Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Electrochemistry of rechargeable aqueous zinc/zinc-sulphate/manganese-oxide batteries and methods for preparation of high-performance cathodes

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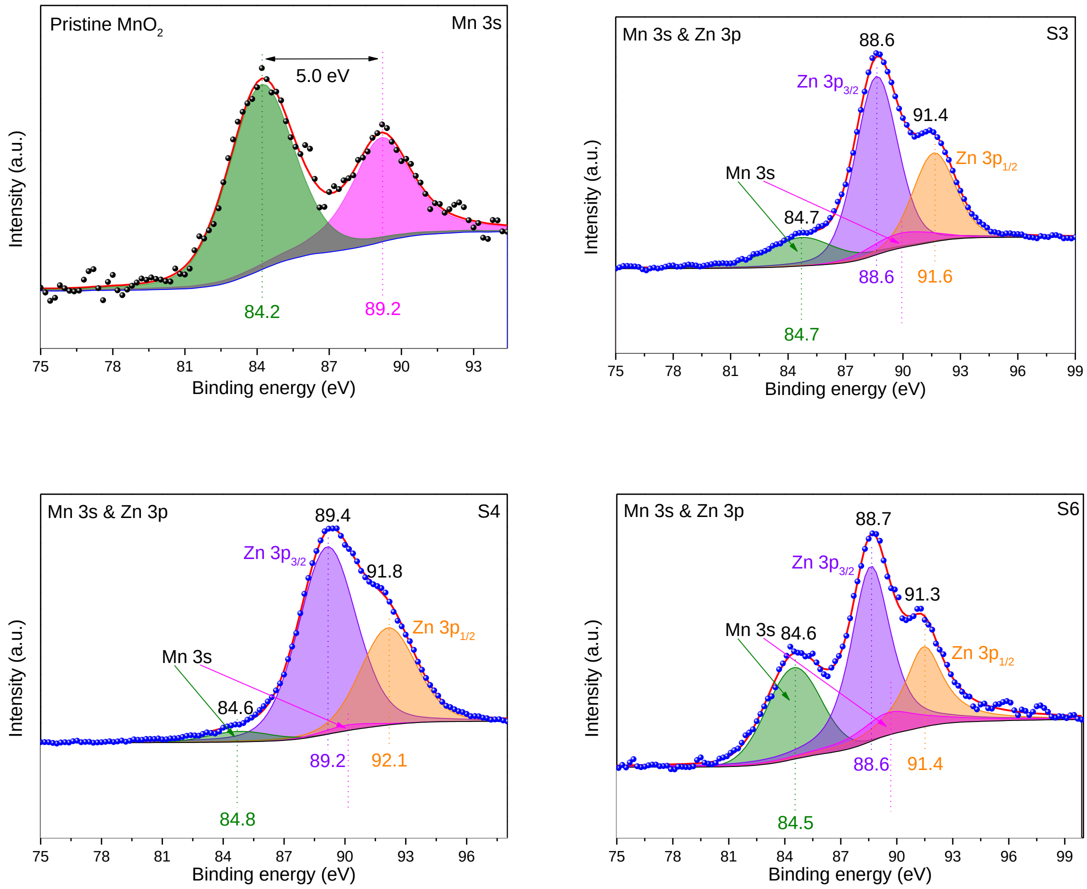
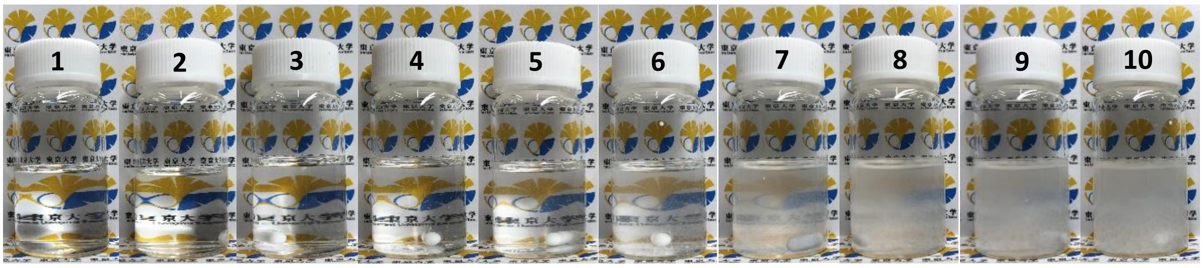


Figure S1. X-ray photoelectron spectroscopy of the MnO_2-based cathode. XPS spectra of Mn 3s in the MnO_2-based cathode at different states.



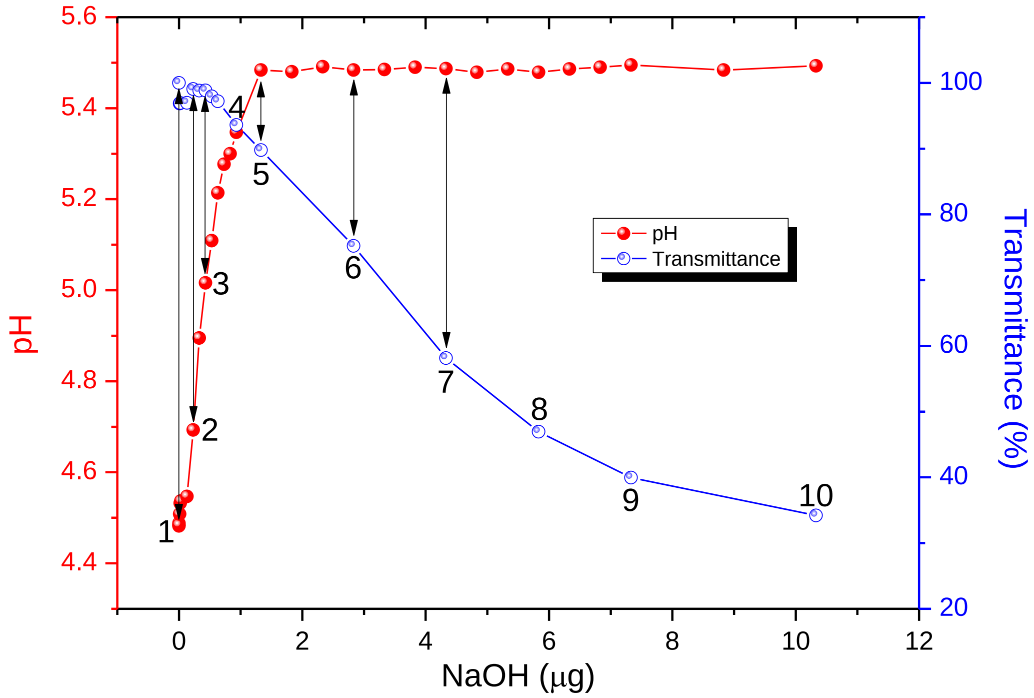


Figure S2. Changes of pH (red colour, measured using a pH meter) and transmittance (blue colour, measured at 600 nm) of the electrolyte while adding NaOH.

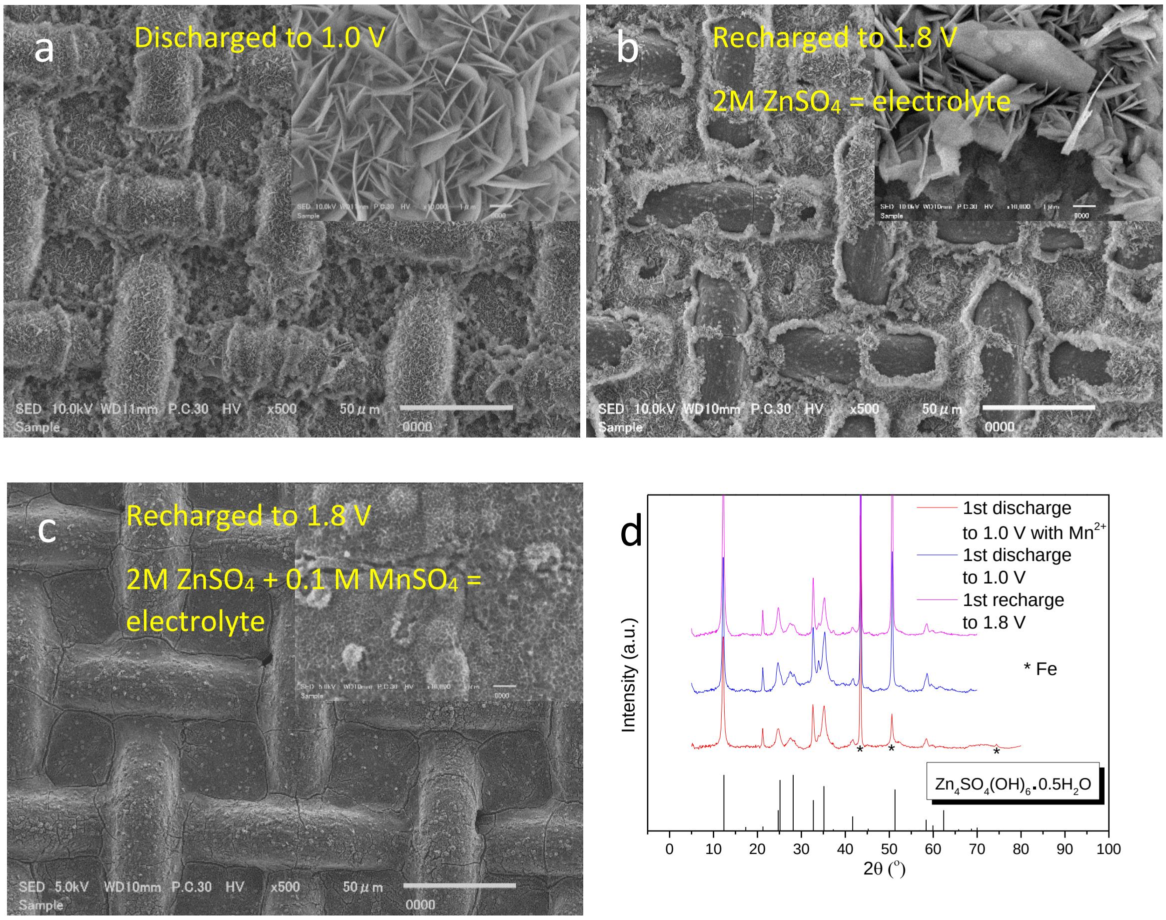


Figure S3. Electrolyte with and without $MnSO_4$. (a,b) SEM images of MnO_2 cathode after discharge (a) and recharge (b) in 2 M $ZnSO_4$ electrolyte without containing $MnSO_4$. (c) SEM images of the MnO_2-based cathode after recharged to 1.8 V with 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ as electrolyte. The insets of (a-c) show the corresponding highly magnified SEM, respectively. (d) XRD of the MnO_2-based cathode at three stages of discharge and recharge: 1^{st} discharged to 1.0 V with 2 M $ZnSO_4$ + 0.1 M $MnSO_4$ as electrolyte (red), 1^{st} discharged to 1.0 V with 2 M $ZnSO_4$ as electrolyte (blue), and 1^{st} recharged to 1.8 V with 2 M $ZnSO_4$ as electrolyte (pink), respectively . In case of the full discharge, zinc sulphate hydroxide (ZSH) was identified unconditionally, however, in case of the full recharge, ZSH was identified only when the electrolyte without $MnSO_4$ was used.

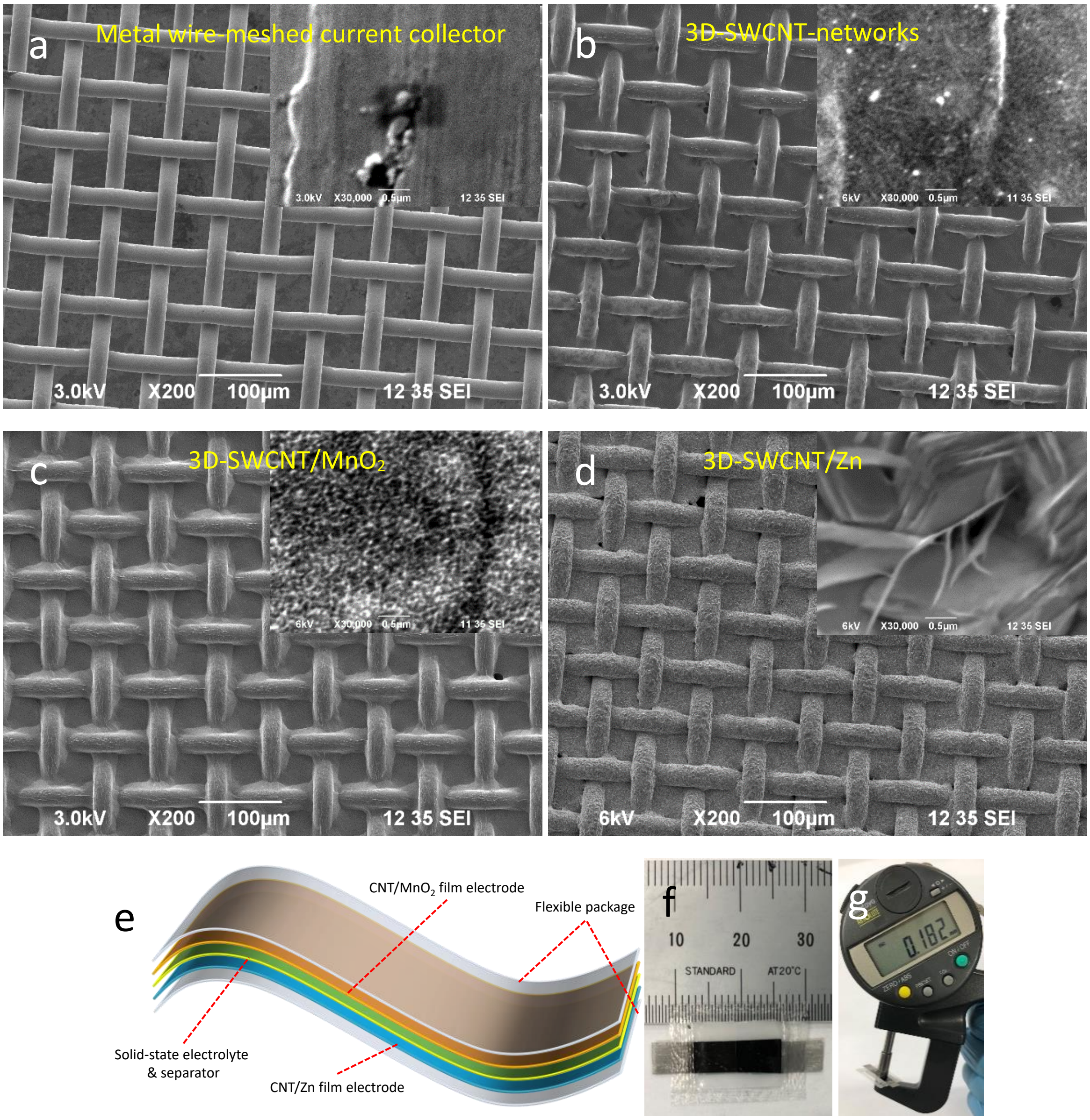


Figure S4. Structural and morphological characterization of 3D-SWCNT/MnO_2 and 3D-SWCNT/Zn based electrodes and the packed cell. (a,b,c,d) SEM images of the wire-meshed current collectors (a), 3D-SWCNT-networks on the wire-meshed current collectors (b), 3D-SWCNT/MnO_2 on the wire-meshed current collectors (c), and 3D-SWCNT/Zn on the wire-meshed current collectors (d). The insets of (a-d) show the corresponding highly magnified SEM, respectively. (e) Schematic illustration of a flexible 3D-SWCNT/Zn/3D-SWCNT/MnO_2 cell. (f,g) Photographs of the size of the Zn/MnO_2 battery device.

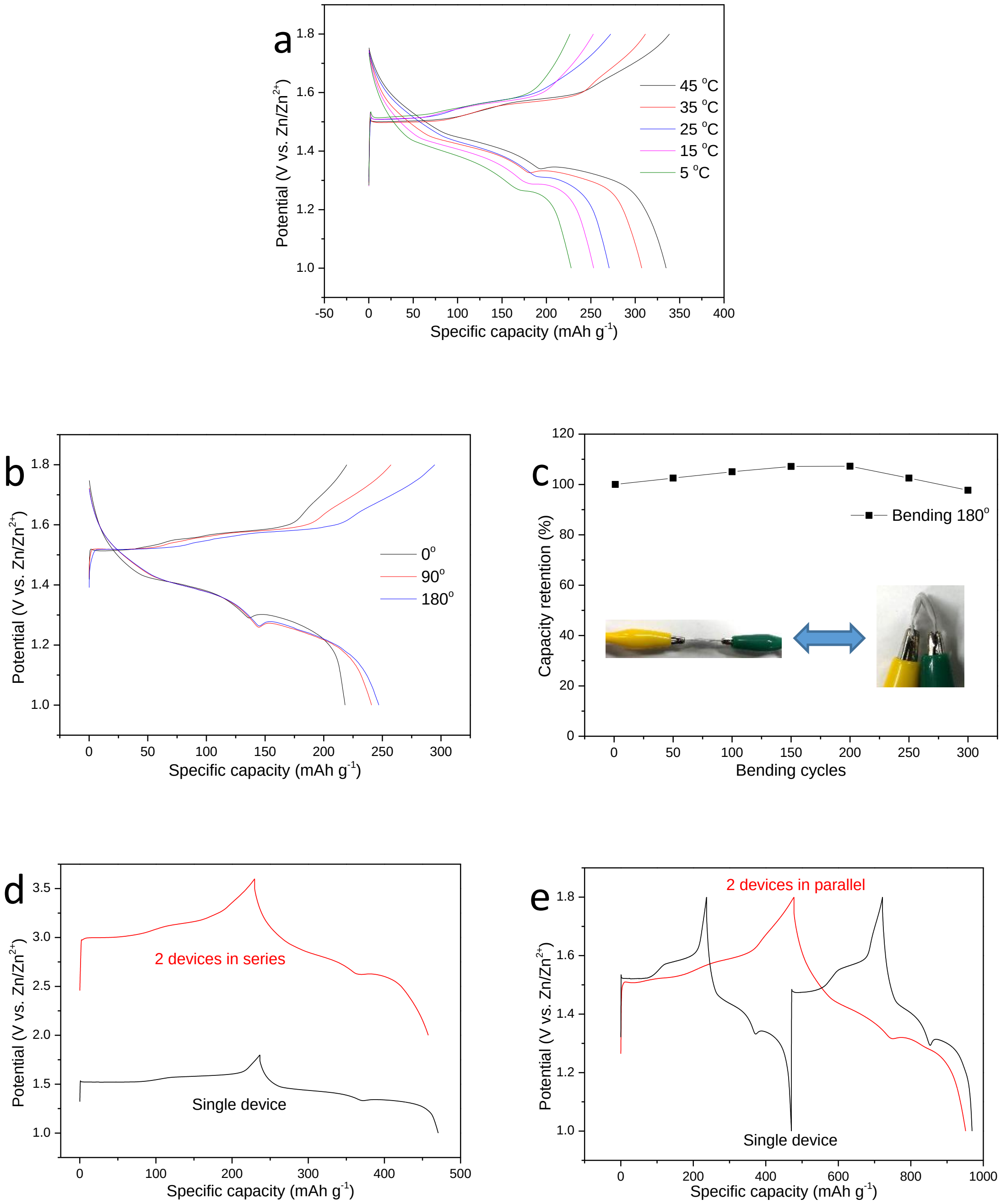


Figure S5. Electrochemical performance of $Zn/ZnSO_4$-$MnSO_4/MnO_2$ cells. (a) Galvanostatic discharge-recharge curves under different environmental temperatures (5°C ~ 45°C). (b) GCD curves with different bending angles (0°, 90°, 180°). (c) Capacity retention after 300 bending cycles from 0° to 180° bending angle; the inserted photos show non-bent and after bending (180° bending degree) of the model cell used in the bending cycle evaluation. (d,e) GCD curves of a single cell and two cells being linked in series (d) and in parallel (e).

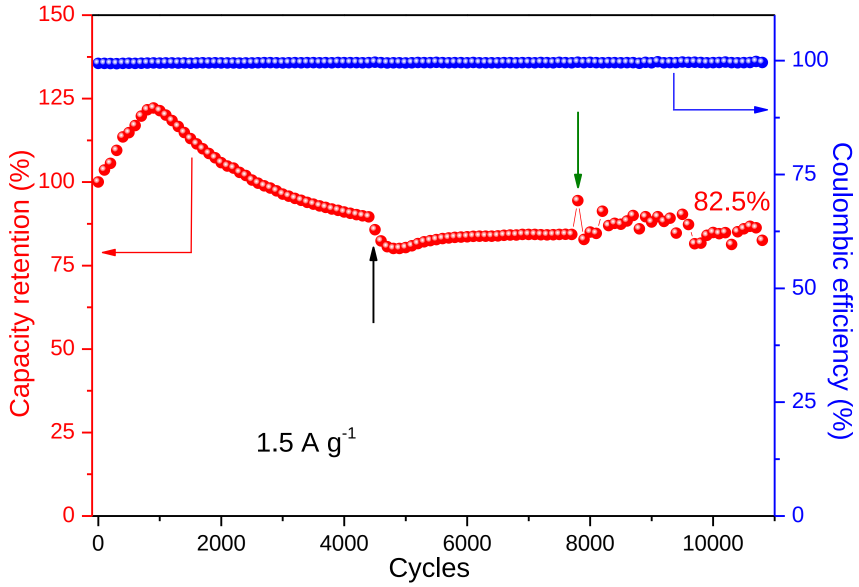


Figure S6. Long-term cyclic performance tests of a CR2032 coin cell based Zn/ $ZnSO_4$-$MnSO_4$/MnO_2 single cell. The cell was being discharged/recharged for 11000 cycles. The cell was paced in a constant 25 °C oven and continuously ran for 4800 cycles. After the running being stopped for two days (pointed by a black arrow), the cell ran continuously to 8000 cycles. The cell was paced under ambient conditions (without control of temperatures, pointed by a green arrow) and then continuously ran for another 3000 cycles. Capacity retention was 82.5% after 11000 cycles. Discharge/recharge rate: 1.5 A g^{-1}.