Evaluating Battery-like Reactions to Harvest Energy from Salinity Differences using Ammonium Bicarbonate Salt Solutions

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Mixing entropy batteries (MEBs) are a new approach to generate electricity from salinity differences between two aqueous solutions. To date, MEBs have only been prepared from solutions containing chloride salts, owing to their relevance in natural salinity gradients created from seawater and freshwater. We hypothesized that MEBs could capture energy using ammonium bicarbonate (AmB), a thermolytic salt that can be used to convert waste heat into salinity gradients. We examined six battery electrode materials. Several of the electrodes were unstable in AmB solutions or failed to produce expected voltages. Of the electrode materials tested, a cell containing a manganese oxide electrode and a metallic lead electrode produced the highest power density (6.3 mW m⁻²). However, this power density is still low relative to previously reported NaCl-based MEBs and heat recovery systems. This proof-of-concept study demonstrated that MEBs could indeed be used to generate electricity from AmB salinity gradients.

Introduction

A salinity difference between two aqueous solutions is a potential source of energy owing to the system-wide entropy increase when the solutions mix. Salinity differences can occur naturally (e.g., when freshwater reaches seawater) or be engineered using thermolytic salts that have highly temperature-dependent solubilities. Relative to natural salinity gradients, those engineered using thermolytic salt solutions, such as ammonium bicarbonate (NH₄HCO₃, AmB), can generate larger salinity differences and be used at sites that produce waste heat.[15] Salinity differences using AmB solutions can be created by conventional distillation and condensation at low temperatures (≥ 40 °C),[1,2] making them a viable means to capture low-grade waste heat (temperatures < 130 °C). Currently, a tremendous amount of low-grade waste heat is generated at industrial sites and power plants, equivalent to approximately half of the current U.S.A energy demand (2.9 x 10¹³ kWh in 2013).[3] Therefore the use of AmB solutions in salinity gradient energy processes could potentially produce a significant amount of electrical power from existing waste heat sources.

Three main approaches have been used to capture energy from engineered salinity differences derived from thermolytic salts: pressure-retarded osmosis (PRO),[2] reverse electrodialysis (RED),[1,4] and capacitive mixing (CapMix).[5] PRO captures energy from salinity differences by creating pressure differences between two waters with different salinities using semi-permeable membranes. RED captures energy by developing electrochemical potentials in solutions with high and low salinities that cross a stack of alternating cation- and anion-exchange membranes. The term CapMix refers to technologies that use electrodes to directly capture electricity from ion-electrode interactions. There are three fundamentally different types of interactions that can be used to capture energy with CapMix: capacitive double layer expansion (CDLE),[6,7] capacitive energy extraction based on Donnan potentials (CDP) established using ion-exchange membranes or coatings on electrodes,[5,6,10] and pseudo-capacitive faradaic (i.e., redox) interactions in devices called mixing entropy batteries (MEBs).[11–14] CapMix has the potential to be an advantageous alternative to PRO or RED because it enables energy capture without the need for additional converters. PRO requires a turbine to generate electricity and is susceptible to membrane fouling, whereas RED has a complex cell configuration consisting of electrodes combined with suitable redox couples and stacks of ion-exchange membranes. Of the CapMix approaches, MEBs are particularly attractive because they can develop a stable electrode potential (as opposed to a highly variable potential in CDLE) and typically do not require ion-exchange membranes (which are necessary for CDP). The electrode materials that have been used in MEBs to date include metal oxides,[11,13] Prussian blue analogues,[12,14] a metal,[15] and a precious metal.[11–15] A depiction of how energy is captured in an MEB using low concentration (LC) and high concentration (HC) salt solutions over a four-step cycle is shown in Figure 1.
To date, MEBs have only been used to capture salinity gradient energy from chloride salts (i.e., NaCl, LiCl, and ZnCl₂).\textsuperscript{[11–15]} In these studies, Ag metal electrodes were used to facilitate a Cl⁻-dependent redox reaction (i.e., AgCl(s) + e⁻ → Ag⁰ + Cl⁻). To capture energy from changes in cation concentrations, researchers have used intercalation reactions (e.g., 5 MnO₂ + 2e⁻ + 2Na⁺ → Na₃Mn₂O₄)\textsuperscript{[16, 17]} and corrosion/deposition reactions (e.g., Zn²⁺ + 2e⁻ → Zn²).\textsuperscript{[18]} Using MEBs to capture salinity gradient energy from thermolytic salts, such as AmB, requires fundamentally different electrode–ion redox reactions to occur and hence different electrode materials. To identify potential electrode materials that undergo redox reactions with ammonium (NH₄⁺) or carbonate (CO₃²⁻) ions, we evaluated six electrode materials used in conventional batteries: manganese oxide (MnO₂), copper hexacyanoferrate (CuHCF), ferrous phosphate (FePO₄), lead dioxide (PbO₂), metallic lead (Pb), and metallic silver (Ag⁰). Based on known reactions for these electrode materials and thermodynamic calculations, we hypothesized that MnO₂, CuHCF, and FePO₄ would undergo redox reactions with ammonium, and that PbO₂, Pb, and Ag would undergo redox reactions with bicarbonate or carbonate. MnO₂, CuHCF, and FePO₄ undergo faradaic reactions with Li⁺ and Na⁺.\textsuperscript{[19]} Redox reactions of NH₄⁺ with MnO₂\textsuperscript{[18]} and CuHCF\textsuperscript{[18]} have been reported, but not in the presence of carbonate. Pb and PbO₂ participate in faradic reactions with carbonate,\textsuperscript{[20]} and Ag can be oxidized in carbonate solutions to form Ag₂CO₃.\textsuperscript{[21]} For each electrode material, we tested if it underwent reversible redox reactions when exposed to varying concentrations of ammonium or bicarbonate/carbonate. Of these materials, promising candidates were made into electrodes and their compatibility, reactivity, and concentration-dependent potential were investigated using AmB solutions at high and low concentrations. We further evaluated a subset of these materials for energy recovery.

**Results and Discussion**

**Half-cell performance of electrodes that undergo redox reactions with NH₄⁺**

We initially determined if each of the three proposed positive electrode materials (CuHCF, FePO₄, MnO₂) underwent reversible faradaic reactions with NH₄⁺ when exposed to HC (1 M) and LC (0.02 M) AmB solutions by constructing composite electrodes (details in the Methods section) and using cyclic voltammetry or galvanostatic charge/discharge tests. CuHCF, a Prussian blue analog, is known to intercalate several cations (i.e., Li⁺, Na⁺, K⁺, and NH₄⁺).\textsuperscript{[19]} However, when we exposed the CuHCF composite electrode to a 1 M AmB solution, it dissolved, as indicated by the clear solution becoming yellow. The dissolution of CuHCF was likely as a result of the AmB solution having a slightly basic pH (~8). To test this, we exposed CuHCF to more acidic NH₄Cl solutions (pH ~5). At this pH, the electrode was stable and underwent a reversible electron transfer reaction in galvanostatic charge/discharge experiments, indicating that the alkaline solution, and not NH₄⁺, led to the dissolution of CuHCF. For FePO₄, an electrochemically delithiated form of LiFePO₄,\textsuperscript{[22]} we obtained a very small charging capacity (data not shown) in galvanostatic tests conducted in 1 M AmB solution, which may have been because the NH₄⁺ was too large to be intercalated into the FePO₄ olivine structure. Consequently, both CuHCF and FePO₄ were ruled out as possible positive electrode materials.

In contrast, the MnO₂ composite electrode was stable in AmB and underwent a reversible redox reaction with NH₄⁺. In MnO₂, structural Mn⁴⁺ can be reduced to Mn²⁺ by cations, such as NH₄⁺, intercalating in the structure (i.e., MnO₂ + NH₄⁺ + e⁻ → MnOONH₄).\textsuperscript{[23]} For this reaction, the electrode potential is controlled by the activity of the ammonium cation, and can be described by the following Nernst equation:
\[ E = E^0 + (RT/F) \ln \left\{ \frac{[\text{NH}_4^+]}{[\text{OH}^-]} \right\} \]  

(1)

where \( E \) is the reduction potential, \( E^0 \) is the standard reduction potential, \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday constant, and curly brackets denote activity. The energy harvesting performance of the MnO\(_2\) electrode with NH\(_4\)Cl was tested by applying a constant current and alternating HC and LC solutions. We observed a large potential gain (\( \Delta E_c \approx 65 \text{ mV} \)) and a relatively small ohmic loss (\(-17 \text{ mV} \)), yielding an overall potential difference (\( \Delta E = \Delta E_c - \text{ohmic loss} \)) of approximately 48 mV (Figure 2a). However, the electrode performance in AmB solutions showed a significantly decreased potential difference despite using the same salinity difference as in the case of the NH\(_4\)Cl solutions (Figure 2b). This low potential difference for AmB was surprising, as we expected the electrode potential to be described by Equation (1). According to this equation, the electrode potential should be approximately 100 mV more positive in the HC solution relative to the LC solution without activity corrections. However, the potential (\( \Delta E_c \)) obtained by changing the pH between the HC and LC solutions was only approximately 20 mV, which was too low to be useful in an MEB because ohmic resistances within the cell would further diminish this value to nearly 0 mV.

To investigate why the MnO\(_2\) electrode yielded large potential differences in NH\(_4\)Cl, but not in AmB, we investigated the differences between the pH of the solutions. AmB solutions are approximately pH 8, whereas NH\(_4\)Cl solutions are approximately pH 5. To test if pH affected the MnO\(_2\) electrode potential, we examined the energy harvesting performance and compared the gained potential (\( \Delta E_c \)) and potential difference (\( \Delta E \)) in several HC and LC ammonium solutions: NH\(_4\)Cl (pH 5), NH\(_4\)HCO\(_3\) + HCl (pH 7), NH\(_4\)HCO\(_3\) (pH 8), and NH\(_4\)HCO\(_3\) + NH\(_4\)OH (pH 9) (Figure 2c and Figure S1, Supporting Information). Both \( \Delta E_c \) and \( \Delta E \) decreased, and even reversed, when the pH increased from 5 to 9. This pH-dependent potential rise and fall explained the surprising low potentials found for AmB solutions. Under alkaline conditions, water can react with the MnO\(_2\) composite electrode, which can be written as: MnO\(_2\) + H\(_2\)O + e \( \rightarrow \) MnOOH + OH\(^-\)\(^{24}\) with a corresponding Nernst equation:

\[ E = E^0 - \frac{RT}{F} \ln \left[ \frac{[\text{OH}^-]}{[\text{H}_2\text{O}]} \right] \]  

(2)

When both NH\(_4\)\(^+\) and OH\(^-\) are present, the Nernst equation can be written by combining Equations (1) and (2) as:

\[ E = E^0 - \frac{RT}{F} \ln \left[ \frac{[\text{NH}_4^+]}{[\text{OH}^-]} \right] \]  

(3)

According to this equation, the electrode potential should be determined by the activities of both NH\(_4\)\(^+\) and OH\(^-\). Based on these experiments conducted at pH 5–9, the results suggested that Equation (3), and not Equation (1), controlled the electrode potential in the AmB solutions when hydroxide activities were sufficiently high. Although the Nernst equation cannot completely explain the low voltage rise and fall, the fact that AmB is a pH buffer could provide one possible reason. The pH (and hence OH\(^-\) activity) of HC and LC AmB solutions were the same (data not shown), whereas NH\(_4\)\(^+\) activity was different, and therefore the dominant species determining the electrode potential could be different in HC and LC AmB solutions. We could not calculate the exact potential change for each of these equations because the activity coefficient for ammonium in HC and LC AmB solutions was difficult to estimate\(^{25}\). According to Equation (3), both hydroxide and ammonium can react with the MnO\(_2\) electrode, and therefore the solution composition of AmB such as pH could change between cycles. However, we expected that the major reaction would be with NH\(_4\)\(^+\), considering the relatively low activity of OH\(^-\) (10\(^{-9}\) M at pH 8). More electrochemical characterizations...
would be necessary to better understand the reaction of the MnO₂ electrode with both NH₄⁺ and OH⁻. By conducting similar experiments in sodium chloride and bicarbonate solutions, we also observed that the solution pH influenced the MnO₂ electrode potential (see Figure S2). The voltage profiles of NaCl (Figure S2a) followed the concentration of Na⁺, but the increasing pH of NaHCO₃ significantly decreased the voltage rise and fall, and even reversed at pH 10 (Figure S2d), supporting the conclusion that the MnO₂ electrode potential is not simply determined by the activities of the cations in alkaline solutions.

**Half-cell performance of electrode materials that undergo redox reactions with CO₃²⁻**

We evaluated three electrode materials (Ag, PbO₂, and Pb) that undergo faradaic redox reactions in the presence of carbonate. Ag was expected to react with carbonate according to: Ag₃CO₃(s) + 2e⁻ → 2Ag + CO₃²⁻. However, in 0.02 and 1 M AmB solutions, we did not observe sufficient potential gains to harvest energy. Instead, we observed a net energy consumption (i.e., the potential difference was negative) owing to ohmic losses (Figure 3a). We observed similar large ohmic losses for the Ag electrode in HC and LC NaHCO₃ solutions (Figure 3b). We suspect that the reason for the reduced performance with AmB relative to NaHCO₃ was complexation of silver ions with ammonia [i.e., Ag(NH₃)₂⁺ + e⁻ → Ag + 2NH₃; ΔE° = 0.37 V vs. SHE]. Moreover, to confirm that the Ag electrode was viable in chloride solutions, we replicated previous findings that it exhibits a Cl⁻-dependent potential in HC and LC NaCl solutions, and found our results to be consistent with previous reports (Figure 3c). Because of the inability of a Ag electrode to yield positive potential gains in AmB, we ruled it out as a potential negative electrode material.

Both Pb and PbO₂(s) are used as electrode materials in lead-acid batteries because they both undergo redox reactions with H₂SO₄ to form PbSO₄(s). According to thermodynamic calculations, they should undergo similar redox reactions with CO₃²⁻ to form PbCO₃(s). PbO₂ reacts with carbonate ions according to the reaction PbO₂(s) + CO₃²⁻ + H₂O + 4e⁻ → PbCO₃(s) + 2OH⁻, suggesting that PbO₂ could function as a positive electrode with AmB (Figure S4a). As predicted by the Nernst equation, exposing the PbO₂ electrode to a HC AmB solution yielded a more positive potential (10–20 mV) compared to a LC solution (Figure S4b). However, net energy was consumed because the ohmic losses were larger than the potential difference, ruling out PbO₂ as a potential electrode material.

Pb reacts with carbonate according to PbCO₃(s) + 2e⁻ → Pb + CO₃²⁻, which yields the Nernst equation:

\[ E = E^0 - \left( \frac{RT}{2F} \right) \ln \left( \frac{[CO_3^{2-}]}{[Pb]} \right) \]  

As predicted from the Nernst equation, the Pb electrode exhibited a CO₃²⁻-dependent potential in HC and LC AmB solutions (Figure 4a), suggesting that it was a promising electrode material. In cycling experiments, however, we found that repetitive charging and discharging irreversibly changed the electrode potential. The potential shifted to more negative (charge) and more positive (discharge) values with electrode cycling, which decreased the energy and power recovery over time (Figure 4a). This deterioration in potential was likely because of the irreversible reaction between Pb and PbCO₃ in the potential range used here. As shown in the current profile obtained by cyclic voltammetry (CV) in 1 M AmB (Figure 4b), less current was delivered during the cathodic sweep, meaning that the PbCO₃ was only partially reduced to Pb. This irreversibility is an intrinsic property of Pb in a carbonate solution; on the cathodic sweep, the base layer is reduced first and a more negative potential is required to further reduce the deposited layer. Therefore, the accumulation of PbCO₃ layer was inevitable because the potential range was quite narrow during the energy harvesting cycles, which would gradually increase the resistance and require more voltage for the reactions (Figure S3).
Despite this limitation, Pb was the most promising negative electrode material analyzed.

The use of cation-exchange membrane for MnO₂ and Pb electrodes in a full-cell

Our half-cell experiments indicated that MnO₂ and Pb were the most promising electrode materials for a MEB harvesting energy from AmB salinity gradients. However, the MnO₂ electrode potential gain in these experiments was very low. To address this issue, we hypothesized that we could increase the potential gain for the MnO₂ electrode by placing a cation exchange membrane (CEM) at the MnO₂-solution interface to selectively allow NH₄⁺ to be transported across the membrane and dictate the electrode potential. To test the effect of the CEM on the MnO₂ potential, we compared the half-cell energy harvesting performance of an MnO₂|CEM electrode in 1 m AmB solutions. The potential profiles obtained during a cycle under these conditions showed a larger voltage gap (~40 mV) between charging and discharging potentials (each for 100 s) with a CEM (dashed line), whereas only a small difference in potential (~5 mV) was obtained without a CEM (solid line) (Figure 5). When the MnO₂ electrode with a CEM was sequentially exposed to HC from LC solutions, ammonium ions diffused through the membrane and produced a more positive or negative potential in response to the solution concentration. This mechanism is similar to the CDP approach, in which capacitive electrodes are used in NaCl solutions and a Donnan potential is created using membranes.[8]

Based on these promising results, we examined the performance of a full battery cell containing the MnO₂|CEM and Pb electrodes. The potential profiles of each electrode in a full cell showed a typical potential rise and fall upon changing solutions between HC (1 m AmB) and LC (0.02 m AmB) during the cycle (Figure 6a). In the HC AmB solution, the potential of the MnO₂ electrode increased, and the potential of the Pb electrode decreased, as expected. The positive MnO₂ electrode showed a greater potential difference than the Pb electrode upon changing the solution (58 vs. 44 mV), and lower ohmic losses (15 vs. 31 mV in 0.02 m AmB). The lower performance of the Pb electrode was likely because Pb oxidation to form PbCO₃ is a two-electron transfer (i.e., \(n = 2\) in the Nernst equation). Consequently, the effect of changing the CO₃²⁻ concentration will be half that of a single-electron transfer reaction according to the Nernst equation. The larger ohmic loss of the Pb electrode may be related to the pH chemistry of carbonate. Because HCO₃⁻ is the dominant species at pH 8, the relatively low CO₃²⁻ concentration should contribute to the higher ohmic loss because it requires more potential to drive the reaction.

The potential profile of the full cell during a cycle using these two electrodes is shown in a closed-loop potential vs. charge plot in Figure 6b. In this plot, the size of the inside area shows the energy harvested in a cycle. Integration of this area yielded a power density of 6.3 ± 0.2 mW m⁻² (normalized to the electrode area), which is lower than previously reported power densities for NaCl-based MEBs (105 mW m⁻²).[11] Although the gained potential (ΔEG) from two different solutions (0.02 and 1 m AmB) was approximately 100 mV, the available potential (ΔE) was significantly reduced owing to ohmic losses in the low conductivity LC solution. Consequently, the power density is still low, especially compared to the amount of thermal energy needed to distill NH₃ and CO₂. We estimated the thermal energy necessary to distill AmB solutions using HYSYS simulation software (454 kJ L⁻¹, Figure S6). This value was large relative to the maximum available mixing free energy.
when combining 0.02 and 1 M AmB solutions (1.4 kJ L\(^{-1}\)), indicating a maximum energy efficiency of approximately 0.3 % (see the Supporting Information sections F and G for detailed calculations).\(^{[11,28,29]}\) In practice, the energy efficiency may be lower owing to the internal resistance, the rate of charging and discharge, dead zones, and non-ideal flows inside the reactor (see the Supporting Information section H for detailed calculations).\(^{[28,30]}\) Theoretical energy efficiency for converting heat to current reported in previous heat recovery studies range from approximately 1 % (thermally regenerative ammonia-based battery system\(^{[31]}\)) to 10 % (ZnCl\(_2\)-based MEB system\(^{[19]}\)), with power densities in the order of 1–60 W m\(^{-2}\). Therefore, the performance of the current system needs further improvements to obtain an enhanced power density with reasonable energy efficiency. However, it should be pointed out that low temperature heat is currently a waste product, and therefore a low energy efficiency is not necessarily a limitation of the technology.

### Outlook for using AmB solutions in MEB processes

Identifying suitable electrode materials is a key challenge for using AmB solutions in an MEB. Our evaluation of several battery electrodes, summarized in Table 1, provides general guidelines for selecting these materials. First, the electrodes must undergo reversible redox reactions with NH\(_4^+\) or HCO\(_3^-\)/CO\(_3^{2-}\) that can produce substantial potential rise and falls in AmB solutions. Although this potential change can in theory be predicted using the Nernst equation, we found that such calculations are not always sufficient. In the case of the MnO\(_2\) electrode, two different reaction mechanisms could be written [Eqs. (1) and (2)], and there was no intuitive means to determine which reaction dictated the cell potential without conducting the experiments. Second, the electrodes should not be adversely impacted by side reactions. For example, silver reacted not only with carbonate, but also with ammonia. Third, the electrode material must be stable in a weak base solution, as the pH of AmB is approximately 8. Many metal-based materials are known to be quite unstable under such conditions. These chemical conditions were the reason why most conventional battery electrodes that were considered here for use in the MEB with NaCl solutions, such as CuHCF, could not be successfully translated to an AmB-based process. Even for electrode materials that satisfy these requirements, a large, favorable electrochemical reaction must be obtained to produce sufficiently large potential differences in LC and HC solutions to offset ohmic losses. Although our results demonstrate that MEBs can be used to capture energy from AmB salinity gradients, there are many avenues to increase the power densities in subsequent studies. For example, the large ohmic loss could be minimized in future tests by decreasing the distance between the electrodes or adding an inert background electrolyte.

### Table 1. Summary of the battery electrodes used in this study.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Polarity</th>
<th>Target ion</th>
<th>Working voltage [V vs. Ag/AgCl]</th>
<th>Potential rise and fall</th>
<th>Limitation</th>
<th>Feasibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO(_2)</td>
<td>+</td>
<td>NH(_4^+)</td>
<td>0.3–0.8</td>
<td>yes (small)</td>
<td>interference of OH(^-)</td>
<td>yes (w/CEM(^{[2]}))</td>
</tr>
<tr>
<td>CuHCF</td>
<td>+</td>
<td>NH(_4^+)</td>
<td>–0.8(^{[29]})</td>
<td>yes</td>
<td>electrode dissolution</td>
<td>no</td>
</tr>
<tr>
<td>FePO(_4)</td>
<td>+</td>
<td>NH(_4^+)</td>
<td>N/A(^{[29]})</td>
<td>no reactions w/NH(_4^+)</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>PbO(_2)</td>
<td>+</td>
<td>CO(_3^{2-})</td>
<td>–0.65</td>
<td>yes (small)</td>
<td>high overpotential</td>
<td>no</td>
</tr>
<tr>
<td>Pb</td>
<td>–</td>
<td>CO(_3^{2-})</td>
<td>–0.65</td>
<td>yes</td>
<td>poor cycle life</td>
<td>yes (short term)</td>
</tr>
<tr>
<td>Ag</td>
<td>–</td>
<td>CO(_3^{2-})</td>
<td>0.35</td>
<td>yes (small)</td>
<td>high overpotential, side reaction w/NH(_4^+)</td>
<td>no</td>
</tr>
</tbody>
</table>

\(^{[a]}\) CEM = cation-exchange membrane. \(^{[b]}\) Midpoint of potentials showing cathodic and anodic peak currents in previous study\(^{[32]}\) \(^{[c]}\) De-lithiated form of LiFePO\(_4\). \(^{[d]}\) Not available.
Conclusions

Battery-like reactions were evaluated to harvest energy from HC and LC AmB solutions. Among various electrode materials examined, MnO₂ (with a CEM) and Pb were the most feasible electrode materials, although the power densities obtained were lower than previous NaCl-based MEBs and heat recovery systems. Evaluation of several different materials as battery electrodes demonstrated the challenges in developing a MEB process based on AmB solutions. These include finding materials stable in an alkaline solution containing ammonia and showing good faradaic reactions that provide large potential differences depending on ammonium and carbonate (or bicarbonate) concentrations. Further improvements in materials and reactor architecture could allow AmB solutions to be used for energy production by employing battery-like reactions in MEBs.

Experimental Section

Electrode materials

MnO₂ powder was synthesized using the co-precipitation method. An aqueous solution of 0.2 M MnSO₄ (120 mL, Alfa Aesar) was poured into another aqueous solution of 0.2 M KMnO₄ (80 mL, Alfa Aesar) while continuously agitating the solution. The resulting MnO₂ precipitates were washed and collected by centrifugation and dried in a vacuum oven at 100 °C for 12 h. Copper hexacyanoferrate (CuHCF) was also synthesized by co-precipitation. Two aqueous solutions of 0.1 M Cu(NO₃)₂ (80 mL, Sigma–Aldrich) and 0.05 M K₃Fe(CN)₆ (80 mL, J.T. Baker) were added dropwise to deionized water (40 mL) with vigorous stirring. The CuHCF precipitate was collected by following the same procedure as for the MnO₂. Pb (9032K272, McMaster-Carr) and Ag (326984, Sigma–Aldrich) plates were purchased and cut into square pieces (4 cm x 4 cm). These plates were ground with sandpaper before use to obtain a fresh surface. For powder materials including MnO₂, CuHCF, PbO₂ (Sigma–Aldrich), and LiFePO₄ (Sigma–Aldrich), composite electrodes were fabricated by mixing 70 wt % electrode material, 20 wt % carbon black (Vulcan XC72R, Cabot), and 10 wt % polyvinylidene fluoride (Kynar HSV 900, Arkema Inc.) with approximate 5 mL of 1-methyl-2-pyrrolidinone per gram of electrode material (anhydrous, 99.5 %, Sigma–Aldrich). The mixture was mixed using a mortar and pestle until a homogeneous slurry was obtained. The resulting mixture was cast onto a graphite sheet with a doctor blade (Microm II, Gardco, USA) and dried in a vacuum oven at 100 °C for 12 h. The electrodes had an approximate thickness of 200 μm and were cut into round pieces with a diameter of 3.8 cm.

Reactor construction

A custom-built reactor was prepared with a 3 cm diameter and 2 cm long chamber (Figure S5). The reactor contained two electrodes constructed from MnO₂ and Pb. A cation-exchange membrane (CEM; Selemon CMV, Asahi Glass, Japan) was cut into a round piece (3.8 cm in diameter) and placed in front of the MnO₂ composite electrode. To assemble the cell, two electrodes were placed at each end of the chamber with graphite sheets as current collectors. The assembled cell was firmly pressed by two end plates with nuts and bolts. An additional porous support layer was placed between the CEM and MnO₂ to aid the physical contact of the CEM with the electrode. A reference electrode (Ag/AgCl in 3 M NaCl, RE-58, BAS) was installed in the middle of the chamber for recording the potential of each electrode. For a three-electrode system, a working electrode was attached to one end of the reactor chamber. The counter electrode was platinum mesh (Princeton Applied Research), which was located at the other end of the chamber, with a wire connected through a small hole.

Energy harvesting from salinity differences

To harvest energy from salinity differences, HC (1 M) and LC (0.02 M NH₄HCO₃ (AmB, Alfa Aesar)) solutions were prepared by dissolving AmB in deionized water. The system was controlled using a potentiostat (Solartron 1470E). Before starting the experiments, the electrode was discharged (reduction for a positive electrode and oxidation for a negative electrode) in a half-cell containing the HC solution. One cycle consisted of four steps (see Figure 1a). First, the cell was charged in the LC AmB solution (0.2 mA for 100 s; step 1). Then, the solution was replaced by the HC AmB solution (step 2), followed by discharging the cell (−0.2 mA for 100 s; step 3). Finally, the solution was replaced by the LC AmB solution (step 4), which was the condition before step 1. When exchanging between HC and LC AmB solutions, the cell was rinsed 3 times to remove as much of the previously filled solution as possible because a residual solution could have affected the performance. The cycle was repeated several times and the third cycle was used as representative data.

From the voltage profiles of the cycle, the area between charge and discharge steps was used to calculate the harvested energy (see Figure 1b). The energy density was calculated by the following equation:

\[ W = -\int_0^{100s} \Delta E \, dq \]

where \( W \) is the energy density, \( \Delta E \) is the cell voltage difference during the charging/discharging, \( q \) is the charge stored and collected from the cell, and \( A \) is the projected surface area of the electrode (−7 cm²). The average power density was calculated from the energy density divided by the time taken for both charging and discharging (200 s).

Energy harvesting was also performed in a three-electrode system to examine the performance of only the working electrode (MnO₂ w/o CEM, Pb, and Ag). For MnO₂, ammonium-based solutions with different pH (NH₄Cl, pH 5; NH₄HCO₃, pH 7; NH₄HCO₃, pH 8; and NH₄HCO₃ + NH₄OH, pH 9) were used to see the effect of pH on the voltage profiles and harvesting energy. The potential difference (\( \Delta E \)) and gained potential (\( \Delta E_\text{G} \)) were calculated from the potential profiles. The same experiment was also performed in sodium chloride and carbonate solutions (Figure S2). The energy harvesting performance of a Ag plate was also examined in NaCl (Macron Fine Chemicals) and NaHCO₃ (BDH Chemicals) solutions.

Electrochemical characterization of electrodes

Electrochemical characterizations were performed in the three-electrode system. CV tests were performed for the metallic Pb (1 M NH₄HCO₃, 10 mV s⁻¹) and PbO₂ composite electrode (1 M NH₄HCO₃, 5 mV s⁻¹). Cycle performance of the Pb in 1 M NH₄HCO₃ was examined by charging/discharging the electrode at 0.2 mA each for 100 s (Figure S3). Between each step, the circuit was off and the open circuit voltage was recorded for 50 s.

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