Supporting Information

Sodium-ion-stabilized 2 × 4 tunnel manganese oxide nanorods as cathodes for high-performance aqueous zinc-ion batteries

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1. EDX

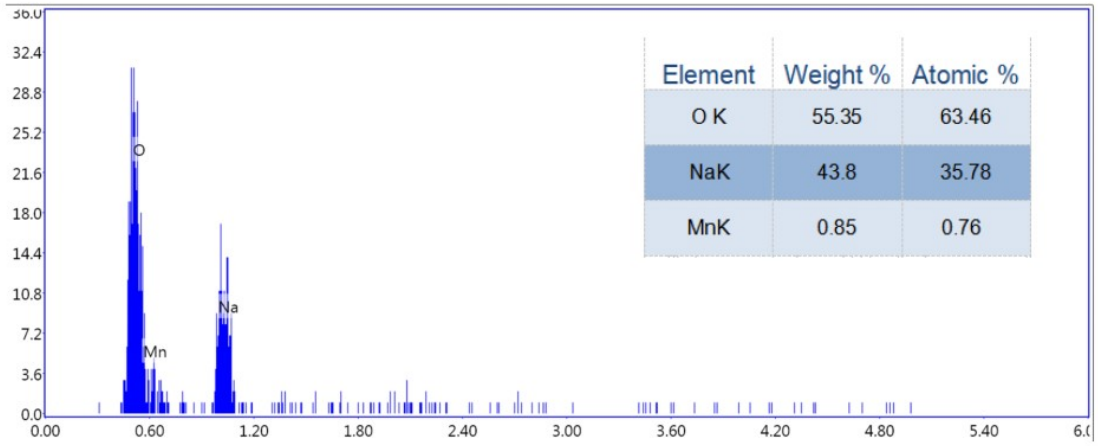

Fig. S1 EDX of the $Na_{0.4}MnO_2$ and the corresponding elemental content .

2. ICP-AES

ICP-AES	Atomic Percentage (%)	
	Na	Mn
$Na_{0.4}MnO_2$	28.57	71.43
Na-birnessite	10.77	89.23

Table S1 Contents of the manganese oxide

3. XRD

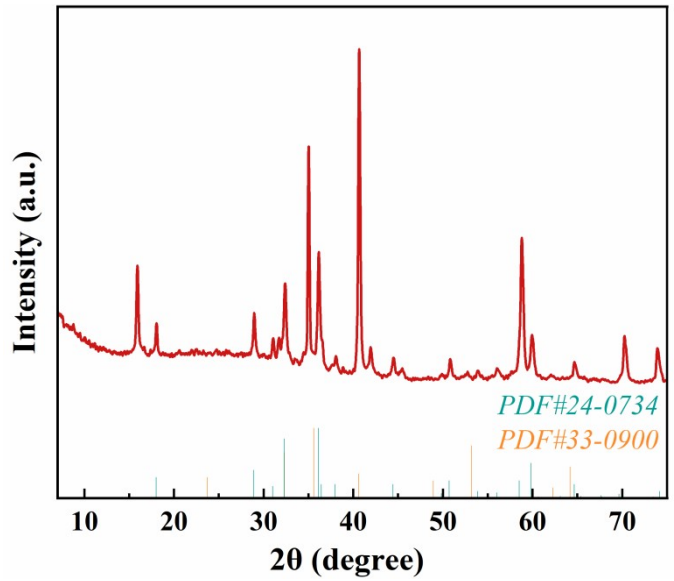

Fig. S2 XRD of the $Na_{0.4}MnO_2$ after 550 °C

After annealed at 550 °C , the $Na_{0.4}MnO_2$ powders is converted into Mn_2O_3 and Mn_3O_4.The $Na_{0.4}MnO_2$ powder was annealed at 550 °C for 2h and XRD patterns are shown in **Fig. S2**.

4. SEM

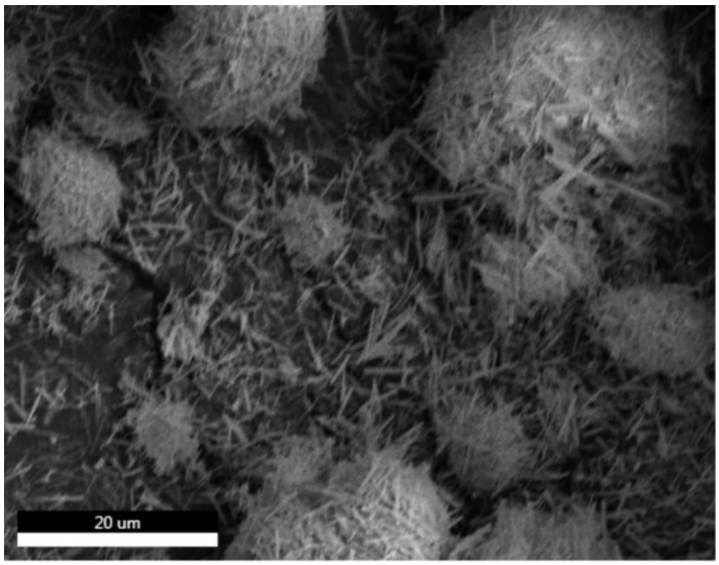

Fig. S3 SEM of the $Na_{0.4}MnO_2$

5. Electrochemistry

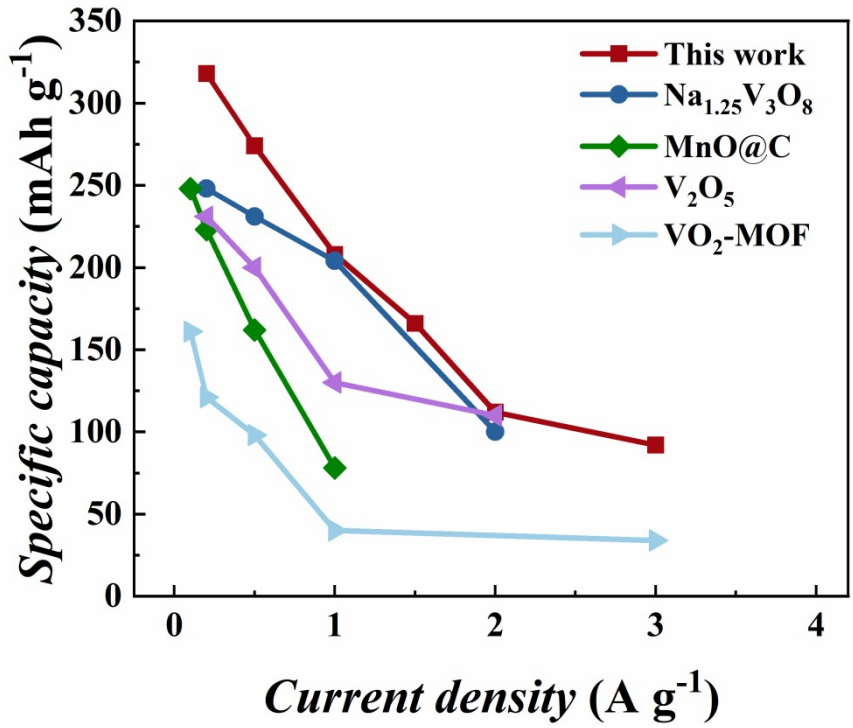

Fig. S4 Compared with other ZIBs Mn-based electrodes previously reported, the specific capacity (stable capacity) of $Na_{0.4}MnO_2$ is higher at different current densities.

[1] Zhao Yanming, Liao Jinhui. Rubidium-doped $Na_{1.25}V_3O_8$ Electrochemical properties of nanorods as cathode materials for zinc-ion batteries[J].Journal of South China University of Technology:Natural Science Edition, 2023, 51(3):63-73.)

[2] Guo Pingchun, Han Xing, Jiang Hedong, et al. Research on vanadium-based metal-based organic framework materials as cathode materials for aqueous zinc-ion batteries[J].Acta Ceramic Sinica, 2023, 44(5):920-927.)

[3] Huang Yongfeng, Huang Wenting, Liu Wenbao, et al.Energy storage mechanism and capacity attenuation reasons of Zinc-ion battery cathode material V_2O_5[J].Chem. J. Chinese Universities, 2020, 41(8):7.

[4] Ma Qiuchen, Liu Jun. MnO@C for research on cathode materials for zinc-ion batteries[J].Mining and Metallurgical Engineering, 2021, 41(1):4.

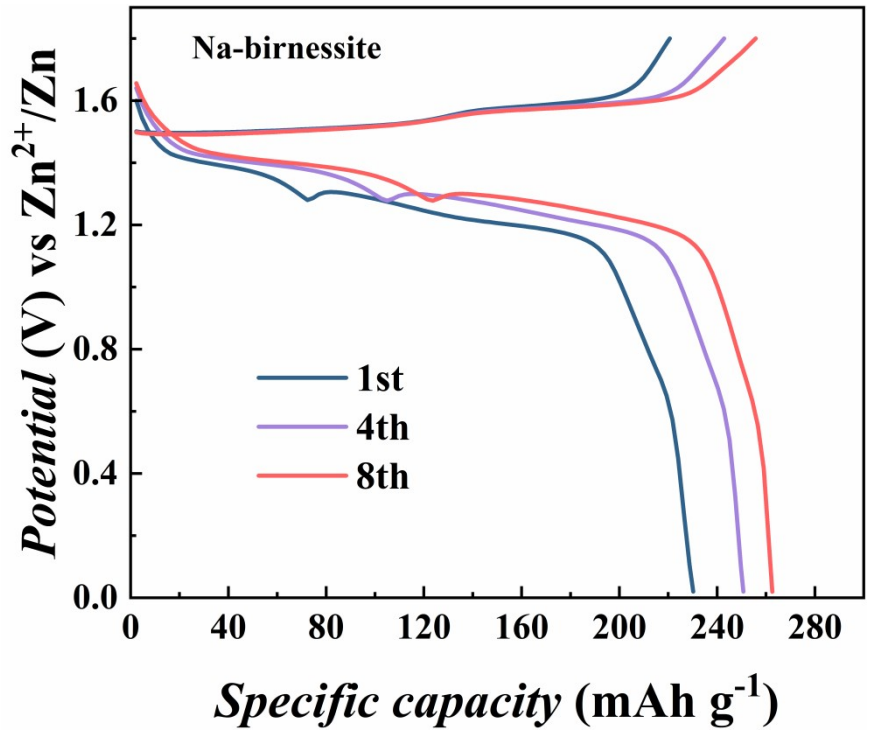

Fig.S5 GCD profiles of the Na-birnessite electrode obtained at 0.2 A g^{-1}.

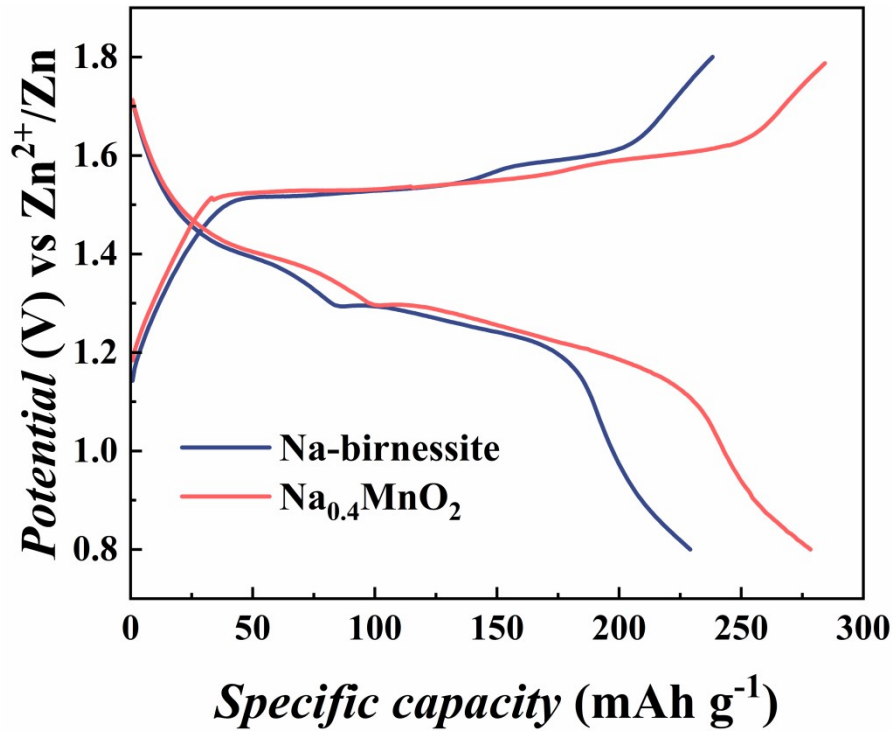

Fig.S6 Comparison of GCD profiles between $Na_{0.4}MnO_2$ and Na-birnessite at 0.2 A g^{-1}.

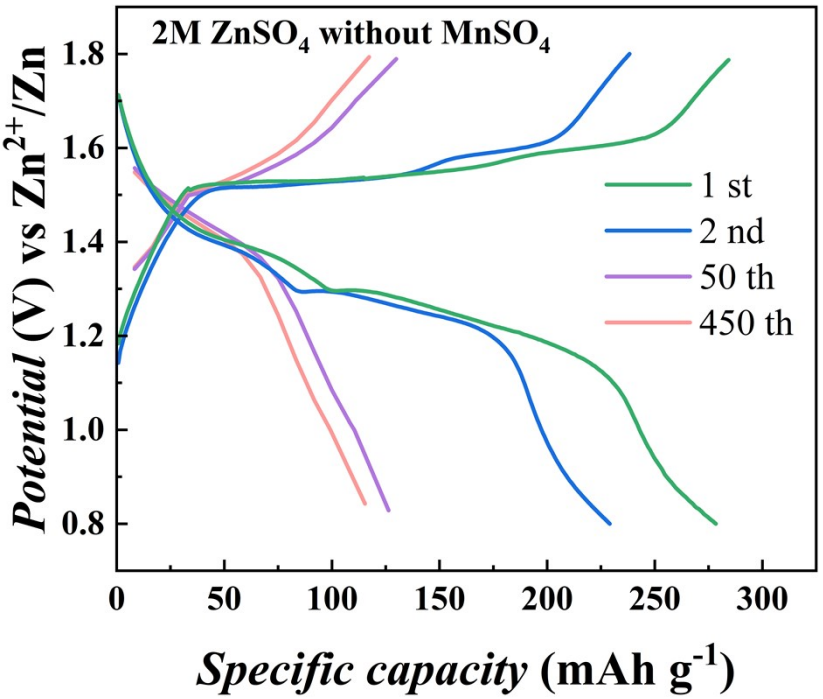

Fig.S7 GCD profiles of the $Na_{0.4}MnO_2$ electrode obtained in aqueous electrolyte (2 M $ZnSO_4$) at a scan of 0.2 A g^{-1}.

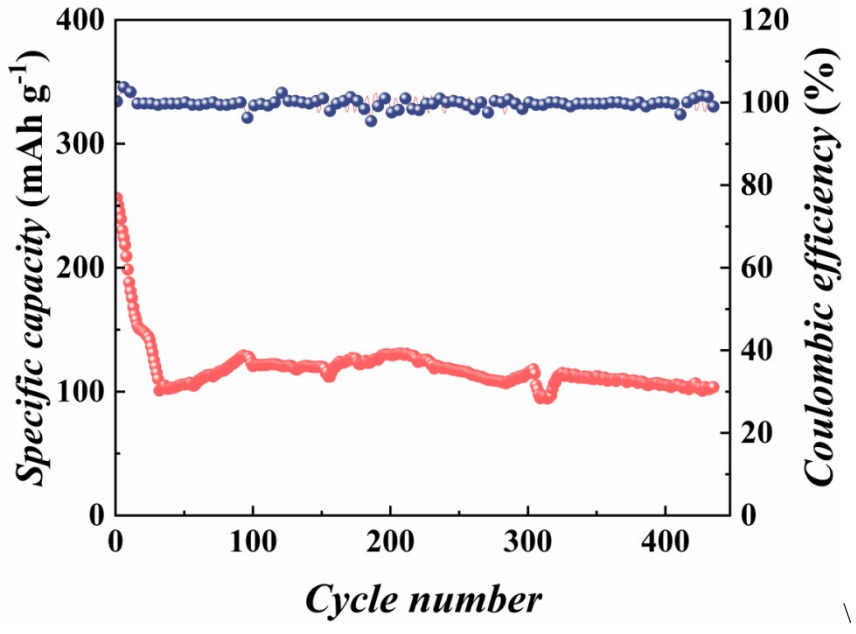

Fig.S8 Cycling performance of the $Na_{0.4}MnO_2$ at 0.2 A g^{-1} in aqueous electrolyte (2 M $ZnSO_4$).

the battery was tested for 450 cycles at 0.2 mA g^{-1} in **Fig S8**. It was found that the capacity of the $Na_{0.4}MnO_2$ sample gradually decreased from 258 mAh g^{-1} to 114 mAh g^{-1} when without Mn^{2+} was added to the electrolyte, the capacity retention rate is only 44.1%.

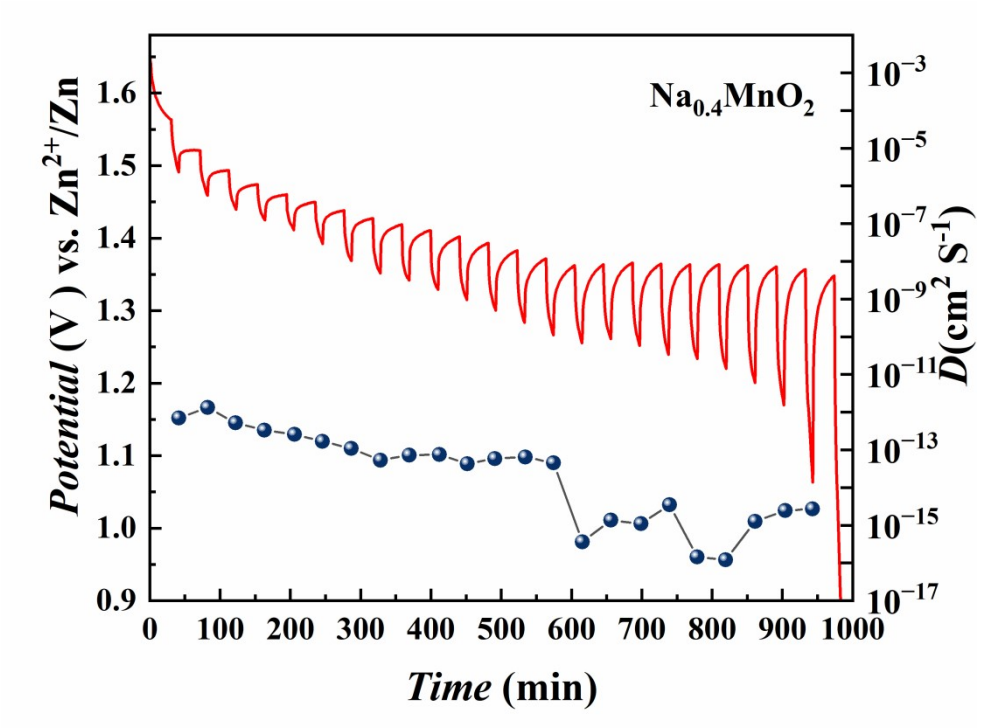

Fig S10. GITT curve and the corresponding diffusion coefficients in discharge process of the ZIB with $Na_{0.4}MnO_2$

The GITT measurement of $Na_{0.4}MnO_2$ electrode was conducted at the current density of 0.1 A g^{-1}. The charging time and rest time are 10 min and 30 min, respectively. When discharged to 1.45 V, the diffusion coefficient of H^+ is 7.52 × 10^{-13} cm^2 s^{-1}, and when discharged to 1.35 V, the diffusion rate of Zn^{2+} is 6.49× 10^{-15} cm^2 s^{-1}. As shown in Fig. S10, the voltage (ΔE_τ) exhibits a linear behavior with the square root of the titration time ($\tau^{1/2}$). Therefore, the diffusion coefficient can be calculated based on the Equation (S3):

$$D = \frac{4}{\pi}\left(\frac{m_B V_M}{\tau M_B A}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \quad \text{(S4)}$$

Here, τ is the constant pulse time 30 min, m_B is the mass of the active material, V_M is the molar volume, m_B is the molecular weight, A is the surface area of electrode with electrode, and ΔE_τ is the difference of stabilized open-circuit for the corresponding step. Accordingly, in this $Na_{0.4}MnO_2$ battery, the relationship between diffusion coefficient and $(\Delta E_s/\Delta E_\tau)^2$ can be described as Eq. S4:

$$\frac{D_1}{D_2} = \frac{(\frac{\Delta E_{S,\ 1}}{\Delta E_{\tau,\ 1}})^2}{(\frac{\Delta E_{S,\ 2}}{\Delta E_{\tau,\ 2}})^2} \quad \text{(S5)}$$

[1] Heubner C, Schneider M, Michaelis A. SoC dependent kinetic parameters of insertion electrodes from staircase—GITT [J]. Journal of Electroanalytical Chemistry, 2016, 767: 18-23.

[2] Deiss E. Spurious chemical diffusion coefficients of Li^+ in electrode materials evaluated with GITT [J]. Electrochimica Acta, 2005, 50(14): 2927-2932.

6.BET

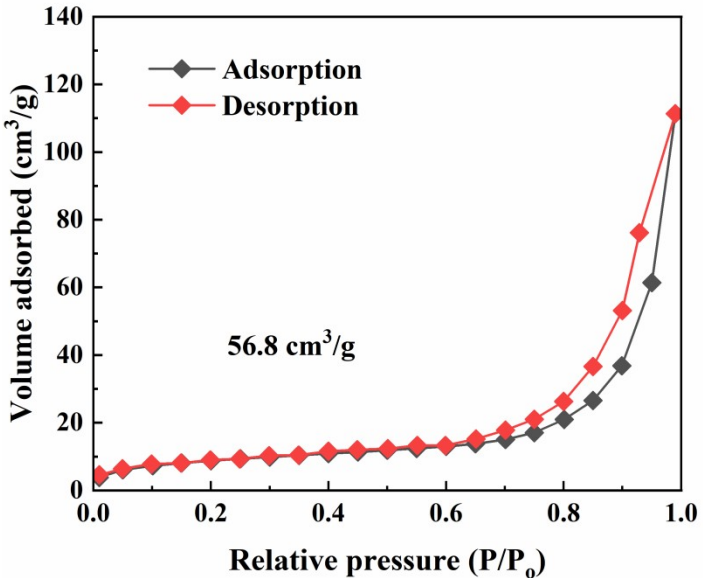

Fig S11. BET pattern of Na-birnessite sample

Fig. S11 displays the BET results of Na-birnessite. The N_2 adsorption-desorption isothermal curve of Na-birnessite belongs to type II, which is a material with large pores or no pores.

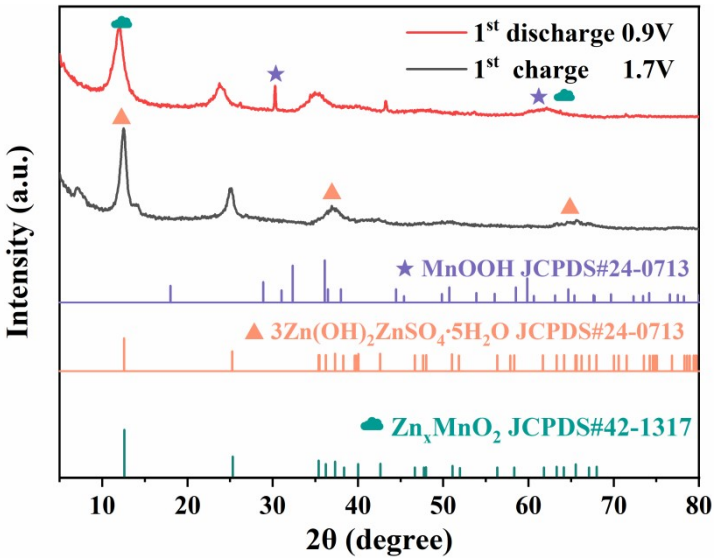

Fig .S12 the ex-situ XRD at different charge–discharge stages

The ex-situ XRD plots of the material in different charge/discharge states are shown in Fig.S12. These nanosheets are identified as $ZnSO_4{\cdot}3Zn(OH)_2{\cdot}5H_2O$ (BZSP), and its formation is associated with the increase in local pH induced by H^+ insertion. At 1.7 V, the flakes gradually disappear, which is attributed to the conversion of BZSP to $ZnMn_3O_7{\cdot}3H_2O$ as indicated by the XRD analysis in Fig. S12. In addition, MnOOH and Zn_xMnO_2 phases are also detected from the fully discharged $Na_{0.4}MnO_2$ anode(Fig. S12), During the first discharging stage at 0.9V, the intercalation of Zn^{2+} and H^+ occurs in $Na_{0.4}MnO_2$ to form layered Zn_xMnO_2, MnOOH and the byproduct BZSP.

[1] Lee B, Seo H R, Lee H R, et al. Critical Role of pH Evolution of Electrolyte in the Reaction Mechanism for Rechargeable Zinc Batteries [J]. Chemsuschem, 2016.

[2] Li Y, Li X, Duan H, et al. Aerogel-structured MnO_2 cathode assembled by defect-rich ultrathin nanosheets for zinc-ion batteries [J]. Chemical Engineering Journal, 2022, 441: 136008-.

[3] Sun W, Wang F, Hou S, et al. Zn/MnO_2 battery chemistry with H^+ and Zn^{2+} coinsertion [J]. Journal of the American Chemical Society, 2017, 139(29): 9775-9778.

Parameter	
Chemical formula	$Na_{0.4}MnO_2$
Space group	C2/m
Step scan increment (°)	0.03
2θ range (°)	5-80
a (Å)	14.28
b (Å)	2.84
c (Å)	23.84

Table 2. Crystal data for $Na_{0.4}MnO_2$.