# Mitigation of the effects of multivalent ion transport in reverse electrodialysis

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## ABSTRACT

Reverse electrodialysis (RED) is a sustainable method to harvest energy using the salinity gradient between fresh and seawater. RED technology is developing but efficiencies are still limited when using natural feed water sources. One significant constraint is induced by the presence of multivalent ions in sea and river water (i.e. $Mg^{2+}$, $Ca^{2+}$, $SO_4^{2-}$). Uphill transport and an increase in membrane resistance in the presence of magnesium ions significantly reduce the power density output obtainable. The choice of cation exchange membrane determines the magnesium transport and as such the power density. Here we investigate four cation exchange membrane types and relate their properties to the stack performance using three different magnesium concentrations on either river and/or seawater side: 1) a highly cross-linked styrene-divinyl benzene monovalent selective cation exchange membrane (Neosepta CMS); 2) a monovalent selective cation exchange membrane that contains a thin polyethyleneimine (PEI) anion exchange layer (Selemion CSO); 3) a multivalent ion (e.g. magnesium) permeable cation exchange membrane with an engineered molecularly open structure facilitating the transport of multivalent ions as recently developed (T1 Fujifilm); 4) a standard cation exchange membrane (Type I Fujifilm (reference)). The first two membranes both retain magnesium ions, while the other two membranes are considered permeable for magnesium ions.

The results show that power density strongly depends on the composition of both river and seawater. Power density decreases in the presence of magnesium, an effect being strongest with magnesium at both river and seawater side, followed by the river water side and the seawater side. The negative effect of multivalent ion transport against the concentration gradient, so called uphill transport, in RED can be significantly minimized when monovalent selective membranes such as the highly cross-linked Neosepta CMS membrane or the AEM coated Selemion CSO membrane are used. However, the use of such membranes directly results in a strong increase in membrane resistance due to the lower ion mobility of magnesium ions inside these membranes. As a consequence, power densities in RED are not improved. Especially at high magnesium concentrations, this effect is very strong at higher concentrations, the membranes are no longer able to retain magnesium ions effectively.

More beneficial is the application of multivalent permeable membranes with a more 'open' structure that allow the free movement of both sodium and magnesium ions through the membrane. Maybe somewhat counter intuitively, such membranes (especially the Fujifilm multivalent permeable T1 membrane) have low resistance values combined with reasonable OCV values leading to high power densities under almost all magnesium concentrations, especially at long term applications. Highest power densities well exceeding 0.3 W/m² are still obtained when only sodium is present. However, when magnesium ions are present power densities in the order of 0.2–0.25 W/m² can still be obtained for these membranes.

## 1. Introduction

Reverse electrodialysis (RED) is a sustainable method to harvest energy using the salinity gradient between fresh and sea water [1–3]. Ion exchange membranes (IEMs) separate the concentrated salt solution (sea water) from the diluted salt solution (river water) in RED. Anion exchange membranes (AEMs) are alternated with cation exchange membranes (CEMs) and river and seawater flow alternatively on either side of the membranes. The chemical potential difference created across the membranes is the driving force for this process: ions permeate through the membranes in accordance with their charge. At the electrodes, the ionic current is converted into an electrical current through

redox reactions generating electricity when closing the external electric circuit. Ion exchange membranes are non-porous dense structures, composed of a polymer matrix containing ionic groups, either negatively charged (CEMs) or positively charged (AEMs). Ion exchange membranes transport ions with the opposite charge as the membrane charge, the so-called counter ion transport. So cation exchange membranes are negatively charged and transport cations (e.g. $Na^+$, $Mg^{2+}$, $Ca^{2+}$), while anion exchange membranes are positively charged and transport anions (e.g. $Cl^-$, $SO_4^{2-}$). CEMs normally contain sulfonic or carboxylic acid groups, whereas AEMs contain quaternary amine groups. As the membranes are never 100% selective, also limited transport of ions with the same charge as the membrane occurs, the so-called co-ion transport. The ratio of the amount of charge transported by the counter-ions and by the co-ions is called the membrane permselectivity.

RED technology is developing but energy efficiencies are still limited when using natural feed water sources [4]. One significant constraint is due to the presence of multivalent ions in sea and river water (i.e. $Mg^{2+}$, $Ca^{2+}$, $SO_4^{2-}$). The presence of these multivalent ions in river water causes uphill ion transport in IEMs [5,6]. Uphill transport refers to the process of ion transport in the direction opposite to the concentration gradient, i.e. from low to high concentration (Fig. 1).

In uphill transport, counter-ions are transported in both directions until the electromotive forces of the ionic species are balanced (equilibrium) and a net flux of electrical charges no longer exists. Donnan dialysis uses uphill ion transport phenomena as driving force of the process [7]. In the system under study, using artificial river and sea water, 2 $Na^+$ ions (downhill transport in the direction of the concentration gradient) are exchanged by 1 $Mg^{2+}$ or 1 $Ca^{2+}$ ion (uphill transport opposite the direction of the concentration gradient). In RED, uphill transport leads to significant energy efficiency losses. Vermaas et al. [6] reported a loss in power density up to 50% at laboratory scale using standard membranes and synthetic feed waters containing 10% $MgSO_4$ in a RED stack. This power density loss was basically attributed to a loss in OCV and barely to an increase in electrical resistance of the membrane. Post et al. [5] studied the RED stack voltage response, the electrical resistance and the effluent ionic concentration when multivalent ions are present. Post et al. [5] concluded that monovalent ion selective membranes could be a good alternative for reverse electrodialysis and particularly if high multivalent ion concentrations are present in the diluted side. However, the improvement on power density might not be as high as expected, due to a loss in monovalent permselectivity and increase on stack resistance in time.

Uphill ion transport causes a reduction in the stack voltage, but also an increase in membrane electrical resistance due to lower diffusion coefficients of $Mg^{2+}$ and $SO_4^{2-}$ compared to $Na^+$ and $Cl^-$. Also multivalent ions get bonded to ion exchange groups inside the membrane.

Therefore, a significant decrease in the obtained power density is observed [8]. The influence of multivalent ions on IEMs has been reported to be more significant in CEMs than in AEMs due to the larger voltage drop [6].

Recently the research on membrane development to minimize the effect of multivalent ions in RED by modifying ion selective membranes has intensified. For instance Güler et al. [9] increased the monovalent ion selectivity through the formation of a highly cross-linked CEM layer on top of an AEM by photo-polymerization (UV). Monovalent ion selectivity was improved by implementing a CEM layer on the top of an AEM, in order to increase the electrostatic repulsion between multivalent ions and membrane surface charge. Higher gross power density was not obtained, however, an improvement on antifouling properties was achieved. Rijnaarts et al. [10] presented a new strategy to overcome the unwanted effects of multivalent ions in RED, by ordering the CEM negative charged groups and providing pathways for ion transport. This so-called multivalent ion permeable membrane has a low membrane electrical resistance and binding of multivalent ions to the charged groups of the membrane was reduced [11]. As a continuation of this research, we here investigate and compare systematically three different membrane strategies to mitigate the effect of multivalent ions in RED (Fig. 2).

The first strategy relies on the use of a highly cross-linked CEM that blocks the transport of multivalent ions and allows the transport of monovalent ions only. Such a membrane acts as an ion sieve when differences in hydrated ionic radii are present [6]. The effective membrane pore size (i.e. membrane ion pathaway) decreases with increasing cross-linker agent concentration (i.e. phenol, divinylbenzene) and so the permeation of multivalent ions decreases. This increase in cross-links increases the permselectivity for monovalent ions over multivalent ions. However, electrical resistance and concentration polarization increase with the content of cross-linker.

The second strategy relies on the application of an oppositely charged top layer on the membrane surface (i.e. a layer with a charge opposite to the membrane charge). Sata et al. [12,13] investigated this strategy by forming a cationic charged layer on the CEM surface to increase the electrostatic repulsion of multivalent ions. A layer of polyethyleneimine (PEI) was formed by acid-amide bonding or adsorption (ion exchange or monolayer adsorption) and creates multivalent ion rejection due to the higher charge density of the multivalent ions. The third, novel strategy, is a multivalent ion permeable membrane i.e. no rejection towards multivalent ions but facilitation of multivalent transport. This approach has only recently been developed especially for application in RED [10]. Till now, almost all IEM membranes used in RED were designed or optimized for other applications (such as desalination or electrodialysis (salt production or acid recovery)). The multivalent ion permeable membrane is an IEM intentionally designed to overcome the challenges of using real feed waters in RED. For this purpose, the membrane is designed such that multivalent ion transport across the membrane is facilitated by fabricating a membrane with a more open structure not increasing the electrical membrane resistance when multivalent ions are transported.

The effect of these three approaches on open circuit voltage, stack resistance and RED power density are investigated. All data are compared to the reference case using a standard CEM. Also, to provide insight in the mass transport mechanisms and consequences of the presence of multivalent ions, measurements were performed with NaCl solutions only on both river and seawater side, 1) with $MgCl_2$ on both sides; 2) with $MgCl_2$ on the river water side and NaCl on the sea water side and 3) with $MgCl_2$ on the seawater side and NaCl on the river water side. $MgCl_2$ concentrations of 10%, 25% and 50% were used in all cases. Additionally, for the 25% $MgCl_2$ case the mass transfer of sodium ions and magnesium ions is monitored in time to unravel the ion transport directions.



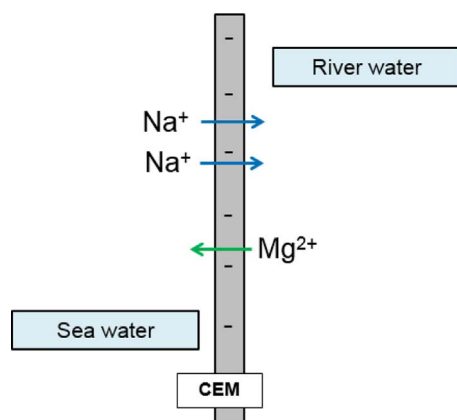**Fig. 1.** Uphill transport of one multivalent $Mg^{2+}$ ion to replace two monovalent $Na^+$ ions in a cation exchange membrane.