



Experimentally obtainable energy from mixing river water, seawater or brines with reverse electrodialysis



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ABSTRACT

Energy is released when feed waters with different salinity mix. This energy can be captured in reverse electrodialysis (RED). This paper examines experimentally the effect of varying feed water concentrations on a RED system in terms of permselectivity of the membrane, energy efficiency, power density and electrical resistance. Salt concentrations ranging from 0.01 M to 5 M were used simultaneously in two stacks with identical specifications, providing an overview of potential applications. Results show a decrease of both permselectivity and energy efficiency with higher salt concentrations and higher gradients. Conversely, power density increases when higher gradients are used. The resistance contribution of concentration change in the bulk solution, spacers and the boundary layer is more significant for lower concentrations and gradients, while membrane resistance is dominant for high concentrations. Increasing temperature has a negative effect on permselectivity and energy efficiency, but is beneficial for power density. A power density of 6.7 W/m² is achieved using 0.01 M against 5 M at 60 °C. The results suggest that there is no single way to improve the performance of a RED system for all concentrations. Improvements are therefore subject to the specific priorities of the application and the salt concentration levels used. Regarding ion exchange membranes, higher salinity gradients would benefit most from a higher fixed charge density to reduce co-ion transport, while lower salinity gradients benefit from a thicker membrane to decrease the osmotic flux.

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1. Introduction

Salinity Gradient Power (SGP) refers to the renewable production of electricity, utilizing the energy generated by mixing two salt streams of different concentration. Several technologies have been developed to obtain electricity from mixing water streams with different salinity [1–7]. One of these technologies is reverse electrodialysis (RED). RED makes use of ion exchange membranes in a stack to capture the Gibbs energy released during mixing. Initial estimates of the theoretical SGP potential were calculated to be in the order of 1.4–2.7 TW [8,9]. Recently, the potential of SGP was

estimated as 983 GW [10,11] on a global scale by taking into account technical and physical limitations.

A RED stack comprises of a series of anion and cation exchange membranes, which form compartments of alternating concentrated and diluted salt water solutions respectively. Anion exchange membranes (AEM) are selective for anions, while cation exchange membranes (CEM) allow the transport of cations. The difference in concentration generates a transport of ions from the concentrated towards the diluted compartment which is controlled by the membranes. Cations are transported towards one side and anions towards the other, creating an ionic flux that can be converted at the electrodes, by using for example a reversible redox reaction, to power an electrical circuit.

Two indices are of key importance for electricity generation using RED, i.e. power density, meaning the power per membrane area (W/m²) and energy efficiency defined as the fraction of the potentially available energy from the salinity difference that is converted into electrical energy (%).

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Research regarding RED has mainly focused on the use of seawater and river water as a feed, due to the availability of large volumes of these water types. Efforts have mostly been focused on determining power density values [12–18], since this is a major indicator of technological progress and economic viability. Measured power densities up to 2.2 W/m² are reported by using artificial feed water solutions representative of seawater and river water [17].

Energy generation with RED from other combinations of feed water concentrations, for example using highly concentrated streams (brines) versus seawater or versus river water, has been considered earlier in literature [19–21]. The use of such feed waters has a practical application at locations where relatively fresh water flows naturally into a salt lake (e.g. Dead Sea or Great Salt Lake), or where brine streams are available from salt mining. The theoretical potential for energy generation from brine (5 M NaCl) versus river water (0.01 M NaCl) is approximately ten times larger than the energy that can be obtained from seawater (0.5 M NaCl) and river water [22]. However, to our best knowledge, no experimental data have been presented before for power density and energy efficiency achievable over the full range of possible concentrations. Power densities obtained with RED using solutions other than river and seawater are mostly estimated values [20,22–25], while only a few combinations have been actually evaluated [19,21] or the results do not include recent developments [26] in terms of membrane performance, hydraulic design and intermembrane distance.

In this paper we present, for the first time, an overview of experimentally determined power density and energy efficiency values over a wide spectrum of feed water concentrations that can be used in RED. The gained insight reveals how the process of reverse electrodialysis is affected by different concentrations in terms of membrane properties, stack resistances and system specifications, while possible paths for future improvements are highlighted. The experiments are based on a typical set of membranes, using a constant flow rate and the same stack specifications for all tests.

2. Theory

The amount of energy released after mixing two streams with a salinity difference (diluted and concentrated solutions) can be calculated based on the equation of the Gibbs energy of mixing [27]:

$$\Delta G_{\text{mix}} = \sum_i [c_{i,c} V_c R \cdot T \cdot \ln(x_{i,c}) + c_{i,d} V_d R \cdot T \cdot \ln(x_{i,d}) - c_{i,b} V_b R \cdot T \cdot \ln(x_{i,b})] \quad (1)$$

where c is the concentration (mol/m³) of species i , V is volume (m³), R is the gas constant (J/mol·K), T is the temperature (K), x is the molar fraction (–) and the subscripts are c for concentrated, d for diluted, b for brackish water.

The experimentally obtainable energy W (J) is calculated according to [27,28]:

$$W = \sum_{t_0}^{t_{\text{end}}} U \cdot I \cdot \Delta t_0 \quad (2)$$

where U is the voltage produced by the RED system (V), I is the current (A), Δt is the time interval (s) and t_0 and t_{end} are the moments the current is started and stopped respectively. The retrieved energy is therefore the product of the voltage obtained under a certain current density, the current density applied and the time during which the current density was applied and energy was

produced. Subsequently, the energy efficiency is calculated as the ratio between the actual energy W and the theoretical energy for an ideal process, derived from the Gibbs equation [22].

The actual energy efficiency is limited by the ohmic loss in the stack, the unused available energy in the effluent [29] and, in case of non-perfect membranes, transport of co-ions and water through the ion exchange membranes. Perfect membranes should only allow ions with opposite charge to pass. The Coulombic efficiency quantifies how much charge transport is used for electricity production and hence indicates the loss due to charge transport of co-ions. The Coulombic efficiency η_{CE} (–) is defined as:

$$\eta_{\text{CE}} = \frac{I}{\Delta c \cdot Q \cdot F} \quad (3)$$

in which Δc is the concentration difference between inflow and outflow of the feed water (mol/m³), Q is the volumetric feed water flow rate (m³/s) and F is the Faraday constant (96485 C/mol). Also an ionic short-cut current [30] reduces the Coulombic efficiency.

The voltage that is produced by the RED system when no current is allowed (open circuit voltage, OCV) is given by the Nernst equation, multiplied with the apparent permselectivity of the membranes, to correct for the non-ideal membrane behaviour (i.e. ion exchange membranes are not 100% selective for either anions nor cations, but allow the transport of the oppositely charged ion to some extent as well) [28]. This yields:

$$\text{OCV} = \alpha \frac{N_m \cdot R \cdot T}{z \cdot F} \ln \left(\frac{a_c}{a_d} \right) \quad (4)$$

in which α is the average apparent membrane permselectivity (–), which stands for the ratio between the obtained membrane voltage and the theoretical voltage, N_m is the total number of membranes, z is the valence of the ions (–), F is the Faraday constant (96485 C/mol) and a is the activity (effective concentration) of the concentrated (a_c) and diluted (a_d) solutions (mol/m³). The maximum obtainable power density can be derived from the OCV and the internal resistance of the RED system. Normalized for the membrane area, power densities are computed by Ref. [28]:

$$P = \frac{\text{OCV}^2}{4 \cdot R_i \cdot N_m} \quad (5)$$

in which R_i is the total electrical area resistance per stack ($\Omega \cdot \text{cm}^2$). The total resistance inside the stack can be split into three different parts according to [17,18]:

$$R_i = R_{\text{ohmic}} + R_{\Delta c} + R_{\text{BL}} \quad (6)$$

where R_{ohmic} is the ohmic area resistance per cell ($\Omega \cdot \text{cm}^2$), $R_{\Delta c}$ is the area resistance caused by the concentration change in the bulk solution ($\Omega \cdot \text{cm}^2$) and R_{BL} is the area resistance caused by the concentration change in the boundary layer ($\Omega \cdot \text{cm}^2$). The latter two non-ohmic resistances account for the reduced electromotive force, as the salinity gradient over the membrane reduces when an electrical current is drawn. The total internal resistance R_i and the ohmic resistance R_{ohmic} are derived from experimental data using the generated voltage, the electrical current and Ohms law.

The resistance $R_{\Delta c}$ is calculated based on [17,18]:

$$R_{\Delta c} = \frac{N_m}{2} \cdot \alpha \frac{R \cdot T \cdot A}{z \cdot F \cdot I} \ln \left(\frac{\Delta_d}{\Delta_c} \right) \quad (7)$$

in which A is the area of one membrane (m²), and $\Delta_d = 1 + (I/(F \cdot Q_d \cdot c_d))$, $\Delta_c = 1 - (I/(F \cdot Q_c \cdot c_c))$, in which Q is the volumetric flow rate per cell (m³/s). The equation uses the average salt

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