+ depletion. The supplementary information (Section S-3) describes the rationale for the selection of the current program. Figure 4b shows the recovery as a function of the amount of charge passed in this experiment as well as for an experiment with a constant current of 0.8 mA/cm^2. The lower applied currents give rise to higher recovery for a given amount of charge passed, which indicates a higher current efficiency. In fact, the calculated current efficiency is as high as 1.4 during the ED with lower currents. The current efficiency >1 suggests that ion-coupled diffusion to the receiving phase as well as exchange of K^+ with H^+ in the ion-exchange membrane are significant at these lower current densities. The final recovery based on the receiving-phase concentration is 104%, but the final source phase concentration at the end of the experiment suggests the recovery is around 90%. This difference likely stems from K^+ initially loaded in the membrane leaching into the receiving phase. Section S-4 of the supplementary information further discusses these issues. Most important, with the applied current program in Figure 4a, even at high recovery the current efficiency is around 1. Although these separations take many hours, section S-5 of the supplementary information shows that increasing the ratio of membrane surface area to cell volume could decrease the residence time required for 90% recovery by two orders of magnitude.

A subsequent experiment with the same membrane and the low applied currents showed no decrease in purity and recovery (see Section S-6 in the supplementary information). This suggests at least short-term stability. Longer-term stability studies are needed for exploring

practical applications. One paper showed that membranes coated with multilayers containing quaternary-ammonium polyelectrolytes are stable for more than 100,000 ppm hours of NaOCl [42].

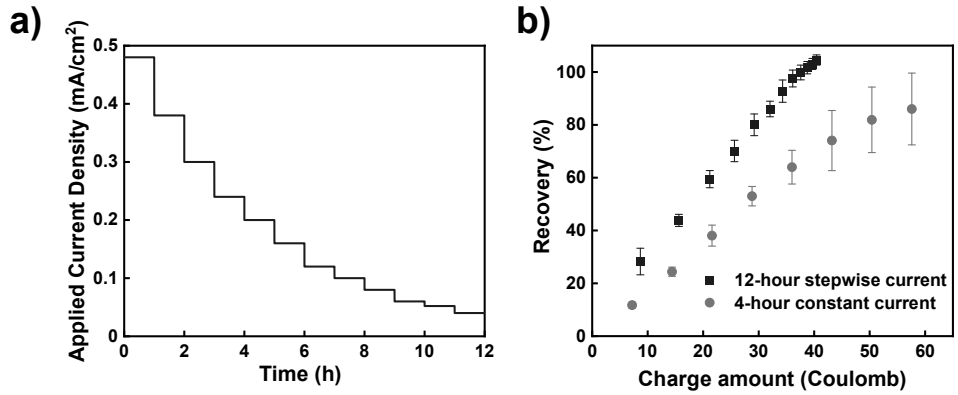

Fig. 4. (a) Current-density program applied to avoid exceeding the limiting current. **(b)** K^+ recovery as a function of charge passed during ED with the current program in Fig. 4a (blue squares) or a constant current density of 0.8 mA cm^{-2} (red circles). The initial source phase contained 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$, and the receiving phase was 0.03M HNO_3. The membrane area was 5 cm^2, and the source- and receiving-phase volumes were 45 mL. Error bars are standard deviations from 3 experiments with at least two membranes.

3.3. ED with a large-volume source phase and higher ion concentrations

To further demonstrate that decreasing K^+ fluxes and current efficiencies at high recoveries result from the declining source-phase K^+ concentration, we performed ED with a 10-fold higher source-phase volume. This gives a much smaller drop in the K^+ source-phase concentration when performing ED for the same amount of time as with a lower-volume source phase. Additionally, when the receiving-phase volume is much smaller than the source-phase volume, ED can concentrate the desired species in the receiving phase. As Figure 5 shows, when performing ED with a current density of 0.8 mA/cm^2 for 6 h and a source-phase volume of 450 mL, the K^+ flux is approximately constant over the course of the experiment. This occurs because the K^+ depletion in the source phase is only 25%. The current efficiency is 85%. Remarkably, the K^+/Mg^{2+} selectivity is > 1000, and the K^+ purity in the receiving phase (relative to Mg^{2+} and K^+) is >99.9% in these experiments. Additionally, because in this experiment the source-phase volume is 15 times the receiving-phase volume, the K^+ concentration in the receiving phase after 6 h is ~4 times the initial concentration in the source phase. With longer ED times and smaller receiving-phase volumes, a much higher concentration factor should be possible. Doubling the source-phase salt concentration to 0.02 M KNO_3 and 0.02 $MgNO_3$ and using the 450-mL source phase leads to even higher current efficiencies, but increased diffusion at the higher concentration likely artificially increases the current efficiency.

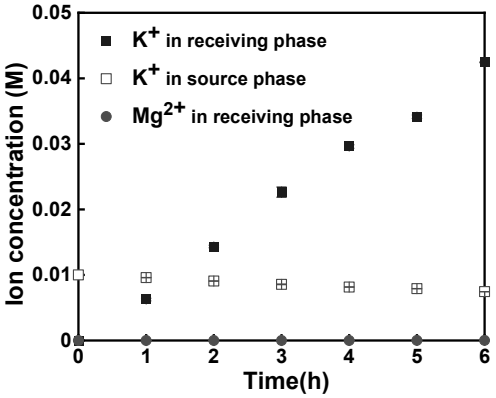

Fig. 5. Concentrations of K^+ in the source (open squares) and receiving phases (filled blue squares) and Mg^{2+} in the receiving phase (red circles) during ED through a $(PAH/PSS)_5PAH$-coated Nafion membrane. The current density was 0.8 mA cm^{-2}, the source phase was initially 0.01 M KNO_3 and 0.01 M $Mg(NO_3)_2$, and the receiving phase was 0.03 M HNO_3. The volumes of the source and receiving phases were 450 ml and 30 mL, and the membrane area was 7.5 cm^2. Error bars, which are typically smaller than the symbols, show the range of values with two membranes. Section S-7 in the supplementary information shows the Mg^{2+} concentration on an expanded scale.

We also performed ED with a source phase containing 0.05 M KNO_3 and 0.05 M $Mg(NO_3)_2$). Because the limiting current is proportional to the cation concentration in the source phase, we increased the current density to 4 mA/cm^2 in these studies. Application of a constant current for 3.5 hours gives a K^+ recovery of 86±2% along with a K^+ purity of 98.2±0.1%. The K^+/Mg^{2+} selectivity decreases to 55±4 in this case, perhaps because the higher current densities greatly exceed the limiting current upon K^+ depletion. Additionally, the higher source-phase concentration may lead to less Donnan exclusion of the divalent cation.

3.4 Recovering Li^+ from Li^+/Mg^{2+} mixtures

Separation of Li^+ from Mg^{2+} or other divalent ions may prove important in recycling or purifying Li^+. The high K^+/Mg^{2+} selectivities described above bode well for Li^+/Mg^{2+} separations. Nevertheless, the Stokes radius of hydrated Li^+ is almost twice as large as that for K^+ [4], so fractionation of Li^+ and Mg^{2+} is more challenging than separation of K^+ and Mg^{2+}. The relatively low diffusion coefficient of Li^+ should also lead to limiting currents that are lower than with K^+. Case 1 in Table 2 shows that application of a constant current of 0.8 mA/cm^2 leads to a Li^+ purity (relative to Li^+ and Mg^{2+}) of 96.9% at a recovery of 48%. As expected, the Li^+/Mg^{2+} selectivity is less than the K^+/Mg^{2+} selectivity with these membranes, and the Li^+ recovery is also lower than the K^+ recovery. A similar experiment with a bare Nafion membrane showed a Li^+/Mg^{2+} selectivity of only 0.75, demonstrating that the MPF greatly increases the selectivity.

Decreasing the current in steps over the course of the separation significantly increases both the purity and recovery of Li^+ in the receiving phase (compare cases 1 and 2 in Table 2). Halving the current every 2 h leads to a Li^+ purity around 99%, and the Li^+/Mg^{2+} selectivities with four different membranes were 30, 160, 230 and 550.

Table 2 Overall Li^+/Mg^{2+} selectivity, Li^+ recovery and Li^+ purity after ED using a source phase containing 0.01 M $LiNO_3$ and 0.01 M $Mg(NO_3)_2$.[a]

Case	Concentration of MPFs (M)	Current Program (mA/cm^2)	Li^+/Mg^{2+} selectivity	Transference number (Li^+ %)	Li^+ recovery (%)	Li^+ purity (%)
1	0.02	0.8 for 6 h	31±3	29±1	48±2	96.9±0.3
2	0.02	0.8, 0.4, 0.2 for 2,2,2 h	240±190	60±9	58±7	98.8±1.3
3	0.04	0.8 for 6 h	48±11	34±2	58±5	97.8±0.6
4	0.04	0.8, 0.4, 0.2 for 2,2,2 h	990±540	68±3	63±4	99.9±0.1
5	0.04	0.8, 0.4, 0.2 for 2,2,6 h	140±30	54±4	63±3	99.3±0.1

[a]The Li^+ recovery is based on source-phase concentrations at the beginning and end of the experiment. Recoveries based on the receiving phase are higher. Samples were removed periodically for analysis.

MPF formation and film structure depend on multiple adsorption parameters including polymer concentration, pH, and supporting electrolyte concentration [44]. We briefly examined the effect of polyelectrolyte concentration on transport properties. Specifically, we doubled the polyelectrolyte repeating unit concentrations in adsorption solutions from 0.02 M to 0.04 M during Nafion modification and examined ED with a solution containing Li^+ and Mg^{2+}. Comparison of cases 1 and 3 in Table 2 suggests that even at a constant current density of 0.8 mA/cm^2, depositing the MPF from solutions with higher polyelectrolyte concentrations gives higher recovery and Li^+ purity.

With the current-step program (Table 2, case 4), the Li^+/Mg^{2+} separation is especially selective when using MPFs deposited from polycation and polyanion solutions containing 0.04 M repeating units. In this case, the receiving phase contains 99.9% pure Li^+ with a recovery of 63%. We attempted to increase the recovery by extending the last current step from 2 to 6 h (Table 2, case 5), but this had no significant effect on recovery and decreased the Li+ purity, presumably because the current exceeds the limiting value at the end of the experiment. The reason for the significant increase in selectivity and recovery when using a higher polyelectrolyte concentration during MPF deposition is not yet clear. Another study showed that polyelectrolyte molecular weight may change how MPFs cover pores [45], and a related effect might occur with different polyelectrolyte concentrations. Ellipsometric thicknesses of "dry" $(PAH/PSS)_5PAH$ films assembled on a Au-coated substrate were not significantly different for deposition from polyelectrolyte solutions containing 0.02 and 0.04 M polymer repeating units. The average film thicknesses were 20 and 21 nm.

3.5 Li^+ extraction from solutions with excess Mg^{2+}

The Li^+ extraction described above employed source-phase solutions containing equimolar Li^+ and Mg^{2+}, whereas in some brines the Mg^{2+} concentration is significantly greater than that of Li^+ (section S-8 of the supplementary information provides more detail about the ion compositions of brines). For example, the molar ratios of Mg^{2+} to Li^{2+} in the Great Salt Lake and Smackover, USA are ~40 and ~6, respectively. Current production of lithium mainly occurs at lakes where the molar ratio of Mg^{2+}/Li^+ is less than 2 [46]. We conducted ED with a Mg^{2+} to Li^+ ratio of 20 to see whether membranes can maintain their selectivity in excess Mg^{2+} and also at a higher ionic strength. These experiments employed a polyelectrolyte repeat unit concentration of 0.04 M during membrane modification, as this condition gave rise to highly selective membranes in experiments with equimolar Li^+ and Mg^{2+}.

Figure 6a shows ED results for an experiment using a source phase initially containing 0.01 M $LiNO_3$ and 0.2 M $Mg(NO_3)_2$ (ionic strength of 0.6 M) In this case the source-phase volume was relatively large (450 mL), and the Li^+ depletion in the source phase was <20% over the course of the experiment. The ratio of Li^+ to Mg^{2+} in the receiving phase was around 5, so when taking into account the Li^+/Mg^{2+} ratio of 0.05 in the initial source phase, the selectivity is around 100. Moreover, because the receiving-phase volume is 15 times that of the source phase, the Li^+ concentration in the receiving phase at the end of the experiment is around 3 times (0.03 M) the initial source-phase concentration, even though the recovery is only 18%.

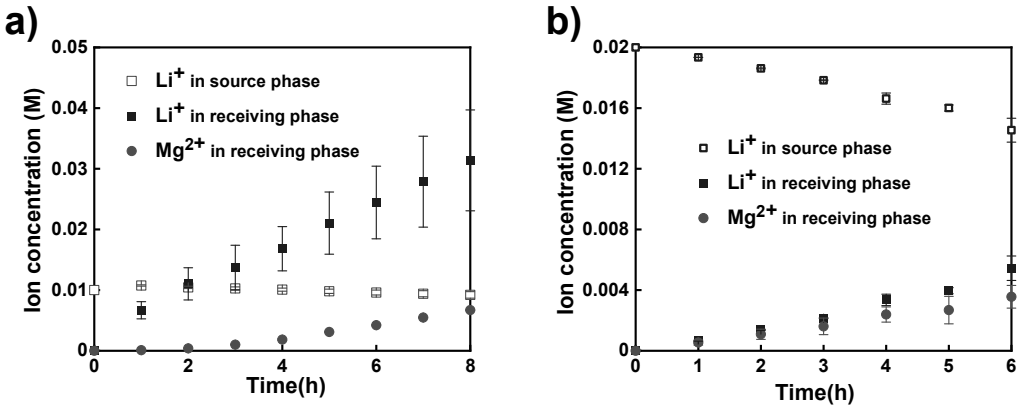

Fig. 6. Concentrations of Li^+ in the source (open squares) and receiving phases (blue squares), and of Mg^{2+} in the receiving phase (red circles) during ED through a $(PAH/PSS)_5PAH$-coated Nafion membrane. (a) ED used a current density of 0.8 mA cm^{-2} with an initial source phase containing 0.01 M $LiNO_3$ and 0.2 M $Mg(NO_3)_2$, and a receiving phase of 0.03 M HNO_3. The source- and receiving-phase volumes were 450 ml and 30 mL, respectively. (b) ED used a current density of 1.2 mA cm^{-2}, with an initial source phase containing 0.02 M $LiNO_3$ and 0.4 M $Mg(NO_3)_2$, and a receiving phase of 0.03 M HNO_3. The volumes of source and receiving phase were 45 mL each. The membrane area was 7.5 cm^2

in (a) and 5 cm^2 in (b). Error bars show the range from experiments with 2 different membranes.

A separate ED experiment employed a source phase containing 0.02 M $LiNO_3$ and 0.4 M $Mg(NO_3)_2$ to see if selectivity decreases further at high ionic strengths. As Figure 6b shows, at this ionic strength of 1.2 M the selectivity was only around 30, suggesting that high ionic strength may decrease selectivity. This effect might arise from less electrostatic exclusion of the divalent ion at high ionic strengths.

3.6. Comparison to other selective membranes

A few studies show extraordinary Li^+/Mg^{2+} selectivities in metal-organic frameworks or ionic conductors [47,48], but this section compares commercial monovalent-selective CEMs and MPF-modified Nafion membranes. Nie et al. used a commercial monovalent permselective CEM (Asahi Glass Selemion) to separate Li^+ and Mg^{2+} and achieved a Li^+ recovery of ~95%, a current efficiency of 50% and a Li^+/Mg^{2+} selectivity of ~20 when the Mg^{2+}/Li^+ feed molar ratio was ~40 [49]. Their work is oriented towards some salt lakes in west China with high concentrations of magnesium. Chen et al. studied the performance of ASTOM CIMS cation-selective membranes in the ED of Li^+ and Mg^{2+}. They achieved a Li^+ recovery of 80%, a current efficiency of 30% and a Li^+/Mg^{2+} selectivity of 60 when the concentrations of Li^+ and Mg^{2+} were similar in the feed [50]. However, when the concentration of Mg^{2+} was 10 times larger than that of Li^+, these values decreased to 60% recovery, 10% current efficiency and a selectivity of 5. Among monovalent selective CEMs, the MPF-coated Nafion shows the highest selectivities and current efficiencies when the Li^+/Mg^{2+} ratio is nearly equal, but the performance is similar to that of other membranes when Mg^{2+} is in excess or the ionic strength is high (Table 3).

Table 3. Comparison of MPF-coated Nafion with other monovalent-selective cation exchange membranes.

Refs	Membrane type	Lithium concentration and molar ratio of cations	Li^+/Mg^{2+} selectivity	Li^+ recovery (%)	Current efficiency (%)
Nie et al	Asahi Glass Selemion (CSO)	0.02 M Li^+ with Mg^{2+}/Li^+ ratio of 40	20	95	50
Chen et al	ASTOM CIMS	0.05 M Li^+ with a Mg^{2+}/Li^+ ratio of 1 or 10	60 or 5	80 or 60	30 or 10
This work	MPF/Nafion membrane	0.01M Li^+ with Mg^{2+}/Li^+ ratio of 1 or 20	700 or 100	75 or 20	70 or 45

Section S-9 of the supplementary materials discusses the relatively low energy consumption for lithium extraction using ED. We should note, however, that incorporation of ED in current evaporation/precipitation processes with brines will prove challenging because Mg^{2+} is usually removed from brines prior to Na^+ [51]. The presence of Na^+ will greatly decrease the

current efficiency for separating Li^+ from Mg^{2+} [50]. Monovalent/divalent ion separations might prove more useful in recycling Li^+ from batteries [52].

4. Conclusions

Coating of Nafion membranes with $(PAH/PSS)_5PAH$ films leads to K^+/Mg^{2+} and Li^+/Mg^{2+} selectivities >200 even with monovalent ion recoveries of 80%. Moreover, when using a low receiving-phase volume, one can concentrate the monovalent ion in the receiving phase. Limiting currents decrease at high recoveries, so ED with a gradually decreasing applied current enhances current efficiency. Assembly of the $(PAH/PSS)_5PAH$ film using higher polyelectrolyte concentration likely leads to higher monovalent/divalent ion selectivities. When the initial ratio of Mg^{2+} to Li^+ in the source phase is 20, ED with these membranes shows a selectivity of around 100, but selectivity decreases at higher ionic strengths.

Supplementary Materials: The supplementary materials contain a PDF file that serves as electronic supporting information.

Author Contributions: Dong Ding: Methodology, Experimentation, Data Interpretation, Writing-Original Draft; **Andriy Yaroshchuk**: Data Interpretation, Writing-Review and Editing; **Merlin L. Bruening**: Conceptualization, Data Interpretation, Writing-Review and Editing.

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