Electronic Supplementary Information

In-situ BaSO₄ coating enabled activation-free and ultra-stable δ -

MnO₂ for aqueous Zn-ion battery

Lele Liu^a, Shouxiang Ding^a, Lu Yao^a, Mingqiang Liu^b, Shunning Li^a, Qinghe Zhao^{*a}, Runzhi Qin ^{*a}, Feng Pan^{*a}

a. School of Advanced Materials, Peking University Shenzhen Graduate School Shenzhen 518055, P. R. China.

b. Electrochemical Innovation Lab, University College London, London WC1E 7JE, UK.

EXPERIMENTAL SECTION

Material Synthesis.

 Ba^{2+} pre-intercalated layered MnO₂ (BMO) is synthesized by microwave-assisted hydrothermal method with multi-flux microwave chemistry workstation (MDS-6G). In a typical synthesis procedure, 6 mmol KMnO₄, 2 mmol MnCl₂·4H₂O, and 2 mmol $BaCl_2 \cdot 4H_2O$ were added into 35 mL of deionized water and stir vigorously for 30 minutes. Then the mixed solution was transferred into a 100 mL microwave-assisted hydrothermal reaction kettle to hydrothermal at 160°C for 2 hours with the microwave power of 1000 W. The synthesized powder was collected by filtration and washed with deionized water and absolute ethanol three times, respectively. The obtained product was dried at 70°C in vacuum for 12 hours.

The contrast sample KMO is also synthesized by microwave-assisted hydrothermal method as the BMO synthesized without adding BaCl₂·4H₂O.

The mixture of KMO and BaSO₄ (KMO+*ex*-BSO) was prepared according to the atomic number ratio of Ba: Mn of 0.35. In a typical synthesize procedure, 0.5916 g MnSO₄·H₂O was added into 20 ml deionized water and stirred until fully dissolved as solution A; add 0.7288 g BaCl₂·4H₂O into 20ml deionized water and stir until fully dissolved as solution B; then add 0.9836 g KMO into the solution A and stir vigorously for 5 minutes to make it evenly mixed; next add the solution B into the mixed solution; last collect powder by filtration and washed with deionized water and absolute ethanol three times respectively and then dried at 70°C in vacuum for 12 hours.

Material Characterization.

X-ray diffraction measurements were performed to investigate the crystallographic structure using a Bruker D8 ADVANCE X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectroscopy (XPS) was tested by ESCALAB 250Xi (Termofisher) to analyze the valence states of the elements. A scanning electron microscope (SEM, ZEISS SUPRA55) and transmission electron microscope (TEM, JEM-3200FS) with an OxfordX-Max20 EDS mapping were used to

determine the micromorphology and microstructure of the products and distribution of elements. The atomic ratios and the structural water contents of products were detected by inductively coupled plasma optical emission spectroscopy (ICP-OES, JY2000-2) and simultaneous thermal analyzer (TGA, SII STA7300 analyzer) measurements which were recorded in the air using a 10°C min⁻¹ heating rate.

Electrochemical measurements.

The electrochemical properties were characterized by assembling CR2032 coin cells in air, with zinc metal of a 16 mm diameter and 0.2 mm thickness as the anode and 3.0 M ZnSO₄+0.2 M MnSO₄ as the electrolyte. The cathode electrodes were prepared with the mass ratio of 70% active material, 20% acetylene black, and 10% polyvinylidene difluoride (PVDF). The loading of active material is about 0.90 mg·cm⁻². CV was conducted using an electrochemical workstation (ParStat2273) over the potential range from 0.95 to 1.85 V vs. Zn/Zn²⁺. Galvanostatic charge/discharge tests were performed using a multichannel battery testing system (Neware, CT2001A/1C).

Diffusion kinetics calculation from GITT curves

The solid diffusion coefficient of layered MnO_2 cathodes is conducted by Galvanostatic Intermittent Titration Technique (GITT) and calculated based on Equation S1.

$$D = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \tag{S1}$$

Where τ is the pulse duration, n_m is the molar number of BMO, V_m is the molar volume, and S is the electrode/electrolyte contact area. ΔE_S and ΔE_t can be obtained from the GITT curves.



Figure S1. Characterization of KMO: (a, b) SEM and (c) EDS mapping.



Figure S2. TGA results of (a) BMO and (b) KMO.



Figure S3. CV curves of KMO at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$.



Figure S4. galvanostatic discharge-charge curves at 0.1C: (a) KMO; (b) BMO.



Figure S5. galvanostatic discharge-charge curves at 1C: (a) KMO; (b) BMO.



Figure S6. (a) Galvanostatic discharge/charge curve of KMO at 0.1C;(b) corresponding *ex-situ* XRD patterns.



Figure S7. ex-situ SEM patterns of different charge/discharge sites of BMO.



Figure S8. *Ex-situ* SEM patterns of different charge/discharge sites of KMO.



Figure S9. XRD patterns of different charge/discharge points of BMO after acid

washing



Figure S10. XRD pattern of f BMO after acid washing at point B



Figure S11. Characterization of KMO+*ex*-BSO: (a, b, c) SEM images and (d) EDS mapping.



Figure S12. Cycling performance of KMO+*ex*-BSO, BMO, and KMO at 1C.



Figure S13. Electrochemical impedance spectroscopy results of KMO and BMO.



Figure S14. CV curves at stepwise scan rates (0.1 to 1.0 mV s⁻¹) of (a) BMO and (b) KMO; The relation between log(i) and log(v) of (c) BMO and (d) KMO; (e) GITT curves and (f) corresponding calculated diffusion kinetics of BMO and KMO.



Figure S15. SEM images of BMO after 150 cycles at 1C.

	K	Mn	Ba	K:Mn	Ba:Mn	molecular formula
BMO	0.23	25.63	22.14	0.01	0.35	$K_{0.01}Ba_{0.35}MnO_2 \cdot 0.39H_2O$
КМО	7.83	78.46		0.14		$K_{0.14}MnO_2 \cdot 0.35H_2O$

Table S1. Rate capacity

Note: K:Mn and Ba:Mn indicate atomic number ratio.

	0.1C	0.25C	0.5C	1C	2C	4C	6C	8C	10C	0.25C
КМО	281	263	233	198	142	68	34	18	12	219
BMO	347	279	243	210	178	137	108	88	73	257

Table S2. Rate capacity of BMO and KMO

Unit: mAh·g⁻¹.