

## Supporting information

### **Effect of divalent cations on RED performance and cation exchange membrane selection to enhance power densities**

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Summary

Number of pages: 14, Figures: 8, Tables: 3

## S1. Equilibrium concentrations of uphill transport through electromotive force calculations

When a cation exchange membrane is in contact with different cations, they can be exchanged, as seen in figure S1.1. The driving force for each ion depends on the concentration on each side of the membrane. The final equilibrium concentrations for the cations are calculated numerically by equating the Donnan potentials of sodium and magnesium across a (perfectly permselective) CEM.

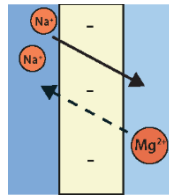


Figure S1.1. Uphill transport of magnesium by exchanging for sodium across a CEM. Left depict the high concentration (seawater) and right the low concentration (river water).

Two cases are studied: one where both the river and seawater contain 10 mol%  $\text{Mg}^{2+}$  (Figure S1.1 left side of the membrane) and where only the river contains 10 mol%  $\text{Mg}^{2+}$  (Figure S1.1 right side of the membrane). The overall salt concentration in the river water is 0.017 M and in the seawater is 0.5 M. In the following figure the approximation is shown from initial  $\text{Mg}^{2+}$  concentration in the river water to the point where the Donnan potentials are equal. This point is approximately at  $0.1 \cdot 10^{-3}$  M, which is slightly less than 1% of the total cation concentration. This shows that nearly full uphill transport should be achieved if the system is in total equilibrium, which matches with the agreement between experimental and calculated OCV values. In the right case where only  $\text{Mg}^{2+}$  is in the river water, the initial electromotive force is actually pushing the  $\text{Mg}^{2+}$  from the river water to the seawater since there is no  $\text{Mg}^{2+}$  in the seawater. As expected, the Donnan potential of  $\text{Mg}^{2+}$  is 0 when about half of the  $\text{Mg}^{2+}$  (5%) is transported to

the seawater side since in this case both concentrations of  $Mg^{2+}$  are equal. We can see that the final equilibrium is nearly complete uphill transport, only 0.01% of  $Mg^{2+}$  is left at equilibrium in the river water.

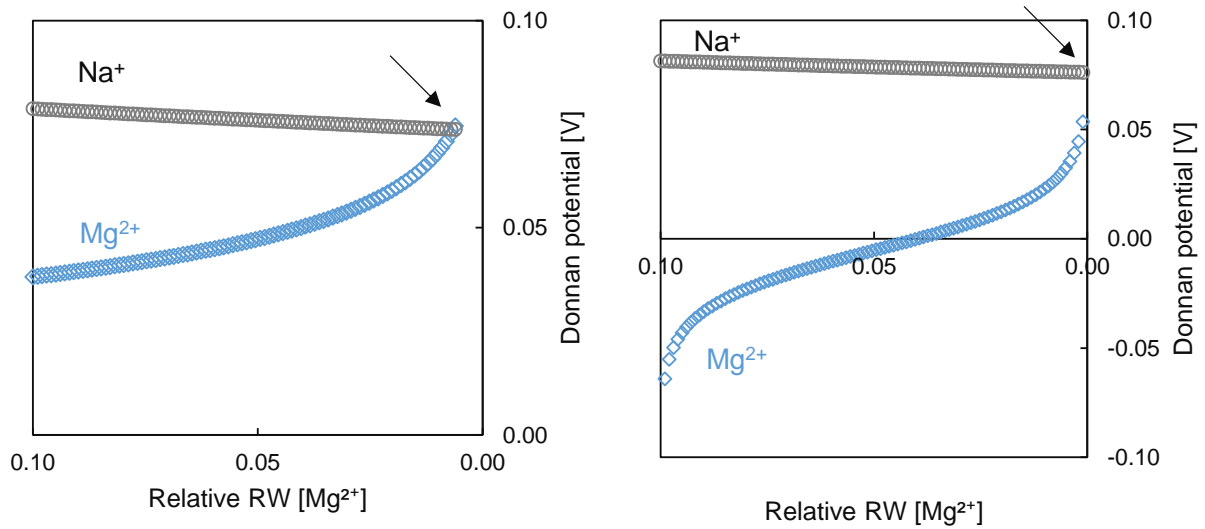


Figure S1.2. Donnan potentials (V) for sodium (black circles) and magnesium (blue squares) as a function of relative  $Mg^{2+}$  concentration of the river water (%). Arrows indicate equilibrium concentrations between  $Na^+$  and  $Mg^{2+}$  Donnan potentials. Initially the concentration of  $Mg^{2+}$  in the river water is 10%. Left figure shows the case for  $Mg^{2+}$  in river and seawater and right figure shows the case for  $Mg^{2+}$  in only the river water.

## S2. Feed water and electrode (rinse) solution composition and conductivities

As an electrode rinse redox pair solution, 0.1 M  $\text{K}_4\text{Fe}(\text{CN})_6$  / 0.1 M  $\text{K}_3\text{Fe}(\text{CN})_6$  with 0.25 M NaCl aqueous solution was used. Feed solutions for river and seawater are given in Table S2.1. In this case we based our experiments on the water conditions of the pilot plant of REDstack on the Afsluitdijk, the Netherlands, which has feed water from the IJsselmeer lake and from the Waddensea.

Table S2.1. Feed water compositions in [M] for seawater and river water with standard NaCl and with divalent cations. Compositions are in mol%. Measured conductivities ( $\pm 0.1$  mS/cm) for the feed streams are given as well (using a conductivity meter Cond 3310 of WTW, Germany).

	<b>[sea water]</b>			<b>[river water]</b>		
	NaCl	90% NaCl + 10% $\text{MgCl}_2$	90% NaCl + 10% $\text{CaCl}_2$	NaCl	90% NaCl + 10% $\text{MgCl}_2$	90% NaCl + 10% $\text{CaCl}_2$
<b>NaCl</b>	0.50	0.45	0.45	0.017	0.015	0.015
<b><math>\text{MgCl}_2</math></b>	0.00	0.05	0.00	0.000	0.002	0.000
<b><math>\text{CaCl}_2</math></b>	0.00	0.00	0.05	0.000	0.000	0.002
<b>Conductivity [mS/cm]</b>	47.9	49.7	50.5	1.9	2.2	2.2

### S3. Typical IV and power density plots (data shown here for T1 CEM)

Lines are shown by fitting effective OCV and resistance. The data agrees quite well, if we fit the resistance and OCV over the complete current (density) range with positive power densities. The fitted OCV (at  $I = 0A$ ) is always lower than the measured OCV in open-circuit conditions, because of current and thus ion migration. The measured OCV is used for calculating (net) power densities and the measured (relative) OCV used in table 1.

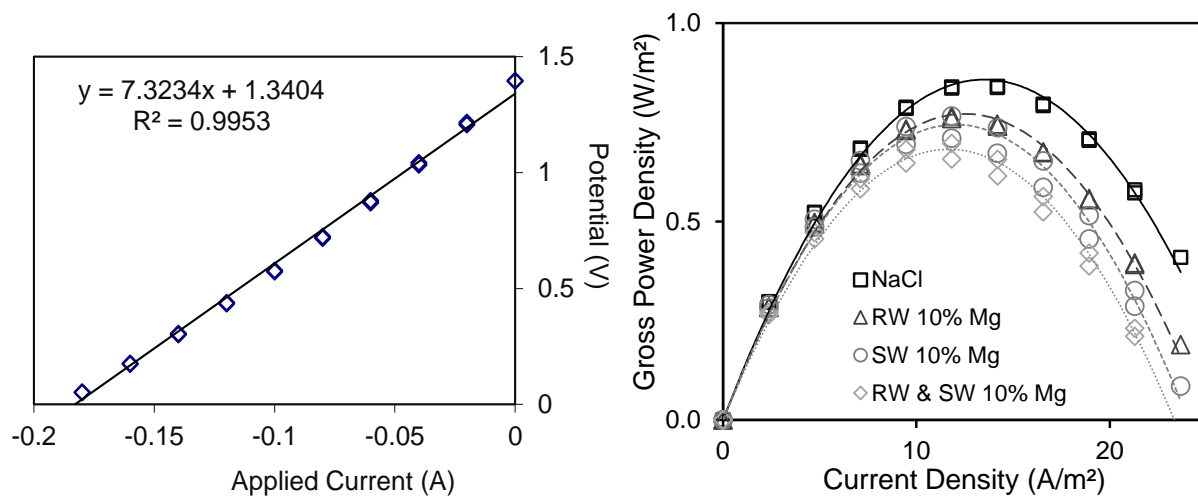


Figure S3.1. Typical IV curve for measured stack of 10 cells with T1 CEM and NaCl solutions (left panel), with fit for effective OCV and total stack resistance. Right panel shows gross power density versus current density for the T1 CEM stack with different feed compositions.

## S4. Detailed ion exchange membrane characterization

### S4.1 Method

The water content of the CEMs was measured by thermal gravimetric analysis (TGA, Perkin Elmer TGA 4000, The Netherlands). A small piece of membrane (~10 mg) was soaked in milliQ water overnight. The supernatant water was removed by briefly blotting the membrane by filter paper on each side. The membrane was then assembled rapidly, to minimize evaporation, in the TGA holder intended for the measurement. The measurements were performed through a temperature sweep of 30 to 120°C at a heating rate of 10°C/min under N<sub>2</sub> atmosphere, followed by an isothermal period of 30 minutes at 120°C to ensure complete drying of the membrane without decomposition. Measurements were taken twice. The relative water content (%) was calculated as the wet mass minus the dry mass, which is then divided by the dry membrane weight.

The ion exchange capacity (mmol/g) of the CEMs was measured according to the procedure described in the literature using ion exchange between H<sup>+</sup> and Na<sup>+</sup>.<sup>1</sup> The total quantity of released H<sup>+</sup> was determined by titrating the exchanging solution. This capacity is divided by the dry membrane mass. Permselectivity is measured according to a procedure reported in the same paper using the ratio of the experimental over the theoretical potential for a 100% permselective membrane with on either side a 0.1 or 0.5 M NaCl solution.<sup>1</sup>

### S4.2 Results

In Table S4.1, the relevant properties of the membranes considered in this study are shown. Interestingly, T1 membranes have lower ion exchange capacities (IEC) compared to Type I, which was not expected from the resistance measurements. Conventionally, higher IEC

membranes have a lower resistance. However in this case electrical resistances (in Na<sup>+</sup>- and especially Mg<sup>2+</sup>-form) are lower, which suggests that in T1 enhanced order is created with less charges in the membrane volume. Similar results were observed by Lee *et al.* where they created order through aligning a polyelectrolyte by using an electric field and obtained membranes with lower resistance but similar IEC<sup>2</sup>.

Table S4.1. Membrane properties of the studied cation exchange membranes. Ohmic area resistance is measured by AC in 0.5 M NaCl and repeat errors are < 0.1 Ω·cm<sup>2</sup>.

	Wet thickness (μm)	Ion exchange capacity (mmol/g)	Water content (wt %)	Apparent permselectivity (%)	Ohmic area resistance (Ω·cm <sup>2</sup> )	Selectivity Na <sup>+</sup> /Mg <sup>2+</sup> (-)
CMH-PES	680	2.34 <sup>1</sup>	31 <sup>3</sup>	93 ± 1	9.4	2.3
FUJI Type I	125	1.7 ± 0.1	61 ± 1	94 ± 1	1.6	2.9
FUJI T1	125	1.4 ± 0.1	58 ± 2	90 ± 1	1.2	2.0
CMS	145	2.2 <sup>4</sup>	22-30 <sup>4</sup>	97 <sup>4</sup>	3.1	34
AEM FUJI Type 1	125	-	-	90 ± 1	1.2	-

Moreover, there is a clear difference in the water content between hydrophobic ion exchange membranes (CMH-PES and CMS) and hydrophilic ion exchange membranes. The FUJI membranes (Type I and T1) are crosslinked charged aliphatic hydrogels and possess a very high water content (around 60%), whereas the styrene-based CMH-PES and CMS have water contents of around 30%. In terms of selectivity of Na<sup>+</sup>/Mg<sup>2+</sup>, CMS clearly has a very high selectivity, which means that it is able to conduct monovalent cations better than divalent cations. On the other hand T1, which has a very low Na<sup>+</sup>/Mg<sup>2+</sup> selectivity and is able to transport both ions as there is no major difference in transport resistance for monovalent and divalent cations.

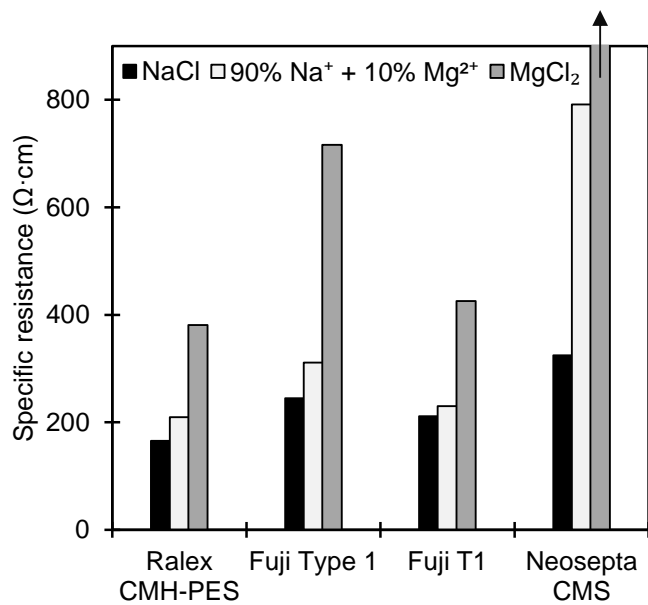


Figure S4.1. Specific resistance of CEMs in 0.5M NaCl, MgCl<sub>2</sub> and a mixture of 90% NaCl and 10% MgCl<sub>2</sub>. The specific resistance of CMS in MgCl<sub>2</sub> is 10923 Ω·cm.



## S5. Ion exchange isotherms for $\text{Na}^+/\text{Mg}^{2+}$ and $\text{Na}^+/\text{Ca}^{2+}$ mixtures in CEMs.

### S5.1 Method

SEM-EDX measurements were performed on a JEOL JSM-6010LA instrument to measure cation affinities of the membranes. The membranes were soaked overnight in solutions of 0.5M total salt concentration of pure salts and mixtures of NaCl,  $\text{MgCl}_2$  or  $\text{CaCl}_2$ . The supernatant water was removed with filter paper quickly, as this method does not pump out the electrolyte from the membrane but does remove excess water, as described by Dammak *et al.*<sup>5</sup>. The membranes were then placed on SEM holders with double-sided carbon tape and dried overnight in vacuo at room temperature. The samples were Pt-sputtered with JEOL JFC-1300 and EDX analysis was performed at 15 kV with >1000 counts/sec (with >5 EDX spectra taken per sample).

### S5.2 Results

The cation affinity of the membranes was investigated for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and shown in Figure S5.1. By comparing the solution concentration and the relative concentration in the membrane, one can study the competitive interactions of cations and CEMs. In this case similar results are observed as in literature, namely higher affinities for divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ )<sup>6-8</sup>. There is a minor difference between Type I and T1, the latter has a small decrease in affinity for  $\text{Mg}^{2+}$  (see Figure S6.1), possibly due to lower possibility of multiple binding of divalent cations. This could be related to the enhanced divalent transport of T1. Similar trends are observed for  $\text{Ca}^{2+}$ , albeit with higher affinity for  $\text{Ca}^{2+}$  (see S5.1). For this study the values for 10% magnesium are relevant (mol fraction  $x = 0.1$ ) as this is the concentration used in stack measurements and typically 30-50% of cations in the membrane are magnesium, which shows

that small amounts of divalent cations in solution can have a very large impact in these membranes.

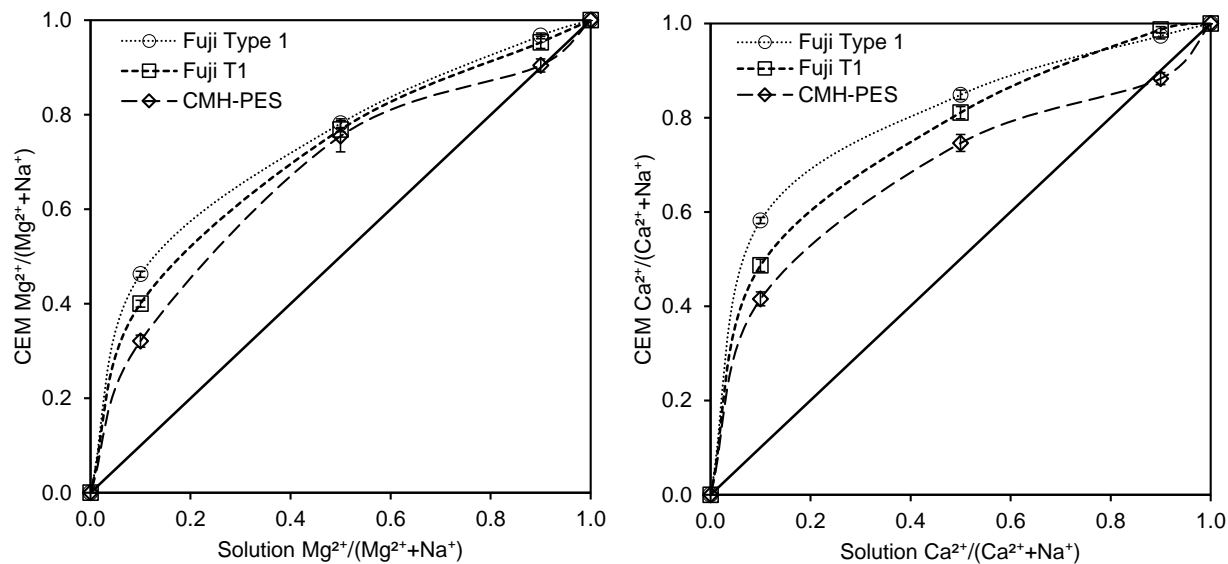


Figure S5.1. Ion exchange isotherms of selected in CMH-PES, Type I and T1 CEMs in NaCl and MgCl<sub>2</sub>, and NaCl and CaCl<sub>2</sub> solutions. Lines are drawn to guide the eye. Error bars represent standard deviations of over 5 measurements. On the x-axis the molar fraction of Mg<sup>2+</sup> or Ca<sup>2+</sup> in solution of and on the y-axis is the molar fraction Mg<sup>2+</sup> or Ca<sup>2+</sup> in the membrane. Total ion concentration is 0.5M.

## S6. Total stack resistance of membranes used with feed waters with NaCl and MgCl<sub>2</sub>

In Figure S6.1, the total stack resistances for the different membranes are shown for feed waters with pure Na<sup>+</sup> and with Mg<sup>2+</sup> in the feed streams. The CMH-PES membrane (with a Na<sup>+</sup>/Mg<sup>2+</sup> selectivity of 2.3) and T1 (with a Na<sup>+</sup>/Mg<sup>2+</sup> selectivity of 2.0) experience the smallest relative effect of Mg<sup>2+</sup> as the stack resistance only increases by 10%, whereas for Type I and CMS membranes with higher selectivities, the stack resistance increases up to as 40 and 15% respectively when Mg<sup>2+</sup> was in the feed streams. For RED application the lowest total stack resistance is desired in the presence of Mg<sup>2+</sup>, in this case the multivalent-permeable T1 has the lowest total stack resistance of all CEMs.

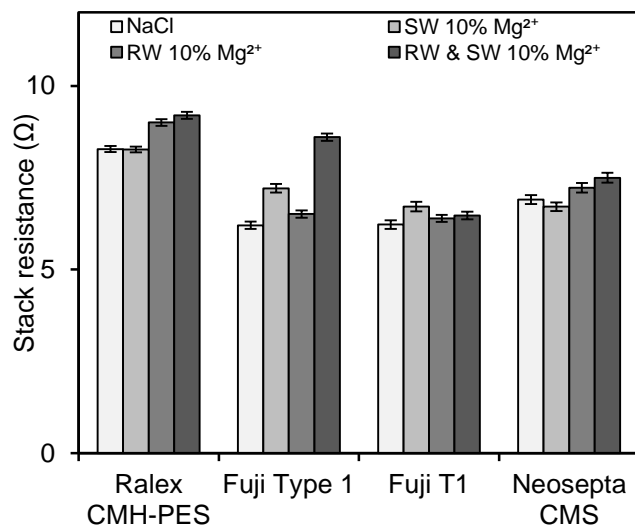


Figure S6.1. Stack resistance in NaCl and 10% Mg<sup>2+</sup> in river and/or seawater streams for different CEMs.

S7. Stack data (OCV, stack resistance and power density) for feed waters with NaCl and CaCl<sub>2</sub>

The experimental procedures for both the membrane resistance and the stack performance measurements are exactly the same for Ca<sup>2+</sup> as it is for Mg<sup>2+</sup>, as described in the main document.

In Figure S7.1, open circuit voltages and stack resistances of the standard-grade Type 1 and multivalent-permeable T1 CEMs are shown with feed of Ca<sup>2+</sup>. In Figure S7.2 the power density is shown for a 10 cell-pair stack.

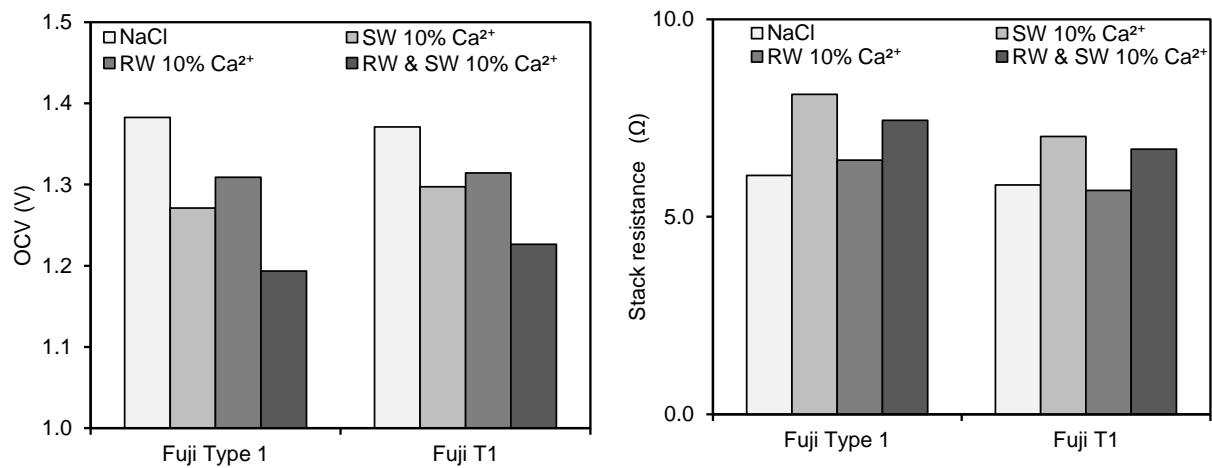


Figure S7.1. Open circuit voltages and stack resistance with Ca<sup>2+</sup> in feed streams with Fuji Type I and T1 CEMs.

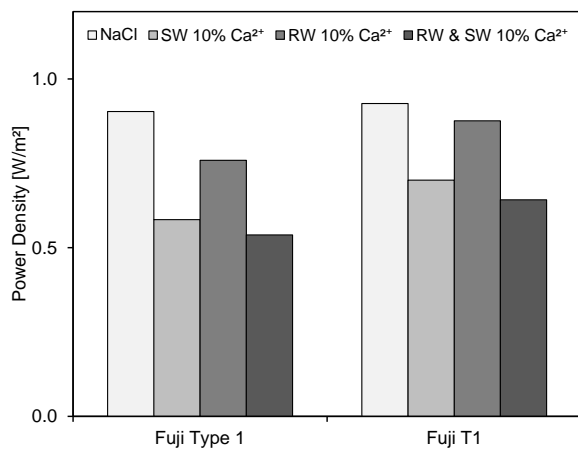


Figure S7.2. Net power densities with Ca<sup>2+</sup> in feed streams with Fuji Type I and T1 CEM. To obtain net power densities, 0.27 W/m<sup>2</sup> pumping losses need to be subtracted.

## S8. Theoretical and experimental absolute OCV values

In table S8.1 the absolute values of table 1 are given. The theoretical values are calculated (Eq 1) based on feed concentrations (see S2) and permselectivity data (see S4). Experimental values are around 90% of theoretical values, this decrease is due to concentration differences over the stack length due to co-ion leakage which decrease the effective concentration gradient and thus OCV.

Table S8.1. Solutions used in studies and the theoretical and experimental OCV per cell pair [V/cp]. Experimental values are triplicate measurements and typical errors are  $\pm 0.002$  V/cp due to concentration and temperature fluctuations.

Na <sup>+</sup>	10% Mg <sup>2+</sup>	uphill	Rel. theory [-]	CMH-PES		CMS		T1		Type I	
				Theory [V/cp]	Exp [V/cp]	theory [V/cp]	exp [V/cp]	theory [V/cp]	exp [V/cp]	theory [V/cp]	exp [V/cp]
SW & RW	-	N	1.00	0.143	0.121	0.146	0.135	0.144	0.136	0.145	0.136
RW	SW	N	1.00	0.143	0.123	0.146	0.133	0.144	0.132	0.145	0.130
SW	RW	Y	1.00	0.143	0.105	0.146	0.134	0.145	0.131	0.145	0.131
			0.97	0.138		0.141		0.140		0.141	
	SW & RW	Y	1.00	0.143	0.107	0.146	0.134	0.144	0.124	0.145	0.125
			0.97	0.138		0.141		0.140		0.140	

## References

1. Güler, E.; Elizen, R.; Vermaas, D. A.; Saakes, M.; Nijmeijer, K., Performance-determining membrane properties in reverse electrodialysis. *Journal of Membrane Science* **2013**, *446*, 266-276.
2. Lee, J.-Y.; Kim, J.-H.; Lee, J.-H.; Kim, S.; Moon, S.-H., Morphologically Aligned Cation-Exchange Membranes by a Pulsed Electric Field for Reverse Electrodialysis. *Environmental Science & Technology* **2015**, *49*, (14), 8872-8877.
3. Długolecki, P.; Nijmeijer, K.; Metz, S.; Wessling, M., Current status of ion exchange membranes for power generation from salinity gradients. *Journal of Membrane Science* **2008**, *319*, (1-2), 214-222.
4. Tuan, L. X.; Mertens, D.; Buess-Herman, C., The two-phase model of structure microheterogeneity revisited by the study of the CMS cation exchange membrane. *Desalination* **2009**, *240*, (1-3), 351-357.
5. Dammak, L.; Lteif, R.; Bulvestre, G.; Pourcelly, G.; Auclair, B., Determination of the diffusion coefficients of ions in cation-exchange membranes, supposed to be homogeneous, from the electrical membrane conductivity and the equilibrium quantity of absorbed electrolyte. *Electrochimica Acta* **2001**, *47*, (3), 451-457.
6. Miyoshi, H.; Chubachi, M.; Yamagami, M.; Kataoka, T., Characteristic coefficients for equilibrium between solution and Neosepta or Selemion cation exchange membranes. *Journal of Chemical & Engineering Data* **1992**, *37*, (1), 120-124.
7. Miyoshi, H.; Yamagami, M.; Chubachi, M.; Kataoka, T., Characteristic Coefficients of Cation-Exchange Membranes for Bivalent Cations in Equilibrium between the Membrane and Solution. *Journal of Chemical & Engineering Data* **1994**, *39*, (3), 595-598.
8. Hannachi, C.; Hamrouni, B.; Dhahbi, M., Ion exchange equilibrium between cation exchange membranes and aqueous solutions of  $K^+/Na^+$ ,  $K^+/Ca^{2+}$ , and  $Na^+/Ca^{2+}$ . *Ionics* **2008**, *15*, (4), 445-451.