Supporting Information

Functioning Mechanism of the Secondary Aqueous Zn - β-MnO₂ Battery

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Figure S1. The charge-discharge curves of the $\beta$-MnO$_2$ cathode (a) and the ex situ XRD results of the cathode during the first cycle (b).
Figure S2. The 5th discharge/charge curves and the corresponding CV result of the MnO$_2$ cathode in the ZnSO$_4$ electrolyte before (a) and after adding sodium trimetaphosphate into the electrolyte. The comparison of the XRD result of the 5th Dis electrode, the 5th Dis@ electrode, and the 200th Dis@ electrode (c) and the cycle performance of the 5th Dis electrode and the 5th Dis@ electrode under 200 mA g$^{-1}$ (d).
Figure S3. The SEM result of the 5\textsuperscript{th} Dis\# cathode (a), the 100\textsuperscript{th} Dis\# cathode (b). The re-test result of the cycle performance of the 5\textsuperscript{th} Dis\# cathode (c), and the 200\textsuperscript{th} Dis\# cathode (d) at 200 mA g\textsuperscript{-1}.

**Calculation of the diffusivity**

The diffusivity of the WE was obtained through AC impedance test and it can be calculated according to the Equation S1:

\[
D = \frac{RT}{\sqrt{2}n^2F^2A\sigma C}
\]  

(S1)

where \(D\) is the diffusivity, \(R\) is the gas constant, \(T\) is absolute temperature, \(n\) is the number of transferred electrons, \(F\) is the Faraday constant, \(A\) is the area of the coated layer on the WE, \(C\) is the concentration of hydrogen ion which is calculated from the pH value of the electrolyte, and \(\sigma\) is the Warburg factor which has relationship with \(Z_{re}(\omega=2\pi f, f\text{ is frequency})\):

\[
Z_{re} = R_s + R_{ct} + \sigma \omega^{-0.5}
\]  

(S2)

where \(R_s\) is the electrolyte resistance, and \(R_{ct}\) is the charge transfer resistance, which are obtained by fitting the EIS curves with the Zview software. By liner fitting the relationship between \(-Z_{re}\) and \(\omega^{0.5}\) in the low frequency region, the \(\sigma\) value can be obtained. The EIS plots and their fitting results of the WE at the charged state of 1.5 V and 1.9 V in different electrolytes for the first 4 cycles are shown in Figure S4 and S5.
Figure S4. The EIS plots of the WE at the charged state of 1.5 V and 1.9 V, respectively, in the Zn electrolyte for the first 4 cycles (a) and the plots of -$Z_{re}$ vs. $\omega^{0.5}$ and their fitting results (b).
Figure S5. The EIS plots of the WE at the charged state of 1.5 V and 1.9 V, respectively, in the Zn+Mn electrolyte for the first 4 cycles (a) and the plots of \(-Z_{re} \text{ vs. } \omega^{-0.5}\) and their fitting results (b).

**Calculation of the current fraction resulted from different contributions**

The Equation 13 can be reformulated as

\[
i(V)/\nu^{1/2} = k_1 \nu^{1/2} + k_2
\]

(S3)

Therefore by liner fitting the results of \(i(V)/\nu^{1/2} \text{ vs. } \nu^{1/2}\) at different potentials (Figure S6), the values of \(k_1\) and \(k_2\) can be obtained from the slope and the intercept, and the fraction of the current due to the surface capacitive effect at specific potentials can be further quantified.
Figure S6. The fitting results of $i (V)/v^{1/2}$ v.s. $v^{1/2}$ at different potentials.

**Calculation of the activation energy ($E_a$)**

The activation energy ($E_a$) of the interface between the electrode and the electrolyte can be calculated based on the following equation:

$$\log \frac{T}{R_{ct}} = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$  \hspace{1cm} (S4)

where $T$ is the absolute temperature, $A$ is the pre-exponential factor indicative of the number of charge carries, $R$ is the universal gas constant, and $R_{ct}$ is the charge transfer resistance obtained by fitting the EIS curves with the Zview software. The AC impedance tests were carried out on the WE at different temperatures between 20 °C and 50 °C. The $E_a$ value can be obtained by linearly fitting the curve according to $\log(T/R_{ct})$-1000 $T^{-1}$. The AC impedance and its fitting result are shown in Figure S7.
Figure S7. The AC impedance and its fitting result of the Zn system (a, b) and the Zn+Mn system (c, d).

Figure S8. The surface morphology of the bare graphite foil after the 1st charge process.