Supplementary Information

Performance of a Mixing Entropy Battery Alternately Flushed with Wastewater Effluent and Seawater for Recovery of Salinity-gradient Energy

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Synthesis of sodium manganese oxide (NMO)

The NMO powder was synthesized by the solid-state reaction[S1]:

$$8Na_2CO_3 + 18Mn_2O_3 + 5O_2 \rightarrow 4Na_4Mn_9O_{18} + 8CO_2$$

The precursor powders were mixed with Na:Mn molar ratio of 0.44 then heated in air in a Lindberg Moldatherm Box Furnace (Fisher Scientific) at a rate of 20 °C/min to 300 °C, held at 300°C for 2 hours, then heated at a rate of 20 °C/min to 800 °C. This temperature was held constant for 12 hours, and the sample cooled was then cool to room temperature[S1]. Fig. S1 illustrates the SEM image of the sample. .

Fabrication and pre-cycle of electrodes

The NMO and Ag electrodes were prepared through an ink coating process followed by electrochemical pre-cycle. The ink was prepared by mixing synthesized NMO (85% wt.) or silver nanoparticles (85% wt.) with Super-P (TIMCAL, 8% wt.) and PVDF (7% wt.). N-methyl pirrolidone (NMP) was added to the mixture as solvent, and the ink was stirred overnight before using[S2]. Carbon cloth (3cm×3cm) was used as the current collector. The electrodes were prepared by coating NMO or Ag ink onto carbon cloth then dried in a vacuum for 24 hours. The loading of active materials was ~14mg/cm^2. As shown in Fig. S2, the oxidation and reduction of NMO electrodes involved two voltage plateaus. The NMO electrode was pre-oxidized in 0.6M NaCl solution to the beginning of a 0.3 V voltage plateau where experiments were conducted. As shown in Fig. S3, the Ag electrode was also pre-cycled in 0.6 M NaCl solution to oxide part of the Ag to AgCl. The measured potential of 0.045 V vs. Ag/AgCl (3.5 M KCl) indicates that the reaction at the silver electrode is dominated by interaction with chloride ions.

Electrochemical properties of NMO

As the cycle time increased to 20 hours (Fig. S4) the slope of voltage-charge curve increased, and the charge curve crossed the discharge curve. Appreciable energy loss resulted. These losses were attributed to transitions between voltage plateaus. For NMO, two voltage plateaus were observed during the charge/discharge cycle (Fig. S2). The transitions between plateaus were irreversible and resulted in energy losses. To prevent these losses, the charge/discharge cycle was maintained at a lower plateau

(0.3 V in this case). When operated at a voltage above the plateau transition, the voltage ratio decreased from >80% to 22%, and overall energy recovery was just 0.08 kWh/m^3. To avoid this loss with NMO electrodes, the voltage was maintained within the 0.3 V plateau. For these conditions,, the utilized specific capacity was only ~1/3 of the total NMO specific capacity of 35 mAh/g. These results underscore the need for new cationic electrode materials.

Derivation of Theoretically Extractable Energy from Mixing

The theoretically extractable energy is:

$$\Delta G_{mix} = 2RT[V_E C_E ln\frac{C_E}{C_M} + V_S C_S ln\frac{C_S}{C_M}]$$

where the first term inside the parentheses is the work required for salination of the wastewater effluent, and the second term is the work required for dilution of the seawater. The coefficient 2 reflects the product of the anion and cation concentrations, where these values must be equal to maintain a charge balance. C_E is the NaCl concentration in the wastewater effluent (0.032 M, in this study); C_S the NaCl concentration in seawater (0.6 M); V_E the volume of wastewater effluent; V_S the volume of seawater; R the universal gas constant; and T the absolute temperature. C_M is the NaCl concentration after complete mixing of wastewater effluent and seawater:

$$C_M = \frac{V_E C_E + V_S C_S}{V_E + V_S}$$

As shown in Fig. S5, when the volume of wastewater effluent is fixed, the available free energy increases with the volume ratio between seawater and wastewater effluent. The maximum available free energy approaches ~0.65kWh/m^3 as the volume ratio approaches infinity.

Calculation of Theoretical Voltage Rise

We used the Nernst equation to calculate the voltage rise for the following reaction:

$$4AgCl + 10Na_4Mn_9O_{18} + \text{energy in} \rightarrow 18Na_2Mn_5O_{10} + 4NaCl + 4Ag$$

The computed voltage rise is:

$$\Delta E = \frac{RT}{zF} \ln \left(\frac{c_{Na^+,seawater} \cdot c_{Cl^-,seawater}}{c_{Na^+,wastewater} \cdot c_{Cl^-,wastewater}} \right)^4$$

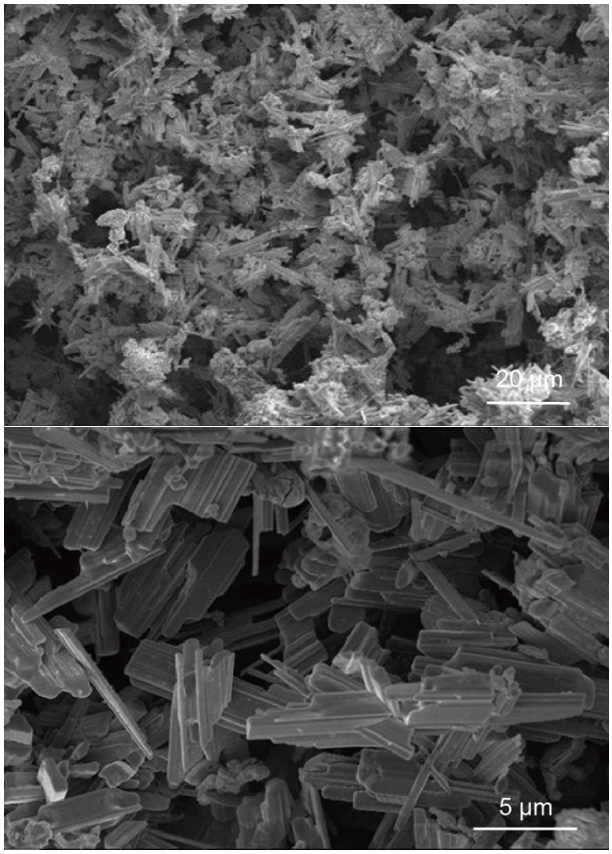
where z is the number of moles of electrons transferred in the cell reaction, F the Faraday constant, R the universal gas constant, and T the absolute temperature. In this study, the concentrations of Na+ and Cl- are each equal to 0.6 M in seawater and 0.032 M in wastewater effluent. The computed voltage rise when changing the solution from wastewater effluent to seawater is 0.151 V. In the operation of MEBs, the wastewater effluent becomes more saline after the charge step, so the voltage rise is calculated using the concentrations of Na+ and Cl- in the wastewater effluent after the charge step (denominator of the above equation) and the numerator is the the concentrations of Na+ and Cl- in the seawater.

References

S1 D. Tevar, J. F. Whitacre, *Journal of The Electrochemical Society*, 2010, **157**, A870.

S2 F. La Mantia, M. Pasta, H. D. Deshazer, B. E. Logan, Y. Cui, *Nano Lett.*, 2011, **11**, 1810.

Supplementary figures

1 

2

3 **Figure S1** Scanning electron microscope (SEM) image of the $Na_4Mn_9O_{18}$ powder

4 showing the nanorod morphology.

5

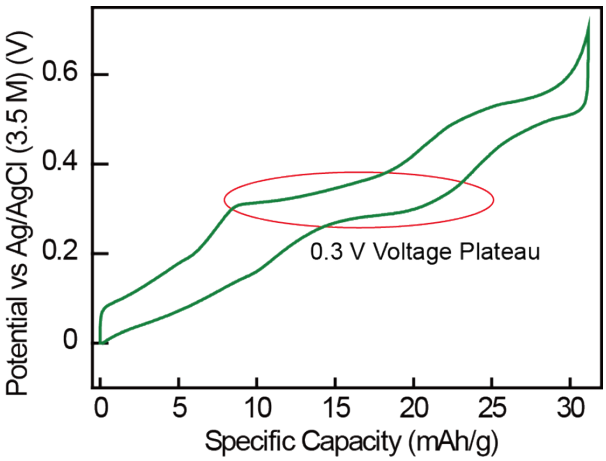


Figure S2 Galvanostatic (1mA) cycles of $Na_4Mn_9O_{18}$ electrode.

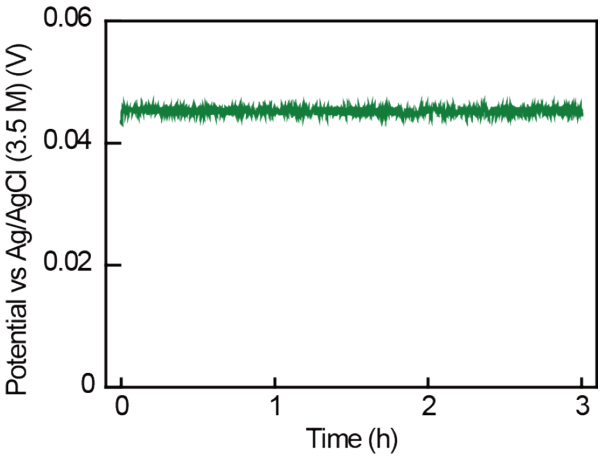


Figure S3 Pre-cycle of Ag/AgCl electrode.

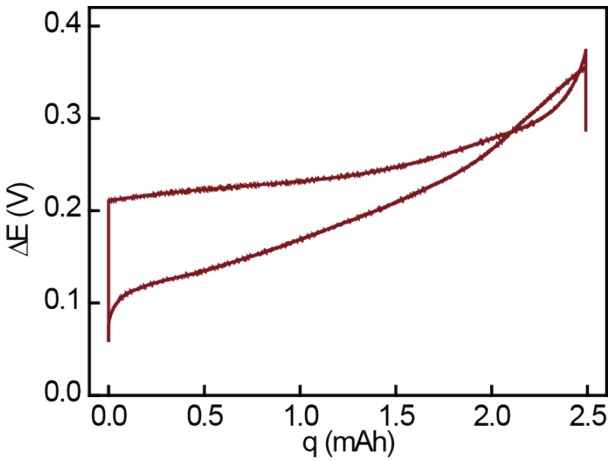


Figure S4 Plot of ΔE vs. q showing energy extraction at cycle times of 20 h.

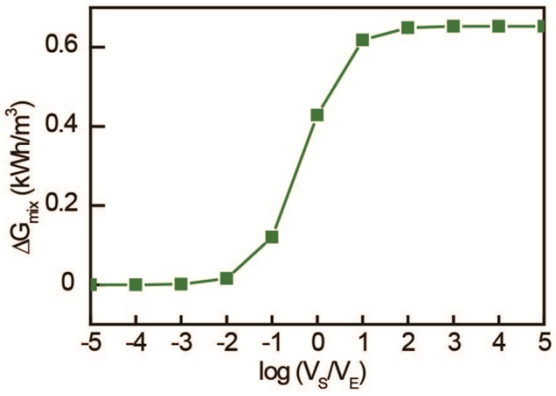


Figure S5 Plot of theoretically extractable energy vs. logarithm of mixing ratio.

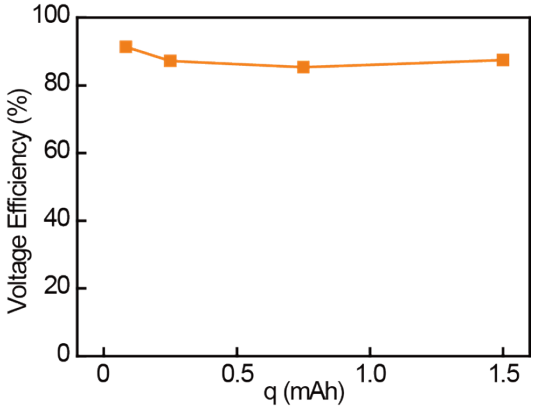


Figure S6 Voltage ratio of each cycle with different cycle time.

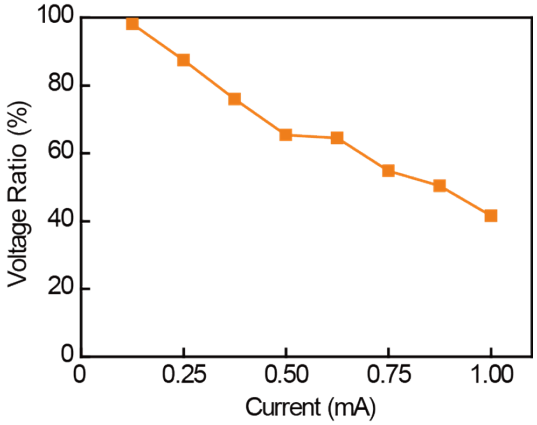


Figure S7 Voltage ratio of each cycle at different applied currents.

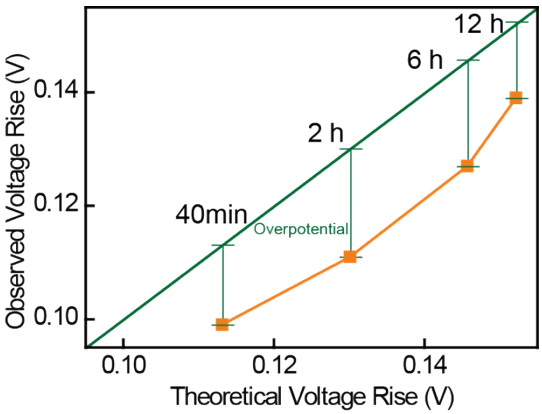


Figure S8 Observed voltage rise vs. theoretical voltage rise with different cycle time: the orange line shows the observed voltage rise with different cycle time. The difference between the ideal voltage (straight line) and the actual voltage (curved line with squares) represents the overpotentials in different scenarios.