Blue Energy: The effect of monovalent ion selectivity in membranes on salinity gradient energy generation

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Introduction

- Salinity gradient power is a clean source of "blue energy."
- Reverse electrodialysis uses ion movement across membranes to generate voltage and power.
- Ion-exchange membrane performance depends on how efficiently ions pass through the membrane.
- This study focuses on chloride ion (Cl^-) transport through an anion-exchange membrane.
- Key parameters studied include diffusion coefficient, separation efficiency, and transport number.
- The results provide baseline data for understanding monovalent ion transfer.
- This helps support the development of better membranes for blue energy generation.

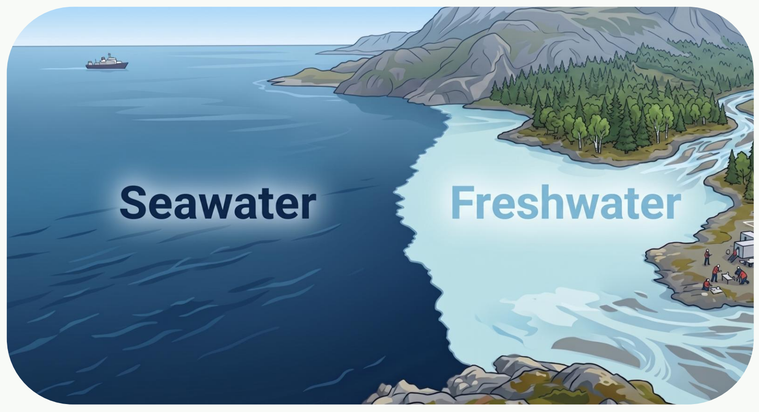

Figure 1. Illustration of the salinity gradient between seawater (high salinity) and freshwater (low salinity), which drives ion transport in processes like reverse electrodialysis.

Literature

- **RED potential:** Salinity gradient energy has been estimated to have a theoretical worldwide potential of approximately 2.6 TW when all river water resources are assumed to be accessible. When technical and physical limitations are included, this potential is reduced to about 983 GW.
- **Renewable energy value:** Salinity gradient energy has been reported to be significantly larger than tidal energy and comparable to wave energy, making it an important marine renewable energy source.
- **Technology development:** Reverse electrodialysis has been identified as one of the main technologies for converting salinity gradient energy into electricity, and it has already been tested at pilot scale.
- **Commercial limitation:** Although pilot-scale results have been obtained, RED has not yet reached full commercialization because several technical barriers still need to be overcome.
- **Membrane performance:** The efficiency of RED is mainly controlled by ion-exchange membrane properties, especially low membrane resistance, high permselectivity, and effective counter-ion transport.
- **Multivalent ion effect:** The presence of multivalent ions, such as Mg^{2+}, Ca^{2+}, and SO_4^{2-}, has been shown to reduce RED performance by lowering power generation and increasing ion transport losses.
- **Monovalent selectivity:** Monovalent ion-selective membranes are therefore required to promote the transport of ions such as Cl^- while limiting the negative effects of multivalent ions.
- **Selectivity mechanisms:** Monovalent ion selectivity can be achieved through electrostatic repulsion, size exclusion, hydration effects, membrane mobility differences, and surface modification.

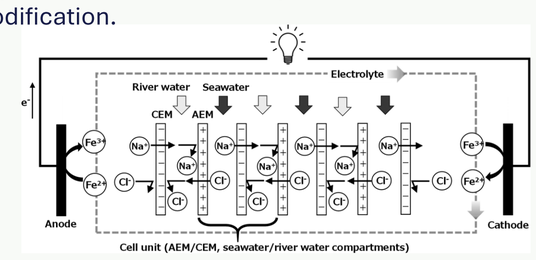

Figure 2. Schematic illustration of RED stack with three cell pairs

Experimental Method

A two-compartment diffusion cell was used to evaluate the ion transport behaviour of the Fumasep® FAA-3-PK-75 anion exchange membrane. The membrane, with an effective diameter of 2.6 cm (corresponding to an exposed surface area of 5.31 cm^2), was mounted between the two compartments of the cell, separating them completely.
One compartment was filled with 300 mL of 0.1 M NaCl solution to serve as the feed, while the opposite compartment was filled with 300 mL of deionized water to act as the receiver. To ensure homogeneous concentration distribution and to minimise concentration polarisation at the membrane surfaces, both compartments were continuously stirred using magnetic stirrers throughout the experiment.
Conductivity readings were recorded at 30-minute intervals over a total experimental duration of 180 minutes, allowing sufficient time for measurable ion transport across the membrane to be detected. The temperature of the solutions was monitored at each sampling point, and all measurements were performed under ambient laboratory conditions.

Equipment Used

- Two-compartment diffusion cell
- Fumasep® FAA-3-PK-75 anion exchange membrane (75 µm, 2.6 cm exposed diameter)
- Magnetic stirrer (×2)
- Conductivity meter with probe (has embedded thermometer)



Figure 3. Fumasep® FAA-3-PK-75 anion exchange membrane immersed in 0.1 M NaCl solution during the pretreatment step, used to hydrate the membrane and convert it into the chloride form prior to the diffusion experiment.

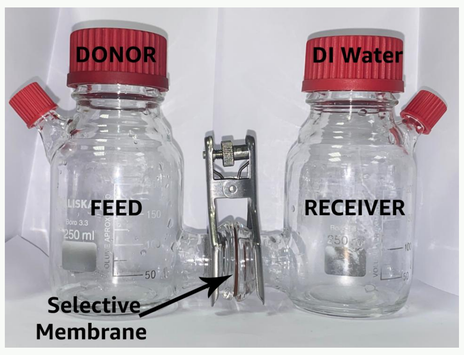

Figure 4. Two-compartment diffusion cell setup consisting of a donor (feed) and receiver (DI water) chamber separated by a selective membrane, used to study ion transport across ion-exchange membranes.

Results

Raw Experimental Data

Time (min)	Receiver σ (µS/cm)	Feed σ (µS/cm)	Temperature (°C)	C_n (mol/L)
0	0	9880	16.0	0
30	26	9880	17.8	2.65×10^{-4}
60	26	9710	19.1	2.65×10^{-4}
90	40.5	9710	19.1	4.13×10^{-4}
120	42.6	9700	19.1	4.35×10^{-4}
150	58	9700	21.1	5.92×10^{-4}
180	60	9690	21.1	6.12×10^{-4}

- The deionized water initially had very low conductivity because it contained very few ions.
- A concentration gradient existed between the 0.1 M NaCl solution and the deionized water.
- Chloride ions gradually moved through the anion-exchange membrane toward the dilute side.
- The increase in conductivity shows that ions were accumulating in the deionized water compartment.
- The table therefore confirms a slow but steady ion transfer through the membrane.

Kohlrausch's Law of Independent Migration of Ions

$$C\ (\text{mol/L}) = \frac{\sigma\ (\mu\text{S/cm})}{98,000} \quad \text{at 20°C}$$

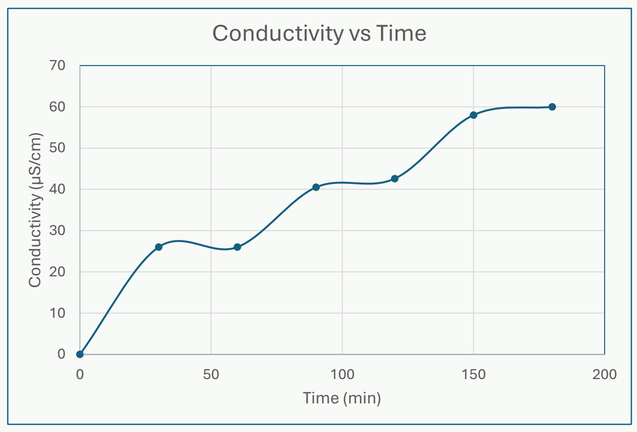

Figure 5. Conductivity over time

Diffusion Coefficient (D_i)

Fick's First Law under pseudo-steady-state conditions.

Step 1 — Calculate molar flux (J_i):

$$J_i = \frac{(\Delta C_n \times V)}{(A \times \Delta t)}$$

$$J_i = \frac{0.18367}{57{,}315.6} \quad J_i = \frac{(6.122 \times 10^{-4}\ mol/L \times 0.300\ L)}{(5.307\ cm^2 \times 10{,}800\ s)}$$

$$\mathbf{J_i = 3.204 \times 10^{-6}\ mol\ cm^{-2} s^{-1}}$$

Step 2 — Calculate diffusion coefficient (D_i):

$$D_i = \frac{(J_i \times \delta)}{\Delta C}$$

$$D_i = \frac{(3.204 \times 10^{-6} \times 7.5 \times 10^{-3})}{(1.0 \times 10^{-4})}$$

$$\boldsymbol{D_i = 2.40 \times 10^{-7}\ cm^2/s = 2.40 \times 10^{-11}\ m^2/s}$$

Separation Efficiency (S)

$$S(\%) = \frac{1 - C_{feed}}{C_{receiver}} \times 100$$

Transfer Efficiency (S)

$$\eta_{transfer} = \frac{C_{feed}}{C_{receiver}} \times 100\%$$

C_n (mmol/L)	C_{feed} (mmol/L)	S (%)	$\eta_{transfer}$
0.265	100.82	99.74	0.00%
0.265	98.98	99.73	0.27%
0.413	98.98	99.58	0.42%
0.435	98.98	99.56	0.44%
0.592	98.98	99.40	0.60%
0.612	98.98	99.39	0.62%

Conclusion

- Cl^- transfer through the Fumasep® FAA-3-PK-75 membrane was characterized under zero-current conditions.
- The membrane showed selective anion transport, allowing Cl^- movement while limiting Na^+ co-ion transport.
- The measured diffusion coefficient was 2.40×10^{-11} m^2/s, indicating slow and steady diffusion driven by the concentration gradient.
- The results confirm that concentration-driven ion transfer can be effectively studied using this membrane.
- The membrane provides a useful baseline for future RED and blue energy studies using more complex salt solutions.
- The gradual increase in conductivity on the dilute side confirmed that ion transfer occurred progressively through the membrane.

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