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Layer-by-layer coatings on ion exchange membranes: effect of multilayer charge and hydration on monovalent ion selectivities

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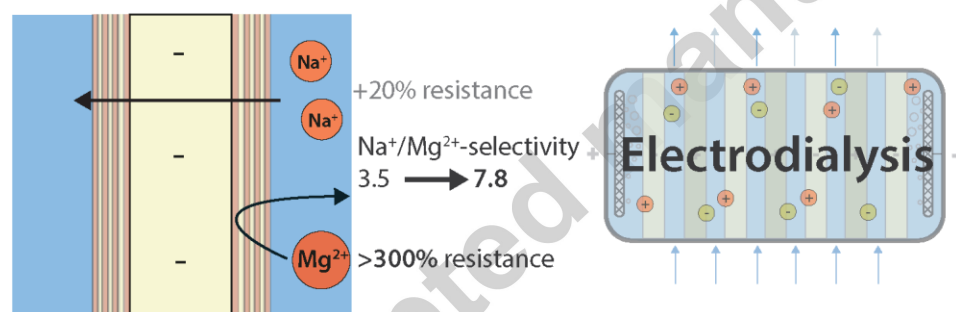
Abstract

Electrodialysis (ED) is an important process to desalinate brackish water, which contains scale-forming divalent ions. Hence, there is an interest in separating mono- and divalent ions. In recent years, layer-by-layer (LbL) polyelectrolyte coatings on ion exchange membranes (IEMs) have provided high monovalent ion selectivities. However, there is a lack of understanding on the structure-property relationships for polyelectrolyte multilayers for membrane applications and lack of evaluation under practical conditions. In this work, we evaluate polyelectrolyte multilayer properties by optical techniques, connect them to monovalent-selectivity using resistance measurements and upscale this to practical monovalent-selectivities for an ED unit. Excess

positive poly(allyl amine) (PAH) was observed in the PAH/PSS (polystyrene sulfonate) multilayer, resulting in a positively charged multilayer. Coated multilayers with low hydrations (0.2) are able to achieve high monovalent-selectivities (of 5.7 up to 7.8) on CEMs comparable to the commercial monovalent-selective CSO (with 6.9). This enhanced selectivity was only observed for cations with LbL-coated CEMs and not for anions with LbL-coated AEMs, which we argue is due to the excess positive charge of the PAH/PSS multilayers. Finally, LbL-coatings show an improved monovalent-selectivity in ED stack experiments with artificial brackish water of 1.7 for LbL-coated CEMs compared to uncoated CEMs (with a monovalent-selectivity of 0.5).

Graphical abstract

LbL-coated ion exchange membranes



Keywords:

Electrodialysis, layer-by-layer, monovalent-selectivity, ion exchange membranes, hydration

1. Introduction

Desalination of aqueous streams is an important process in the production of potable water from brackish water. These aqueous streams typically consist of multiple ionic species, including

monovalent and divalent cations and anions. Divalent ions are abundant in natural water sources and their high concentrations lead to scaling by precipitation that fouls or clogs the desalination process equipment. It is therefore important to be able to separate mono- and divalent ions from the feed streams¹. These separations are performed by ion exchange membranes (IEMs) in electro-dialytic desalination processes. IEMs are thin films composed of a charged and crosslinked polyelectrolyte that contains acidic (e.g. $-\text{SO}_3^-$) groups for cation exchange membranes (CEMs) or basic amine (e.g. $-\text{NR}_3^+$) groups for anion exchange membranes (AEMs). As a result of their high charge densities, IEMs are able to selectively separate cations (such as Na^+ and Ca^{2+}) and anions (such as Cl^- and SO_4^{2-})².

Standard IEMs are not selective for mono/divalent ions with the same charge. In contrast, special-grade CEMs (e.g. monovalent-selective Neosepta CMS and Selemion CSO), and AEMs (e.g. Neosepta ACS and Selemion ASV), are selective to monovalent ions over divalent ions^{3, 4}. Monovalent-selective CEMs can be based on either charge-rejection, where a thin oppositely charged layer is used to hinder the permeation of divalent cations (in the case of CSO a thin poly(ethylene imine) (PEI) layer⁵), or by using a crosslinked layer with lower hydration, where the divalent ions with their larger hydrated ion size are hindered (in the case of CMS)³. These special-grade IEMs, however, are much more expensive than the standard-grade IEMs⁶.

Researchers have studied new methods with the aim to prepare these monovalent-selective IEMs with higher selectivities and with cheaper base polymers or production processes. Monovalent-selectivity for these IEMs can be achieved by tuning the bulk properties or by adding a selective surface coating. The bulk charge densities can be controlled by blending a charged

polyelectrolyte with an uncharged polymer to suppress swelling, which can also lead to monovalent-selectivities^{7, 8}. Surface coatings with an oppositely charged layer can introduce monovalent-selectivity in membranes as well. For these coatings, monovalent-selectivities of crosslinked sulfonated polystyrene CEMs were initially 0.4 for Na^+ over Ca^{2+} and can be improved to 5.0 after a coating with PEI^{5, 9}. Recently, polyelectrolyte multilayers prepared by the layer-by-layer (LbL) process has become a simple and attractive method to coat tunable and selective layers on a variety of membrane surfaces. These LbL-coatings have been applied on IEMs as well, with several research groups showing monovalent-selectivities for multilayer coatings on existing commercially-available IEMs. In lab-scale systems, monovalent-selectivities have been achieved of 1.35¹⁰ for $\text{Na}^+/\text{Ca}^{2+}$, while more recent work achieved diffusion based $\text{K}^+/\text{Mg}^{2+}$ selectivities over 1000 on fluorinated Nafion membranes as well as on aliphatic CEMs^{11, 12}. The crucial step for such high selectivities are the coating procedures that enable defect-free coatings. These coatings have been applied on porous ultrafiltration membranes as well, where they achieve nanofiltration-like performance with selectivity for monovalent ions^{13, 14}.

LbL polyelectrolyte coatings show promising selectivities for monovalent ions in the studies discussed above. However, there is a lack of information regarding structure-property relationships for these multilayers with respect to membrane performance. It is therefore important to characterize polyelectrolyte multilayer formation and multilayer properties relevant for membrane applications, such as hydration, layer thickness and charge. Another crucial step towards practical implementation of these multilayer-coated membranes are measurements under practical conditions resembling ED stacks (electrical-driven transport). To address these

structure-property relationships, it is therefore important that these multilayers are thoroughly characterized, and tested under practical conditions and systems.

In this study, the goal is to elucidate structure-property relationships for PAH/PSS multilayer based IEM coatings and to test them under practical conditions. To this end, detailed layer characterization is combined with membrane characterization and performance studies at the single membrane and at the membrane stack level. The growth and properties of the multilayers were studied on model (silicon with oxide layer) surfaces, with regards to thickness, charge and hydration effects. Aliphatic Type I CEMs and AEMs are coated with multilayers and studied for their specific cation and anion permeation properties. Structure-property relationships for the multilayers and their respective ion transport properties are investigated. Finally, ED experiments are performed with the base membrane (Type I) and the LbL-coated membrane to assess the improvement of the monovalent-selectivity in practical ED stacks.

2. Materials and Methods

2.1. Membranes and chemicals

Ion exchange membranes – Selemion CSO (purchased from Asahi, Japan), Fujifilm Type I CEMs and Type 1 AEMs (received from FUJIFILM, The Netherlands), Neosepta AMX, ACS (purchased from Astom Corp., Japan) – were soaked in 0.5 M NaCl at least 48 h before use. Magnesium chloride hexahydrate, sodium nitrate and calcium chloride (anhydrous) were purchased from Sigma-Aldrich. Sodium chloride (pharmaceutical grade) was kindly supplied from AkzoNobel (Hengelo, The Netherlands).

Poly(4-styrenesulfonic acid) (PSS) with a M_w of ~ 200 kDa was obtained as 30 wt% solution from Sigma Aldrich and poly(allylamine hydrochloride) (PAH) with a M_w of 120 – 200 kDa was obtained from Alfa Aesar. MilliQ water (>18 M Ω) was used to prepare solutions for dip coating. Demineralized water is used to prepare ED feed water.

2.2. Layer-by-layer coating and characterization

2.2.1. LbL-coating procedures

LbL-coating recipe 1

Polyelectrolyte solutions were prepared at concentrations of 1.0 g/L polyelectrolyte with 0.5 M NaCl. The pH was adjusted using HCl to 2.3 (without pH adjustment the polymer solution had a pH of 5.0). It is expected that at this pH (2.3) the weak PAH is nearly fully charged¹⁵. For each coating step, membranes were immersed for at least 15 minutes in the polyelectrolyte solution and were rinsed in water with the same ionic strength (0.5 M NaCl) for 5 minutes in a first rinsing step and 10 minutes in a second rinsing step¹⁴. These two rinsing steps are performed to avoid accumulation of polyelectrolytes in the second rinsing bath. Multilayer build-up started with PAH, as this is a positive polyelectrolyte on a negative CEM. The polyelectrolyte multilayers were coated in an alternating fashion on top of the starting layer. In addition to the standard double-sided coating, a one-sided coating was performed as well. One-side coatings were applied using a custom-made Teflon cell that exposes only one side of the CEM to the coating solutions.

On anion exchange membranes (AEMs), PAH/PSS coatings were coated with polyelectrolyte concentrations of 0.1 g/L in 0.05 M NaNO₃ with pH 2.5, based on earlier work¹⁶. Multilayer

built-up for AEMs started with PSS, as this is the negative polyelectrolyte on a positive AEM. Rinsing steps were performed for 15 minutes in 0.05 M NaNO₃.

LbL-coating recipe 2

In literature, the best results for defect-free coating on aliphatic CEMs have been achieved with a different recipe. Polyelectrolyte solutions for recipe 2 (CEM) according to Zhu et al.¹² were used with solutions of 0.02 M (1.9 g/L) PAH in 1 M NaCl (pH 2.3) and 0.02 M (4.1 g/L) PSS in 0.5 M NaCl (pH 2.3). Coating steps were performed for 5 minutes and rinsed briefly for 1 minute with deionized water from a squirt bottle. The membranes were initially soaked in 0.1 M NaCl for 24 hours.

Both recipe 1 and 2 were coated on membranes and silicon wafers, the latter for comparison using ellipsometry (not for reflectometry, see section 2.2.2). While the substrates are chemically different (although in all cases charged), it is known from literature that the substrate affects only the properties of the first few layers. For a sufficient number of layers, the bulk and surface properties become independent of the substrate¹⁷. Hence, the results on membranes and model surfaces can be readily compared.

The complete overview of all the coating conditions is given in Table 1.

Table 1. Overview of the recipes used for membrane preparations and for characterization of surfaces by ellipsometry and reflectometry. For AEMs, a different recipe is chosen based on earlier work. For reflectometry, a lower concentration polyelectrolyte is selected to avoid large refractive index changes. This should, however, not change the structure of the multilayer.

	Polyelectrolyte concentration	Supporting electrolyte	pH	Rinsing solution	One-sided on membrane?	Ellipsometry?
Recipe 1 (CEM)	1.0 g/L PAH 1.0 g/L PSS	0.5 M NaCl 0.5 M NaCl	2.3 ~6.9	2 x 10 minutes in 0.5 M NaCl	Yes	Yes
Recipe 2 (CEM)	1.9 g/L PAH 4.2 g/L PSS	0.5 M NaCl 0.5 M NaCl	2.3 2.3	1 minute with deionized water	No	Yes
Recipe 1 (AEM)	0.1 g/L PAH 0.1 g/L PSS	0.05 M NaNO ₃ 0.05 M NaNO ₃	2.3 ~6.9	2 x 10 minutes in 0.05 M NaNO ₃	No	No
Recipe 1 (reflecto- metry)	0.1 g/L PAH 0.1 g/L PSS	0.5 M NaCl 0.5 M NaCl	2.3 ~6.9	Flushing with 0.5 M NaCl	No	No

2.2.2. Reflectometry

In this work we employed reflectometry to study the in situ layer-by-layer adsorption process¹⁸. With this technique, the rinsing step must contain the same background salt and pH (to measure at similar refractive indices). Moreover, the coating steps were performed at lower concentrations (0.1 g/L) of polyelectrolyte to prevent precipitation and allow control over salt concentration (polyelectrolytes have associated counter ions)¹⁴. This concentration (of 0.1 g/L polyelectrolyte) is enough to obtain saturated (self-limiting) layer adsorption, where further

adsorption is restricted by charge repulsion. Therefore, multilayer adsorption behavior (as measured by reflectometry) in both 0.1 and 1.0 g/L cases would be the same¹⁹. Specifically for reflectometry, to avoid precipitation and for increased control of salt concentration for measurement accuracy, authors adopted recipe 1 (reflectometry) by decreasing the polyelectrolyte concentration. The reflectometry set-up used a He-Ne JSPU 1108p (632.8 nm) laser, which was linearly polarized and the light was reflected at the Si Brewster angle of 71°. The light was split in parallel and perpendicular components in the detector. The difference between these components, relative to the initial state, is proportional to the adsorbed mass of polyelectrolyte on the silicon wafer, as described by Equation 1:

$$\Gamma = Q \cdot \frac{\Delta S}{S_0} \quad (1)$$

where Γ is the adsorbed mass in mg/m^2 , S_0 is the initial signal of the wafer and ΔS is the signal change and the sensitivity factor Q depends on the refractive indices, thickness and angle of incidence of the multilayers. The Q -factors are calculated for layers of PAH and PSS: PAH has a Q -factor of $28 \text{ mg}/\text{m}^2$ with a dn/dc value of 0.18 and PSS has a Q -factor of $33 \text{ mg}/\text{m}^2$ with a dn/dc value of 0.21²⁰. Silicon wafers (with 100 nm silicon oxide top layer) were used in a flow cell, where the adsorption is measured at the stagnant point. At the stagnant point, convection to the surface is minimal, which mimics LbL-coating conditions. Polyelectrolyte solutions (0.1 g/L polyelectrolyte, 0.5 M NaCl, pH 2.3) were alternately flown, by a Masterflex peristaltic pump, through the flow cell until a stable adsorption plateau was reached. Subsequently, the flow cell was rinsed with background solution (0.5 M NaCl and pH 2.3) to rinse away the excess polyelectrolytes. After the rinsing step, when the adsorbed amount was stable, signals are

recorded for analysis of the mass and molar adsorption. The molar adsorption per m^2 is calculated by dividing the adsorbed mass with the molecular weights of the monomers. The following monomer molecular weights were used (58.1 g/mol for PAH and 183.2 g/mol for PSS).

2.2.3. Ellipsometry

Both recipe 1 (CEM) and 2 (CEM) were coated on silicon wafers with a native oxide layer of 2 nm, in a dip coating fashion exactly like the membranes. An M-2000V spectroscopic ellipsometer (J.A. Woollam Co., USA) was used with a wavelength (λ) range of 370-1000 nm. All samples were measured in air (dry) at three different angles of incidence (65, 70, and 75°) at four different spots on the silicon wafer. Wet measurements were performed in MilliQ water as well as in 0.5 M NaCl in a 5 ml liquid cell at a fixed angle of incidence of 75° and one fixed spot. All measurements were performed in ambient conditions. For layers less than 10 nm, data is deemed inaccurate and is not reported. The data shown was fitted using the CompleteEase software. A standard Cauchy model ($n = A + B/\lambda^2$) was used with input parameters $A = 1.49$ and $B = 0.0045$, according to de Vos et al.²¹. The hydration is calculated using the relationship: $1 - (\text{dry thickness} / \text{wet thickness})$. Therefore, a hydration of 0 means no swelling at all, while a value of 1 is infinite swelling. Here, we choose to report hydration, as it gives a good measure for how open the multilayer is.

2.3. Membrane characterization

Resistance measurements for these membranes are a tool to evaluate the ability to conduct specific ions. A large resistance implies a large driving force (voltage in this case) necessary to

transport these ions. In this work, both ohmic as well as total (including ohmic and non-ohmic) resistance are measured. The ohmic resistance is measured by an alternating current (AC) method, thereby excluding diffusion boundary layers or surface effects²². The total resistance is measured by a direct current (DC) method, where diffusion boundary layers and surface effects are present. This latter situation resembles a practical desalination process, where DC is applied to transport ions. The total resistance (obtained with DC) minus the ohmic resistance (obtained with AC) gives the non-ohmic resistance, which is a measure for diffusion of ions to the membrane surface.

Before each resistance measurement, CEMs were soaked in 0.5 M of NaCl, MgCl₂ or Na₂SO₄ for at least 48 h to exchange them to the Na⁺ or Mg²⁺-form for the CEMs or to the Cl⁻ or SO₄²⁻-form for the AEMs. The same solutions (of 0.5 M of the desired salt) were used to measure the membrane resistances. The electrode rinse consists of 0.5 M Na₂SO₄. The membrane resistances were measured as described in our previous work²³, and the Na⁺/Mg²⁺ monovalent-selectivity, S_{Mg}^{Na} , was calculated by using the total resistances in the Mg²⁺ (R_{Mg}) and Na⁺ forms (R_{Na}) (see Equation 2). The Cl⁻/SO₄²⁻ monovalent-selectivity was calculated in the same fashion. The used six-compartment cell is shown in Fig. 1a.

$$S_{Mg}^{Na} = \frac{R_{Mg}}{R_{Na}} \quad (2)$$

2.4. ED stack experiments

Model brackish water (with 25 mM NaCl and 10 mM MgCl₂) was desalinated using an ED stack. The electrode rinse solution (or electrolyte) was 100 mM NaHCO₃, to acts as pH buffer

and to enhance conductivity. The temperature of the feed water was controlled at 25 °C using a thermostat bath (F12-ED thermostat Julabo, Germany) and pulsation dampeners were used for feed waters, which were flown using peristaltic pumps (Cole Parmer, USA). The ED stack consisted of three cell pairs: the outer two CEMs were Neosepta CMX for their high permselectivity to contain the electrolyte, the middle two CEMs were Fuji Type I with or without LbL-coating, and the AEMs were Fuji Type I AEMs. Woven spacers (Deukum GmbH, Germany) with a thickness of 260 μm and a free void and free area fraction of 0.726 and 0.476 respectively were used.

A cross-flow stack, obtained from REDstack BV (the Netherlands), equipped with Pt-coated Ti mesh electrodes (Magneto Special Anodes BV, the Netherlands) with an active area of 6.5×6.5 cm^2 , as used for the ED experiments. The feed water flow rate was 34 mL/min for all ED experiments, which gives a linear flow speed of 1.5 cm/s and residence time of 4.2 s. The stacks were operated using single-pass (concentrate and diluate outlets are fed back to the feed water tank) at 3.5 V for 10 minutes to reach a steady-state and samples were taken after 500 s from the feed water, as well as from concentrate and diluate outlets of the stack. A schematic drawing of the stack is shown in Fig. 1b. For detailed stack characterization, see Supplementary Information (SI) 1.

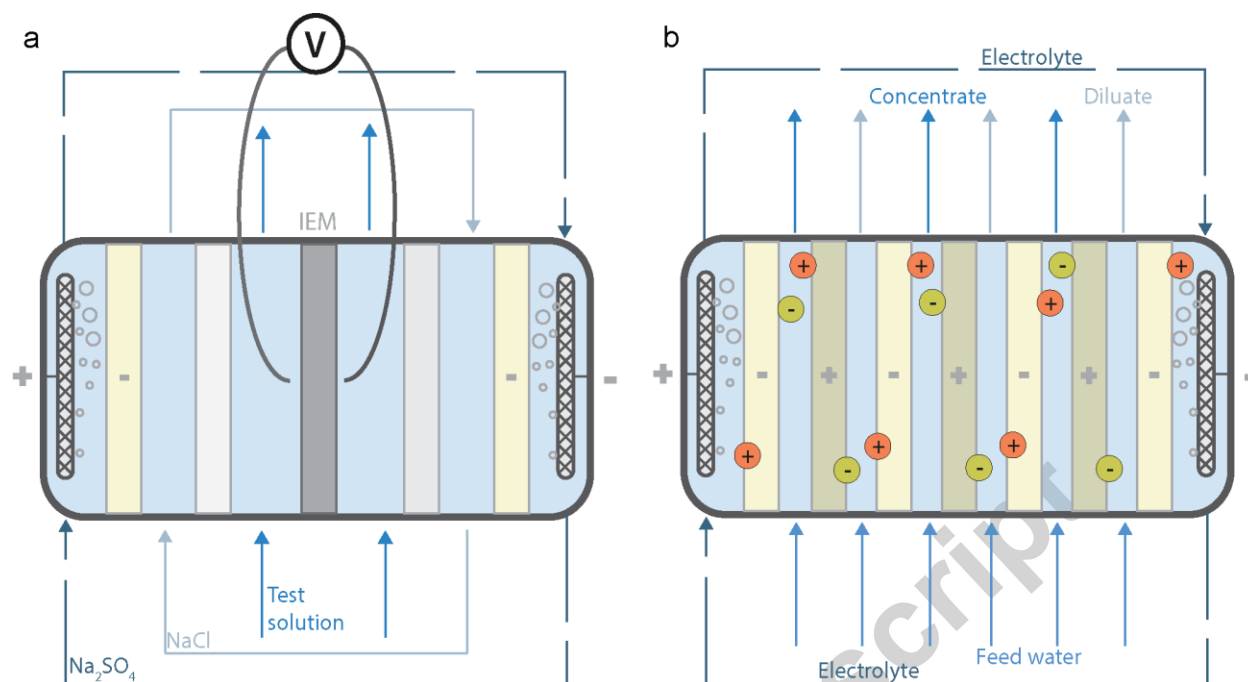


Figure 1. Schematic configuration of six-compartment cell (a) and ED stack (b) used in this study. For the six-compartment cell (active membrane area 23.8 cm^2), the voltage drop of the (coated) IEM is measured by Luggin-Haber capillaries with calomel reference electrodes. For the ED experiments (active membrane area 42.3 cm^2), feed water is supplied to all channels, the enriched/concentrated feed water is the concentrate and the diluate is the desalinated feed. The electrolyte is rinsed between the cathode (-) and anode (+) compartments. Cation (light) and anion (dark) exchange membranes are stacked alternately in an ED stack.

For the ion concentrations, ion chromatography (IC) was used to analyze the cation concentrations. Samples were diluted with 2 mM HNO_3 before the analysis. The instrument used was a Metrohm 850 Professional IC equipped with Metrosep C6 -150/4.0 column with eluent of 1.7 mM HNO_3 and dipicolinic acid.

The monovalent-selectivities for the ED stack are calculated by the following equation:

$$S_{Mg}^{Na} = \frac{J_{Na} \cdot C_{Mg}}{J_{Mg} \cdot C_{Na}} \quad (3)$$

where J_{Na} and J_{Mg} are the sodium and magnesium fluxes (in mol/m²s), C_{Na} and C_{Mg} are the sodium and magnesium concentrations in the diluate (in mol/L) respectively.

3. Results and discussion

In this study, we first discuss the formation of polyelectrolyte multilayers on silicon oxide model surfaces to determine the adsorption, charge, and hydration. Next, CEMs coated with identical multilayers, are measured for their resistances towards Na⁺ and Mg²⁺ to determine the Na⁺/Mg²⁺-selectivity. A similar coating is applied on AEMs (but the first layer is the negative polyelectrolyte) and their resistances for Cl⁻ and SO₄²⁻ are measured to determine Cl⁻/SO₄²⁻ selectivities. Finally, ED experiments are performed with uncoated and LbL-coated CEMs to study the practical selectivities for large-scale separations.

3.1. Formation of polyelectrolyte multilayers

Layer-by-layer assembly of the polyelectrolyte multilayers is studied per layer. In this way, the properties of the layers such as charge, thickness and hydration can be studied as function of coating steps. For reflectometry, rinsing was performed with aqueous solutions of the same ionic strength and pH as the polyelectrolyte solutions (see recipe 1 (reflectometry) in Materials and Methods section). In Fig. 2a, the build-up of the LbL-coating is shown, where the layer mass and molar adsorption increase for an increasing number of layers. In previous work, it was shown

that an excess of PAH, based on monomers, is adsorbed in PAH/PSS multilayers when coated at pHs between 3 and 5.5¹⁵. Moreover, in the same study, it was found that the weak polyelectrolyte PAH is almost fully charged when it adsorbed on a monolayer of negatively charged surfactants. The rejection properties, important for membrane application, depend on the charge density of the multilayer. The total excess of PAH (to PSS) in the layer can be calculated with the molar adsorption per layer; i.e. from the mass adsorption per layer and the molar weights (see Section 2.2.2). If the PAH and PSS compensate each other completely, a 1:1 ratio of monomers would be expected and the charges can compensate each other, which results in a multilayer with a net neutral charge. Initially, this is observed in our experiments, where the multilayer charge switches from negative excess at PSS-terminated layers to positive excess at PAH-terminated layers (see Fig. 2b). However, after eight layers the overall excess of PAH in the multilayer is positive and continues to increase with more layers. From eight layers onwards, there is always an excess of PAH in the multilayer. The weak polyelectrolyte PAH will first compensate the negative charges of the strong PSS. The excess of PAH will be partially charged, which creates a net positive charge in those multilayers. At 11 layers, there is a total layer adsorption of 0.080 mmol/m² with an excess of 0.024 mmol/m² of PAH. This is a ~30% excess of PAH compared to a stoichiometric 1:1 PAH/PSS layer. Clearly, also for recipes where PAH is coated at pH 2.3, the PAH/PSS multilayer will contain a significant excess of positive charges, especially for thicker multilayers.

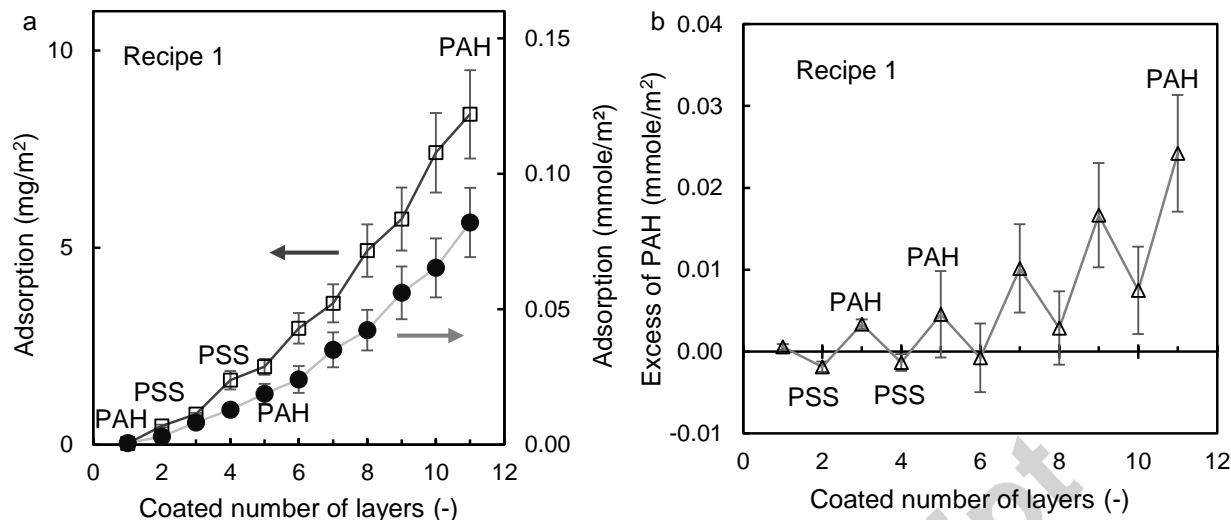


Figure 2. Cumulative adsorption (mass \square and molar \bullet) measured per layer by reflectometry (a) and overall excess of PAH per layer (b). PAH/PSS multilayers are coated according to recipe 1 (reflectometry) at concentrations of 0.1 g/L polyelectrolyte. PAH or PSS written in graph denotes the final layer coating.

In Fig. 3, the hydration of layers formed using both recipes 1 (CEM) and 2 (CEM) is plotted as function of the number of coated layers. From earlier work²⁴, it is known that bulk PAH/PSS multilayers are $\sim 21\%$ hydrated whereas the terminating PAH-layer is $\sim 43\%$ hydrated. If there are more layers, the hydration of the multilayer will approximate the bulk properties and, therefore, the hydration decreases with an increasing number of layers. The difference between the layer hydration in earlier reports is that in these measurements, the humidity in the atmospheric ('dry') measurements is not accounted for. This will swell the multilayer by 5 – 10% depending on the relative humidity²⁵. The limit in hydration is also observed in Fig. 3, where final layer hydrations are in the order of 20 - 23% for recipe 2. For recipe 1 (CEM), the hydration is higher at 37 – 38%

with similar wet thicknesses as recipe 2 (CEM). The main difference between these recipes is that recipe 2 has a fast (1 min) rinsing step in demineralized water, whereas recipe 1 has a slower (15 min) rinsing step in water with 0.5 M NaCl at pH 2.3. By quickly rinsing with demineralized water (recipe 2), intrinsic charge compensation between the polyelectrolytes occurs, and this phenomena is known to lead to denser, less hydrated multilayers¹⁹. Therefore, the hydration of the multilayers with recipe 2 is lower; however, hydrated thicknesses are equal (~ 35 nm) for both recipes at 10 and 11 layers. For the same excess of PAH this could lead to higher positive charge densities in multilayers with recipe 2. The wetted layers are also exposed to 0.5 M NaCl to assess their stability and investigate hydration differences in seawater. For all layers, the hydration increased slightly by 0.03 – 0.05 (data not shown), which means that these multilayers are stable in 0.5 M NaCl as the extent of hydration did not change substantially.

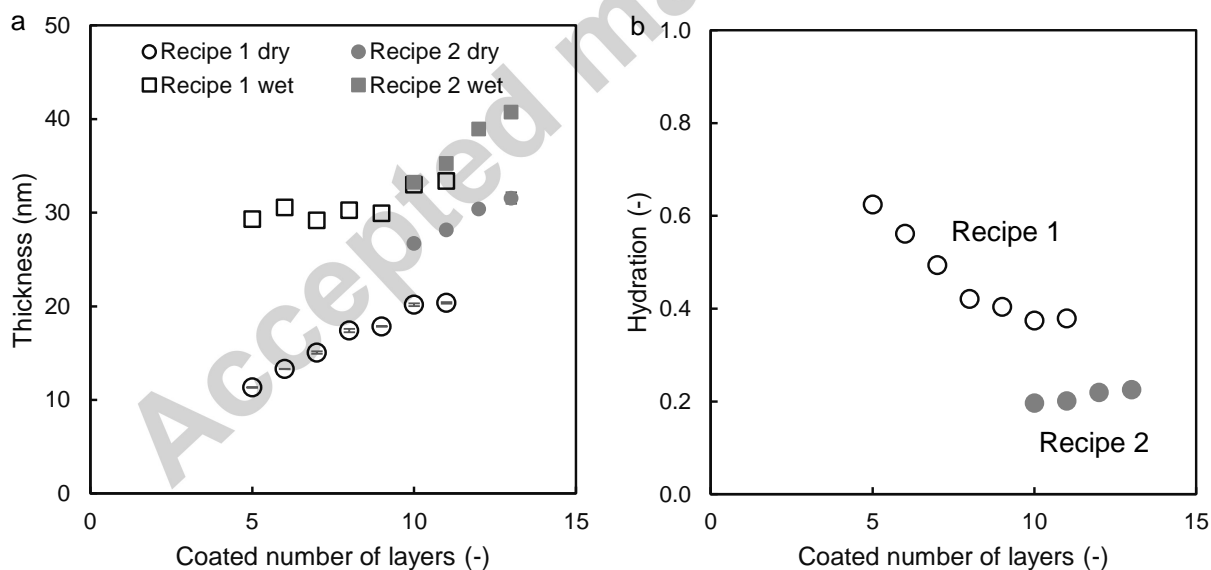


Figure 3. Thickness of dry and wet LbL-coating (a) and hydration of LbL-coating (b) versus number of coated layers for recipe 1 (CEM) and recipe 2 (CEM). All coatings are performed on Si wafers with an oxide layer.

3.2. Resistance of LbL-coated Type I CEMs

Membrane resistance is an important IEM property, as it describes the ability of the membrane to permeate ions. For IEMs, the membrane resistances for different ions allows the evaluation of permeation properties, as seen in previous work^{23, 26}. It is, therefore, an appropriate method to evaluate IEM selectivities. If we discuss membrane resistance in this work, it is the membrane with the multilayer coating included. In Fig. 4, the ohmic and non-ohmic membrane area resistances are shown for bare CEMs (zero layers) and LbL-coated CEMs in Na⁺-form. Thicker layers increase the non-ohmic resistance, which indicates that Na⁺ ions need a higher driving force to diffuse to the membrane surface. Still the effect is small; clearly, the layers have little effect on the transport of Na⁺. It is important to note that the polyelectrolyte multilayers are only 30 – 40 nm thick (see Fig. 3) while the CEMs are 100 – 150 μm thick. The effect these polyelectrolyte multilayer coatings have on the permselectivity is also studied and found to be low, with an observed typical decrease of 2 – 8% (see SI 2).

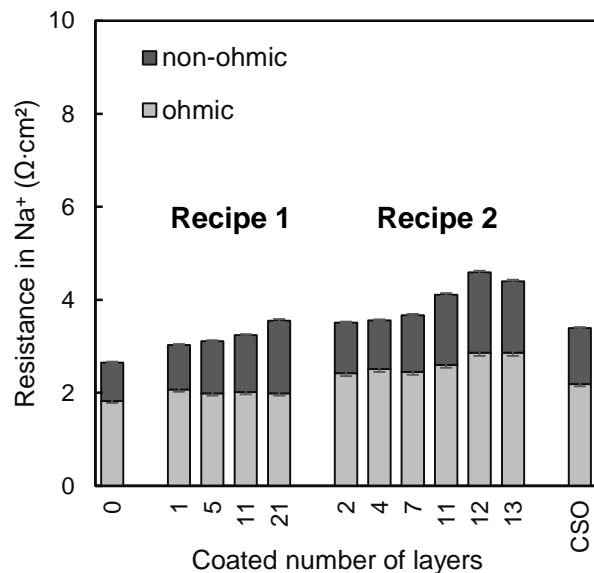


Figure 4. Membrane area resistance in 0.5 M NaCl for LbL-coated Type I CEMs using recipe 1 (CEM) and recipe 2 (CEM). Monovalent-selective CSO is added as a reference membrane.

The same LbL-coated membranes are measured for their Mg^{2+} -resistance, as is shown in Fig. 5. The non-ohmic resistance increases drastically with an increasing number of coated layers. For both recipe 1 and 2 the ohmic resistance does not change ($9.0 - 10 \text{ } \Omega \cdot \text{cm}^2$), whereas the non-ohmic increases from 0.8 up to $25 \text{ } \Omega \cdot \text{cm}^2$. The difference is that, for recipe 2, with more layers, the non-ohmic resistance increases more strongly than recipe 1. The total resistance in NaCl varies less for these coated membranes (from 2.7 to $4.6 \text{ } \Omega \cdot \text{cm}^2$), as seen in Fig. 4. Consequently, the monovalent-selectivities increase drastically, from 3.5 for the initial CEM to 5.7 or 7.8 with recipe 1 or 2 respectively. Especially recipe 2 creates an improved monovalent-selective CEM even compared to the commercially-available monovalent-selective Selemion CSO (with 6.9).

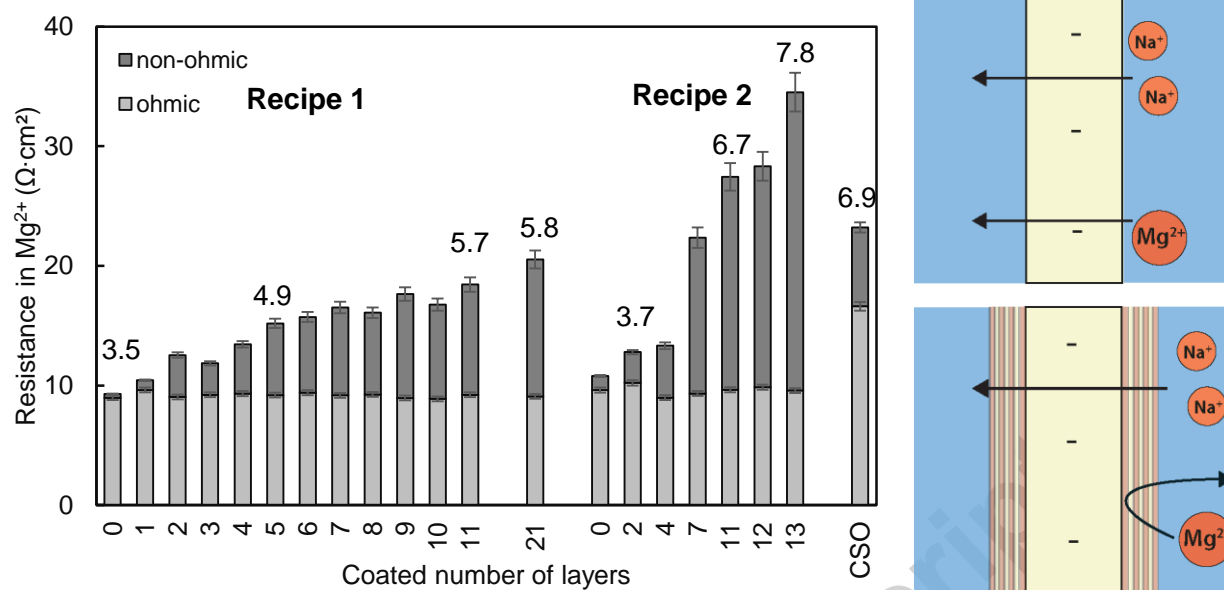


Figure 5. Membrane area resistance in 0.5 M MgCl_2 for LbL-coated Type I CEMs using recipe 1 (CEM) and recipe 2 (CEM). Monovalent-selective CSO is added as a reference membrane. Numbers above the bars are $\text{Na}^+/\text{Mg}^{2+}$ selectivities. Schematic pictures showing uncoated membranes and LbL-coated membranes.

Clearly, LbL-coatings create a barrier for divalent cations that hinders ion transport by means of non-ohmic resistance. The diffusion of divalent cations from the bulk to the surface of the membrane is hindered much more than monovalent cations. The LbL-coating is located at the surface of the IEMs, since IEMs are dense and do not possess a porous structure. The transport of Na^+ is only hindered by a 20% increase in resistance for the highest monovalent-selective LbL-coating, whereas the Mg^{2+} transport is hindered by an increase in resistance of over 300%. In other words, monovalent Na^+ has hardly any transport penalty but the same multilayer hinders transport of divalent Mg^{2+} severely. The selective transport through these multilayers stems from either a hydrated ion size or a Donnan (charge) exclusion. In the case of size exclusion, a dense

multilayer separates ions on size, where the divalent Mg^{2+} diffusion to the membrane is hindered while the diffusion of monovalent Na^+ would be hardly affected. However, the difference in hydrated ionic radii is only $\sim 25\%$ ²⁷, so this separation mechanism is not likely to be the dominant one. In the case of Donnan (charge) exclusion, the positive charge of the multilayer is hindering the diffusion of the cations to the membrane surface. The divalent Mg^{2+} with a higher charge density (six times that of monovalent Na^+ ²⁷) is hindered drastically. The large differences in charge densities can explain why a positively charged multilayer can achieve such differences in non-ohmic resistance between monovalent Na^+ and divalent Mg^{2+} . A certain number of layers is needed to create a multilayer with net positive charge (see Fig. 2b), after eight layers a clear positive charge is observed. This can be seen for the resistance towards Mg^{2+} as well (see Fig. 5), where from seven or more layers a sharp increase in resistance is observed. For this charge exclusion (at the electrical double layer²⁸) to take effect, it is important to have enough layers without defects to create sufficient positive charge density on the CEM surface.

3.2.1. Orientation effect of LbL-coating

LbL-coatings on the CEM surfaces hinder divalent cations diffusion to the membrane surface. However, if the LbL-coating is on the backside of the membrane (the side where the divalent cations diffuse out of the membrane to the concentrated solution), does the resistance for divalent cations increase as well? Previous work shows that it matters if a selective coating is facing the transport direction²⁹. To test this hypothesis, a one-side LbL-coated CEM was prepared with 11 layers using recipe 1 (CEM). In Fig. 6, the result of this approach is shown and compared to the one-side monovalent-selective CSO. Each membrane resistance is measured in

solutions of 0.5 M MgCl_2 and 0.5 M NaCl with the coating against (front) or with (back) the transport direction of Mg^{2+} . There is a remarkable difference between sides facing the Mg^{2+} -transport direction with high non-ohmic resistances (6.6 and 9.3 $\Omega\cdot\text{cm}^2$) and monovalent-selectivities (6.0 and 6.9) for the one-side LbL-coated CEM and the CSO, respectively. The Na^+ resistances are shown in SI 2.

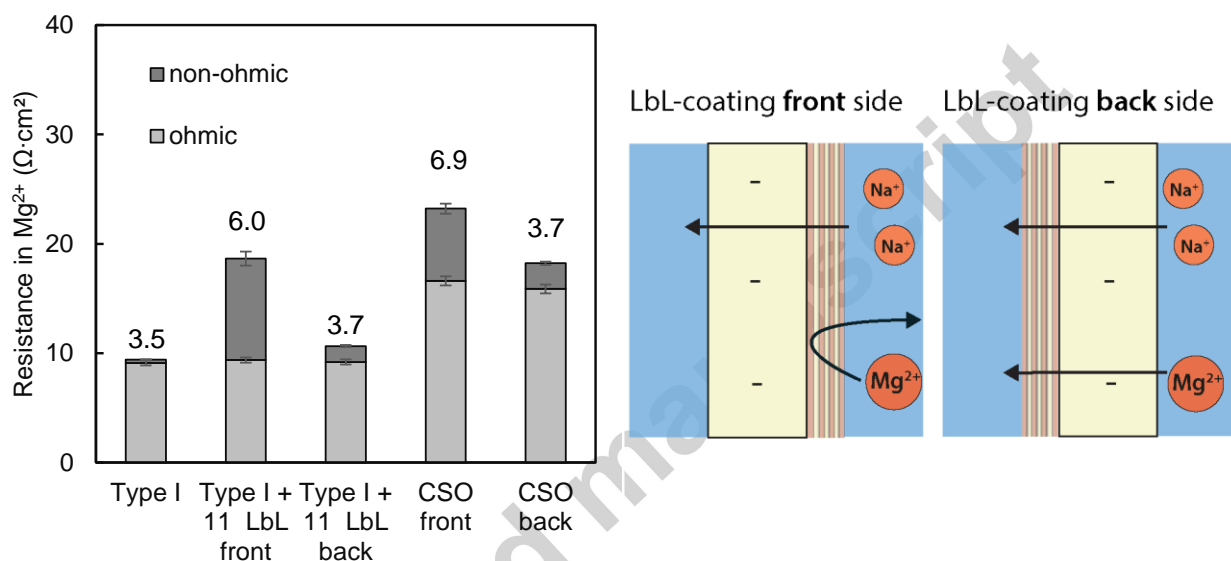


Figure 6. Membrane area resistance in 0.5 M MgCl_2 for one-side monovalent-selective membranes LbL-coated Type I CEMs with 11 layers using recipe 1 (CEM). Monovalent-selective CSO is added for comparison with a commercial monovalent-selective CEM. Numbers above the bars are $\text{Na}^+/\text{Mg}^{2+}$ selectivities. Schematic pictures shows the orientation effect observed in the resistance graph.

The results for the one-side LbL-coated CEM is similar to the double-sided LbL-coated CEM with a selectivity of 5.7. When the one-sided coating is facing the transport direction of the cations it is able to achieve similar resistances for Mg^{2+} (and monovalent selectivities) as double-

sided coatings. However, when the multilayer coating of the CEMs is not facing the transport direction of Mg^{2+} , the non-ohmic resistance as well as the monovalent-selectivity is drastically lower and comparable to standard-grade (uncoated) CEMs. The position of the layer with respect to the transport direction plays a crucial role in the transport properties, and interestingly, if the coating is on the backside of the CEM the Mg^{2+} permeates as if the membrane was uncoated. In other words, the coating only hinders Mg^{2+} diffusion to the membrane, and does not alter the permeation through the membrane nor the diffusion out of the membrane to the concentrated solution. These results show again that the multilayer is hindering divalent cation diffusion towards the membrane, and not in the diffusion inside the membrane itself (as was also observed in section 3.2). Directional monovalent-selective transport is possible with these coatings and this could be beneficial for specific applications where such a property is desired. Alternatively, one can coat the multilayer on both sides of the membrane to avoid the practical difficulty of coating a single side.

3.2.2. Resistance of LbL-coated Type I AEMs

Applying these coatings on anion exchange membranes (AEMs) could introduce changes in selectivities as well. On pressure-driven porous ultrafiltration membranes, it was shown that PSS/PAH coatings can enhance $\text{Cl}^-/\text{SO}_4^{2-}$ selectivities³⁰. For this reason, PSS/PAH multilayers are coated on Fuji Type I AEMs and their resistances in NaCl and Na_2SO_4 are measured, and standard-grade AMX and monovalent-selective ACS are included for reference. In Fig. 7, the resistances in Na_2SO_4 and monovalent-selectivities are shown. The monovalent-selective ACS has a high resistance ($27 \Omega\cdot\text{cm}^2$) as well as monovalent-selectivity (4.9), which shows that the

resistance-based selectivity method is able to distinguish monovalent-selectivity for AEMs as well. Interestingly, the resistance of monovalent-selective ACS is mainly ohmic, while the monovalent-selective CSO has a large non-ohmic contribution. The high ohmic resistance for SO_4^{2-} through ACS indicates that the divalent anion is severely hindered in its permeation through the membrane, in contrast to CSO, which hinders Mg^{2+} diffusion to the membrane surface.

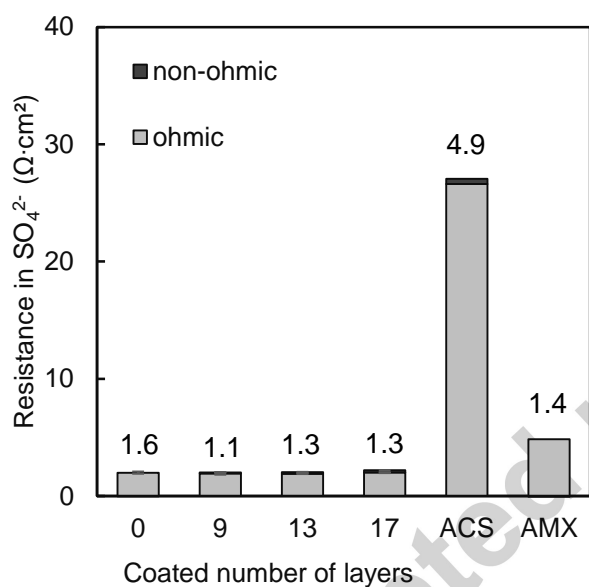


Figure 7. Membrane area resistance in 0.5 M Na_2SO_4 for LbL-coated Type I AEMs using recipe 1 (AEM). Monovalent-selective ACS and standard-grade AMX are added as a reference material. Numbers above the bars are $\text{Cl}^-/\text{SO}_4^{2-}$ selectivities.

The effect of the LbL-coating on the resistance and selectivity of Type I AEM is hardly present, both the membrane resistances in NaCl (see SI 2) and Na_2SO_4 are increasing slightly; hence the selectivity is unchanged or even decreases. There are two explanations for this lack of enhanced

selectivity for anions. Firstly, the excess positive charge of the multilayer does not provide separation based on charge for anions – as is the case for cations. The multilayers with a positive charge, actually lower the monovalent-selectivity slightly to 1.3 (from 1.6). Secondly, Tansel showed that the differences between mono- and divalent anions in hydration radii and charge densities are smaller than for mono- and divalent cations²⁷. Both these reasons could explain why the same PSS/PAH coatings show enhanced monovalent-selectivities for CEMs but not for AEMs. Both reasons are valid and the lack of monovalent selectivity stems from the fact that the layer does not have the right charge to provide Donnan based selectivity, and is too swollen to provide selectivity on the basis of size or hydration. Steric effects induced by a high degree of crosslinking, is an industrially applied technique to create monovalent-selective ACS³. In this work, this was measured as a high ohmic resistance for ACS in SO_4^{2-} -form (see Fig. 7). Designing multilayers for AEMs with enhanced monovalent-selectivity could benefit from such industrially proven membranes. Monovalent-selective layers for AEMs could be prepared using tightly crosslinked multilayers (with low hydration), such that similar steric separations occur as observed for ACS. Moreover, polyelectrolyte multilayer coatings can be designed with an excess of negative charge, using e.g. Chitosan/PAA³¹.

3.3. ED selectivities of LbL-coated Type I CEM

The best monovalent-selective LbL-coated CEMs were achieved with LbL-coating recipe 2 (CEM) where a low hydration and excess PAH was observed. This is expected to lead to a higher positive charge density of the multilayer, which induces the desired monovalent-selectivity. In this work, we aim to demonstrate the benefit of LbL-coatings under relevant process conditions.

Hence, the most promising LbL-coating on CEMs (monovalent-selectivity of 7.8) is coated on two large 11×11 cm CEMs for ED to test the practical selectivities. Artificial brackish water containing 25 mM NaCl and 10 mM MgCl₂ is desalinated with an ED stack consisting of three cells of standard Type I AEMs and uncoated or LbL-coated Type I CEMs to investigate the practical transport selectivities in ED stacks for Na⁺ over Mg²⁺. In Fig. 8, the ion fluxes of ED stacks equipped with uncoated and LbL-coated CEMs are shown. The Mg²⁺ and Na⁺ ion fluxes are very similar for uncoated CEMs, which leads to a low monovalent-selectivity of 0.5. The Mg²⁺ flux reduces by more than 50% while the Na⁺ flux improves by over 60% for the LbL-coated CEMs. This leads to a drastic improvement in monovalent-selectivity to 1.7. At similar current densities equal amounts of charge are transported, and since there is less Mg²⁺ transported with LbL-coated CEMs the Na⁺ transport is greatly enhanced.

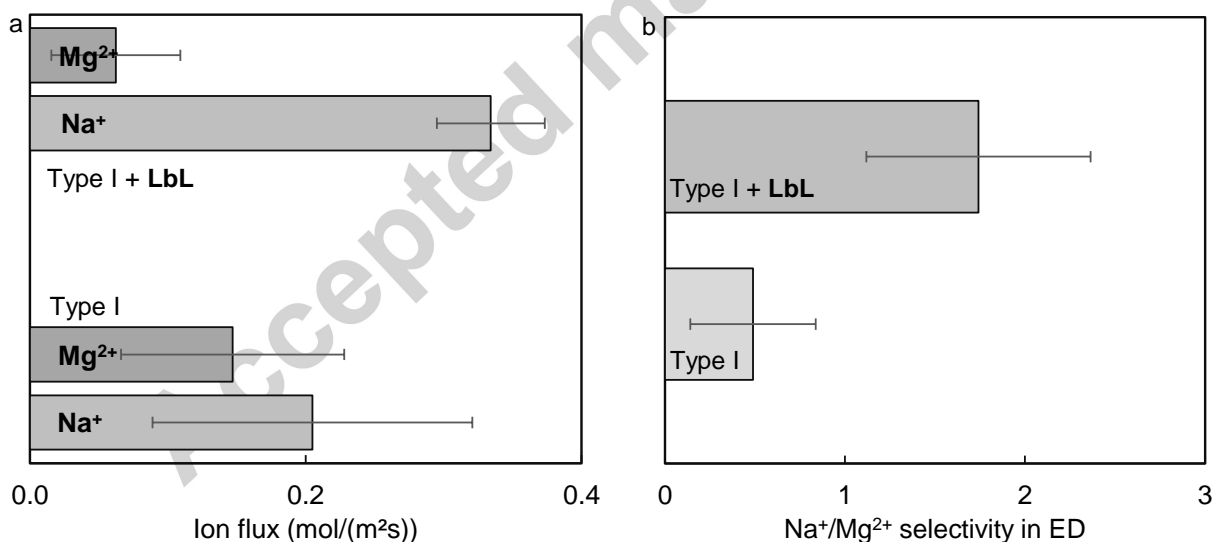


Figure 8. Ion fluxes (a) and selectivities of $\text{Na}^+/\text{Mg}^{2+}$ transport (b) in ED experiment (at 3.5 V) with uncoated and LbL-coated Type I using recipe 2 (CEM). The flux measurements are triplicates and error bars are standard deviations.

Single membranes show the same qualitative trend in monovalent-selectivity as the membrane stacks in ED. However, the monovalent selectivities in ED for both the uncoated and LbL-coated Type I are lower than selectivity based on resistance. This difference in selectivities can be caused by two factors. Firstly, the practical selectivities can be expected to be closer to 1 as mixtures of Na^+ and Mg^{2+} are used instead of pure solutions in ED stacks. Secondly, the concentrations of ions are changing over the length of the stack, such that concentrations of ions that are preferentially transported (Na^+ in this case) decrease more than the others (Mg^{2+}). Therefore, the effective selectivities will be smaller than based on single membranes in pure solutions. The ED stack selectivities are a factor 4.5 – 7.0 lower for uncoated and LbL-coated Type I compared to resistance based selectivities. Despite these effects, the selectivities based on CEM resistances (as described in section 3.2) provide a suitable - though qualitative only - predictor for ED stack selectivities.

We thus show that lab studies with promising LbL-coatings on aliphatic CEMs can achieve monovalent-selectivities of 1.7 in realistic and large scale ED processes. These results show that LbL-coatings are on par with commercial monovalent-selective membranes. Different measurement methods to quantify selectivities makes comparison of different studies difficult. In previous work, CSO had a monovalent transport selectivity of 1.72 (for $\text{Na}^+/\text{Ca}^{2+}$) and PEI/PSS-coated CMX could reach up to a monovalent-selectivity of 1.35 for 21 layers¹⁰. In this work,

using an optimized recipe for PAH/PSS-coated Type I, monovalent selectivities of 7.8 are achieved on membrane level, and are higher compared to CSO (6.9). However, the resistances for these multilayer-coated CEMs is usually higher than CSO, which implies that a higher driving force (and thus power consumption) is required for the same separation. Careful tuning of the coating recipe is required for each membrane to create defect-free, low-hydrated polyelectrolyte multilayers coatings¹². For the final application, both monovalent selectivity and membrane resistance should be investigated for the desired separation.

Conclusions

In this study the formation and application of polyelectrolytes multilayers on ion exchange membranes is studied from the molecular level up to stack-scale desalination. First, multilayer formation on model surfaces is studied to investigate important properties such as layer thickness, hydration and charge. The PAH/PSS multilayers produced with recipe 1 have an excess of positive charge due to an excess of PAH. The layers formed using recipe 2 (CEM) have a lower hydration, as measured by ellipsometry, and are expected to have excess positive charge as well.

Both the LbL-coating recipes are applied on CEMs and their specific ion transport properties were determined using resistance measurements. The main effect of the LbL-coating is the hindrance of Mg^{2+} diffusion to the membrane as seen through the increase in non-ohmic resistance. Multilayers prepared by recipe 2 (CEM) with lower hydration had a promising monovalent-selectivity of 7.8, which is even higher than monovalent-selective CSO (selectivity of 6.9). Moreover, a strong multilayer orientation effect was observed, which showed that the

LbL-coating only hindered diffusion towards the CEM and not through nor out from the CEM. Finally, the uncoated and LbL-coated CEMs were used in an ED stack to assess their monovalent-selectivity at the process-scale. LbL-coated CEMs achieved a monovalent-selectivity of 1.7 compared to 0.5 for the uncoated CEM, showing the applicability of polyelectrolyte multilayers on full-scale ED stacks.

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Highlights

- PAH/PSS Polyelectrolyte multilayers are characterized by their hydration and excess charge
- Multilayer-coated CEMs show increased monovalent-selectivity from 3.5 to 7.8
- Under brackish water ED, coated CEMs still show an increased monovalent-selectivity of 0.5 to 1.7
- These multilayer coatings on AEMs do not result in enhancement of monovalent-selectivity

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