Harvesting Energy from Salinity Differences Using Battery Electrodes in a Concentration Flow Cell

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Supporting Information

ABSTRACT: Salinity-gradient energy (SGE) technologies produce carbon-neutral and renewable electricity from salinity differences between seawater and freshwater. Capacitive mixing (CapMix) is a promising class of SGE technologies that captures energy using capacitive or battery electrodes, but CapMix devices have produced relatively low power densities and often require expensive materials. Here, we combined existing CapMix approaches to develop a concentration flow cell that can overcome these limitations. In this system, two identical battery (i.e., faradaic) electrodes composed of copper hexacyanoferrate (CuHCF) were simultaneously exposed to either high (0.513 M) or low (0.017 M) concentration NaCl solutions in channels separated by a filtration membrane. The average power density produced was 411 ± 14 mW m⁻² (normalized to membrane area), which was twice as high as previously reported values for CapMix devices. Power production was continuous (i.e., it did not require a charging period and did not vary during each step of a cycle) and was stable for 20 cycles of switching the solutions in each channel. The concentration flow cell only used inexpensive materials and did not require ion-selective membranes or precious metals. The results demonstrate that the concentration flow cell is a promising approach for efficiently harvesting energy from salinity differences.

INTRODUCTION

Salinity differences between seawater and freshwater contain an enormous amount of entropic energy, which — if harvested — could produce approximately 1 TW of renewable electricity from coastal sites worldwide.¹ Several salinity-gradient energy (SGE) technologies have been developed to convert this energy into electrical power, including pressure-retarded osmosis (PRO),¹–⁴ reverse electrodialysis (RED),¹,⁴–⁶ and capacitive mixing (CapMix).⁷–¹⁸ In PRO, electrical power is produced by creating pressure differences between two waters with different salinities using semipermeable membranes. In RED, potential differences developed across an array of ion-exchange membranes produce electrical power using electrodes and soluble redox-active compounds. CapMix is a relatively new approach that encompasses several technologies inspired by energy storage devices, such as supercapacitors and batteries. CapMix devices produce electrical power from salt concentration-dependent electrode potentials, which can be created from capacitive (i.e., nonfaradaic) or battery (i.e., faradaic) electrodes or Donnan potentials developed across ion-exchange membranes. Of the SGE technologies, the largest reported electrical power densities have been generated for PRO (∼10 W m⁻²-membrane area) and RED (∼1 W m⁻²-membrane area). However, these two technologies require the use of ion-exchange or semipermeable membranes (i.e., “selective membranes”), which are currently cost-prohibitive or susceptible to fouling.¹,⁴ A significant advantage of some CapMix technologies over PRO and RED is that they can produce electrical power without the need for selective membranes.

Several CapMix approaches have been developed with different reactor configurations and electrode materials. Capacitive energy extraction based on double layer expansion (CDLE) uses two porous carbon electrodes that undergo capacitive charging/discharging reactions, which produce power by exploiting the concentration-dependent double layer thickness and subsequent voltage rise and fall at each electrode.⁷–¹⁰ Generating electrical power using CDLE has major challenges, including charge leakage, low power densities (0.05 W m⁻²), and intermittent power production.⁷ Producing electrical power using capacitive energy extraction based on Donnan Potentials (CDPs) is similar to CDLE, except that potentials are developed across ion-exchange polymers or membranes placed on the surface of carbon electrodes.¹¹–¹⁶ CDP has multiple advantages over CDLE, including higher power densities (∼0.2 W m⁻²) through external electrode charging¹³ and continuous power production using flow electrodes.¹⁵,¹⁶ The major disadvantage of CDP is that, like
RED, it requires expensive ion-exchange membranes. Unlike CDLE and CDP, electrical power production in a mixing entropy battery (MEB) is based on battery electrodes that develop concentration-dependent electrode potentials through faradaic reactions.8,17,18 MEB has shown a reasonable power density of ∼0.1 W m−2 without ion-exchange membranes,17 but electrical power production is intermittent due to the need for periods of charging, and current systems use precious metals, such as silver, as an electrode material. A recently suggested approach inspired by a concentration cell,19 called the same-electrode-kind CapMix (SEK-CapMix), partly addressed these challenges by using two identical chemically modified carbon electrodes,10 but the voltage rise (110 mV) and power density (<0.05 W m−2) were still similar to those found for other cell designs. For CapMix to become a viable means for converting SGE into electrical power, devices must be able to continuously produce electrical power at high densities using inexpensive materials.

To address the limitations of previous CapMix approaches, we designed a concentration flow cell inspired by previous studies.5,17 The flow cell contained identical battery electrodes, composed of nontoxic copper hexacyanoferrate (CuHCF), that were separated by an inexpensive (nonselective) filtration membrane. During operation, one electrode was exposed to a flowing solution of synthetic seawater, while the other electrode was exposed to a flowing solution of freshwater. We examined the energy harvesting performance of this flow cell as a function of operating conditions and cell architecture. Specifically, we examined the influence of hydraulic retention time on power production, the sources of power losses in the system, and how the membrane properties influenced the separations of the solutions within the cell. Collectively, we achieved a power density that was more than double the highest reported value for previous CapMix technologies, indicating that the concentration flow cell is a compelling approach for harvesting salinity gradient energy using inexpensive materials.

**EXPERIMENTAL METHODS**

**Electrode Preparation.** Copper hexacyanoferrate (CuHCF) was synthesized by following a previously reported coprecipitation method.8,19 Briefly, 0.1 M Cu(NO3)2 (Sigma-Aldrich) and 0.05 M K3[Fe(CN)6] (J.T. Baker) solutions (each 80 mL) were simultaneously added dropwise to deionized water (40 mL) under vigorous stirring at room temperature. The resulting precipitates were centrifuged and then dried overnight at 70 °C. Composite electrodes were fabricated by mixing CuHCF (70 wt %), carbon black (20 wt %, Vulcan XC72R, Cabot), and polyvinylidenefluoride (10 wt %, kynar HSV 900, Arkema Inc.) with 1-methyl-2-pyrrolidinone (1 mL per 0.1 g of CuHCF, Sigma-Aldrich). The slurry was poured onto a graphite foil (120 μm thick, 4.4 mg/cm2) and cast using a doctor blade, followed by overnight drying in a vacuum oven at 70 °C. Before using the electrode in energy harvesting tests, the electrode potential was fixed at 0.9 V vs Ag/AgCl in 0.513 M NaCl to remove residual potassium ions. Then, the potential was adjusted to 0.7 V vs Ag/AgCl in a fresh electrolyte.

**Concentration Flow Cell Design.** The flow cell consisted of two channels that could be simultaneously fed by two solutions with different salt concentrations. Each solution was fed to the channels (width = 1 cm; height = 3 cm; area = ~3 cm2; thickness = ~400 μm) that were separated by the filtration membrane (magna nylon, thickness = 110 μm, pore size = 0.22 μm, Micron Separations Inc.; except as noted) preventing instantaneous mixing between solutions. The CuHCF composite electrodes were placed at each end of the channel, and titanium foil behind the electrode served as a current collector. Two end plates were firmly sealed using bolts and nuts.

**Energy Harvesting Performance.** To test the performance of the system, low concentration (LC, 1 g/L or 0.017 M) and high concentration (HC, 30 g/L or 0.513 M) NaCl solutions were used at concentrations that were representative of synthetic freshwater and seawater. These solutions were supplied to the flow cell using a peristaltic pump (Cole-Parmer) at a flow rate of 7.5 mL min−1, which produced a theoretical hydraulic retention time (HRT) of ~0.9 s. Different external resistors (Rext = 10, 14, 16, 22, 30 Ω) were connected between the electrodes for energy harvesting at various rates, with the cell voltage (∆U) recorded per second using a potentiostat (VMP3, Bio-Logic). Instantaneous power production was calculated from the cell voltage and the Rext (P = ∆U2/Rext), and it was divided by the electrode area (~3 cm2) to obtain the power density. The average power density was calculated from the power densities of a cycle. Each cycle started by switching the flow path of LC and HC solutions and ended when the cell voltage decreased below ±30 mV.

**Characterizations of the Flow Cell.** Resistance components of the flow cell were separately analyzed by measuring the overall, solution, and membrane resistances. The overall cell resistance was measured from the voltage drop when applying constant current (±0.5 mA) to the flow cell in three different combinations of feed solutions (LC+HC, HC+HC, LC+LC, see SI, section A). Solution resistance was calculated based on the effluent conductivity and the channel geometry (area = ~3 cm2; thickness = ~400 μm). The membrane resistance was evaluated using a DC current method in a custom-built reactor (see SI, section B).21 The membrane resistance of the flow cell was calculated by measuring the membrane resistances as a function of NaCl concentration for several solutions (0.017, 0.042, 0.141, 0.265, 0.513 M) and assuming that the concentration profile inside the membrane was linear. To examine the ability of filtration membranes to separate HC and LC solutions inside the flow cell, which was achieved by the membrane separating two channels, the effluent conductivity was measured using several commercially available membranes (GVWP, HVLP, RAWP, SMWP, and NY10, Millipore). The effluents were collected only after flowing copious amounts of solution at a flow rate of 7.5 mL/min in a cell without electrodes (channel area = ~3 cm2; thickness = ~500 μm).

**RESULTS AND DISCUSSION**

**Feasibility of Harvesting Energy from Salinity Differences Using the Flow Cell.** To demonstrate the feasibility of the concentration flow cell (Figure 1) for harvesting energy from salinity differences, we recorded the open-circuit cell voltage of the cell while periodically alternating the flow of high concentration (HC, 0.513 M) and low concentration (LC, 0.017 M) solutions in each channel at 60 s intervals. The cell voltage rapidly rose and fell after each switch, equilibrating to approximately 172 mV in less than 30 s (Figure 2a). Approximately 20 mV of this potential difference was due to the liquid junction potential, based on open-circuit cell voltage measurements without electrodes (Figure S3), which was also found in a previous study reporting the similar cell architecture (34 mV).18 Connecting the two electrodes using an external resistor (Rext = 30 Ω) produced electrical power from this cell.
voltage (Figure 2b, left axis). Unlike previously developed MEBs, this power was produced without the need for a power source or potentiostat. While discharging the cell, the cell voltage rapidly developed and gradually decayed, indicating that the potential of each CuHCF electrode was dissipated by reduction (positive electrode) and oxidation (negative electrode) reactions according to the following half reaction:

$$\text{NaCu}[\text{Fe}^{II}(\text{CN})_6] + x\text{Na}^+ + xe^- = \text{Na}_{1+x}\text{Cu}[\text{Fe}^{II}(\text{CN})_6]_x[\text{Fe}^{III}(\text{CN})_6]_{1-x}$$  

(1)

A peak power density of approximately 600 mW m⁻² was achieved at the beginning of the discharge cycle, which gradually decayed over time as the cell voltage decreased (Figure 2b, right y-axis).

The relationship between the cell voltage and salinity was further examined by measuring half-cell electrode potentials as a function of NaCl concentration. The electrode potential became increasingly positive as the NaCl concentration increased, with the potential being linearly proportional to log[NaCl] (Figure 2c). The potential difference between LC and HC solutions was 84 mV, in good agreement with theoretical predictions that the maximum power density can be achieved when R_{ext} equals R_{int}²⁻³⁻.²³

The cycle performance of the concentration flow cell was further examined at the R_{ext} value (14 Ω). The flow cell produced an average power density of 412 ± 12 mW m⁻² for 20 cycles with no trend in the fluctuations among successive cycles (Figure 3b). This continuous power production is a remarkable advantage of using this flow cell, as this approach overcomes a drawback of conventional CapMix technologies that generate electrical power intermittently. In CDLE and CDP, the whole cell was alternatively filled with LC and HC solutions, and the power density was lower in a LC solution than in a HC solution, as the low concentration significantly increased the internal solution resistance. In MEBs, the net electrical power production is obtained after four sequential steps, in which the energy input in a LC solution was subtracted from energy output in a HC solution. Here, solutions are directly changed under continuous flow conditions, rather than in separate steps.

**Effect of Hydraulic Retention Time on Power Production.** The hydraulic retention time (HRT) plays an important role in the concentration flow cell because the salinity difference inside the cell is created by continuously flowing the feed solutions. To evaluate the impact of HRT on power production, we performed energy harvesting experiments at R_{ext} = 14 Ω and varied the flow rates of the feed solutions. At a low HRT (0.5 s), we achieved a peak power density of 679 ± 77 mW m⁻² and an average power density of 435 ± 44 mW m⁻² (Figure 4). Increasing the HRT to 0.9 s reduced the peak power density to 661 ± 47 mW m⁻² and the average power density to 422 ± 24 mW m⁻². At the highest HRT tested (2.0 s), the peak power density was further reduced to 564 ± 7 mW m⁻² and the average power density
The HRT of 0.9 s was considered as the optimal condition because decreasing HRT from 2.0 to 0.9 s increased the average power density by 15%, whereas further decrease in HRT from 0.9 to 0.5 s only increased the average power density by 3%.

In this flow cell, the filtration membrane retards the advective transport of solutions between channels, and therefore a lower HRT led to an increase in HC/LC ratio and $\Delta U$. In addition, HRT can affect the solution exchange between cycles from HC to LC and LC to HC solutions in each channel. According to the Nernst eq (eq S1), the electrode potential is a function of activity of $Na^+$, and thus a lower HRT can enable rapid cell voltage development by quickly exchanging the previously filled solution inside each channel.

**Resistance Components of the Concentration Flow Cell.** To determine where resistive losses occurred in the flow cell, with the aim of identifying the largest resistances that would need to be reduced to improve performance, we measured the internal resistances and function of feed solutions and separator materials. In the regular operating condition (HC + LC), the measured overall internal resistance was 12.0 $\Omega$. The largest contribution to this resistance was the LC solution (5.6 $\Omega$), which had an inherently low conductivity due to its low ionic strength. The resistances from the HC solution (0.3 $\Omega$) and membrane (1.0 $\Omega$) were negligible, and the remaining resistance (5.1 $\Omega$) could be ascribed to the electrodes, contacts, and fixtures (Figure 5). Filling both channels with HC solutions (HC+HC) decreased the overall resistance by approximately 50% (6.4 $\Omega$), furthering indicating that LC solution was a major resistance component. When both channels were filled with LC solutions (LC+LC), the overall resistance was substantially larger (29.5 $\Omega$). This increase was mainly due to the membrane resistance (9.9 $\Omega$), which showed concentration-dependent resistance in separate experiments (Figure S7).

The overall resistance could be reduced by optimizing the cell architecture. For example, 25% of the cell resistance could be eliminated by decreasing the channel lengths to half of their original lengths. If the overall resistance could be reduced by an additional 50%, by further decreasing the resistance of other components, the expected averaged power density would reach approximately 0.8 W m$^{-2}$, which is comparable to that

![Figure 3](image-url)  
**Figure 3.** (a) Average power density vs energy density plot showing energy harvesting performance of the concentration flow cell and (b) cell voltage profile (solid line) and the average power density (rectangles) for 20 cycles ($R_{\text{ext}} = 14 \Omega$).

![Figure 4](image-url)  
**Figure 4.** Effect of hydraulic retention time (HRT) on the energy harvest performance ($R_{\text{ext}} = 14 \Omega$).

![Figure 5](image-url)  
**Figure 5.** Resistance components of the flow cell with different combination of feed solutions. The height of bars refers to the overall cell resistance, which was calculated from a voltage drop when applying constant current to the flow cell while supplying feed solutions. Contribution of HC (black) and LC (light gray) solutions were estimated by measuring effluent conductivity. Membrane resistance (white) was evaluated in separate experiments (see SI, section B). When estimating the membrane of the regular operating condition (HC+LC), we assumed that the concentration profile inside the membrane was linear. Other components (dark gray) were unknown components among the overall resistance, which could be ascribed to electrode, contact, and fixtures.
Membranes with larger pore sizes were used (SMWP, 5.0 μm) with the highest HC/LC ratio of 20.3 for MSI (pore size = 0.22 μm), the membrane showing the best performance (MSI) reduced resistance is insignificant for this system, likely because the membrane resistance was relatively small compared to the total internal resistance (Figure 5). In this regard, a filtration membrane with an even smaller pore size should lead to better separation for solutions with a higher HC/LC ratio and therefore better performance as long as the membrane contribution to the total internal resistance is insignificant. Although the use of the nonselective membrane showing the best performance (MSI) reduced mixing between HC and LC solutions, Na⁺ and Cl⁻ crossover was inevitable (Figure S8). This crossover would occur as a result of multiple processes: diffusion through the membrane, mixing between solutions upon switching the flow path, and Na⁺ migration through the membrane due to the current flow. Collectively, these processes would reduce the energy recovery efficiency of the system. Further optimizing this proof-of-concept device would be necessary to optimize the energy recovery by systematically investigating the influence of several parameters, including the membrane thickness and structure, the channel dimensions, and the hydraulic retention time.

**Comparison of the Concentration Flow Cell with Previous CapMix Devices.** The average power density achieved here (411 ± 14 mW m⁻²) is the highest reported value achieved for a CapMix system to date (Table 2), obtained using RED (∼1.0 W m⁻²) using solutions with similar conductivities to those used here.

**Evaluating Separation Performance of Filtration Membranes.** To better understand filtration membrane’s effectiveness at separating the solutions, we examined the effect of membrane pore size for several commercially available filtration membranes on salt crossover (separation performance) by collecting the effluent of each channel and measuring its conductivity. A smaller pore size resulted in better separation for solutions with a higher HC/LC ratio and therefore better performance as long as the membrane contribution to the total internal resistance is insignificant. Although the use of the nonselective membrane showing the best performance (MSI) reduced mixing between HC and LC solutions, Na⁺ and Cl⁻ crossover was inevitable (Figure S8). This crossover would occur as a result of multiple processes: diffusion through the membrane, mixing between solutions upon switching the flow path, and Na⁺ migration through the membrane due to the current flow. Collectively, these processes would reduce the energy recovery efficiency of the system. Further optimizing this proof-of-concept device would be necessary to optimize the energy recovery by systematically investigating the influence of several parameters, including the membrane thickness and structure, the channel dimensions, and the hydraulic retention time.

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**Table 1. Membrane Properties and the Separation Performance in the Flow Cell**

<table>
<thead>
<tr>
<th>membrane</th>
<th>material</th>
<th>pore size (μm)</th>
<th>thickness (μm)</th>
<th>LC conductivity (mS/cm)</th>
<th>HC conductivity (mS/cm)</th>
<th>HC/LC conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSI</td>
<td>magna nylon</td>
<td>0.22</td>
<td>110</td>
<td>2.1 ± 0.0</td>
<td>42.9 ± 0.1</td>
<td>20.3</td>
</tr>
<tr>
<td>Millipore GVWP</td>
<td>PVDF</td>
<td>0.22</td>
<td>125</td>
<td>2.2 ± 0.2</td>
<td>42.7 ± 0.1</td>
<td>19.1</td>
</tr>
<tr>
<td>Millipore HVLP</td>
<td>PVDF</td>
<td>0.45</td>
<td>125</td>
<td>3.0 ± 0.6</td>
<td>42.2 ± 0.3</td>
<td>14.0</td>
</tr>
<tr>
<td>Millipore RAWP</td>
<td>mixed cellulose esters</td>
<td>1.2</td>
<td>150</td>
<td>3.7 ± 0.3</td>
<td>41.3 ± 0.1</td>
<td>11.3</td>
</tr>
<tr>
<td>Millipore SMWP</td>
<td>mixed cellulose esters</td>
<td>5.0</td>
<td>135</td>
<td>13.7 ± 0.9</td>
<td>32.0 ± 1.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Millipore NY10</td>
<td>nylon</td>
<td>10.0</td>
<td>60</td>
<td>17.0 ± 1.8</td>
<td>29.3 ± 1.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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**Table 2. Overview of Experimental Conditions and Energy Harvesting Performance of CapMix Devices**

<table>
<thead>
<tr>
<th>type of CapMix</th>
<th>electrodes</th>
<th>solutions (M NaCl)</th>
<th>external power source</th>
<th>power production</th>
<th>av power density (mW/m²)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDL</td>
<td>+ AC</td>
<td>− AC</td>
<td>LC 0.024 0.6 25</td>
<td>yes</td>
<td>intermittent</td>
<td>n/a</td>
</tr>
<tr>
<td>CDL</td>
<td>modified AC</td>
<td>modified AC</td>
<td>0.02 0.5 25</td>
<td>yes</td>
<td>intermittent</td>
<td></td>
</tr>
<tr>
<td>spontaneous CDL</td>
<td>ACC</td>
<td>ACC</td>
<td>0.02 0.5 25</td>
<td>no</td>
<td>intermittent</td>
<td></td>
</tr>
<tr>
<td>SEK-CapMix</td>
<td>AC</td>
<td>AC</td>
<td>0.02 0.5 25</td>
<td>no</td>
<td>continuous</td>
<td></td>
</tr>
<tr>
<td>CDP</td>
<td>AC/AEM</td>
<td>AC/CER</td>
<td>0.01 0.51 51</td>
<td>no</td>
<td>intermittent</td>
<td></td>
</tr>
<tr>
<td>forced CDP</td>
<td>AC/AEM</td>
<td>AC/CER</td>
<td>0.01 0.51 30</td>
<td>no</td>
<td>intermittent</td>
<td></td>
</tr>
<tr>
<td>BES’-CDP</td>
<td>AC/AER</td>
<td>AC/CER</td>
<td>0.01 0.5 25</td>
<td>yes</td>
<td>intermittent</td>
<td></td>
</tr>
<tr>
<td>flow electrode-CDP</td>
<td>AC/AEM</td>
<td>AC/CER</td>
<td>0 0.34 n/a</td>
<td>no</td>
<td>continuous</td>
<td></td>
</tr>
<tr>
<td>flow electrode-CDE</td>
<td>AC/AEM</td>
<td>AC/CER</td>
<td>0.02 0.6 30</td>
<td>no</td>
<td>continuous</td>
<td></td>
</tr>
<tr>
<td>MEB</td>
<td>Na₂MnO₂ 0</td>
<td>Ag</td>
<td>0.02 0.6 30</td>
<td>yes</td>
<td>intermittent</td>
<td></td>
</tr>
<tr>
<td>MEB</td>
<td>CuHCF</td>
<td>CuHCF</td>
<td>0.017 0.513 30</td>
<td>no</td>
<td>continuous</td>
<td></td>
</tr>
</tbody>
</table>

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*Influent conductivity of LC = 1.8 ± 0.0 and HC = 42.7 ± 0.1 (HC/LC = 23.7).*

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across ion-exchange membranes can be 10 times higher than
Using a
inexpensive
in technical challenges in existing SGE systems. First, the cell did
eachion a filtration membrane had an additional benefit in
reducing the internal resistance of the cell, as the resistance
across ion-exchange membranes can be 10 times higher than
filtration membranes.21 Second, we used battery electrodes but
avoided the need for precious silver metal electrodes used in
previous studies. Silver is commonly selected as an electrode
material to obtain electrode potentials that depended on the
Cl− activity.9,17,18 In addition, the inadvertent release of silver
into the effluent could be toxic to aquatic life. Here, we used
two identical and benign electrodes that underwent redox
reactions with Na+. Third, the power production was constant
during cycles, whereas previous CapMix systems yielded lower
power densities (411 mW m−2). This superior performance would be due to
the inherent property of battery electrodes enabling the
concentration cell architecture consisting of battery electrodes in this
study showed better performance than that of carbon
electrodes.10 The concentration flow cell achieved a higher voltage rise
(172 vs 110 mV) and a lower cell resistance (35 vs
50 mW m−2). This superior performance would be due to
the inherent property of battery electrodes enabling the
concentration-dependent electrode potential development as
opposed to carbon electrodes which should be chemically
modified to achieve the same goal. Thus, these multiple
advantages of the flow cell could enable cost-effective capture of
salinity gradient energy as electrical power.

**Implications for Enhancing the Power Production of CapMix.** The concentration flow cell demonstrated here
represents a new approach for converting energy from salinity
differences to electrical power, with an average electrical power
density (411 mW m−2) that is twice as high as values previously
reported for other CapMix technologies. The flow cell
architecture allowed for simultaneous feeding of two solutions
and using two identical battery electrodes, and therefore the
power production was nearly continuous over cycles where the
solutions were alternated between the channels. When
compared to conventional SGE technologies, the flow cell
can achieve power densities similar to those produced using
RED, without the need for expensive ion-exchange membranes.
In addition, the use of a filtration membrane as a separator
should reduce fouling compared to PRO, as there is no
advective flow required through the membrane. When
employing the concentration flow cell to produce power from
real seawater, of which pH is typically neutral or mild basic, a
proper pretreatment would be required to adjust pH for
maintaining the performance because the structure of CuHCF
is known to be more stable under mild acidic conditions.24 The
cyanide in ferri/ferrocyanide ions is a nontoxic form of cyanide,
and therefore its impact on aquatic life would be negligible,
while toxic cyanide ions can be released under a strong acidic
condition.25 A simple synthesizing method of CuHCF, mixing
two salt solutions, can enable mass production of electrode
materials, thus an industrial-scale process can be easily
developed using conventional infrastructure. Therefore, this
concentration flow cell should provide an efficient and cost-
effective method of harvesting energy from renewable resources
for sustainable power generation.

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Supporting information for:
Harvesting energy from salinity differences using battery electrodes in a concentration flow cell

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The supporting information contains 8 figures and 16 pages.

A. Evaluating internal resistance of the flow cell ................................................................. 2
B. Evaluating area resistance of membrane using a DC current method ................................. 4
C. Open-circuit cell voltage recorded with and without CuHCF ......................................... 6
D. Estimation of cell voltage development based on activity coefficients ............................ 8
E. Electrochemical characterizations of CuHCF electrode .................................................. 10
F. Cell voltage profiles depending on external resistance values ..................................... 12
G. Area resistance of membrane as a function of NaCl concentration ......................... 13
H. Irreversible mixing of NaCl solutions across the filtration membrane in the flow cell .... 14
References ......................................................................................................................... 16
A. Evaluating internal resistance of the flow cell

Internal resistance of the flow cell was examined by measuring voltage drop when applying constant current. Experiments were conducted by varying combinations of high (HC, 0.513 M NaCl) and low concentration (LC, 0.017 M NaCl) feed solutions: HC+LC, HC+HC, and LC+LC. Feed solutions were continuously supplied to each chamber of the flow cell during the experiments. The flow cell first equilibrated by applying 0 V for 5 min, and the circuit was opened for 1 min. Then, 0.5 mA was applied until the cell voltage approached to 0.03 V. Next, the cell voltage was set to 0.03 V for 5 min followed by open circuit, and discharged by applying –0.5 mA until 0 V. The voltage drop was taken from the linear fit of charging or discharging profiles after the constant slope was achieved (typically in 30 sec, Fig. S1).
Figure S1. Representative voltage profile for obtaining internal resistance of the flow cell by applying constant current (–0.5 mA).
**B. Evaluating area resistance of membrane using a DC current method**

Area resistance of membrane was measured using a DC current method. A membrane was placed between two chambers (each 4 cm long, 3 cm in diameter, inner volume = ~30 ml), where platinum mesh and Ag/AgCl reference electrodes were installed (Fig. S2a). Reference electrodes were placed close to a membrane (2.7 cm apart) and platinum mesh electrodes were placed at each end of chamber (7.8 cm apart). After filling the chambers with the solution, constant current was applied (1–10 mA) to platinum electrodes while the voltage between reference electrodes were recorded using a potentiostat (VMP3, Bio-Logic). The resistance was calculated from the slope of current and voltage ($R = \frac{V}{I}$). The resistance was first measured without a membrane, which is the background resistance mainly due to the solution, and this value was subtracted from the resistance measured with a membrane (Fig. S2b). The area resistance was then calculated by multiplying area of the membrane (7.07 cm$^2$). All experiments were performed in triplicated at room temperature.
Figure S2. (a) A custom-built reactor for measuring area resistance of membrane and (b) representative voltage vs. current plot measured w/ and w/o membrane in 0.017 M NaCl.
C. Open-circuit cell voltage recorded with and without CuHCF

To examine the cell voltage development of the flow cell without CuHCF, open-circuit cell voltage profiles were obtained using graphite foil without CuHCF (Fig. S3). In the regular operating condition (with CuHCF in 0.017 and 0.513 M NaCl, black rectangles), open-circuit cell voltage achieved was approximately 172 mV. The cell voltage of approximately 20 mV was recorded without CuHCF (white rectangles), which can be ascribed to the liquid junction potential. The configuration of the flow cell, high and low concentration NaCl solutions separated by a membrane, can enable the diffusion of ions in the high concentration solution into the low concentration solution through the membrane. Since Cl\(^-\) diffuses faster than Na\(^+\), more positive potential could be developed in the channel filled with high concentration NaCl. To better understand this additional potential, the open-circuit cell voltage was measured using KCl, which has similar cation and anion diffusion rate (grey rectangles). The cell voltage measured was approximately 15 mV, which was comparable to that of NaCl. Thus, the additional cell voltage cannot be explained only by different diffusion rate of Na\(^+\) and Cl\(^-\). A few functional groups of the filtration membrane may facilitate the diffusion of Cl\(^-\) and/or impede that of Na\(^+\).
**Figure S3.** Open-circuit cell voltage profiles recorded w/ CuHCF in NaCl (black rectangles), w/o CuHCF in NaCl (white rectangles), and w/o CuHCF in KCl (grey rectangles).
D. Estimation of cell voltage development based on activity coefficients

The activity-dependent electrode potential can be estimated from the following Nernst equation:

\[ E = E^0 + \frac{RT}{F} \ln[a_{Na^+}] \]  

(S1)

where \( E \) is the electrode potential, \( E^0 \) is the standard electrode potential, \( R \) is the gas constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\), \( T \) is temperature (K), \( F \) is the Faraday constant \((96,485 \text{ C mol}^{-1})\), and \( a \) is activity. In the flow cell, two CuHCF electrodes were simultaneously exposed to HC and LC solutions, and therefore the cell voltage difference (\( \Delta U \)) can be written as:

\[ \Delta U = 2 \frac{RT}{F} \ln \left( \frac{a_{Na_{HC}^+}}{a_{Na_{LC}^+}} \right) \]  

(S2)

The concentration-dependent cell voltage development of this flow cell was estimated based on reported mean activity coefficient values of NaCl solutions \((0.01–1.00 \text{ mol kg}^{-1} \text{ at } 25^\circ\text{C})\).\(^2\) The molality values were converted to molarity, and the arbitrary electrode potential was plotted vs. NaCl concentrations (M) by following Nernst equation,

\[ E = E^0 + \frac{RT}{F} \ln(\gamma_{NaCl}^\pm c) \]  

(S3)

where \( \gamma_{NaCl}^\pm \) is the mean activity coefficient of NaCl, and \( c \) is the concentration. Estimated electrode potential difference between 0.017 and 0.513 M NaCl was approximately 81 mV (Fig. S4), which becomes 162 mV in the flow cell.
Figure S4. Arbitrary potential vs. concentration plot derived from mean activity coefficient values of NaCl.
E. Electrochemical characterizations of CuHCF electrode

Cyclic voltammetry was conducted by using CuHCF electrode painted on Ti foil using a brush. Representative cyclic voltammogram was obtained in 1 M NaCl at a scan rate of 1 mV s\(^{-1}\) (Fig. S5a). Note that small electrode material loading (~1 mg) could have resulted in inaccurate mass based current (A/g). Galvanostatic cycling test was performed by using CuHCF coated on graphite foil in a half-cell consisting of Ag/AgCl reference electrode and activated carbon (YP-50F) counter electrode, and 0.513 M NaCl was used as an electrolyte (Fig. S5b). The cell was charged and discharged at ±3 mA in the range of 0.6–0.8 V (vs. Ag/AgCl) for 50 cycles, and the resulting discharging capacity and coulombic efficiency were calculated. After 50 cycles, the capacity retention was 99% and coulombic efficiency was 99.5% (Fig. S5c). When performed galvanostatic charge/discharge tests in the flow cell by applying ±0.5 mA (0.0–0.05 V), the coulombic efficiency was 76% when flowing HC (0.513 M NaCl) and LC (0.017 M NaCl), and 89% when flowing HC and HC (Fig. S5d). Since the power production in the flow cell was achieved by discharging only, these coulombic efficiency values would not represent the efficiency of the flow cell.
Figure S5. (a) Cyclic voltammogram of CuHCF in 1 M NaCl at a scan rate of 1 mV s\(^{-1}\). (b) Representative galvanostatic charge/discharge profiles at ±3 mA (0.6–0.8 V) in 0.513 M NaCl, (c) capacity and coulombic efficiency for 50 cycles, and (d) galvanostatic charge/discharge profiles recorded in a flow cell by applying ±0.5 mA (0.0–0.05 V) while flowing HC (0.513 M NaCl) and LC (0.017 M NaCl) or HC and HC solutions through each channel at the flow rate of 7.5 ml min\(^{-1}\).
F. Cell voltage profiles depending on external resistance values

Figure S6. Representative voltage profiles depending on external resistance (10, 14, 16, 22, 30 Ω).
G. Area resistance of membrane as a function of NaCl concentration

**Figure S7.** Area resistance of membrane (MSI) as a function of NaCl concentration (0.017, 0.042, 0.141, 0.265, 0.513 M).
**H. Irreversible mixing of NaCl solutions across the filtration membrane in the flow cell**

To examine the irreversible mixing of high and low concentration NaCl solutions across the filtration membrane (magna nylon, thickness = 110 µm, pore size = 0.22 µm, Micron Separations Inc.), we recorded the conductivities of high and low concentration solutions (HC and LC) in the reservoir (each 100 mL) while flowing two solutions through each channel of the flow cell (channel width = 1cm; height = 3 cm; thickness = 400 µm) at the flow rate of 7.5 ml min\(^{-1}\) without electrodes. After flowing the solutions for 100 min, the conductivity of HC decreased from 47.8 to 45.9 mS cm\(^{-1}\), while that of LC increased from 1.98 to 3.76 mS cm\(^{-1}\) (Fig. S8). The HC/LC ratio, which can be converted to the cell voltage in the flow cell, decreased from 24.1 to 12.2, indicating that approximately 35 mV of the cell voltage would be lost due to the irreversible mixing. The average crossover flux evaluated from the initial and final conductivity values of LC was 0.87 mmol m\(^{-2}\) s\(^{-1}\) for the 100 min. The mixing would be affected by various parameters such as membrane porosity, channel dimensions, and hydraulic retention time.
Figure S8. Conductivity values of HC (filled squares, 0.513 M NaCl) and LC (open squares, 0.017 M NaCl) and HC/LC ratio (gray circles) as a function of time.
References
