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Blue energy harvesting and divalent ions: Capacitive Reverse Electrodialysis cell with a single membrane opens a gateway to new applications

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ABSTRACT

A considerable disparity persists between lab-scale studies and the industrial application in the study of Reverse Electrodialysis (RED). A notable distinction arises in the choice of feed solutions. While earlier researches report the power density performances of RED systems fed by ideal artificial solutions predominantly composed of monovalent ions such as NaCl or KCl, real-world applications necessitate the use of complex solutions featuring a mix of multivalent ions. Prior investigations indicate a pronounced decline in electrical potential and power density in RED systems when operated with solution mixed with divalent ions. This study specifically explores the impact of divalent ion mixing on capacitive RED systems. Our findings reveal a membrane voltage drop attributable to the uphill effect, mirroring outcomes observed in similar studies. However, the consistent contribution of capacitive electrodes, constituting 50% of the total voltage, remains unaltered. During the operational cycle involving periodic water chamber switches, the accumulation of cations within the ion exchange membrane remains minimal. Consequently, the decrease in voltage and the associated decline in power density stemming from divalent ion mixing are comparatively modest, suggesting a minor ion trapping and fouling problem in this case. Furthermore, a comprehensive examination of the system’s long-term performance spanning 500 minutes affirms the sustained stability of its energy efficiency. Our findings have important implications on the valorization of salinity gradients in industrial operations.

Please note: Abbreviations should be introduced at the first mention in the main text – no abbreviations lists. Suggested structure of main text (not enforced) is provided below.

Introduction

In the face of global environmental challenges and the looming threat of persistent climate change, there is a growing demand for a decisive shift towards alternative and sustainable energy sources to mitigate these issues. Despite the impressive progress of solar and wind energy, the diversification of renewable energy resources remains a complex objective. In this context, the exploitation of blue energy generated by the mixing of solutions with varying salinities presents a promising avenue for exploration.

Considering factors such as viability, sustainability, and reliability, the potential of blue energy is estimated to generate more than 600 TWh/year, which equivalent to approximately 2.5% of the global electricity consumption in 2021. Introduced by Pattle in the early 1950s, developed as an energy production method by Loeb, RED stands out as one of the most promising methods for harnessing blue energy.

RED devices capitalize on the Donnan potential difference across ion exchange membranes positioned between solutions of differing salinities. This osmotic phenomenon propels ions to migrate from concentrated to diluted solutions. By leveraging selective membranes, an ionic flux is established. In a standard RED setup, the conversion of this ionic flux into electronic flux is achieved through Faradaic electrodes that undergo redox reactions.

To enhance cost-effectiveness, Vermaas et al. suggested the integration of capacitive electrodes within reverse electrodialysis systems (CRED). Carbon-based capacitive electrodes eliminate overpotential losses associated with Faradaic electrodes, and they also prove to be more economically viable than conventional Faradaic systems. This substitution obviates oxidation-reduction reactions at the electrodes, yielding a more ecologically friendly and economical approach. Following this approach, Zhu et al. pioneered the development of capacitive concentration cells employing a single selective membrane. Remarkably, they achieved an average power density of 0.95 W.m$^{-2}$ for salinity levels of 0.017 M and 0.513 M in fresh water and salt water, respectively. These results stand in stark contrast to the performance of Capmixing devices (producing less than 400 mW.m$^{-2}$), and they are comparable to outcomes from RED experiments involving the same salinity gradients. In a
similar vein, we have pursued an analogous approach, devising a novel cell configuration comprised of a solitary selective membrane and two cost-effective capacitive electrodes\(^{26}\). This design yielded a net power density output of 2 W.m\(^{-2}\), achieved with a salinity ratio of 300 (0.017 M and 5.13 M).

Nevertheless, the majority of these studies have been conducted using artificial seawater and freshwater with a predominant presence of NaCl. The use of real-world feed waters (sea water and river water) can lead to different results. When dealing with natural feedwaters in systems like Reverse Electrodialysis (RED), the power output is significantly lower than with artificial solutions due to impurities such as organic particles, clay particles, micro-organisms that may plug the membrane. Beyond those problems in the absence of filtration\(^{27}\), the presence of divalent ions seems to affect the behavior of energy recovery devices. The inclusion of multivalent ions, particularly Mg\(^{2+}\) and Ca\(^{2+}\), has an adverse impact on osmotic energy production efficiency. For example, Post et al.\(^{28}\) observed that the introduction of MgSO\(_4\) into the diluted stream led to a reduction in stack voltage compared to using NaCl alone in the feed. Vermaas et al.\(^{29}\) identified a detrimental effect of multivalent ions on RED performance in real-world feed waters. When using a mixture with a molar fraction of 10% MgSO\(_4\) and 90% of NaCl in both feed waters, the experimentally obtained power density in steady state decreases up to 50% compared to the case where the feed solutions contain only NaCl as a salt. Multivalent ions negatively impact the membrane in RED systems in several ways: they increase membrane resistance, reduce permselectivity, and lead to uphill transport, where ions move against their concentration gradient, causing a loss of power output. Long-term issues arise as multivalent ions become trapped in the membrane, neutralizing fixed charges and reducing ion exchange capacity and permselectivity, ultimately diminishing the system’s efficiency.

The compromised performance in the presence of multi-ionic solutions severely limits the range of application of RED. Multiple industrial processes involve mixing of salinity gradients, such as production water, desalination plants, salt mining, to name a few. However, these applications typically involve high salinity brine, of complex composition, and significant presence of divalent ions, in particular calcium and magnesium divalent cations\(^{30}\). Development of efficient and economically viable technology for partial recovery of osmotic energy in such "harsh" conditions could potentially be a game changer for energy balance and carbon footprint of industrial processes.

In this work, we aim to understand how the presence of divalent ions affects the electrical power recovered in single-membrane systems with capacitive electrodes. We start by recalling the working principle of such device. To address the question, we measure cell potentials, membrane potentials, open-circuit electrode potentials, and cell impedance as a function of monovalent ions concentrations and mixture of monovalent and divalent ions. Maximum recoverable powers are then measured and compared with literature results. We focus on two types of measurements: first, we study the power recovered at short times (i.e. when the membrane is soaking in the electrolyte for less than 1 hour), then we carry out long-time cycling (i.e. over 10 hours). Application cases with real-life solutions are presented.

### Results

#### 0.1 Working principle of a capacitive cell with a single membrane

The general principle of the capacitive salinity-gradient cell with a single membrane is illustrated in Figure 6 (Cell preparation, see Methods). A cationic ion-exchange membrane (CEM) is placed in middle of the cell between two compartments of different salinity. This membrane allows the passage of cations and blocks the anions and water molecules\(^{31,32}\). Thanks to this selectivity, an electrical potential difference appears between these two solutions of different salinity. In open-circuit cases, the cell voltage \(E_{OCV}\) is the sum of the Donnan potential \(E_{mem}\) and of electrode potentials \(E_{elec}\). The Donnan potential is given by the Nernst equation, corrected for the activity of the feed waters and the apparent permselectivity of the non-perfect membrane. It is given by:

\[
E_m = \frac{\alpha RT}{z_i F} \log \frac{a_{i,1}}{a_{i,2}}
\]  

(1)

where \(E_m\) represents the electromotive force across the membrane (in volts, V), \(\alpha\) denotes the apparent membrane permselectivity (dimensionless), \(R\) stands for the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \(T\) is the temperature, \(z_i\) represents the valence of the ionic species \(i\) (dimensionless), \(F\) is the Faraday constant (96,485 C mol\(^{-1}\)), and \(a_i\) signifies the activity of ionic species \(i\) in the feed water (in molarity, M). The subscripts 1 and 2 indicate the side of the membrane. Equation 1 illustrates that a salinity ratio of monovalent ions (such as Na\(^{+}\), Cl\(^{-}\)) results in twice the voltage generated by an equivalent salinity ratio of divalent ions (such as Mg\(^{2+}\), SO\(_4^{2-}\)), assuming constant activities and apparent membrane permselectivity.

\(E_{elec}\) results from the ion adsorption on the electrodes and depends upon the value of the local salt concentration. When the circuit is closed, the potential drop between the two electrodes includes the ohmic ionic dissipation both in the membrane and in the electrolyte, as well as the non-ohmic dissipation in the polarization layers built up around the membrane and the electrode. The closing of the circuit also involves the ohmic potential difference in the load resistance and the capacitive potential jump at
the electrodes. The presence of capacitance causes the electric current to decay over time. When the capacitor is fully charged, the potential difference across its terminals balances the membrane potential $E_{\text{mem}}$ and the potential created by the adsorbed layers $E_{\text{elec}}$. As a result, the produced electric current stops. It is then necessary to switch the fresh water and salt water supplies in order to reverse the membrane and electrode potential to unblock the electricity production. This generates an electric current in the opposite direction.

### 0.2 Divalent ion mixture influence on cell voltages

In order to perform insight studies of the impact of divalent ion mixing on electrical voltages, we conducted measurements to study separately the membrane voltage $E_m$ and capacitive electrode related voltage $E_{\text{OCV} - c}$. This is realized by open-circuit voltage (OCV) measurements both in capacitive and faradaic cells. In the capacitive situation, $E_{\text{OCV} - c}$ is twice the sum of the membrane potential $E_m$ and of the electrode potentials $E_{\text{elec}}$. In the faradaic situation, $E_{\text{OCV} - f}$ is the sum of the membrane potential $E_m$ and of the Ag/AgCl electrode potentials $E_{\text{elec} - f}$. $E_{\text{elec} - f}$ is measured separately in a simple set-up containing two electrodes immersed in two beakers containing solutions of different concentration and linked by a salt bridge. As $E_m$ does not depend upon the nature of the electrode, it is then possible to deduce $E_{\text{elec} - c} = E_{\text{OCV} - c} - E_m$ from the measurement of the open circuit potential performed on a cell equipped with the membrane and capacitive electrodes. A detailed explanation for the voltage measurement and calculation method is available at Methods section.

We carried out a series of 16 experiments with NaCl solutions mixed with MgCl$_2$ and CaCl$_2$ solutions. The compositions of the different solutions used are given in the Table 4. Compared to solutions with only NaCl, part of the NaCl was replaced by MgCl$_2$ or CaCl$_2$, in order to maintain the molarity of the inflowing feed (and hence the conductivity, to a certain degree) constant. The results obtained concerning different electrical voltages under the influence of divalent ion mixing are displayed in the Table 1 and Figure 1.

![Figure 1. Electrical voltage over membrane $E_m$ and over capacitive electrodes $E_{\text{elec} - c}$ as a function of NaCl molar fraction.](image)

(a), (b) and (c) represents the variation of voltage of mixing between NaCl and CaCl$_2$ for salinity ratio of 100, 30 and 10, respectively. (d) represents the mixing case of NaCl and MgCl$_2$ for a salinity ratio of 30. As molar fraction of divalent ions gets higher, $E_m$ drops significantly while $E_{\text{elec} - c}$ remains constant.

Data obtained in the absence of divalent ions are comparable to measurements obtained previously in the literature$^{26}$. In these situations, $E_m$ corrected by measured Ag/AgCl electrode potential are 0.107, 0.074 and 0.05 V for Ra value of 100, 30 and 10 respectively. Based on these values, the selectivities $\alpha$ are calculated to be 0.92, 0.86 and 0.86 for Ra value of
Table 1. Electrical voltage measurement split-up table for mixing between NaCl and CaCl$_2$. The electrical voltages measured by experiments consist of open-circuit voltage of a capacitive cell $E_{OCV-c}$ (which corresponds to $2(E_m + E_{elec})$), open-circuit voltage of a faradaic cell $E_{OCV-f}$, and electrical voltage on faradaic electrodes $E_{elec-f}$. Based on these measurements, it is possible to deduce the electrical voltage across the membrane $E_m$ and the electrical voltage on capacitive electrodes $E_{elec-c}$.

The measurements are conducted by using solution mixing between NaCl and CaCl$_2$ of different molar fractions (1, 0.8, 0.6 and 0.4 for NaCl molar fraction) for salinity ratios of 10, 30 and 100, respectively.

<table>
<thead>
<tr>
<th>NaCl fraction</th>
<th>CaCl$_2$ fraction</th>
<th>Salinity ratio $Ra$</th>
<th>$E_{OCV-c}$ (V)</th>
<th>$E_{OCV-f}$ (V)</th>
<th>$E_{elec-f}$ (V)</th>
<th>$E_m$ (V)</th>
<th>$E_{elec-c}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>100</td>
<td>0.355</td>
<td>0.203</td>
<td>0.096</td>
<td>0.107</td>
<td>0.071</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>100</td>
<td>0.349</td>
<td>0.194</td>
<td>0.094</td>
<td>0.100</td>
<td>0.074</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>100</td>
<td>0.327</td>
<td>0.184</td>
<td>0.091</td>
<td>0.093</td>
<td>0.070</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>100</td>
<td>0.310</td>
<td>0.176</td>
<td>0.090</td>
<td>0.086</td>
<td>0.069</td>
</tr>
</tbody>
</table>

Table 2. Electrical voltage measurement split-up table for mixing between NaCl and MgCl$_2$ for a fixed salinity ratio $Ra$ of 30. Two scenarios are investigated here: The mixing in both concentrated and diluted solutions, and mixing only in the diluted solution.

<table>
<thead>
<tr>
<th>NaCl fraction</th>
<th>MgCl$_2$ fraction</th>
<th>Salinity ratio $Ra$</th>
<th>$E_{OCV-c}$ (V)</th>
<th>$E_{OCV-f}$ (V)</th>
<th>$E_{elec-f}$ (V)</th>
<th>$E_m$ (V)</th>
<th>$E_{elec-c}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing of NaCl-MgCl$_2$ in both solutions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>30</td>
<td>0.265</td>
<td>0.145</td>
<td>0.070</td>
<td>0.075</td>
<td>0.057</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>30</td>
<td>0.252</td>
<td>0.139</td>
<td>0.067</td>
<td>0.072</td>
<td>0.054</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>30</td>
<td>0.230</td>
<td>0.131</td>
<td>0.070</td>
<td>0.061</td>
<td>0.054</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>30</td>
<td>0.212</td>
<td>0.120</td>
<td>0.065</td>
<td>0.055</td>
<td>0.051</td>
</tr>
</tbody>
</table>

| Mixing of NaCl-MgCl$_2$ only in the diluted solution |
| 1             | 0                 | 30                  | /                | 0.144           | 0.070           | 0.074     | /               |
| 0.8           | 0.2               | 30                  | /                | 0.142           | 0.069           | 0.073     | /               |
| 0.6           | 0.4               | 30                  | /                | 0.139           | 0.069           | 0.070     | /               |
| 0.4           | 0.6               | 30                  | /                | 0.131           | 0.069           | 0.062     | /               |
| 0.2           | 0.8               | 30                  | /                | 0.120           | 0.069           | 0.021     | /               |

100, 30 and 10 respectively. $\alpha$ is defined as $E_{mem} = \alpha \frac{RT}{F} \ln \left( \frac{c_H^m c_L^m}{c_H^L c_L^L} \right)$. We recall that $\alpha = 1$ corresponds to a perfect selective membrane, that allows the free passage of cations but blocks anions. In presence of divalent ions, the membrane voltage decreases compared with solutions composed of pure mono-valent ions, as illustrated in Figure 1. As the molar fraction of divalent ions increases, the membrane voltage shows significant further decrease. For a fixed salinity ratio of 100 (30 or 10, respectively), the membrane potential decreases from 107 mV to 86 mV (75 mV to 63 mV in the case of ratio 30 and 50 to 23 mV in the case of 10, respectively) for a molar fraction of 0.4 CaCl$_2$ and a total salt concentration of 1.71 mol/L (0.51 mol/L, 0.17 mol/L, respectively).

It also depends upon the nature of the ions. In presence of MgCl$_2$, the drop of potential is comparable to that in presence of CaCl$_2$. For a NaCl salt fraction of 0.4, $Ra=30$, the membrane potential is equal to 54 mV in presence of MgCl$_2$ and to 57 mV in presence of CaCl$_2$. We have supplemented this series of measurements with membrane potential measurements when divalents are only present in the dilute solution (see Table 2). The results show that the potential is less affected by the presence of divalents in this situation than in the case where divalent ions are present on both sides of the membrane. We will come back to this point in the discussion.
The potential of the electrodes behaves differently. It seems less affected than membrane potential by the presence of divalent ions. It depends little of the amount of divalent added and on the nature of the ions. These results have important implications for cell potential. The cell potential consists the sum of the electrode and membrane contribution. While the molar fraction of NaCl drops from 1 to 0.4, the voltage contribution of membranes $E_m$ shows a significant drop of 19.6%, 27.0% and 54.0% for salinity ratio $Ra$ of 100, 30 and 10, respectively. In the same situations, the voltage contribution of electrodes $E_{elec-c}$ shows a drop of 3%, 19% and 12.4% for salinity ratio $Ra$ of 100, 30 and 10, respectively. While the molar fraction of NaCl drops from 1 to 0.4, this induces for a capacitive cell a decrease of the total cell voltage $E_{OCV-c}$ of 12.8%, 23.4%, and 33.6% for salinity ratio $Ra$ of 100, 30 and 10, respectively. This decrease is thus much less important than the one occurring for the membrane potential. We remind the reader that in a RED-type arrangement with an assembly of a large number of membranes, only the membrane potential comes into play. However, in a capacitive type cell scaling-up, both capacitive electrodes and membrane is considered as a repeating unit, thus the contribution of membrane voltage is less important.

0.3 Divalent ion mixture influence on electrochemical properties

In order to characterize changes in cell resistance $R_{cell}$ and cell capacity $C$ as a function of the nature of the salt solutions, we carried out impedance spectroscopy measurements (see Methods section). As an equivalent $R-C$ circuit can be established for the capacitive cell, for each solution mixture, it is possible to measure the corresponding inner cell resistance and its capacitance by using the Nyquist plot plotted by the PEIS method. Here, by using the impedance result measured at 10 mHz, we characterized $R$ and $C$ for different divalent mixing scenarios. The electrochemical measurement results are illustrated in the Table 3 for two different mixing scenarios: NaCl-CaCl$_2$ and NaCl-MgCl$_2$ with a fixed salinity ratio of 30. It is clear that while the quantity of divalent salts in the mixing is increased, the cell resistance decreases slightly. We believe that this is related to the increase of molar concentration of chloride ions inside the solution.

Table 3. R-C characterization result table for the capacitive cell system with a fixed salinity ratio of 30 of different divalent ion fraction.

<table>
<thead>
<tr>
<th>NaCl-CaCl$_2$</th>
<th></th>
<th>NaCl-MgCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl fraction</td>
<td>CaCl$_2$ fraction</td>
<td>$R$ ($\Omega$)</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>3.750</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2</td>
<td>3.426</td>
</tr>
<tr>
<td>0.6</td>
<td>0.4</td>
<td>3.098</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>2.832</td>
</tr>
</tbody>
</table>

0.4 Divalent ion mixture influence on energy performance

Figure 2. Power density curves as a function of load resistance for divalent ion mixing of NaCl and CaCl$_2$ and (b) mixing of NaCl and MgCl$_2$. The solid lines represent the theoretical prediction based on the R-C equivalent circuit. The dots represent the experimental data obtained for a capacitive salinity gradient cell. The number presented in the legend corresponds to the molar fraction of NaCl. $T_s$ = 45s.
It is important to characterize the energy performance of the capacitive cell. We will firstly explain the power density characterization method for a simple capacitive cell using pure mono-valent ion based solutions.

The mean gross power density $P_{\text{gross}}$ (that is, power density without compensating for pumping losses) is assessed by averaging the signal recorded across the resistance over a time interval of $T_s$. $S$ denotes the area of the membrane. The expression is as follows:

$$P_{\text{gross}} = \frac{1}{T_0} \int_0^{T_s} \frac{E_{\text{load}}^2(t)}{R_{\text{load}}} \, dt$$

(2)

It’s noteworthy that these measurements constitute direct assessments that mirror real-world scenarios. In a previous work, we developed a theoretical model that can account for the measured power and that describes the experimental values well when the cell filling time is small compared to the period. Details about the modeling can be find in the work of Brahmi et al. We recall here only the main point of the theoretical approach. According to an analysis of the electrochemical impedance spectroscopy, a R-C model is proposed as a simplified fitting model for the cell-booster system. The system inner resistance $R_{\text{cell}}$ and capacitance $C$ can be quantitatively characterized by Potentiostatic electrochemical impedance spectroscopy (PEIS) measurement using a potentiostat. $E_{\text{mem}}(t)$ is the potential drop over the membrane, $E_{\text{elec}}(t)$ the electrical potential due to the salt adsorption on the electrodes, $R_{\text{cell}}(t)$ the resistance of the cell (including the ohmic and non ohmic resistance of the salt, the membrane, the carbon felt and the current collector). The temporal variation of $R_{\text{cell}}(t), C_{\text{cell}}(t), E_{\text{mem}}(t)$ and $E_{\text{elec}}(t)$ are due to the temporal variation of the ion concentration profile including osmotic potential, diffuse layer establishment, cell filling process after water compartment switching and etc. In the following we will assume that these characteristic times and the filling time of the cell are negligible compared with the switch half period $T_s$. Thus, these functions will be modeled simply by window functions: for $0 < t < T_s$, $E_{\text{mem}}(t) + E_{\text{elec}}(t) = E_{\text{OCV}}$ and for $T_s < t < 2T_s$, $E_{\text{mem}}(t) + E_{\text{elec}}(t) = -E_{\text{OCV}}$. In this framework, $R_{\text{cell}}(t)$ and $C$ do not depend upon $t$. We recall that $T_s$ is the switch half period.

Following these conditions, we establish the theoretical model for a pure cell-resistor circuit in absence of boosting by the equations below:

For $0 < t < T_s$:

$$(R_{\text{load}} + R_{\text{cell}})I(t) + \frac{q_1(t)}{C} = E_{\text{OCV}}$$

(3)

For $T_s < t < 2T_s$:

$$(R_{\text{load}} + R_{\text{cell}})I(t) + \frac{q_1(t)}{C} = -E_{\text{OCV}}$$

(4)

We solve analytically these equations and calculate the electrical power recovered by the load resistor. We find:

$$P_{\text{th}} = \frac{2}{S T_s} \frac{C E_{\text{OCV}}^2 R_{\text{load}}}{R_{\text{load}} + R_{\text{cell}}} \tanh\left(\frac{T_s}{2 (R_{\text{load}} + R_{\text{cell}}) C}\right)$$

(5)

To assess the influence of divalent ion mixing in the capacitive cell, we measure the harvesting power in various salinity gradients with different divalent ion mixing fraction. As explained earlier, periodic water compartment switching is performed to unblock the saturation state. The measured power densities show classic variations according to the load resistance. For each mixing case, the experimental results are presented by dots in Figure 2. For each mixing case, by the above-explained electrochemical characterizations, we have measured the cell resistance $R_{\text{cell}}$ and capacity $C$. Thus based on the established theoretical model, we simulate the power density performance of the capacitive cell, just by using the measured value $E_{\text{OCV}}$, $R_{\text{cell}}$ and $C$. The theoretical prediction is presented by solid lines in Figure 2, it does not involved any fitting parameters. It is demonstrated that experimental power density performances are perfectly described by the classical modeling. As cell resistance is virtually unchanged and even decreases slightly in the presence of divalent ions, the decrease in recovered power is due to the decrease in the value of the open-circuit potential $E_{\text{OCV}}$.

0.5 Experiments dealing with real solutions

To complete our study, we designed a series of experiments to test the feasibility of CRED in applications, where complex solution mixtures are used. These imaginary scenarios serve as proxies for some real-life applications, as detailed below, or allow to test some bottlenecks expected in these applications.

In the first scenario (Figure 3 (a)) we consider produced water from an oil well mixing with seawater. Here we used synthetic production water and synthetic seawater prepared in a laboratory from data provided from a field (see composition...
The obtained power density 0.35 W.m$^{-2}$ was similar to what was obtained with NaCl solutions at similarly low salinity ratio of around 4. The amount of osmotic energy is low due to the small difference in salinity. We could conclude that although our results show the feasibility of energy harvesting from production water, unaffected by the presence of divalent ions, advantage of further development of this application is site dependent.

In the second scenario we used real water from the evaporation ponds at the Dead Sea, mixed with the same solution diluted by 30 times (Figure 3 (b)). The extreme salinity conditions of this test could be relevant to projects like the Red sea-Dead sea conveyance, or similar. Remarkably, the high power density of over 2 W.m$^{-2}$ indicate the unprecedented feasibility of such application. According to our experimental analysis, the total dissolved salts content in the dead sea solution is on the average 324.9 g.L$^{-1}$. The dominant cation is Mg (62.3 g.L$^{-1}$), followed by Na (32.2 g.L$^{-1}$), Ca (27.5 g.L$^{-1}$) and K (9.3 g.L$^{-1}$). We demonstrated that even in the case where divalent ions (Mg and Ca presenting around 55%) dominate, the measured power density obtained in a capacitive cell is comparable to the value 2.2 W.m$^{-2}$ obtained in a pure solution composed of NaCl salts with similar concentration gradients (300 g.L$^{-1}$ vs. 10 g.L$^{-1}$) as reported by Wu et al. 

In the third scenario we imagine creation of salt caverns, either for salt mining or for subsequent hydrogen storage (see Figure 3 (c)). The caverns are created by dissolution in water, of salinity available on site, injected into the salt deposit. The concentrated solution is therefore saturated brine, mostly composed of NaCl 300 g.L$^{-1}$, and the diluted solution is fresh (used) water or river water, replaced here for simplicity by a 1 g.L$^{-1}$ artificial mixture solution of composed of NaCl (40%) and CaCl$_2$ (60%). In this case, a maximum power density of 3.2 W.m$^{-2}$ is obtained. The power density shows limited decrease compared with NaCl pure solutions of 300 g.L$^{-1}$ and 1 g.L$^{-1}$, which shows a maximum power density of 4 W.m$^{-2}$ in the capacitive cell.

For most real solutions, divalent ions are of low molar fraction (6.7 % in the case of production water and 0.4 % in the case of sea water). The results obtained with the real solutions are thus close to the result obtained with equivalent monovalent ion based solutions. When it comes to Dead Sea water, it is actually dominated by the presence of divalent ions. However, according to our experimental studies, capacitive system presents minor performance decay in this case. We conclude here that in a capacitive cell system, brine composition has a small impact on the performance. We highlight that these performances might be enhanced using an external voltage source.

![Figure 3. Power density curves for real solutions.](image)

(a) Synthetic sea water / production water
(b) Dead sea water
(c) Salt cavern

0.6 Long-term energy performance analysis

Additional studies were carried out to characterize the long-term power density performance of the capacitive cell under the impact of the mixture of divalent ions. Different from the result reported by Vermaas et al., we did not observe any significant transitional response. As illustrated in Figure 4 (a), we operated the capacitive cell in solutions with presence of divalent ions for a fixed salinity ratio of 30. During its total operation time of 10 hours, the power density performance remains constant with a variation rate of 6%. The phenomenon is verified in three different cases, where we varied the membrane types and solution compositions. In case 1 and 2, we used Nafion 117 as membrane while varying solution compositions. We used namely artificial NaCl-CaCl$_2$ mixed solution in the case 1 and production water in case 2. In case 3 we used Fumasep FS720 membrane with artificial NaCl-CaCl$_2$ mixed solution. It is shown that the presence of divalent ions presents limited impact on power density performance of capacitive systems, even in the long term. And this phenomenon is verified for different solution compositions and for different membranes.
Figure 4. Long-term power density performance characterization. (a) Power density measurement of a capacitive salinity gradient cell during an operation duration of 500 min for three different cases. Case 1: the use of artificial NaCl (80%) - CaCl$_2$ (20%) mixed solution with a salinity ratio of 30 g.L$^{-1}$ vs 1 g.L$^{-1}$). The membrane used here is Nafion 117 with a load resistor of 10 $\Omega$. Case 2: the use of production water (equivalent NaCl concentration 107 g.L$^{-1}$) with a salinity ratio of 30. The membrane used here is Nafion 117 with a load resistor of 10 $\Omega$. Case 3: the use of artificial NaCl (40%) - CaCl$_2$ (60%) mixed solution with a salinity ratio of 30 g.L$^{-1}$ vs 1 g.L$^{-1}$). The membrane used here is Fumasep FS720 with a load resistor of 30 $\Omega$. In all cases, we fix the switching period as $T_s = 45$ s. The power density variation after 10h of operation is within 6%. (b) Open-circuit voltage measurement of a faradaic Ag/AgCl electrode based cell with a membrane before and after 24 hour immersion in artificial NaCl (40%) - CaCl$_2$ (60%) mixed solution of 30 g.L$^{-1}$. We noticed a major difference in membrane performance between Nafion and Fumasep membranes. Nafion membranes show stable voltage performance, suggesting a limited membrane poisoning effect by divalent ions, while Fumasep membranes show an important voltage drop after divalent solution immersion, implying a severe membrane poisoning effect. NaCl solutions with a salinity ratio of 30 are used during OCV measurements.

Discussion

Figure 5. Theoretical interpretation of the membrane voltage $E_m$ decreases as a function of divalent ion molar fraction. (a) Theoretical prediction (solid lines) and experimental data (dots) of $E_m$ of different salinity ratio $Ra$ of 100, 30 and 10, respectively, for a mixing between NaCl and CaCl$_2$. (b) Membrane voltage $E_m$ decrease in two different cases: mixture in both concentrated and diluted solutions, and mixture only in the diluted solution. The feed solution used here is a mixture of NaCl and MgCl$_2$ with a fixed salinity ratio $Ra$ of 30.

The preceding analysis and measurements give us a better understanding of why divalent ions affect the performance of our
have proposed a simple modeling for the membrane potential in presence of divalent ions. In their analysis, they propose that the open-circuit equilibrium membrane potential is equal to a potential that cancels out the displacement of divalent ions. This is only possible if a local transfer of matter takes place, inducing a different concentration in the layer near the membrane. More precisely, ion transport across a membrane is a complex phenomenon when monovalent and multivalent ions exist on both sides of an ion exchange membrane. In such situations, ions are exchanged across the membrane to achieve chemical potential equilibrium on both sides. When solutions of NaCl and MgCl are present on either side of a cation exchange membrane (CEM) at varying concentrations but with the same ratio, the electromotive force $E_{OCV}$ resulting from the difference in concentration of Na$^+$ is greater than that of Mg$^{2+}$ due to the valence of the ions. We recall that $E_{OCV} = \frac{aRT}{zF} \log \frac{a_{Na^{+},1}}{a_{Na^{+},2}}$. As a result, Mg$^{2+}$ ions are transported from the dilute to the concentrated solution, while twice as many Na$^+$ ions move in the opposite direction. This exchange ensures electroneutrality on both sides of the membrane and is described in the literature as uphill transport, corresponding to the movement of Mg$^{2+}$ against the concentration gradient. Using Equation 1 and assuming that the apparent permselectivity is equal for both ionic species, this stationary situation is reached when the ion activities at either side of the membrane obey:

$$\frac{aRT}{z_{Na^{+}}F} \log \frac{a_{Na^{+},1}}{a_{Na^{+},2}} = \frac{aRT}{z_{Mg^{2+}}F} \log \frac{a_{Mg^{2+},1}}{a_{Mg^{2+},2}}$$

This leads us to:

$$E_m = \frac{aRT}{z_{Na^{+}}F} \log \frac{a_{Na^{+},1}}{a_{Na^{+},2}}$$

$$a_{Na^{+},2} = \gamma_{Na^{+},2}(c_{Na^{+},2} + 2J/V_2)$$

$$a_{Na^{+},1} = \gamma_{Na^{+},1}(c_{Na^{+},1} - 2J/V_1)$$

$$\gamma_{Na^{+},1}(c_{Na^{+},1} - 2J/V_1) = \gamma_{Mg^{2+},1}(c_{Mg^{2+},1} - 2J/V_1)$$

$$\gamma_{Mg^{2+},2}(c_{Mg^{2+},2} + 2J/V_2)$$

$J$ is the molar transport (mol) of Mg$^{2+}$ towards the seawater compartment, and $V_1$ and $V_2$ are the volume of the compartments.

Figure 5 shows a comparison between the model and membrane potential measurements. An excellent agreement is found between measurements and simulation. Note that in solving these equations, we have assumed that the activity coefficients are equal to one. This choice was made because we were unable to find any models in the literature to describe the ion mixtures and concentration conditions we were studying. A very good agreement between measurements and model is obtained without a correction for the capacitive system to be used at its maximum efficiency.
Table 4. Brine composition

### NaCl - CaCl$_2$ solution composition

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<thead>
<tr>
<th>NaCl molar fraction</th>
<th>NaCl g.L$^{-1}$</th>
<th>NaCl mol.L$^{-1}$</th>
<th>CaCl$_2$ g.L$^{-1}$</th>
<th>CaCl$_2$ mol.L$^{-1}$</th>
<th>NaCl g.L$^{-1}$</th>
<th>NaCl mol.L$^{-1}$</th>
<th>CaCl$_2$ g.L$^{-1}$</th>
<th>CaCl$_2$ mol.L$^{-1}$</th>
<th>Experiment number</th>
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### NaCl - MgCl$_2$ solution composition

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<th>MgCl$_2$ g.L$^{-1}$</th>
<th>MgCl$_2$ mol.L$^{-1}$</th>
<th>MgCl$_2$ g.L$^{-1}$</th>
<th>MgCl$_2$ mol.L$^{-1}$</th>
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### Methods

**Preparation and composition of the salted solutions**

NaCl, MgCl$_2$, CaCl$_2$ and KCl were purchased from Sigma Aldrich. In this study, we prepared solution mixtures of different concentrations. The compositions of these solutions are described in Table 4 and 5.

Table 5. Experiments reproducing possible applications: compositions of solutions

<table>
<thead>
<tr>
<th>Scenario 1: Production water / seawater</th>
<th>NaCl equivalent g.L$^{-1}$</th>
<th>NaCl g.L$^{-1}$</th>
<th>KCl g.L$^{-1}$</th>
<th>CaCl$_2$.2H$_2$O g.L$^{-1}$</th>
<th>MgCl$_2$.6H$_2$O g.L$^{-1}$</th>
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<td>Production water</td>
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<td>107</td>
<td>93.9</td>
<td>0.628</td>
<td>11.25</td>
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<td>Sea water</td>
<td>4.28</td>
<td>25</td>
<td>23.63</td>
<td>0.77</td>
<td>0.11</td>
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</table>

<table>
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<tr>
<th>Scenario 2: Dead Sea water / x30 diluted</th>
<th>NaCl g.L$^{-1}$</th>
<th>K g.L$^{-1}$</th>
<th>Ca g.L$^{-1}$</th>
<th>Mg g.L$^{-1}$</th>
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<tr>
<td>Dead Sea water</td>
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<td>324.87</td>
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<td>Diluted Dead Sea water</td>
<td>30</td>
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<td>0.309</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Scenario 3: Salt caverns</th>
<th>NaCl g.L$^{-1}$</th>
<th>KCl g.L$^{-1}$</th>
<th>CaCl$_2$.2H$_2$O g.L$^{-1}$</th>
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<td>Salt cavern extraction water</td>
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10/14
Capacitive Cell: Description

The experiments are performed in a capacitive cell. A configuration akin to that detailed in the prior study by Brahmi et al. is employed here (Figure 6). The cell exhibits symmetrical geometry, featuring an ion-exchange membrane (Nafion™ 117, Chemours) sandwiched between two water compartments containing varying salt concentrations. The membrane, with a dry thickness of 183 µm, ensures an average conductivity exceeding 0.1 S.cm⁻¹ and a total acid capacity ranging between 0.95 and 1.01 meq.g⁻¹. The effective surface area of the ion-exchange membrane used in our experimentation measures 2.24 cm².

Carbon felt capacitive electrodes (Kynol Activated Carbon Felt) are separately positioned within gaskets on either side of the membrane. These electrodes are situated at a distance of 1.4 mm from the membrane and are directly linked to graphite current collectors. The entire assembly is securely sealed by stainless steel endplates and held together using eight bolts torqued to 2 N.m. Two ports facilitate water inlet and outlet, driven by a peristaltic pump (Longer Multichannel Peristaltic pump) operating at a consistent flow rate of 10 mL.min⁻¹. After the system achieves saturation upon full capacitive charging, an automated 4-port valve switches water compartments at fixed intervals of T. This transition unblocks the saturation state, enabling the cell to deliver periodic alternating current.

Measurement of the Open Circuit Voltage

To evaluate the inherent potential of the circuit, we initially link the two cell electrodes. One compartment is filled with a high salt concentration while the other contains a low salt concentration. We then wait for equilibrium to be established.

Modeling the temporal progression of the potential necessitates understanding the behavior of both the electrodes and the membrane. Across the entirety of the circuit, there is no voltage drop. This can be expressed as follows:

\[ R_{\text{load}} I + R_{\text{cell}} I + \frac{q}{C} = E_m(t) + E_{\text{elec}-c}(t) \] (11)

Here, \( E_m(t) \) represents the voltage drop across the membrane, \( E_{\text{elec}-c}(t) \) signifies the voltage drop across the capacitive layer, \( I \) denotes the current intensity, and \( R_{\text{cell}} \) is the ohmic resistance of the cell, which encompasses the resistance of the solvent, carbon felt, and current collector.

Changes in the concentrations of ions over time cause the temporal evolution of \( E_{\text{elec}-c}(t) \) and \( E_m(t) \). These variations stem from cell filling and the creation of a diffuse ion layer near the electrodes when altering the salt concentration.

At \( t = 0 \), the system is in a stable state with \( I(0) = 0 \) and \( q(0) = q_0 = C(E_m(\infty) + E_{\text{elec}-c}(\infty)) \). For \( t \) less than 0, the sum of membrane and capacitive layer potentials is given by \( E_m(\infty) + E_{\text{elec}-c}(\infty) \); at \( t = 0 \), the flow in both compartments reverses and the signs of membrane and capacitive layer potentials change. Upon reaching steady state after reversal, membrane and capacitive layer potentials are determined by \( -E_m(\infty) - E_{\text{elec}-c}(\infty) \).

The solution to Equation 11 is straightforward. We arrive at:

\[ q = \exp\left(\frac{-E_m(s) + E_{\text{elec}-c}(s)}{R} \right) ds + q_0 \exp\left(\frac{-E_m(\infty) + E_{\text{elec}-c}(\infty)}{R} \right) \] (12)

\[ A(t) = \frac{1}{RC} \exp\left(\frac{-E_m(s) + E_{\text{elec}-c}(s)}{R} \right) ds \] (13)

Figure 6. Schematic illustration of the capacitive cell.
We measure the open-circuit voltage and wait for steady-state. We then apply 10 mV oscillatory perturbations over the open-circuit voltage. We use a logarithmically whole circuit is closed by the use of a home-made salt bridge (KCl saturated). Then the electrode potential difference with different mixing molar fraction. For a faradaic cell, the OCV voltage corresponds to the sum of the membrane voltage and

\[ E_{OCV-m} = 2(E_m + E_{elec-c}) \]  

(15)

Thus in order to obtain the membrane voltage \( E_m \), it is necessary to measure the faradaic electrode related voltage \( E_{elec-f} \). In our experiment, we immersed the two home-made Ag/AgCl electrodes into concentrated solution and diluted solution in two beakers separately. The solutions used in experiments follows the same experimental conditions, i.e. solutions of different salinity ratio with different mixing molar fraction. The whole circuit is closed by the use of a home-made salt bridge (KCl saturated). Then the electrode potential difference \( E_{elec-f} \) is measured by using a potentiostat. Following the above two equations (Eq 15 and Eq 16), we can easily calculate the membrane voltage \( E_m \) and capacitive electrode voltage \( E_{elec-c} \).

### Measurement of the capacitive electrode voltage

This leads to \( RI(\infty) = E_{OCV-c} = -2(E_m(\infty) + E_{elec-c}(\infty)) \). To conclude, as noted in the main text, the open-circuit measurement for a capacitive cell corresponds to twice the steady-state membrane potential and capacitive layer values.

### Measurement of the membrane potential voltage

To gain insight into the individual impact of the membrane and the electrodes on the potential, we conducted separate measurements of the open-circuit potential of the membrane, denoted as \( E_m \). These measurements were performed while subjecting the membrane to salt gradients, utilizing custom-made Faradaic Ag/AgCl electrodes.

In this scenario, the measured potential can be expressed as \( E_{OCV-f} = E_{mem} + E_{elec-Ag/AgCl} \). It corresponds to the Nernst contribution from the Ag/AgCl electrodes. Activity coefficients \( \gamma_L \) and \( \gamma_c \) are calculated using Debye Huckel theory and taken directly from a Dortmund Data Bank database for concentrated solutions.

Here, the symbols \( R \), \( T \), \( z \), \( F \), \( \gamma \), and \( c \) stand for the gas constant, temperature, ion valence, Faraday constant, mean activity coefficient, and salt concentration, respectively. The subscript \( H \) pertains to the concentrated solution, while \( L \) pertains to the dilute one. Knowing the salt concentrations it is possible to measure using Ag/AgCl electrodes the potential drop of potential across the membrane. We measured directly \( E_{elec-f} \) eventually. To gain insight into the individual impact of divalent ion mixing on membrane voltage and electrode voltage, we conducted separate electrochemical measurements with both capacitive cells and faradaic cells. The capacitive cell assembly is described above and we measure the open-circuit voltage \( E_{OCV-c} \) for solutions of different salinity ratio with different mixing molar fraction. As explained above, the OCV voltage of a capacitive cell corresponds to twice the sum of the membrane voltage and capacitive electrode voltage.

\[ E_{OCV-m} = 2(E_m + E_{elec-c}) \]  

(14)

\[ q_0 = C(E_m(\infty) + E_{elec-c}(\infty)) \].

### Measurements of the impedance of the cell

Each compartment of the cell is supplied with a different saline solution under a constant flow rate. The circuit is open, and we wait for steady-state. We then apply 10 mV oscillatory perturbations over the open-circuit voltage. We use a logarithmically spaced frequency range from 200 kHz to 10 mHz for a fixed salinity ratio of 30 g.L\(^{-1}\) vs. 1 g.L\(^{-1}\) situation with different divalent ion mixing fraction. A Nyquist plot can be plotted corresponding all to a sweep over a frequency range from 200 kHz to 10 mHz. Note that the exact value of the impedance depends on the tightening. Here, we used the impedance data measured at 10 mHz to characterize the cell inner resistance and capacitance. Variations of 0.5 (\( \Omega \) cm\(^2\)) in real part are measured on consecutive experiments despite the care taken to make the clamping procedure repeatable.

### Measurement of the maximal harvested power

The system under consideration embodies a capacitive configuration. To restore current, a cyclic process reminiscent of cap mixing procedures is employed, where distinct brine flows with varying concentrations are directed into the two compartments. The experimental apparatus incorporates a rotary valve that permits the passage of highly concentrated saltwater into the first compartment for a duration of \( T_s \), succeeded by the circulation of fresh water for an equivalent \( T_s \) duration. This procedure is
reversed in the second compartment. Here, $T_s$ represents the half period of the salt gradient. The direction of the current shifts with each cycle, which is a distinctive trait of capacitive currents. The use of capacitive electrodes prompts a reevaluation of the methodology employed for measuring the recovered power. The mean gross power density $P_{\text{gross}}$ (that is, power density without compensating for pumping losses) is assessed by averaging the signal recorded across the resistance over a time interval of $2T_s$. The parameter $A$ denotes the area of the membrane. The expression is as follows:

$$P_{\text{gross}} = \frac{1}{2T_s} \cdot A \int_{0}^{2T_s} \frac{E_{\text{load}}^2(t)}{R_{\text{load}}} dt$$  \hspace{1cm} (17)$$

It’s noteworthy that these measurements constitute direct assessments that mirror real-world scenarios. These experiments are conducted across various salinity gradients, oscillation periods, and flow rates.

References
Acknowledgements

N.W acknowledges funding from CSC. Y.B acknowledges funding from Total Energies. M.L and Y.B thank C.Desplombins and M.Questel for their help conducting the experiments in PERL.

Author contributions statement

M.L, A.C conceived the experiments, N.W, Y.B conducted the experiments. N.W, M.L, Y.B, C.T, A.C analyzed the data. N.W, M.L, A.C wrote the manuscript. All authors reviewed the manuscript.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on request.