Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

The back-deposition of dissolved Mn^{2+} to MnO_2 cathodes for stable cycling in aqueous zinc batteries

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1. Experimental Section

1.1 Synthesis of MnO_2. The α-phase MnO_2 was obtained by mixing 0.3506 g $KMnO_4$, 1.65 mL HCl (36 ~ 38 %) and 35 mL water in a 50 mL autoclave, followed by heat treatment at 140 °C for 16 h.[1] The β-phase MnO_2 was obtained by mixing 1:1 volume ratio of 0.1 M $MnSO_4$ solution and 0.1 M $(NH_4)_2S_2O_8$ solution in a 50 mL autoclave, followed by heat treatment at 140 °C for 12 h.[2] After the hydrothermal reactions, the product was filtered, washed with water and ethanol repeatedly, and dried at 60 °C for 24 h.

1.2 Characterizations. The crystal structures were analyzed by X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer with Cu-Kα radiation. The morphologies were investigated by HITACHI SU 8010 scanning electron microscope. The high resolution transmission electron microscopy (HRTEM) images were recorded on a JEM-ARM200F transmission electron microscope. The Mn concentrations in electrolytes were measured on an Avio500 inductively coupled plasma optical emission spectrometer. The specific surface areas were obtained by the Brunauer-Emmett-Teller (BET) method, and the isotherms were recorded by the DFT method to calculate the pore size distributions.

1.3 Electrochemical characterization. MnO_2 were mixed with KB or SP carbon, PVDF at the weight ratio of 7:2:1 in 1-methyl-2-pyrrolidinone (NMP). The slurry was drop casted on graphite paper substrate and dried at 90 °C. The BET area of the graphite paper was 19.45 $m^2\ g^{-1}$. The mass loading of MnO_2 active material was around 1.1 mg cm^{-2}. Two-electrode cells were assembled with MnO_2 cathode, zinc foil anode, 1 M $ZnSO_4$ electrolyte and glass fiber separators. The glass fiber separators also enhanced the cycling stability of MnO_2 when comparing to filter paper (Figure S5), which would result from the different Mn^{2+} ion mobilities. EIS was obtained in 3-electrode cells with saturated calomel electrode (SCE) as the reference on Biologic VMP3. Galvanostatic charge-discharge tests were carried out on Land CT-2001A battery cyclers.

2. Supporting Figures

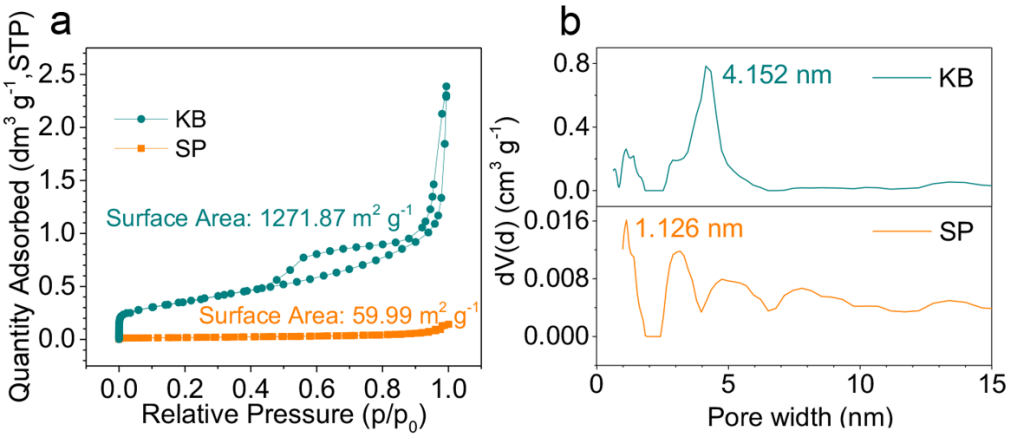

Figure S1 a) N_2 adsorption-desorption isotherms and b) pore size distributions of KB and SP carbons.

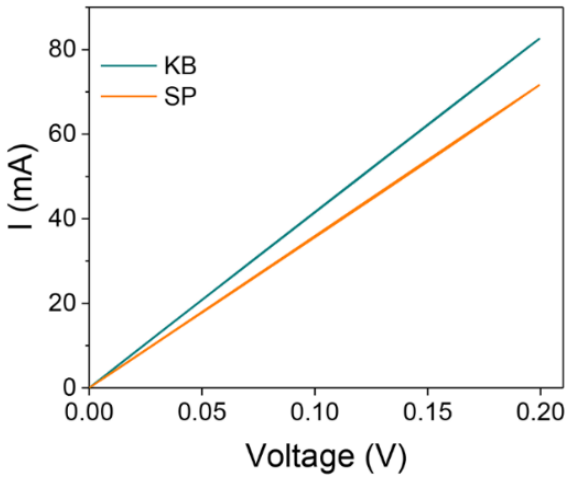

Figure S2 *I-V* plots of KB and SP carbons.

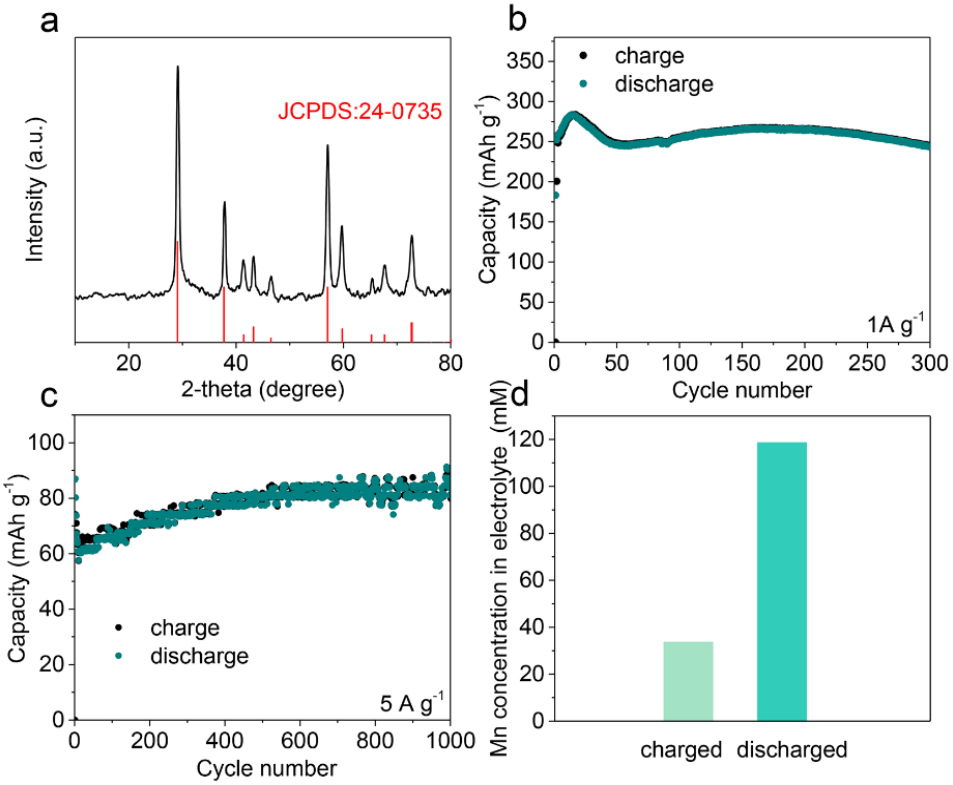

Figure S3 a) XRD pattern of β-MnO_2. Cycling performance of β-MnO_2 cathode with KB conducive agent in aqueous zinc batteries with 1 M $ZnSO_4$ electrolyte at b) 1 A g^{-1}, c) 5 A g^{-1}, and d) Mn concentrations in the electrolyte at the fully charged and discharged states of the 200th cycle of 1 A g^{-1} test from ICP.

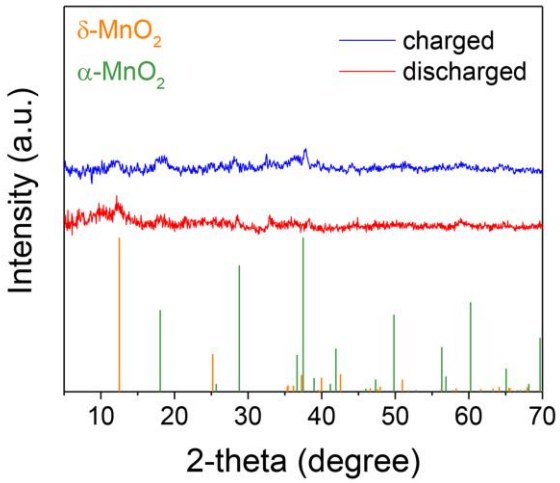

Figure S4 XRD patterns of the MnO_2/KB cathode at the charged and discharge states.

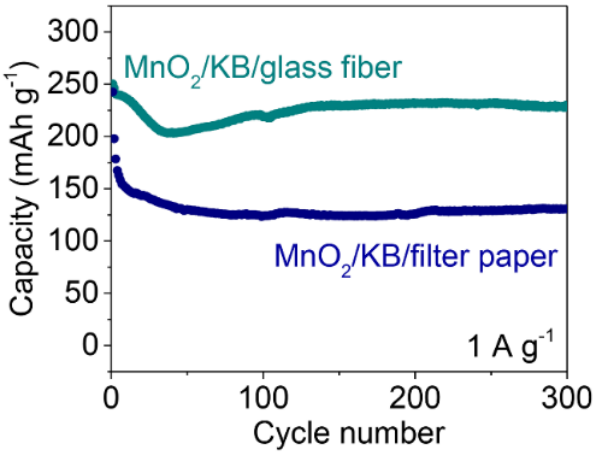

Figure S5 Cycling performance of MnO_2/KB with different separators in aqueous zinc batteries with 1 M $ZnSO_4$ electrolyte at 1 A g^{-1}.

3. References

1. W. Chen, R. B. Rakhi, H. N. Alshareef, *J. Mater. Chem. A*, 2013, **1**, 3315-3324.
2. W. Liu, X. Zhang, Y. Huang, B. Jiang, Z. Chang, C. Xu, F. Kang, *J. Energy Chem.*, 2021, **56**, 365-373.