Charge-Free Mixing Entropy Battery Enabled by Low-Cost Electrode Materials

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Supporting Information

Preparation of Prussian Blue (PB) Electrode

We prepared Prussian Blue powder using a solution based reaction:

$$Na_3[Fe(CN)_6] + FeCl_3 \rightarrow 3NaCl + Fe[Fe(CN)_6]$$

0.5 M sodium ferricyanide solution was mixed with 0.5 M ferric chloride in a hydrochloric acid solution at pH=2. A green precipitate was observed immediately. After 24 h, the sample was centrifuged and washed three times with deionized water, then dried in a vacuum oven. The synthesized PB powder was then coated onto a carbon cloth current collector through a slurry-coating method. The slurry was prepared by mixing PB powder (85% wt.) with Super-P ((TIMCAL, 8% wt.) and PVDF (7% wt.). We then added N-methyl pirrolidone (NMP) to the mixture as solvent, and stirred the ink overnight before use. The current collector was a 3 cm x 3 cm carbon cloth with titanium wire connected. The electrode was prepared by coating the slurry onto the current collector and dried in a vacuum oven for 24 h. The loading of PB was ~ 7 mg/cm^2. To prevent attrition of the PB

particles on the electrode, a Na^+ permeable polyvinyl alcohol/sulfosuccinic acid (PVA/SSA) coating was also used, and prepared according to the literature[1,2]. A solution of PVA (10% wt.), SSA (30% wt.) and DI water (60% wt.) was stirred vigorously for 24 hours, then coated on the PB electrode with a scalpel blade. The PVA concentration was also varied (2-12% wt.) to determine the impact of coating composition. The electrode was then placed in an oven at 60 ºC for one hour, 130 ºC for another hour, and cooled to room temperature prior to using.

Preparation of Polypyrrole (PPy) Electrode

We prepared the PPy electrode by electrochemically polymerizing PPy onto a carbon cloth current collector. The supporting solution was pyrrole (0.1 M) in the presence of NaCl (1 M). An anodic current of 1 mA/cm^2 was applied for six hours for polymerization of PPy. The PPy electrode was then electrochemically reduced in a 0.6 M NaCl solution to a potential of 0.2 V vs Ag/AgCl (3.5 M KCl).

Mixing Entropy Battery (MEB) Construction and Operation

We constructed a MEB in a plate-shape glass chamber with the dimension of 3 cm × 3 cm × 0.3 cm. The volume of the chamber was 1.5 mL after embedding the PB electrode and the PPy electrode. For a long-term study of the MEB, two peristaltic pumps on programmable timers alternately flushed the MEB with seawater and wastewater effluent, enabling automatic and continuous operation.

Theoretical Potential Calculation

The calculated theoretical potential is found by the Nernst Equation for the PB and PPy electrodes, respectively, as:

$$E_{PB} = E^0 + \frac{RT}{zF}\ln\left(a_{Na,\epsilon}\right)$$

and

$$E_{PPy} = E^0 + \frac{RT}{zF}\ln\left(a_{Cl,\epsilon}\right)$$

Where E^0 is the standard reduction potential, R is the universal gas constant, T is the temperature, z is the charge transfer coefficient, F is Faraday's constant, $a_{Na,\epsilon}$ and $a_{Cl,\epsilon}$ are the activities for sodium and chloride in solution, respectively. Molarity was used in lieu of activity, in the range of 0.032 M to 2 M for Na^+ and Cl^-. Standard reduction

potentials were taken from the literature[3,4].

References

(1) Kim, D. S.; Guiver, M. D.; Nam, S. Y.; Yun, T. Il; Seo, M. Y.; Kim, S. J.; Hwang, H. S.; Rhim, J. W. Preparation of Ion Exchange Membranes for Fuel Cell Based on Crosslinked Poly(Vinyl Alcohol) with Poly(Styrene Sulfonic Acid-Co-Maleic Acid). *J. Memb. Sci.* **2006**, *281* (1–2), 156–162.

(2) Kim, Y.-J.; Choi, J.-H. Improvement of Desalination Efficiency in Capacitive Deionization Using a Carbon Electrode Coated with an Ion-Exchange Polymer. *Water Res.* **2010**, *44* (3), 990–996.

(3) Ellis, D.; Eckhoff, M.; Neff, V. D. Electrochromism in the Mixed-Valence Hexacyanides. 1. Voltammetric and Spectral Studies of the Oxidation and Reduction of Thin Films of Prussian Blue. *J. Phys. Chem.* **1981**, *85* (9), 1225–1231.

(4) Wernet, W.; Wegner, G. Electrochemistry of Thin Polypyrrole Films. *Makromol. Chemie-Macromolecular Chem. Phys.* **1987**, *188* (6), 1465–1475.

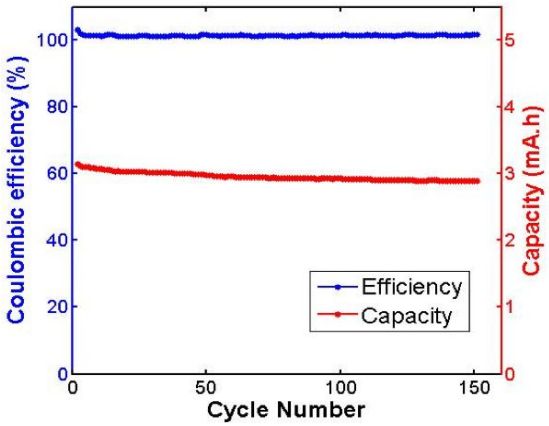

Figure S1 Cycling performance of the PB electrode with a PVA/SSA coating: showing the coulombic efficiency and discharge capacity over 150 cycles.

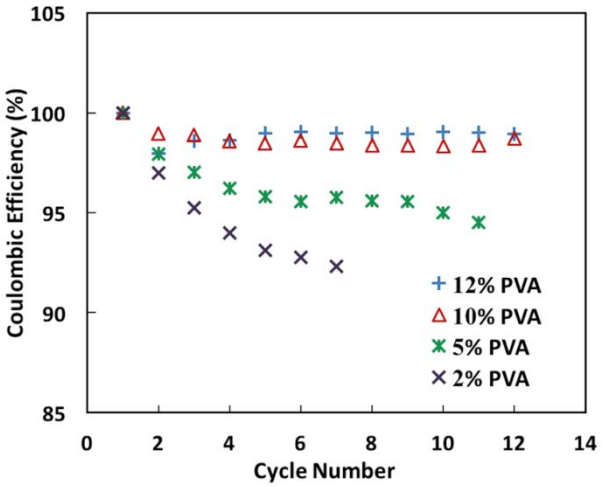

Figure S2 Impact of PVA concentration in PVA/SSA coating on coulombic efficiency of PB cathode cycling.

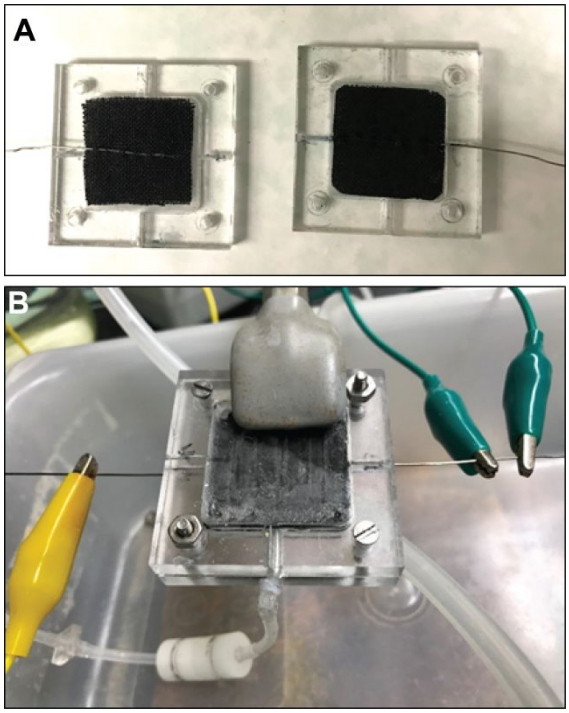

Figure S3 (A) 3 cm × 3 cm MEB electrodes, Prussian Blue (left), PPy (right), plastic mesh separator not shown; (B) Charge-free MEB in operation. No input step requirement allows for simplified operation without a potentiostat or charge-input control mechanism. Photograph by M. Ye.

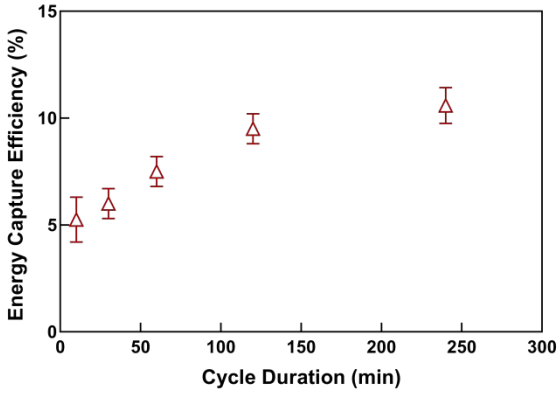

Figure S4 Impact of duration on net energy recovery efficiency for single full-cell cycle, seawater salinity = 0.6 M NaCl, freshwater salinity = 0.032 M NaCl.

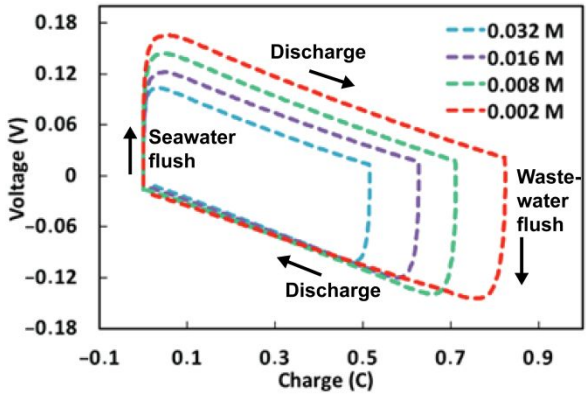

Figure S5 Impact of freshwater salinity on energy extraction with PVA/SSA coating, seawater salinity = 0.6 M NaCl.

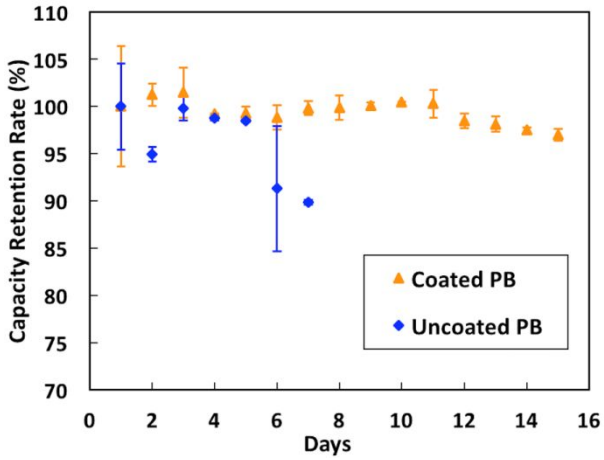

Figure S6 Impact of PVA/SSA coating on full-cell capacity retention over 15 days (180 cycles), seawater salinity = 0.6 M NaCl, freshwater salinity = 0.032 M NaCl. Error bars indicate standard deviation.