

Batteries for Efficient Energy Extraction from a Water Salinity Difference

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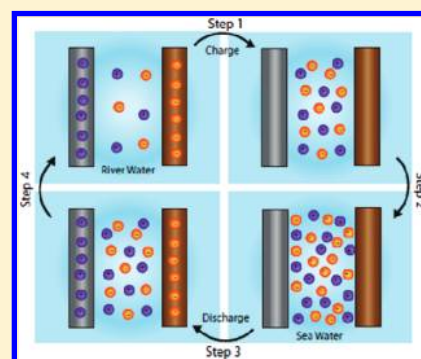
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S Supporting Information

ABSTRACT: The salinity difference between seawater and river water is a renewable source of enormous entropic energy, but extracting it efficiently as a form of useful energy remains a challenge. Here we demonstrate a device called “mixing entropy battery”, which can extract and store it as useful electrochemical energy. The battery, containing a $\text{Na}_{2-x}\text{Mn}_5\text{O}_{10}$ nanorod electrode, was shown to extract energy from real seawater and river water and can be applied to a variety of salt waters. We demonstrated energy extraction efficiencies of up to 74%. Considering the flow rate of river water into oceans as the limiting factor, the renewable energy production could potentially reach 2 TW, or $\sim 13\%$ of the current world energy consumption. The mixing entropy battery is simple to fabricate and could contribute significantly to renewable energy in the future.

KEYWORDS: Salinity-gradient power, mixing entropy, sodium intercalation, energy harvesting



Technologies to utilize renewable energy such as solar, wind, geothermal, and biomass sources have attracted great attention recently. The large scale chemical energy stored as the salinity difference between seawater and freshwater is another renewable source which can be harvested. The major components of the global water cycle involve distillation of water from oceans by evaporation, precipitation, and collection of this freshwater in rivers, lakes, and aquifers, with mixing of freshwater and salt water in estuaries. Solar energy drives this cycle, creating a significant salinity difference between seawater and freshwater. The entropic energy created by the difference in water salinities is normally dissipated when river water flows into the sea. This reduction in free energy due to the mixing is estimated at 2.2 kJ of free energy per liter of freshwater.

To date this significant and completely renewable energy source has not been fully harnessed, although since Pattle's pioneering studies in 1954¹ several types of technologies have been proposed in order to take advantage of this renewable energy source. Past suggestions for capturing energy from the mixing of seawater and freshwater include: hydroelectric pile,¹ based on acidic and basic membranes; pressure-retarded osmosis,² based on semipermeable membranes; reverse electrodialysis,³ based on ion selective membranes; concentration electrochemical cells;⁴ and devices exploiting differences in vapor pressures.⁵ Nowadays, the most reliable methods use membranes as separator between the seawater and the freshwater, to prevent the mixing of the two streams. Therefore, the application of these technologies is strongly based on the energy efficiency, cost, and lifetime of the membranes themselves.⁶

Recently, Brogioli has proposed a new and interesting method based on the electrochemical double layer capacitor technology, using activated carbon electrodes.⁷ This technology has intrinsic technical challenges, like high sensitivity to impurities and dissolved oxygen, causing self-discharge phenomena and the use of the electrode/electrolyte interface for energy storage. Sales et al. employed a membrane-modified electrochemical double layer capacitor, improving the energy conversion efficiency of the Brogioli system.⁸ Finally, Guo et al. have proposed a technology based on single ion selective nanopores for powering biomedical devices through salinity difference in body fluids.⁹

In this work, we demonstrate a novel electrochemical cell named a “mixing entropy battery”, which extracts energy from the difference in concentration of two solutions and stores it as chemical energy inside the electrode material's bulk crystal structure. This approach allows us to overcome the challenges of supercapacitor electrodes based on activated carbon. This device consists of a reversible electrochemical system where the salts in the electrolyte are the reactants and the electrode stores ions. We employed two different electrodes: an *anionic electrode*, which interacts with Cl^- ions selectively; and a *cationic electrode*, which interacts with Na^+ ions selectively. These electrodes are initially submerged in a low ionic strength solution (river water) in their discharged states, when the electrode materials contain the respective ions incorporated in their structures. In this dilute

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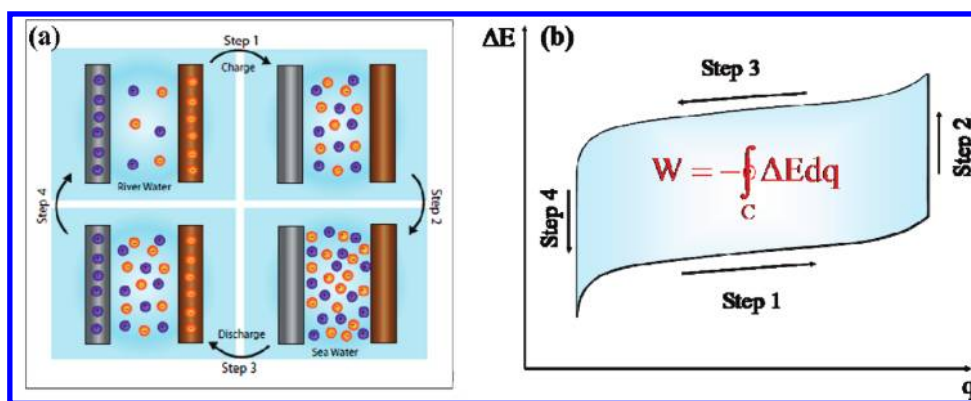


Figure 1. (a) Schematic representation of the working principle behind a complete cycle of the mixing entropy battery, showing how energy extraction can be accomplished: step 1, charge in river water; step 2, exchange to seawater; step 3, discharge in seawater; step 4, exchange to river water. (b) Typical form of a cycle of battery cell voltage (ΔE) vs charge (q) in a mixing entropy battery, demonstrating the extractable energy.

solution, the battery is charged by removing the Na^+ and Cl^- ions from the respective electrodes (Figure 1a, step 1). Successively, the dilute electrolyte is exchanged for a concentrated solution (seawater), which is accompanied by an increase in the potential difference between the electrodes (Figure 1a, step 2). At this higher potential difference, the battery is discharged, as the anions and cations are reincorporated into their respective electrodes (Figure 1a, step 3). The concentrated solution is then removed and substituted by the dilute electrolyte (river water), which results in a decrease in potential difference between the electrodes (Figure 1a, step 4). We note that the exchange of solution could also be carried out via a flow process, which could be attractive for large scale energy extraction.

This closed cycle produces energy, as shown by a schematic of the expected shape of the battery cell voltage (ΔE) versus charge (q) during one cycle in Figure 1a. We observe that during steps 2 and 4 no energy is produced or consumed. During step 1, the battery requires energy to drive the ions out of the crystal structure, while during step 3 the battery produces energy by incorporation of the ions. Therefore, the energy gain is due to the fact that the same amount of charge is released in step 3 at a higher voltage than consumed in step 1. The energy gain is given by the integral along the cycle of the voltage with respect to the charge

$$W = - \oint_C \Delta E dq \quad (1)$$

The difference in the Gibbs free energy per unit of volume (ΔG) between the solution after mixing seawater and river water and the separate seawater and river water before mixing can be calculated as a function of the volumetric fraction of seawater, χ . The minimum in Figure 2a, which is the maxima of mixing entropy of the two solutions, is obtained at $\chi \approx 0.4$ and is equal to $\Delta G \approx -0.85 \text{ kJ dm}^{-3}$ with respect to the mixed solution. Figure 2a is based on the equation

$$\frac{\Delta G}{RT} = c_T \ln(c_T) - \chi c_1 \ln(c_1) - (1 - \chi)c_2 \ln(c_2) \quad (2)$$

where R is the universal gas constant, T the absolute temperature, c_T the concentration of the mixed solution, c_1 the concentration of the first solution, and c_2 the concentration of the second solution. The activity coefficient can be considered to be unity over the

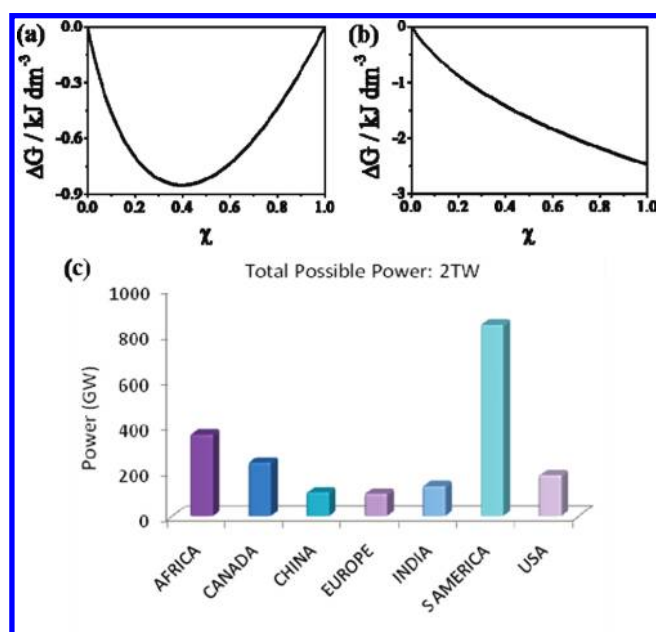


Figure 2. Gibbs free energy of mixing as a function of the volumetric fraction of seawater (χ), calculated at 298 K, mixing a 0.6 M solution and a 0.024 M solution for per unit volume of (a) final solution and (a) low concentration solution. (c) Estimated extractable power (GW) from the difference of salinity in different countries, based on flow of river water emptying into the ocean.

range of salt concentrations examined here (0.024 M for river water, and 0.60 M for seawater; see Supporting Information).

In order to calculate the maximum extractable energy per unit volume of river water, which is the limiting reagent in this process, the Gibbs free energy of mixing is plotted with respect to the volume of river water consumed in Figure 2b. The energy needed to mechanically exchange river water and seawater in the device is assumed to be negligible compared to the total energy produced. For an excess of seawater reagent, the maximum energy extractable is $\Delta G \approx -2.5 \text{ kJ dm}^{-3}$ of river water (obtained for $\chi \approx 1$). This means that a power plant processing $40 \text{ m}^3 \text{ s}^{-1}$ of river water could produce up to 100 MW.

To demonstrate experimentally the validity of our mixing entropy battery design, we constructed an electrochemical cell

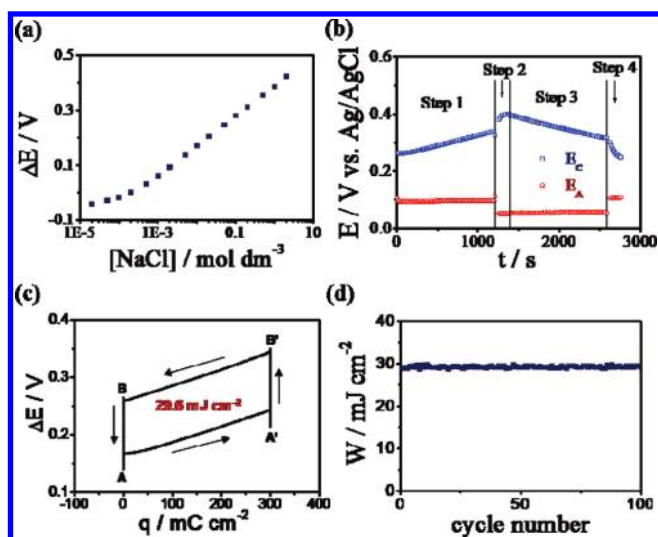


Figure 3. (a) Measured open circuit potentials for the AgCl/ $\text{Na}_2\text{Mn}_5\text{O}_{10}$ system at different concentrations of NaCl in aqueous solution. (b) Measured potential (E) of individual Ag/AgCl (red) and $\text{Na}_{2-x}\text{Mn}_5\text{O}_{10}$ (blue) electrodes vs Ag/AgCl reference electrode during the cycle of energy extraction. (c) Energy extraction cycle for the AgCl/ $\text{Na}_2\text{Mn}_5\text{O}_{10}$ system in a ΔE vs q plot (the area is equal to the extracted energy). (d) Energy per area extracted vs number of cycles for the AgCl/ $\text{Na}_2\text{Mn}_5\text{O}_{10}$ system.

employing the following reaction



where the $\text{Na}_{2-x}\text{Mn}_5\text{O}_{10}$ electrode made of nanorods was used to capture Na^+ ions and the Ag electrode to capture Cl^- ions. (See Supporting Information for detailed electrode preparation.) Among other Na^+ intercalation materials, we selected $\text{Na}_2\text{Mn}_5\text{O}_{10}$ because of its energy density, low cost, and benign environmental impact. The Ag/AgCl electrode was used because it was readily available, although it would not be ideal for capturing Cl^- ions in practice since silver is a precious metal. The equilibrium potential difference of the reaction was measured as a function of the concentration of NaCl in the electrolyte (Figure 3a). As expected, the equilibrium potential difference increased with NaCl concentration (see Supporting Information for further details). The gain in energy was correlated to the change in the potential difference obtained at different NaCl concentrations. We refer to the change in potential difference as the gained potential, V_G . In the case of seawater (0.6 M NaCl solution) and river water (0.024 M NaCl solution), the thermodynamic gained potential was $V_G \approx 0.135$ V (see Supporting Information). This value corresponds to about 3–4 times the gained potential obtained using a supercapacitor material (activated carbon) for the electrodes ($V_G \approx 0.033\text{V}^6$, $V_G \approx 0.040\text{V}^8$).

In Figure 3b the typical cycle of the Ag/AgCl and $\text{Na}_2\text{Mn}_5\text{O}_{10}$ system is reported for the two separate electrodes (vs Ag/AgCl/KCl 3.5 M reference electrode). In the presence of the dilute electrolyte, the potential difference of the two electrodes is small. In step 1 the battery is charged by removing the ions from AgCl and $\text{Na}_2\text{Mn}_5\text{O}_{10}$, thus gradually increasing the potential difference of the two electrodes. The current density applied is $250 \mu\text{A cm}^{-2}$, and a time limit of 20 min is imposed (see Supporting Information). During step 2, the dilute solution is substituted with the concentrated one, and consequently the potential

difference between the two electrodes increases significantly. During step 3, the battery is discharged, and the ions are captured by the electrodes, while the potential difference gradually decreases. The applied current density is $-250 \mu\text{A cm}^{-2}$, with a time limit of 20 min. The voltage difference between the Ag/AgCl and $\text{Na}_2\text{Mn}_5\text{O}_{10}$ electrodes is plotted during this cycling process (ΔE vs q) in Figure 3c. After one full cycle, the energy density produced is about 29 mJ cm^{-2} (power density $10.5 \mu\text{W cm}^{-2}$).

The spikes in the potential difference observed at the beginning and end of step 1 (A and A') and step 3 (B and B') are due to electrochemical losses, known as overpotential. Due to this loss, the practical gained potential is $V_G \approx 0.100$ V (74% efficiency, as compared to the thermodynamically predicted potential gain). It is possible to optimize the experimental configuration to improve this gain as well, as the electrodes are currently at a distance of approximately 1 cm from each other. The resistance of the solution was 75Ω for the diluted solution (75% of the total internal resistance of the device) and 5Ω in the concentrated one (20% of the total internal resistance of the device), creating a high overpotential. This overpotential could be greatly decreased (and thus the power and/or energy efficiency significantly increased) by designing a more optimized cell geometry using closer electrode spacing and allowing a small amount of seawater to remain in the cell when adding the river water to reduce the resistance of the solution (see Supporting Information). Thus, this system can be further optimized in order to increase the energy recovery in each cycle. The experimental energy produced with respect to cycle number is reported in Figure 3d. It is important to note that the system operation was very stable for 100 cycles, with essentially no observable loss in energy production over this period. This consistent power production is expected, since both anionic and cationic electrodes are always operating within the stability window of water, and the electrode materials are very stable in the aqueous environment.

In order to probe possible complications which could exist in a real system, we also conducted measurements with real water samples collected from local natural water sources (see Supporting Information). There was no decrease in cycling performance when these samples were used, and we observed no electrode degradation, self-discharge, or other detrimental phenomenon. The energy conversion efficiency of this cell was 75%.

The extractable power from the difference of salinity of river and seawater that could be obtained in many different countries around the world is summarized in Figure 2c (data from ref 10). If the energy from mixing entropy was harnessed from all these rivers, the power obtained could reach up to 2 TW, which is $\sim 13\%$ of the current total global energy requirement.¹¹ This energy can also be easily harvested at low temperatures, and is completely renewable, since the ultimate source is the solar energy which powers the water cycle.

Thus far, we have only considered the possibility of energy production by harvesting the free energy dissipated by mixing seawater and river water. However, this system could be modified to operate on a smaller scale using solar energy to distill water, with complete recycle of the electrolyte to achieve conversion of solar energy into electrical energy. To further examine this concept, we investigated electrolytes based on the reaction



LiCl is highly soluble (832 g dm^{-3} in water) and $\text{LiFePO}_4/\text{FePO}_4$ is a two-phase system with a well defined potential capable of rapid

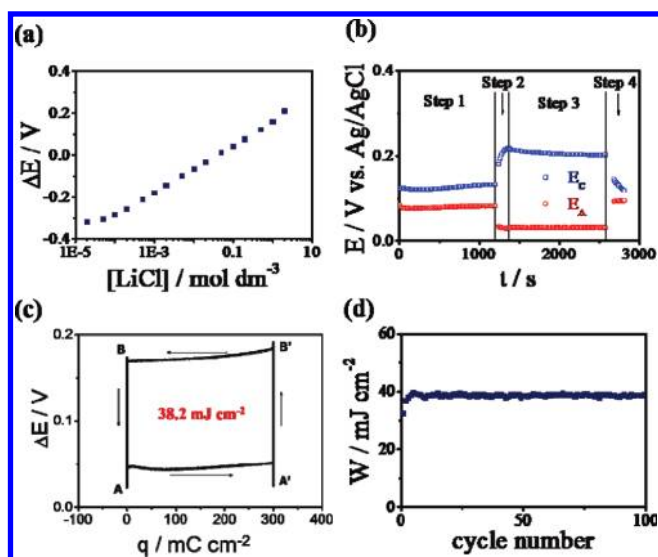


Figure 4. (a) Measured open circuit potential for the AgCl/LiFePO₄ system at different concentrations of NaCl in aqueous solution. (b) Measured potential of individual Ag/AgCl (red) and FePO₄/LiFePO₄ (blue) electrodes vs Ag/AgCl reference electrode during the cycle of energy extraction. (c) Energy extraction cycle for the AgCl/LiFePO₄ system in a ΔE vs q plot (the area is equal to the extracted energy). (d) Energy extracted vs number of cycles for the AgCl/LiFePO₄ system.

charging and discharging. With the exception of Ag, these materials are inexpensive and environmentally benign. In tests with 0.03 and 1.5 M solutions, we produce an energy density of 38.2 mJ cm⁻² (power density 13.8 μ W cm⁻²) that was stable over 100 cycles (Figure 4). These results indicate that this system has significant potential as a method of harnessing solar energy, and has the possibility to be completely renewable, due to repeated cycling of the materials with no loss of reagent.

The mixing entropy battery and other processes described here represent not only a novel type of electrochemical system compared to existing technologies but also a very promising technology whose practical application can make a significant contribution to the field of renewable energy production. This process for generating electrical energy (Figure 1a) could also be reversed, and exploited as a method for water desalination. Future work will focus on cell geometry optimization and the development of materials which can be used to replace silver as the anionic electrode.

■ ASSOCIATED CONTENT

S Supporting Information. Additional details on electrochemical thermodynamics details, synthesis and characterization of the Na⁺ capturing electrodes, electrode preparation and electrochemical characterization, and tests with collected water samples and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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F.L., M.P., and Y.C. conceived and designed the experiments. F. L., M.P., and H.D.D. performed the experiments. All authors contributed to the discussion and writing of the paper.

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