Highly Selective Separations of Multivalent and Monovalent Cations in Electrodialysis Through Nafion Membranes Coated with Polyelectrolyte Multilayers

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ABSTRACT:

Nafion membranes coated with 5.5-bilayer poly(4-styrenesulfonate) (PSS)/protonated
poly(allylamine) (PAH) films show $\text{Li}^+/\text{Co}^{2+}$ and $\text{K}^+/\text{La}^{3+}$ selectivities >1000 in electrodialysis
(ED). The corresponding selectivities of bare Nafion are <2 . Even with adsorption of only 3
polyelectrolyte layers, Nafion membranes exhibit a $\text{Li}^+/\text{Co}^{2+}$ selectivity >23 . However, the
resistance to monovalent-ion passage does not decrease significantly with fewer polyelectrolyte
layers. At overlimiting currents, water splitting near the polyelectrolyte/Nafion interface reduces
current efficiency because protons and hydroxide ions carry current in the membrane. Moreover,
hydroxides from water splitting form insoluble metal hydroxides to foul the membrane. With 0.1
M source-phase salt concentrations, transference numbers for monovalent cations approach unity

and selectivities are >5000 because the diffusion-limited K^+ or Li^+ currents exceed the applied current. However, ED selectivities gradually decline with time. Thus, future research should aim to increase membrane stability and limiting currents to fully exploit the remarkable selectivity of these membranes.

Keywords: Electrodialysis, selectivity, polyelectrolytes, ion-exchange membranes, layer-by-layer

1. Introduction

Electrodialysis (ED) is a membrane-based separation technique for applications such as brackish-water desalination,¹⁻³ wastewater treatment,⁴ dairy-byproduct demineralization,⁵ and production of organic acids⁶ and concentrated brines.^{7,8} Typical commercial ED systems employ feed solutions flanked by cation and anion-exchange membranes, and an applied current leads to migration of both cations and anions out of the feed solution.⁹ Although ED effectively removes charged species from feed streams, commercial ED membranes exhibit low selectivities among different cations or anions. Such selectivities are important in applications such as preventing vanadium crossover in redox flow batteries or purifying salts or drinking water.¹⁰⁻¹³

Several groups employed polyelectrolyte adsorption to enhance the selectivity of ion-exchange membranes. Sata and coworkers showed that polyanion coatings on cation-exchange membranes enhance the selectivity for cations over anions, and polycation coatings have the opposite effect.¹⁴⁻¹⁶ Polyethyleneimine (PEI) deposition on AMX anion-exchange membranes increased monovalent anion selectivity, and modification under basic conditions

1 led to $\text{NO}_3^-/\text{SO}_4^{2-}$ selectivities up to 20.¹⁷ Other studies using PEI coatings on cation-
2 exchange membranes showed that cross-linking of the film and control over hydrophobicity
3 give $\text{Na}^+/\text{Ca}^{2+}$ selectivities as high as 7.¹⁶ Additionally, electrochemical deposition of PEI
4 films on Nafion cation-exchange membranes produced $\text{Na}^+/\text{Cr}^{3+}$ selectivities >10 .¹⁸
5 However, these selectivities are relatively modest, so in this study we explore adsorption of
6 multilayer polyelectrolyte films on cation-exchange membranes to increase selectivity.

7 The discovery of simple layer-by-layer polyelectrolyte adsorption¹⁹ spurred exploration
8 into whether polyelectrolyte multilayers (PEMs) can act as selective barriers for ion
9 transport,²⁰⁻²⁵ and a few groups deposited PEMs on ion-exchange membranes to impart
10 selectivity. Mulyati *et al.* reported that modification of an anion-exchange membrane with
11 $(\text{PSS}/\text{PAH})_7\text{PSS}$ films reverses the $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity from 0.8 to 2.5.¹⁰ Other work with
12 60-bilayer poly(styrenesulfonate) (PSS)/protonated poly(allylamine) (PAH) films on
13 poly(acrylonitrile)/poly(ethylene terephthalate) produced $\text{Na}^+/\text{Mg}^{2+}$ selectivities exceeding
14 100 in diffusion dialysis.²⁶ Abdu and coworkers modified Neosepta CMX ion-exchange
15 membranes with polyethylenimine/PSS films to alternate ion permselectivity based on the
16 terminal layer, but $\text{Na}^+/\text{Ca}^{2+}$ selectivities were less than 1.5.²⁷

17 This research builds on our previous studies of PEM-coated membranes that show
18 remarkable $\text{K}^+/\text{Mg}^{2+}$ ED selectivities >1000 .^{28,29} In this paper, we first demonstrate that
19 $(\text{PAH}/\text{PSS})_5\text{PAH}$ -modified Nafion also exhibits $\text{Li}^+/\text{Co}^{2+}$ and $\text{K}^+/\text{La}^{3+}$ selectivities >1000 .
20 Using these pairs of ions, we investigate the effect of the source-phase salt concentrations on
21 selectivity and transference numbers because concentration polarization greatly affects ED.
22 Current-voltage curves and elemental characterization of fouled membranes give insight into
23 limiting currents and water-splitting near the PEM-Nafion interface, a phenomenon that

decreases the current carried by target ions.²⁷ Additionally, longer-term (48 h) ED reveals challenges to PEM stability, possibly because the electric field causes electromigration of the charged polyelectrolytes to degrade the film. We also study how varying the number of bilayers in the PEM affects the flux, transference number, and selectivity of coated membranes. The high selectivities of PEM-coated membranes make them very attractive for ED separations, and future work should aim at increasing limiting currents and membrane stability.

2. Experimental section

2.1. Materials

Poly(sodium 4-styrenesulfonate) ($M_w = 70000$ Da), poly (allylamine hydrochloride) ($M_w = 15000$ Da), sodium nitrate, lanthanum(III) acetate ($\text{La}(\text{OAc})_3$) hydrate, and potassium acetate ($\text{K}(\text{OAc})$) were purchased from Sigma-Aldrich. Magnesium nitrate was obtained from Mallinckrodt, and lithium nitrate was purchased from Spectrum. All salts were used as received without further purification. For the acidic receiving phase, 69% HNO_3 (Fisher) was diluted with deionized water to give 0.01 M HNO_3 . Nafion 115 membranes were acquired from Ion Power (New Castle, DE, thickness 127 μm), and deionized water (Milli-Q Reference Ultrapure Water Purification System, 18 $\text{M}\Omega\cdot\text{cm}$) was used to prepare aqueous solutions. For membrane oxidation, 30% H_2O_2 (Fisher) and 98% H_2SO_4 (Macron) were separately diluted to 3% H_2O_2 and 1.0 M H_2SO_4 . The pH of polyelectrolyte solutions was adjusted with 0.1 M HCl or 0.1 M NaOH. Nafion 117 solution (5% w/w) was purchased from Sigma-Aldrich and diluted to 0.5% with isopropanol.

2.2. Film formation and characterization

As previously described,²⁹ Nafion membranes were cut into 25-mm disks with a mechanical die and pretreated according to literature methods to oxidize and clean the surface. Membranes were first rinsed with deionized water then sequentially immersed for 30 min in the following solutions heated to 100 °C: 3% H₂O₂, deionized water, 1.0 M H₂SO₄, and deionized water.^{13,30} Rinsing with room-temperature deionized water also occurred after each immersion. All experiments with unmodified and modified Nafion employed oxidized membranes.

We performed layer-by-layer adsorption by sequentially immersing membranes in 0.02 M PAH in 1.0 M NaCl, rinsing with deionized water to remove weakly adhered polyelectrolyte, immersing in 0.02 M PSS in 0.5 M NaCl, and again rinsing with deionized water. This process was repeated to form multiple bilayers, and films were terminated with PAH adsorption to give them a positive surface charge. In one case noted in the text, the final immersion in PAH was eliminated to yield a negatively-charged film.

Reflectance FTIR spectra were obtained using a Thermo Nicolet 6700 FTIR spectrometer with a Pike grazing angle (80°) apparatus. Bare Au-coated silicon wafers treated with UV/O₃ served as a background. To create substrates for polyelectrolyte adsorption, wafers were spin-coated with a 0.5% v/v Nafion solution for 30 s at 2000 rpm before pretreatment with H₂O₂/H₂SO₄ and polyelectrolyte adsorption using the procedure employed for modifying Nafion membranes.

2.3. Electrodialysis

1 Nafion membranes were sandwiched between two 100-mL homemade glass cells
2 separated by an o-ring (3.1 cm² effective membrane area). Platinum wire electrodes were
3 placed in each compartment such that upon application of an electric field cations could
4 move across the membrane from the source phase to the receiving phase. Using a CH
5 Instruments model 604 potentiostat, a specific potential between working and reference
6 electrode terminals was applied across a 499 Ω resistor to generate a constant current during
7 ED. The reference electrode terminal was also attached to the Pt electrode in the source
8 phase, and the counter electrode terminal was attached to the Pt electrode in the receiving
9 phase.²⁹ To produce current-voltage curves, the voltage across the resistor was varied from
10 0.05 V to 4.0 V. Both source and receiving phases were stirred briskly to minimize
11 concentration polarization. During ED, sample aliquots were removed periodically over 2 h
12 from both the source and receiving phases, but generally only the receiving phase was
13 analyzed. The source phase was periodically analyzed to verify the salt concentration.
14 Metal-cation analysis was accomplished with an axial Varian 710-ES Inductively Coupled
15 Plasma Optical Emission Spectrophotometer equipped with a Varian SPS 3 autosampler.
16 Individual cation standards were prepared from nitrate (Li⁺ and Co²⁺) or acetate (La³⁺ and
17 K⁺) salts, and serial dilutions were performed to make a calibration curve. Each experiment
18 was performed in triplicate using a different membrane each time, and uncertainties in the
19 results represent standard deviations of values for the different membranes.

20 ED data are plotted as total moles of cation in the permeate phase as a function of time,
21 and fluxes were calculated by dividing the slope of this line by the membrane area. To allow
22 for ion exchange and equilibration between the membrane and solution, slopes were
23 determined from only the final 90 min of 2 h of ED. The reported selectivities represent the

ratios of monovalent to multivalent ion fluxes when the source phase contains equal concentrations of both cations. Selectivities are shown as $>$ values to show the minimum selectivity observed with three different membranes because variations in the very low multivalent ion flux can lead to large deviations in calculated selectivities. Furthermore, transference numbers, t_i , were calculated using equation 1, where J_i is the flux of ion i in moles $\text{cm}^{-2} \text{s}^{-1}$, z_i is the ion charge, F is the Faraday constant, and I is the current density in A cm^{-2} .

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

Parallel experiments with current-voltage curves were performed using the four-point method in a homemade two-compartment electrodialysis cell similar to the one described above. Haber-Luggin capillaries filled with 1 M KCl and fitted with borosilicate glass frits (Ace glass, size E) to minimize leakage were used to bring the capillary-filling solution/source phase interface to within ~ 4 mm of the membrane surface. The capillaries containing the reference electrodes (Ag/AgCl, 3 M KCl, CH Instruments model 111) were attached to ground-glass joints to ensure their reproducible placement near the center of the membrane. Platinum wire electrodes were used for both the anode and cathode. Current-voltage curves were obtained with solutions containing 0.01 M LiNO_3 or K(OAc) and 0.1 M $\text{Co(NO}_3)_2$ or La(OAc)_3 on both sides of the membranes. The current was increased stepwise and held at a constant value for at least 30 s to reach a constant voltage. Between steps to new current values, the applied current was turned off until the transmembrane potential was < 10 mV. The excess multivalent cation in these experiments decreases solution resistance,

1 but due to its low permeability it should not greatly affect K^+ or Li^+ transport through the
2 PEM.

3 In a few ED experiments, membranes modified with (PAH/PSS)₅PAH films were
4 deliberately fouled using a high current density (2.54 mA cm^{-2}) with 0.01 M $LiNO_3$ and 0.01
5 M $Co(NO_3)_2$ in the source phase and 0.01 M HNO_3 in the receiving phase. A blue precipitate
6 formed on the membrane within 30 minutes, but the current was maintained for 1 h to ensure
7 a thicker coating. Subsequently, the membrane was air-dried before coating with 8 nm of
8 gold using a Pelco SC-7 Auto Sputter Coater coupled to a Pelco FTM-2 Film Thickness
9 Monitor. The fouled membrane was characterized with a JEOL 7500F scanning electron
10 microscope (SEM) equipped with a cold field-emission emitter (2 kV accelerating voltage,
11 4.5 mm working distance), and elemental analysis of the precipitate was performed with
12 energy dispersive spectroscopy (EDS) and INCA software.

14 2.4. Membrane durability

15 Experiments aimed to evaluate the stability of PEMs in electric fields employed the two-
16 compartment electrodialysis cell described previously. ED was performed for a total of 48 h
17 with the same (PAH/PSS)₅PAH membrane at a current density of 0.63 mA cm^{-2} . These
18 experiments used 0.02 M $LiNO_3$ and 0.02 M $Co(NO_3)_2$ in the source phase and 0.01 M
19 HNO_3 in the receiving phase. At 2-h ED intervals the cell was rinsed with deionized water,
20 and ED solutions were replaced. Sample aliquots were taken at the end of each 2-h period
21 and analyzed for cation content. After 12, 22, and 30 h of ED, the membrane was stored
22 overnight in deionized water while still mounted in the cell. Ions probably diffuse out of the
23 membrane during storage, causing a 'lag effect' after which the membranes must re-

1 equilibrate with the source and receiving solutions. In Figure 6, small dips in ion passage at
2 22 and 30 h likely occur due to this overnight storage.

3. Results and Discussion

5 Our previous work showed monovalent/divalent-ion selectivities >300 in ED through
6 porous alumina membranes coated with (PSS/PAH)₅ films,²⁸ and selectivities as high as
7 20,000 with Nafion membranes coated with (PAH/PSS)₅PAH films.²⁹ High selectivities
8 originate from both the large hydration sphere of the divalent ion and electrostatic exclusion
9 of multiply-charged ions. However, those studies only investigated K^+ and Mg^{2+} transport.
10 This section first examines whether the high selectivities previously observed with K^+ and
11 Mg^{2+} also occur with Li^+ and Co^{2+} as well as K^+ and La^{3+} . We also investigate limiting
12 currents and water splitting, which creates metal-hydroxide precipitates on membrane
13 surfaces. Finally, we explore membrane durability and how ED varies with the number of
14 adsorbed PAH/PSS bilayers on Nafion membranes.

3.1. Electrodialysis with bare and modified cation-exchange membranes

17 Initial ED experiments with bare and modified membranes employed a 2-compartment
18 cell with 0.01 M $LiNO_3$ and 0.01 M $Co(NO_3)_2$ in the source phase (anode compartment) and
19 0.01 M HNO_3 in the receiving phase (cathode compartment). The acidic receiving phase
20 maintains electrical conductivity while neutralizing hydroxide produced at the cathode to
21 prevent $Co(OH)_2$ precipitation. We used nitrate salts because ED with chloride sometimes
22 generates Cl_2 which may damage the PEM.²⁸ Figure 1 shows the amounts of Li^+ or Co^{2+} in
23 the receiving phase as a function of ED time. Unmodified Nafion membranes show high

passage of both Li^+ and Co^{2+} . In experiments with three replicate membranes, the average fluxes of Li^+ ($1.9 \pm 0.4 \text{ nmol cm}^{-2} \text{ s}^{-1}$) and Co^{2+} ($3.0 \pm 0.7 \text{ nmol cm}^{-2} \text{ s}^{-1}$) indicate an average $\text{Li}^+/\text{Co}^{2+}$ selectivity of only 0.66 ± 0.08 at the applied current density of 0.63 mA cm^{-2} . Interestingly, the $\text{K}^+/\text{Mg}^{2+}$ selectivity of bare Nafion membranes is >1 .²⁹ The $\text{Li}^+/\text{Co}^{2+}$ selectivity of 0.66 likely reflects a low Li^+ electrical mobility. In aqueous solutions, K^+ is about twice as mobile as Li^+ .³¹

Figure 1. Moles of Li^+ and Co^{2+} in the receiving phase as a function of time during ED (current density of 0.63 mA cm^{-2}) through bare Nafion membranes (open symbols) or Nafion coated with a $(\text{PAH/PSS})_5\text{PAH}$ film (filled symbols). The source phase initially contained 0.01 M LiNO_3 and $0.01 \text{ M Co(NO}_3)_2$, and the receiving phase was initially 0.01 M HNO_3 . The membrane area was 3.14 cm^2 .

1 With (PAH/PSS)₅PAH-coated Nafion, the Li⁺ concentration increases approximately
2 linearly after a brief induction period. In one experiment, we immersed the membrane
3 overnight in the source phase prior to ED, and the induction period disappeared. In all
4 experiments, plots of Li⁺ receiving-phase concentration versus time were linear ($R^2 > 0.995$)
5 over the final 90 min of ED. Nevertheless, at the end of the ED, the Li⁺ flux may decline
6 slightly because the source-phase pH decreases from 4.7 to 2 over the course of the
7 experiment, presumably due to protons generated at the anode. As the pH decreases, protons
8 should carry a larger fraction of the current.

9 Based on the last 90 min of ED in Figure 1 and in other replicate experiments, the Li⁺
10 flux through (PAH/PSS)₅PAH-coated Nafion is $3.0 \pm 0.2 \text{ nmol cm}^{-2} \text{ s}^{-1}$ (current density of
11 0.63 mA cm^{-2}). The Li⁺ flux through the PEM-coated Nafion is higher than through the
12 native membrane because Co²⁺ carries >50% of the current through the bare Nafion. In
13 contrast, the Co²⁺ flux was $<2 \text{ pmol cm}^{-2} \text{ s}^{-1}$ through three replicate (PAH/PSS)₅PAH-coated
14 Nafion membranes, so the Li⁺/Co²⁺ selectivity of these membranes is >1500. This value is
15 similar to the K⁺/Mg²⁺ selectivities of >1000 reported²⁹ for the same membranes and is much
16 higher than the typical monovalent/divalent-ion selectivities of <10 for monovalent-ion
17 selective ion-exchange membranes.^{16,18,32-35} Interestingly, in ED with PSS-terminated
18 coatings ((PAH/PSS)₅ films), the Co²⁺ flux rises to $116 \pm 34 \text{ pmol cm}^{-2} \text{ s}^{-1}$ whereas the Li⁺
19 flux is again $\sim 3.0 \text{ nmol cm}^{-2} \text{ s}^{-1}$, so the Li⁺/Co²⁺ selectivity is only 23.5 ± 6.8 . Thus,
20 positively-charged terminal layers are essential for achieving very high selectivities among
21 cations, presumably because of electrostatic exclusion of the more highly charged ion.
22 Additionally, swelling of (PAH/PSS) multilayers is likely lower for films terminated with a
23 polycation,^{36,37} and low swelling will increase size exclusion of highly hydrated divalent ions.

1 High current efficiencies are important for minimizing power consumption in ED
2 separations. The current efficiency, quantified through the transference number, t_i , is the
3 fraction of current carried by a particular ion. For (PAH/PSS)₅PAH-modified Nafion
4 membranes at a current density of 0.63 mA cm⁻², t_{Li^+} is 0.45 whereas $t_{Co^{2+}}$ is essentially
5 zero. Thus, other ions carry about 50% of the current in ED through (PAH/PSS)₅PAH-
6 coated membranes. Assuming that anions do not pass through Nafion, protons (the only
7 cations present besides Li⁺ and Co²⁺) must carry about 55% of the current in this cation-
8 exchange membrane. Large proton transference numbers are reasonable at highly acidic pH,
9 but this condition appears only toward the end of the ED experiments after electrolysis at the
10 anode has generated sufficient protons for the source-phase pH to approach 2. At the initial
11 source-phase pH of 4.7, protons generated at the anode should not carry a significant fraction
12 of the current.

13 In the beginning of the ED, protons and hydroxide ions generated from water splitting
14 near the PEM-Nafion interface probably carry much of the current. Inside the Nafion, only
15 cations will carry current if this cation-exchange substrate is ideally selective, but the PEM
16 allows transport of both anions and monovalent cations.²⁹ In fact, Cheng et al. showed that
17 PEMs are somewhat anion-selective in the case of 1:1 salts.²⁸ Even assuming that Li⁺ and
18 NO₃⁻ have the same electrophoretic mobilities in the PEM, Li⁺ should carry only half the
19 current in this region (Figure 2). The disparity between the Li⁺ transference number in
20 Nafion (where it approaches unity) and in the PEM leads to an ion-depleted region near the
21 PEM-Nafion interface (i.e. cation and anion electromigration away from this interface is
22 greater than toward it). To maintain a constant current throughout the membrane, the electric
23 field in the ion-depleted region must be high and may reach the levels needed to cause water

splitting, a non-electrode process characterized by water dissociation and separation to H^+ and OH^- . Furthermore, Wessling and coworkers showed that some PEMs can act as water-splitting catalysts.^{27,34}

Figure 2. Ion transport through (PAH/PSS)₅PAH-modified cation-exchange membranes. Imbalanced Li^+ and NO_3^- electromigration at the PEM-Nafion interface generates an ion-depletion zone in the PEM. J_{mig} arrows represents the local flux of the ions due to electrical migration.

3.2. ED with different source-phase concentrations

We further examined selectivity and current efficiency in ED through (PAH/PSS)₅PAH-modified Nafion membranes with source phases containing 0.01 M, 0.02 M, or 0.1 M salts. We maintained at least 0.01 M salt concentrations to prevent excessive solution resistance, and the current density was 0.63 mA cm^{-2} in all of these experiments. Salts were either $LiNO_3$ and $Co(NO_3)_2$ or $K(OAc)$ and $La(OAc)_3$ in the source phase, and the receiving phase remained 0.01 M HNO_3 for all experiments. Table 1 presents the Li^+ and Co^{2+} fluxes and the

1 corresponding transference numbers and $\text{Li}^+/\text{Co}^{2+}$ selectivities from these experiments.
2 Interestingly, Li^+ flux is almost constant when the source-phase LiNO_3 and $\text{Co}(\text{NO}_3)_2$
3 concentrations increase from 0.01 to 0.02 M, but it nearly doubles when the source
4 concentrations increase from 0.02 to 0.1 M. The Li^+ transference number approaches 1.0 at
5 0.1 M salt concentrations but is only ~ 0.45 at the lower source-phase salt concentrations.
6 These data suggest that the current density is overlimiting for both 0.01 M and 0.02 M
7 source-phase concentrations, giving rise to water splitting at the PEM-Nafion interface.
8 However, we would expect the limiting current and the transference number to
9 approximately double on doubling the source-phase salt concentrations from 0.01 to 0.02 M.
10 Perhaps precipitation of $\text{Co}(\text{OH})_2$ increases upon doubling the source-phase concentration
11 and thus limits membrane permeability to Li^+ more with 0.02 M $\text{Co}(\text{NO}_3)_2$ rather than 0.01 M
12 $\text{Co}(\text{NO}_3)_2$ in the source phase. We could not see any precipitate on membranes during ED
13 under these conditions, but even a thin layer of precipitate might reduce ion flux. The
14 increase in Co^{2+} flux on going from 0.01 M to 0.02 M salts might stem from formation of
15 $\text{Co}(\text{OH})^+$ or some soluble $\text{Co}(\text{OH})_2$ that can pass through the membrane more readily than
16 Co^{2+} . At 0.1 M source-phase salt concentrations, the current density should be
17 underlimiting, so water splitting will not occur to generate OH^- that precipitates Co^{2+} . Most
18 remarkably, the $\text{Li}^+/\text{Co}^{2+}$ selectivity is >600 for all conditions (Table 1).
19

Table 1. Li^+ and Co^{2+} fluxes, Li^+ transference numbers,^a and $\text{Li}^+/\text{Co}^{2+}$ selectivities as a function of source-phase cation concentrations during ED^b through Nafion membranes coated with (PAH/PSS)₅PAH films.

Li^+ or Co^{2+} Concentration (M)	Li^+ Flux ($\text{nmol cm}^{-2} \text{s}^{-1}$)	Co^{2+} Flux ^c ($\text{pmol cm}^{-2} \text{s}^{-1}$)	Li^+ Transference	Selectivity ^d
0.01	2.95 ± 0.21	1.29 ± 0.51	0.45 ± 0.03	>1600
0.02	3.18 ± 0.30	2.55 ± 1.71	0.48 ± 0.05	>630
0.1	6.79 ± 0.18	< 1	1.03 ± 0.02	>6500

^a Co^{2+} transference numbers were <0.0013 for all replicates

^bThe source phase contained equal concentrations of LiNO_3 and $\text{Co}(\text{NO}_3)_2$, the receiving phase was 0.01 M HNO_3 , and the current density was 0.63 mA cm^{-2} .

^c Co^{2+} fluxes are close to the minimum detectable value, which leads to large uncertainties in selectivity.

^dThese values are the minimum selectivity observed in experiments with three replicate membranes.

Table 2 shows data for ED with $\text{K}(\text{OAc})$ and $\text{La}(\text{OAc})_3$ in the source phase. Constant-current ED leads to greatly increasing K^+ flux when the source-phase $\text{K}(\text{OAc})$ and $\text{La}(\text{OAc})_3$ concentrations change from 0.01 M to 0.02 M or 0.1 M. Remarkably, despite a constant current density, the K^+ flux increases nearly ten-fold from 0.46 ± 0.27 to $4.40 \pm 0.02 \text{ nmol cm}^{-2} \text{s}^{-1}$ when the salt concentration in the source phase doubles from 0.01 M to 0.02 M. Flux increases further when the source phase contains 0.1 M $\text{K}(\text{OAc})$ and $\text{La}(\text{OAc})_3$, and t_{K^+} exceed unity. Transference numbers >1 suggest that diffusive transport of ions across the membrane is significant compared to electromigration. Our calculation of the transference number (see the experimental section) assumes that all of the K^+ in the receiving phase appears there due to electromigration. However, significant coupled diffusion of K^+ to the receiving phase and protons to the source phase could occur.

Table 2. K^+ and La^{3+} fluxes, K^+ transference numbers,^a and K^+/La^{3+} selectivities as a function of source-phase cation concentrations during ED^b through Nafion membranes coated with (PAH/PSS)₅PAH films.

K^+ or La^{3+} Concentration (M)	K^+ Flux (nmol cm ⁻² s ⁻¹)	La^{3+} Flux ^c (pmol cm ⁻² s ⁻¹)	K^+ Transference	Selectivity ^d
0.01	0.46 ± 0.27	1.58 ± 1.00	0.07 ± 0.04	>93
0.02	4.40 ± 0.02	1.27 ± 0.46	0.69 ± 0.01	>2400
0.1	7.85 ± 0.69	<1	1.19 ± 0.10	>7000

^a La^{3+} transference numbers were <0.0008 for all replicates

^bThe source phase contained equal concentrations of K(OAc) and La(OAc)₃, the receiving phase was 0.01 M HNO₃, and the current density was 0.63 mA cm⁻².

^c La^{3+} fluxes are close to the minimum detectable value, which leads to large uncertainties in selectivity.

^dThese values are the minimum selectivity observed in experiments with three replicate membranes or the maximum detectable selectivity.

Compared to ED with Li^+ and Co^{2+} , the monovalent ion flux from a source phase of 0.01 M K(OAc) and La(OAc)₃ is very low, so t_{K^+} is below 10%. This low current efficiency presumably results from interfacial precipitation that decreases membrane permeability to both K^+ and La^{3+} much more than to hydroxide or protons. Hydroxide generated through water splitting near the PEM-Nafion interface likely forms La(OH)₃, which is highly insoluble in water.³⁸ In a separate set of experiments with 0.01 M KOAc and 0.01 M La(OAc)₃ in the source phase, the K^+ flux increased from 0.46 ± 0.27 nmol cm⁻² s⁻¹ to 1.05 ± 0.47 nmol cm⁻² s⁻¹ upon *decreasing* current density from 0.63 mA cm⁻² to 0.32 mA cm⁻². Additionally t_{K^+} increased from 0.07 ± 0.04 to 0.32 ± 0.14 leading to a K^+/La^{3+} selectivity >500 for three replicate membranes at the lower current density. These results provide strong evidence that overlimiting current densities cause formation of hydroxide compounds that adversely affect the permeability of PEM-coated membranes to monovalent cations.

Decreasing the current density results in less precipitation to provide a more permeable film and, hence, higher K^+ flux despite the lower current.

In contrast to ED with nitrate salts where the source-phase acidity increases with time, in ED with acetate salts the source-phase pH remains around 5.5 throughout the experiment, so proton transport from this phase should not decrease K^+ transference numbers substantially. Thus, with 0.01 M and 0.02 M acetate salts in the source phase, transference numbers significantly <1 must stem predominantly from water splitting. Moreover, the formation of $La(OH)_x$ species due to water splitting might explain why La^{3+} flux increases at low source-phase concentrations where water splitting is most prevalent. As Table 2 shows, the selectivity of the films increases from ~ 100 with 0.01 M source-phase solutions to >2400 with 0.02 M solutions. Further increasing the source-phase concentration to 0.1 M increases selectivity to >7000 . For comparison, the K^+/La^{3+} selectivity of unmodified Nafion membranes with 0.01 M $K(OAc)$ and 0.01 M $La(OAc)_3$ in the source phase is only 1.61 ± 0.26 .

We should note that K^+/La^{3+} selectivities stem in part from the formation of $La(OAc)_x$ complexes in the source phase. These large complexes likely have low electrophoretic mobilities in the PEM. Based on literature values for La^{3+} -OAc association constants,³⁹ we estimate that in a solution prepared with 0.01 M $La(OAc)_3$ and 0.01 M $K(OAc)$ only $\sim 15\%$ of the $La(III)$ exists as La^{3+} ions. $La(OAc)^{2+}$ and $La(OAc)_2^+$ complexes account for $\sim 57\%$ and $\sim 28\%$ of the $La(III)$, respectively. In solutions made from 0.1 M $La(OAc)_3$ and 0.1 M $K(OAc)$, the fractions of La^{3+} , $La(OAc)^{2+}$, $La(OAc)_2^+$, and $La(OAc)_3$ are around 3%, 25%, 42%, and 31%, respectively. The supplementary material provides the details of these estimations.

3.3. Effect of bilayer number on selectivity and current efficiency

Figure 3 shows reflectance-FTIR spectra of (PAH/PSS)_xPAH-modified Nafion films. Although subtraction of absorbances from the underlying Nafion leads to some uncertainty in the spectra (small negative peaks), the figure clearly shows that sulfonate absorbances of PSS (1200, 1130, 1033, and 1008 cm⁻¹) increase in intensity with the number of adsorbed PAH/PSS bilayers.⁴⁰ Previous X-ray photoelectron spectroscopy analysis showed the disappearance of fluorine signals after adsorption of (PAH/PSS)₃PAH films, confirming that such films are at least 5 nm thick, or greater than the escape depth of Nafion fluorine photoelectrons.^{29,41}

Figure 3. Reflectance-FTIR spectra (1700-900 cm⁻¹) of (PAH/PSS)₅PAH, (PAH/PSS)₃PAH, and (PAH/PSS)PAH-modified Nafion films on Au-coated Si wafers. The spectra were plotted after subtracting the spectrum of a Nafion film to minimize absorbances from Nafion. Wafers were spin-coated with a Nafion solution and oxidized prior to film deposition. The

peaks at 1200, 1130, 1008 and 1033 cm^{-1} are due to the sulfonate groups in PSS, and additional peaks around 1500-1650 cm^{-1} stem from aromatic ring modes in PSS.

Because the amount of adsorbed polyelectrolyte increases with the number of deposited layers, we compared selectivity, flux, and current efficiency in ED through Nafion membranes coated with (PAH/PSS)₅PAH, (PAH/PSS)₃PAH, and PAH/PSS/PAH films. Surprisingly, at a constant applied current density, Li^+ flux through modified Nafion membranes decreases as the number of PAH/PSS bilayers in the film decreases (Table 3). As a result, Li^+ transference numbers decrease as well. Conversely, Table 3 shows that the Co^{2+} flux increases as the number of bilayers decreases, so the membrane $\text{Li}^+/\text{Co}^{2+}$ selectivity declines from at least 1600 for all three replicate membranes with (PAH/PSS)₅PAH films to only ~50 with PAH/PSS/PAH coatings. Nevertheless, the Co^{2+} transference number is <0.02 in all cases. Evidently, protons and hydroxide from water splitting carry an increased fraction of current as the number of bilayers declines.

Table 3. Li^+ and Co^{2+} fluxes, transference numbers, and $\text{Li}^+/\text{Co}^{2+}$ selectivities during ED^a through Nafion membranes coated with (PAH/PSS)₅PAH, (PAH/PSS)₃PAH, or (PAH/PSS)PAH films.

Film	Li^+ Flux ($\text{nmol cm}^{-2} \text{s}^{-1}$)	Co^{2+} Flux ($\text{pmol cm}^{-2} \text{s}^{-1}$)	Li^+ Transference	Co^{2+} Transference	Selectivity
(PAH/PSS) ₅ PAH	2.95 ± 0.21	1.29 ± 0.51	0.45 ± 0.03	< 0.0006	$>1600^b$
(PAH/PSS) ₃ PAH	2.39 ± 0.10	3.85 ± 2.49	0.36 ± 0.02	< 0.002	$>430^b$
(PAH/PSS)PAH	1.62 ± 0.10	37.3 ± 25.5	0.25 ± 0.01	< 0.018	23, 54, 108 ^c

^aThe source phase contained 0.01 M LiNO_3 and 0.01 M $\text{Co}(\text{NO}_3)_2$, the receiving phase was 0.01 M HNO_3 , and the current density was 0.63 mA cm^{-2} .

^bThese values are the minimum selectivity observed in experiments with three replicate membranes.

^cThese are the values from three replicate measurements. With adsorption of only a few polyelectrolyte layers, film coverage may differ significantly among replicate membranes and lead to large variations in selectivity.

Table 4 shows the trends in fluxes with the number of PAH/PSS bilayers during ED of K^+ and La^{3+} (acetate salts) through Nafion membranes. As noted above, flux and K^+ transference numbers are low with the (PAH/PSS)₅PAH film on Nafion due to formation of a precipitate that decreases permeability. The K^+ Flux increases nearly 10-fold upon going from (PAH/PSS)₅PAH to (PAH/PSS)₃PAH films on the membrane, perhaps because of less precipitation on the membrane surface due to a higher limiting current. However, PAH/PSS/PAH-coated membranes exhibit lower K^+ fluxes than (PAH/PSS)₃PAH-coated Nafion. La^{3+} flux increases slightly from $<1 \text{ pmol cm}^{-2} \text{ s}^{-1}$ to $2.7 \pm 1.9 \text{ pmol cm}^{-2} \text{ s}^{-1}$ upon changing from (PAH/PSS)₃PAH to PAH/PSS/PAH films. Nevertheless, selectivity remains >500 even with only 1.5 bilayers on the Nafion (Table 4). K^+ transference numbers decline similarly to those of Li^+ upon moving from (PAH/PSS)₃PAH to PAH/PSS/PAH films, but the transference numbers are higher for K^+ than for Li^+ , probably because of the larger electrophoretic mobility of K^+ .³¹

Table 4. K^+ and La^{3+} fluxes, transference numbers, and K^+/La^{3+} selectivities during ED^a through Nafion membranes coated with (PAH/PSS)₅PAH, (PAH/PSS)₃PAH, or (PAH/PSS)PAH films.

Film	K^+ Flux ($\text{nmol cm}^{-2} \text{ s}^{-1}$)	La^{3+} Flux ^b ($\text{pmol cm}^{-2} \text{ s}^{-1}$)	K^+ Transference	La^{3+} Transference	Selectivity ^c
(PAH/PSS) ₅ PAH	0.46 ± 0.27	1.58 ± 1.00	0.07 ± 0.04	< 0.0009	>90
(PAH/PSS) ₃ PAH	4.32 ± 0.38	<1	0.66 ± 0.06	< 0.0003	>3500

(PAH/PSS)PAH	2.82 ± 0.14	2.70 ± 1.90	0.43 ± 0.02	< 0.0015	> 500
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^aThe source phase contained 0.01 M K(OAc) and 0.01 M La(OAc)₃, the receiving phase was 0.01 M HNO₃, and the current density was 0.63 mA cm⁻².

^bLa³⁺ fluxes are close to the minimum detectable value, which leads to large uncertainties in selectivity.

^cThese values are the minimum selectivity observed in experiments with three replicate membranes or the maximum detectable selectivity.

Although all of the membranes are essentially impermeable to multivalent ions, we expected the K⁺ and Li⁺ fluxes to increase with decreasing film thickness. A thinner film should lead to a stronger concentration gradient across the PEM to increase the supply of monovalent ions to the PEM-Nafion interface, thus increasing the maximum current carried by that ion. This in turn should decrease the amount of water splitting at a specific current density. Experiments are not in accord with these expectations, and we are currently trying to understand why monovalent ion fluxes usually decrease with a decreasing number of bilayers in a PEM on Nafion. These unusual behaviors may stem from a low PEM thickness that is comparable to the thickness of an electrical double layer that forms inside this film.

3.4. Current density-voltage curves

Current density-voltage (*I-V*) curves often provide insight into limiting currents. *I-V* curves for ion-exchange membranes frequently exhibit three regions. At the lowest current densities, the potential drop across the membrane increases nearly linearly with increasing current density. As the applied current increases, cation electromigration inside Nafion increasingly exceeds the cation electromigration through the PEM, and a strong depletion zone forms near the interface (Figure 2). Equation (2) describes the theoretical limiting current density, I_{lim} , which occurs when the concentration of ions at the interface goes to

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

1 zero.²⁹ In this equation, P_s is the diffusion salt permeance of the PEM, c is the monovalent
2 cation concentration in the source phase, F is the Faraday constant, and Δt_+ is the difference
3 in the monovalent cation transference numbers in the PEM and the Nafion.

4 Attainment of limiting conditions gives rise to a ‘plateau’ region in the I - V plot because
5 further increases in current density require a large increase in potential. The intersection of
6 the best-fit lines through the plateau and linear regions approximates the limiting current
7 density (see the example in the inset of Figure 4). Further increases in current density lead
8 to an overlimiting region where the potential drop across the film rises less dramatically with
9 increases in current, presumably because water splitting or electroconvective forces supply
10 additional ions at the interface.^{34,42,43}

11 As Figure 4 shows, the I - V curves for membranes coated with (PAH/PSS)₅PAH,
12 (PAH/PSS)₃PAH, and PAH/PSS/PAH films exhibit linear, ohmic regions only at very low
13 current densities and transmembrane potentials <100 mV (inset). “Plateau” regions then
14 appear where the transmembrane potential drop increases more rapidly with increasing
15 current density. The limiting current in all three cases is <0.2 mA cm⁻² and does not increase
16 with a decreasing number of bilayers. As with measurements of ion flux (see Table 3),
17 decreasing the film thickness unexpectedly does not increase permeability. Finally, Figure
18 4 shows that extensive water splitting at high current densities requires lower transmembrane
19 potentials with thinner films. Wessling *et al.* recently reported a similar trend with poly(3,4-
20 ethylenedioxythiophene):PSS/PEI multilayer films.²⁷

Figure 4. Current density as a function of transmembrane potential drop during electrodialysis through Nafion membranes coated with (PAH/PSS)₅PAH, (PAH/PSS)₃PAH, and PAH/PSS/PAH films. Electrodialysis employed solutions containing 0.01 M LiNO₃ and 0.1 M Co(NO₃)₂ in both the source and receiving phases. The inset shows an expanded view at low current densities along with best-fit lines from ohmic and “plateau” regions for the (PAH/PSS)₃PAH-coated membrane.

3.5. Characterization of membrane fouling

At overlimiting currents, water splitting near the PEM-Nafion interface gives protons that migrate toward the cathode and hydroxide ions that move toward the anode. When the source phase contains transition-metal or lanthanide cations, insoluble hydroxide salts may form in the PEM or at its surface. Figure 5 shows SEM images of a fouled, (PAH/PSS)₅PAH-coated membrane after 1 h of ED at a highly overlimiting current. A thick cake-layer forms (images 5a and 5b), and EDS analysis of the precipitate confirms extensive amounts of cobalt (image 5c) and oxygen (image 5d) across the membrane. Table 5 shows

the composition of the foulant in Figure 5b, and atomic percentages are reasonably consistent with $\text{Co}(\text{OH})_2$, strongly suggesting that hydroxides from water splitting form insoluble cobalt hydroxides on the membrane surface at overlimiting current densities. The blue color of the foulant also suggests the presence of $\text{Co}(\text{OH})_2$.

Figure 5. SEM images of fouled, $(\text{PAH}/\text{PSS})_5\text{PAH}$ -modified Nafion membranes at (a) low and (b) high magnifications. EDS imaging of the area in (b) shows extensive deposition of (c) cobalt (L_α line) and (d) oxygen (K_α line) in the fouled area. Fouling occurred during 1 h of ED at a current density of 2.54 mA cm^{-2} with 0.01 M LiNO_3 and 0.01 M $\text{Co}(\text{NO}_3)_2$ in the source phase and 0.01 M HNO_3 in the receiving phase.

Table 5. EDS elemental surface composition of a (PAH/PSS)₅PAH-modified Nafion membrane after fouling during 1 h of ED at 2.54 mA cm⁻² with 0.01 M LiNO₃ and 0.01 M Co(NO₃)₂ in the source phase and 0.01 M HNO₃ in the receiving phase.

Element	C	O	F	Co
Weight %	4.67	30.06	1.94	63.33
Atomic %	11.29	54.5	2.96	31.20

3.6. Durability of membranes during ED

We evaluated the durability of membranes during 48 h of constant-current ED. Figure 6 shows the total quantity of Li⁺ or Co²⁺ that passed into the receiving phase during 24 2-h periods (every 2 h, an aliquot of the receiving phase was collected for analysis prior to rinsing the cell with deionized water and adding fresh source- and receiving-phase solutions). During the first 6 h of ED, the total micromoles of Li⁺ passing through the membrane during 2 h increased about 20%, perhaps due to conditioning of the membrane. The Co²⁺ flux was negligible initially but increased steadily after ~12 h of total ED, and the Li⁺ flux decreased concurrently. Membrane selectivity during the first 12 h was >1000 but declined to ~25 after 48 h of ED. Electromigration of polyelectrolytes out of the PEM may lead to this selectivity decline. After 48 h, the selectivity is similar to that of a membrane coated with either PAH/PSS/PAH or a PSS-terminated film ((PSS/PAH)₅). This lack of durability is a significant challenge, but either less hydrophobic base membranes or cross-linked PEMs may increase stability.

Figure 6. Total Li⁺ and Co²⁺ passage (μmol) per 2-h sampling period during electro dialysis through a Nafion membrane modified with a (PAH/PSS)₅PAH multilayer film. Electro dialysis used 0.02 M LiNO₃ and 0.02 M Co(NO₃)₂ in the source phase and 0.01 M HNO₃ in the receiving phase along with a current density of 0.63 mA cm⁻². Source- and receiving-phase solutions were changed after each 2-h interval prior to again performing electro dialysis with the same membrane.

4. Conclusions

Alternating adsorption of polycations and polyanions on Nafion yields membranes with high ED monovalent-ion selectivities for several pairs of monovalent/multivalent cations. Below overlimiting current densities, Li⁺/Co²⁺ and K⁺/La³⁺ selectivities are >1000 for ED through (PAH/PSS)₅PAH-coated Nafion membranes. Selectivities are >25 even for membranes modified with only 3 polyelectrolyte layers (PAH/PSS/PAH films). Transference numbers reach ~1 and selectivity is >5000 with high source-phase concentrations and underlimiting current densities. However, water splitting in the PEM

reduces current efficiency at high current densities or low source-phase ion concentrations. Hydroxides formed from water splitting lead to precipitation of insoluble metal hydroxides on the membrane, which decreases current efficiency for monovalent ion transport. Current-voltage curves show that the limiting current does not increase with fewer bilayers in the (PAH/PSS)_nPAH film, perhaps because the thickness of the electrical double layer inside the PEM is significant relative to the film thickness. Finally, ED for 48 h with the same membrane suggests that the films may be unstable in strong electric fields, as selectivity declines with extended ED time. To enhance the possible impact of these membranes, future work will explore methods to increase limiting current, stabilize PEMs, and form highly selective membranes on less-expensive cation-exchange substrates.

Associated Content

Discussion of La(OAc)_x complex formation and a table of critical stability constants.

This information is available free of charge via the internet at <http://www.elsevier.com/>.

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Notes

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