High valence MnO_2 for aqueous zinc ion battery cathode by secondary hydrothermal method

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The calculation of ionic diffusion coefficients

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); V_m is the molar volume of the WBEC ($cm^3\ mol^{-1}$); ZA is the charge number; F is the Faraday's constant (96485 C mol^{-1}); S is the electrode/electrolyte contact area (cm^2); dE/dδ 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); V_m is the molar volume of the electrode ($cm^3\ mol^{-1}$); S is the electrode/electrolyte contact area (cm^2); ΔEs is the steady-state voltage change, due to the current pulse and ΔE_τ is the voltage change during the constant current pulse, eliminating the iR drop.

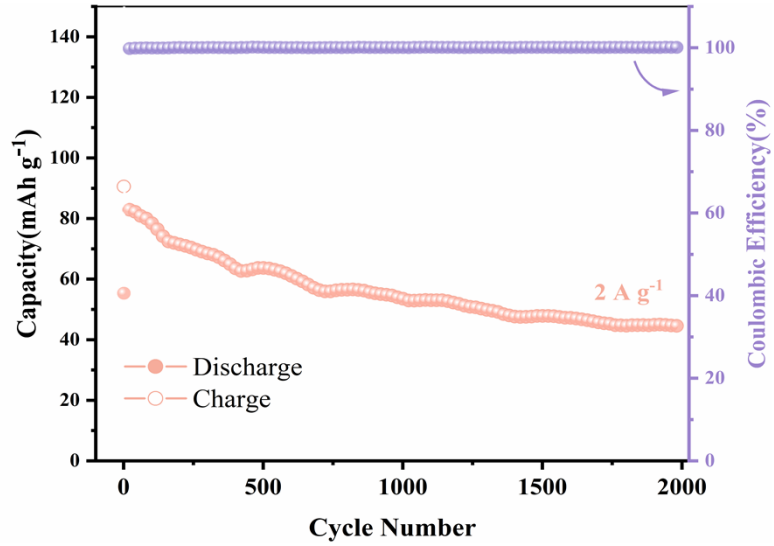

Fig S1. long cycle performance diagram of MnO_2

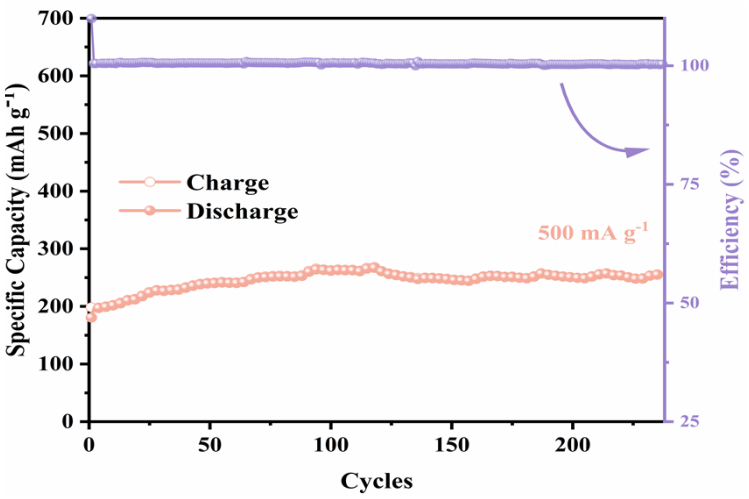

Fig S2. long cycle performance diagram of H-MnO_2