Supporting information

Doubled power density from salinity gradients at reduced inter-membrane distance

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Appendix A: Experimental setup

The RED stack was comprised of 5 CEMs and 5 AEMs. Additionally, at the end of the stack next the electrode, one additional CEM was used as shielding membrane to close the last compartment. Two Ti mesh 1.0 electrodes coated with Ir/Ru and an area of 10x10 cm^2 (Magneto Special Anodes BV, The Netherlands) were used as the anode and the cathode. Figure S1 shows the configuration of the RED stack. The resistance of the electrodes, its corresponding compartments and the last shielding membrane was measured and used a correction for all measurements.
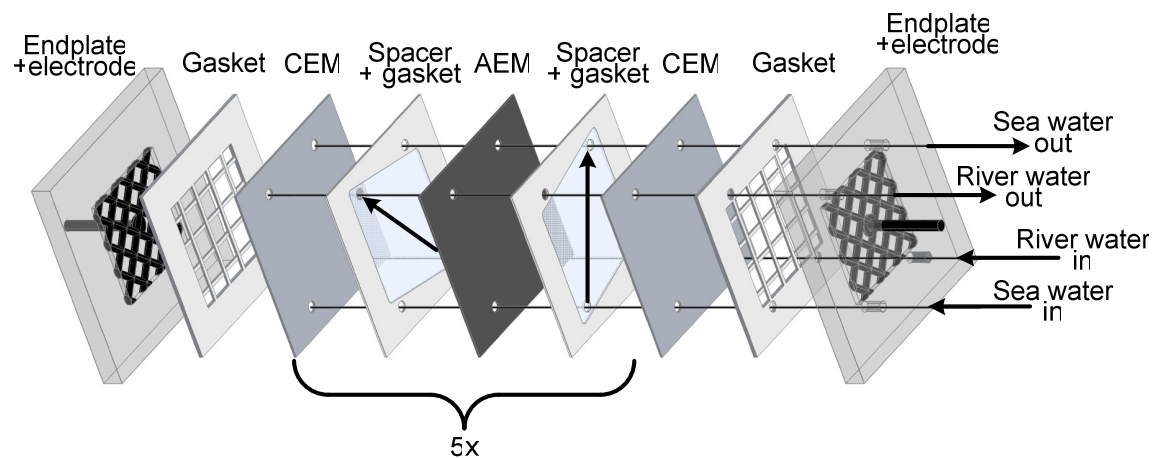

Figure S1: Configuration of the RED stack.

The river water and sea water compartments were fed by inlets at the right bottom and left bottom respectively. A drawing of the compartment shape is given in previous work (4). A gasket made of silicone rubber (Special Silicone Fabricators, USA), with a thickness equivalent to the spacer thickness, was used to seal all compartments. The stack was closed with plates of PMMA (poly(methyl methacrylate)) and 8 bolts, all tightened with a torque key at 2 N.m.

Artificial sea and river water was prepared by dissolving NaCl (technical grade, 99.5% purity, ESCO, The Netherlands) in demineralized water. The concentration NaCl in the sea water was 0.507 M (30.0 g NaCl per kg water) and the concentration NaCl in the river water was 0.017 M (1.00 g NaCl per kg water). The water was stored at 25 ($\pm$1) ℃.

The feed waters were pumped through the stack by using peristaltic pumps (Cole-Parmer, Masterflex L/S Digital drive, USA) at 10 different flow rates between 0.017 and 4.17 cm^3/s. The pressure drop between inflow and outflow of both feed waters was measured by a differential pressure meter (Endress+Hauser Deltabar S, Germany). A pressure meter with a range of 0-500 mbar was used for the inter-membrane distance of 200 and 485 μm, whereas a pressure meter with a range of 0-3000 mbar was used for the inter-membrane distance of 60 and 100 μm.

The electrode rinse solution was made from 0.025 M $K_3Fe(CN)_6$, 0.025 M $K_4Fe(CN)_6$ and 0.25 M NaCl in demineralized water. This solution was circulated at ca. 2 cm/s along the electrodes and stored in a bottle at 25 ($\pm$0.1) ℃. The RED stack was located in an isolated chamber (Friocell, Germany), which was kept at 25 ($\pm$0.1) ℃.

The internal resistance (R_i) and the ohmic resistance (R_{ohmic}) of the RED stack were determined using chronopotentiometry. A fixed current density was set, in steps of 0, 2.5, 5 … 65 A/m^2, and applied for at least 60 seconds till a constant value was reached by using a potentiostat (Ivium Technologies, The Netherlands). The sampling interval time was 4 ms. For low flow rates, it took up to 1200 seconds for the voltage to equilibrate. In between every step, the current was interrupted. The sudden jump in voltage when the current is interrupted reveals the ohmic resistance, whereas the remaining change in voltage is attributed to the non-ohmic resistances. Figure S2 shows a typical example of such a measurement series. Because R_i and R_{ohmic} can be determined from the chronopotentiometric measurements, and $R_{\Delta C}$ can be calculated, the remaining contribution can be attributed to R_{BL}.

$$R = \frac{\Delta U}{\Delta I}$$

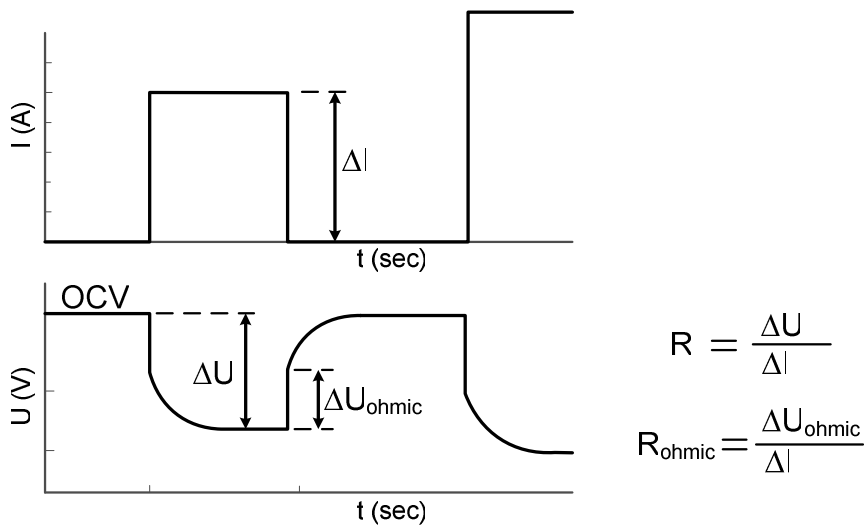$$R_{ohmic} = \frac{\Delta U_{ohmic}}{\Delta I}$$

Figure S2: Typical example of chronopotentiometric measurement series, showing the current in the upper graph and the corresponding voltage obtained from the stack in the lower graph as a function of the measurement time.

Appendix B: Derivation of $R_{\Delta C}$

The contribution of $R_{\Delta C}$ can be estimated from theory. The derivation of eq 1 as given in the research paper is presented here.

The salt concentrations at the inflow of sea water and river water are defined as c_s and c_r, respectively. The concentration at the outflow, when ions are exchanged under influence of a direct current (assuming no leakage), can be calculated by:

$$c_{s,out} = c_s - \frac{J \cdot L}{F \cdot q_s} \tag{S1a}$$

$$c_{r,out} = c_r + \frac{J \cdot L}{F \cdot q_r} \tag{S1b}$$

In which J is the current density (A/m^2), L is the cell length (m) and q is the flow rate per cell per unit width (m^2/s).

The theoretical value for the electromotive force is dependent on the concentrations on either side of the membrane, as described by the Nernst equation (e.g. (13)). Considering membranes with an average apparent permselectivity α (-), as defined by e.g. (13), and using monovalent ion species, the electromotive force E per cell can be calculated by:

$$E = 2 \cdot \frac{\alpha \cdot R \cdot T}{F} \cdot \ln\left(\frac{c_s \cdot \gamma_s}{c_r \cdot \gamma_r}\right) \tag{S2}$$

In which R is the universal gas constant (8.314 J/(mol·K)), T is the temperature (K), F is the Faraday constant (96485 C/mol), c is the concentration (mol/L) and γ represents the

activity coefficient (-).The subscripts s and r refer to sea water and river water, respectively.

The feed water in the stack has a concentration in between the extreme concentrations at the inflow and outflow. Hence the local electromotive force over the membranes varies spatially. The effective electromotive force is an average value of this spatially varying field. The highest value for the electromotive force is based on the inflow concentrations. If the outflow concentrations from eq S1a and S1b are considered, the electromotive force is lower. As a rough estimate, the average electromotive force is approximated by the average of these two extreme values. This average electromotive force per cell is given by:

$$
\begin{aligned}
E_{average} &= 2\frac{\alpha \cdot R \cdot T}{F} \cdot \frac{1}{2} \cdot \left[\ln\left(\frac{\gamma_s \cdot c_s}{\gamma_r \cdot c_r}\right) + \ln\left(\frac{\gamma_s}{\gamma_r} \cdot \frac{c_s - \dfrac{J \cdot L}{F \cdot q_s}}{c_r + \dfrac{J \cdot L}{F \cdot q_r}}\right) \right] \\
&= 2\frac{\alpha \cdot R \cdot T}{F} \cdot \frac{1}{2} \cdot \ln\left(\frac{\gamma_s^{\,2} \cdot c_s^{\,2}}{\gamma_r^{\,2} \cdot c_r^{\,2}} \cdot \frac{1 - \dfrac{J \cdot L}{F \cdot q_s \cdot c_s}}{1 + \dfrac{J \cdot L}{F \cdot q_r \cdot c_r}}\right) &\text{(S3)} \\
&= 2\frac{\alpha \cdot R \cdot T}{F} \cdot \ln\left(\frac{\gamma_s \cdot c_s}{\gamma_r \cdot c_r} \cdot \frac{\sqrt{1 - \dfrac{J \cdot L}{F \cdot q_s \cdot c_s}}}{\sqrt{1 + \dfrac{J \cdot L}{F \cdot q_r \cdot c_r}}}\right)
\end{aligned}
$$

This approach neglects changes in the activity coefficient within a compartment and assumes a linear decrease in electromotive force from the inflow to outflow of feed waters. These assumptions are reasonable for small changes in concentration between the inflow and outflow.

The area resistance ($\Omega \cdot m^2$) per cell due to the change in bulk concentrations can be calculated according to:

$$R_{\Delta C} = \frac{E - E_{average}}{J} \tag{S4}$$

Substitution of eq S2 and eq S3 in eq S4 subsequently yields:

$$
\begin{aligned}
R_{\Delta C} &= 2\frac{\alpha \cdot R \cdot T}{F \cdot J} \cdot \left[\ln\left(\frac{\gamma_s \cdot c_s}{\gamma_r \cdot c_r}\right) - \ln\left(\frac{\gamma_s \cdot c_s}{\gamma_r \cdot c_r} \cdot \frac{\sqrt{1 - \frac{J \cdot L}{F \cdot q_s \cdot c_s}}}{\sqrt{1 + \frac{J \cdot L}{F \cdot q_r \cdot c_r}}}\right) \right] \\
&= 2\frac{\alpha \cdot R \cdot T}{F \cdot J} \cdot \ln\left(\sqrt{\frac{1 + \frac{J \cdot L}{F \cdot q_r \cdot c_r}}{1 - \frac{J \cdot L}{F \cdot q_s \cdot c_s}}} \right) \\
&= \frac{\alpha \cdot R \cdot T}{F \cdot J} \cdot \ln\left(\frac{1 + \frac{J \cdot L}{F \cdot q_r \cdot c_r}}{1 - \frac{J \cdot L}{F \cdot q_s \cdot c_s}} \right)
\end{aligned} \tag{S5}
$$

Or, in short:

$$R_{\Delta C} = \frac{\alpha \cdot R \cdot T}{F \cdot J} \cdot \ln\left(\frac{\Delta a_r}{\Delta a_s}\right) \tag{S6}$$

In which $\Delta a_r = 1 + \frac{J \cdot L}{F \cdot q_r \cdot c_r}$ and $\Delta a_s = 1 - \frac{J \cdot L}{F \cdot q_s \cdot c_s}$

This first order approach should be considered only as a rough estimate due to the assumptions made. For the current research, in which $R_{\Delta C}$ is estimated only as a rough indication and where no information is available about the local concentration gradients, this model satisfies.