Supporting Information

Aqueous Proton Battery Stably Operates in Mild Electrolyte and Low-Temperature Condition

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The calculation details about the utilization rate of electrolyte

In this work, the active material is Mn$^{2+}$ in electrolyte. For example, 50 μL (73.06 mg) 3.5 M Mn(ClO$_4$)$_2$ electrolyte is added in coin cell. Theoretically, this electrolyte can provide a capacity of 9.3819 mAh. The calculated process can be summarized as follow:

1. The mole of Mn$^{2+}$: $3.5 \text{ mol L}^{-1} \times 50 \text{ μL} \times 10^{-6} = 1.75\times10^{-4} \text{ mol}$

2. The mole of formed MnO$_2$ in theory: $1.75\times10^{-4} \text{ mol}$

3. The theoretical capacity of Mn$^{2+}$/MnO$_2$: $C = \frac{96500 \times n}{3.6 \times \text{Mr}_{\text{MnO}_2}} = 96500\times2/(3.6\times87)=616.22 \text{ mAh g}^{-1}$

4. The max capacity which can be provided by electrolyte: $616.22 \text{ mAh g}^{-1} \times 1.75\times10^{-4} \text{ mol} \times 87 \text{ g mol}^{-1}=9.3819 \text{ mAh}$

5. The PANI//CF battery obtains a capacity of 0.122 mAh at 2 C. It implies that the utilization rate of electrolyte only has 1.3% ($0.122\div9.3819\times100\%$).

PANI is selected to verify the feasibility of the cathode (based on conversion reaction of Mn$^{2+}$/MnO$_2$) in full battery. Considering practical application value, suitable anodes with higher theoretical capacity should be developed and applied to match this cathode.
**Figure S1.** The stretching vibration of H$_2$O.

Following the order of Mn(CH$_3$COO)$_2$-MnSO$_4$-Mn(NO$_3$)$_2$-Mn(ClO$_4$)$_2$, the peak at low wavenumber, corresponding to strong hydrogen bond, gradually decrease. The peak at high wavenumber, corresponding to weak hydrogen bond, gradually increase.
Figure S2. The fitted O-H stretching vibration of H₂O in a) 1 M Mn(CH₃COO)₂; b) 1 M MnSO₄; c) 1 M Mn(NO₃)₂; d) 1 M Mn(ClO₄)₂.

Figure S3. The charge curves of CF electrodes in different electrolytes.
Figure S4. The cycling stability of CF electrode in a) 1 M Mn(ClO$_4$)$_2$; b) 1 M Mn(CH$_3$COO)$_2$; c) 1 M MnSO$_4$; d) 1 M Mn(NO$_3$)$_2$.

Figure S5. The cycling stability of CF electrode at 4 mA cm$^{-2}$ in 1 M Mn(ClO$_4$)$_2$. 
Figure S6. The charge curves of CF electrodes in different concentrations Mn(ClO$_4$)$_2$ electrolyte.

Figure S7. The freezing point of a) 1 M Mn(ClO$_4$)$_2$; b) 2 M Mn(ClO$_4$)$_2$; c) 3 M Mn(ClO$_4$)$_2$; d) 3.5 M Mn(ClO$_4$)$_2$; e) 4 M Mn(ClO$_4$)$_2$. 
**Figure S8.** The cycling stability of CF electrode in a) 2 M Mn(ClO$_4$)$_2$; b) 3 M Mn(ClO$_4$)$_2$; c) 3.5 M Mn(ClO$_4$)$_2$; d) 4 M Mn(ClO$_4$)$_2$.

**Figure S9.** The charge-discharge curves of CF electrode in 3.5 M Mn(ClO$_4$)$_2$ electrolyte.
Figure S10. The different scan-rate CV curves of CF electrode in 3.5 M Mn(ClO$_4$)$_2$ electrolyte.

Figure S11. The deposition morphology of MnO$_2$ on the surface of CF electrode in different concentrations Mn(ClO$_4$)$_2$ electrolytes.

Figure S12. The XPS spectrum of O 1s.
**Figure S13.** The ESP of PANI.

**Figure S14.** The LUMO-HOMO energy gap of PANI.
Figure S15. The possible reaction mechanism of PANI.

Figure S16. The ex-site XRD patterns of PANI electrodes.
Figure S17. The CV curves of PANI electrode.

Figure S18. The cycling stability of PANI electrode.

Figure S19. The charge-discharge curves of PANI electrode.
Figure S20. The rate capability of PANI electrode.

Figure S21. The different scan-rate CV curves of PANI electrode.

Figure S22. The calculated $b$ values of PANI electrode.
**Figure S23.** The calculated capacitance contribution ratio of PANI electrode.

**Figure S24.** a) the optical images of cell shells; b) the XRD patterns of stainless steel current collector (SS).

**Figure S25.** The charging curves of PANI//CF battery at a) 0.1 C; b) 0.5 C; c) 1C; d) the charge-discharge curve of PANI//CF battery at 2 C.
**Figure S26.** The different scan-rate CV curves of PANI//CF battery.

**Figure S27.** The calculated $b$ values of PANI//CF battery.

**Figure S28.** The calculated capacitance contribution ratio of PANI//CF battery.
**Figure S29.** The cycling performance of CF//PANI battery.

**Figure S30.** The charge-discharge curves of PANI//CF battery at -50 °C.

**Figure S31.** The rate capability of PANI//CF battery at -70 °C.
Table S1. The comparison of this work and reported works.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Discharge capacity /current density</th>
<th>Ref.</th>
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<tr>
<td>MnO$_2$@GF</td>
<td>PTO</td>
<td>2 M H$_2$SO$_4$+ 2 M MnSO$_4$</td>
<td>208 mA h g$^{-1}$/0.16 mA cm$^{-2}$</td>
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<td>MnO$_2$@GF</td>
<td>MoO$_3$</td>
<td>2 M H$_2$SO$_4$+ 2 M MnSO$_4$</td>
<td>209.6 mA h g$^{-1}$/1 A g$^{-1}$</td>
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<tr>
<td>MnO$_2$@CF</td>
<td>ALO</td>
<td>2 M HBF$_4$+ 2 M Mn(BF$_4$)$_2$</td>
<td>145.5 mA h g$^{-1}$/1 A g$^{-1}$</td>
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<td>MnO$_2$@CF</td>
<td>Zn</td>
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<td>MnO$_2$@CF</td>
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<td>0.5 M H$_2$SO$_4$+ 1 M MnSO$_4$</td>
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<tr>
<td>MnO$_2$@CF</td>
<td>PANI</td>
<td>3.5 M Mn(ClO$_4$)$_2$</td>
<td>130 mA h g$^{-1}$/0.7 A g$^{-1}$</td>
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Table S2. The ex-situ DES of PANI electrodes at different states.

<table>
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<tr>
<th>Element</th>
<th>State</th>
<th>Atomic Fraction (%)</th>
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<th>discharge</th>
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<td>0.00</td>
<td>0.00</td>
<td></td>
<td>0.18</td>
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</tbody>
</table>

Reference


