Silver and Manganese Dioxide composite with Oxygen Vacancies as a high-performance cathode material for an aqueous zinc-ion battery

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Supplementary Figures



Figure S1 Ag3d XPS spectrum of Ag@MnO₂

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Figure S2 Enlarged parts of the GITT curves at the two platforms of the charge process.

In our GITT study, a cell was charged or discharged at 100 mA g⁻¹ rate for 10 min, followed by a 30 min open circuit step to allow relaxation back to equilibrium. The procedure was continued until the charge (or discharge) voltage reached 1.9 V (0.9 V). The Zn^{2+} diffusion coefficients could be calculated using the following equation first outlined by Weppner and Huggins:

$$D = \frac{4}{\pi} \left(I \frac{V_m}{Z_A FS} \right)^2 \left(\frac{dE/d\delta}{dE/d\sqrt{t}} \right)^2$$

where I is the current (A); Vm is the molar volume of the WBEC (cm³ mol⁻¹); ZA is the charge number; F is the Faraday's constant (96485 C mol⁻¹); S is the electrode/electrolyte contact area (cm²); dE/d δ is the slope of the coulometric titration curve, found by plotting the steady state voltages E (V) measured after each titration step δ ; $dE/d\sqrt{t}$ is the slope of the linearized plot of the potential E (V) during the current pulse of duration t (s). If sufficiently small currents are applied for short time intervals, so that $dE/d\sqrt{t}$ can be considered linear and the coulometric titration curve can be also considered linear over the composition range involved in that step, the above equation can be simplified into:

$$D = \frac{4}{\pi^{\tau}} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_{\tau}} \right)^2$$

Here, τ is the duration of the current pulse (s); nm is the number of moles (mol); Vm is the molar volume of the electrode (cm³ mol⁻¹); S is the electrode/electrolyte contact area (cm²); Δ Es is the steady-state voltage change, due to the current pulse and Δ Et is the voltage change during the constant current pulse, eliminating the iR drop.



 $Figure \ S3 \ {\rm SEM} \ {\rm images} \ of the discharged state (a). \ {\rm SEM} \ {\rm images} \ of the charged state (b).$



Figure S4 EPR spectra of MnO₂ and Ag@MnO₂.



