

Supporting Information

of the paper entitled

**MOF-derived Porous Carbon Inlaid with MnO₂ Nanoparticles as
Stable Aqueous Zn-ion Battery Cathodes**

Experimental Section

1. Materials

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99 %, National Medicine Co., Ltd.), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99 %, National Medicine Co., Ltd.), Manganese sulfate (MnSO_4 , 99 %, National Medicine Co., Ltd.), Zinc sulfate (ZnSO_4 , 99 %, National Medicine Co., Ltd.), CH_3OH and HCl in this experiment were acquired from Aladdin Ltd., Poly-(vinylidene fluoride) (PVDF) and carbon black were purchased from National Medicine Co., Ltd.. All of the reagents were of analytical purity and were used as received.

2. Preparation of CoMOF

4 mmol of cobalt nitrate and 20 mmol of 2-methylimidazole were dissolved in 100 mL of methanol, mixed rapidly and stirred vigorously for 30 s. After stirring, the mixture was left to stand at 25°C for 24 h. After standing, the mixture was washed by alternate filtration with methanol and deionised water and dried, and the purple powder was collected as CoMOF.

3. Preparation of C-CoMOF

Some of the CoMOF obtained in step 2 was calcined under Ar atmosphere at $2^\circ\text{C}/\text{min}$ to 100°C for 1h and then continued to calcine at a rate of 5°C min^{-1} to 900°C for 4h. The black powder collected above was crushed and dispersed in 1 M HCl , stirred and sonicated for 24h, then washed three times with deionised water and collected as C-CoMOF.

4. Preparation of C-CoMOF-MnO₂

An appropriate amount of C-CoMOF homogeneous powder was dispersed into a 50% solution of manganese nitrate, stirred and sonicated for 24 h. After stirring, the black viscous gelatinous mixture was collected by filtration and calcined in air at $1\text{ }^{\circ}\text{C min}^{-1}$ to $150\text{ }^{\circ}\text{C}$ for 2 h. After burning, the solid was ground and collected to obtain C-CoMOF-MnO_x (which contains a small amount of cobalt metal monomers).

5. Preparation of MnO₂

A 50% solution of manganese nitrate is calcined directly in air at $1\text{ }^{\circ}\text{C min}^{-1}$ up to $150\text{ }^{\circ}\text{C}$ for 2h, after which the solid is ground and collected homogeneously to obtain MnO₂.

6. Preparation of anode and electrolyte

High purity zinc flakes (99%) are first soaked in acetone for 15min and then dried by ultrasonic cleaning with alcohol for 10 minutes. The electrolyte was easily mixed with 3 M ZnSO₄ + 0.1 M MnSO₄.

7. Characterization of Materials

The crystal structure of the products are identified by X-ray diffraction (XRD) using a Bruker/Vertex 70 X-ray diffractometer with range of 5° - 80° . The morphology and microstructure are observed by the field emission scanning electron microscope (JEOL JEM-2100F). Transmission electron microscope (TEM) and high resolution Transmission electron microscope (HRTEM) were performed on Titan G2 60-300. Valence states measurements were analysed with X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). And binding energies (BEs) of the elements were calibrated against the reference BE at 284.8 eV for the C 1s peak. FT-IR spectrums were

performed on IRAffinity-1/SHIMADZU. Thermogravimetric analysis (TGA) was conducted under air atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ on a MS coupled thermogravimetric analyser (TA Instruments Q600SDT).

8. Electrochemical Performance Characterization

The batteries were assembled using the C-MnO₂ electrode as the cathode, organic glass fiber as the separator and Zn foil (thickness: 0.1mm, diameter: 15mm) as the anode in CR 2016 coin cells. 3 M ZnSO₄ + 0.1 M MnSO₄ aqueous solution was used as the electrolytes. The working electrode was prepared by mixing carbon coated C-MnO₂ (70 wt%), conductive carbon (Super-P, 20 wt%), and polyvinylidene flluoride (PVDF, 10 wt%), using N-methyl-2-pyrrolidone as solvent. The obtained slurry was cast onto stainless steel wire mesh (sswm) and dried in a vacuum oven at 80°C for 12 h. Cyclic voltammetry (CV) was carried out using CHI 660E electrochemical work station. Galvanostatic charge/discharge (GCD) tests were performed in the potential range of 0.8 to 1.8 V. The galvanostatic intermittent titration technique (GITT) was applied to analyze the reaction and diffusion kinetics at a current density of 100 mA g⁻¹ and a charge/discharge time and interval of 10 min for each step.

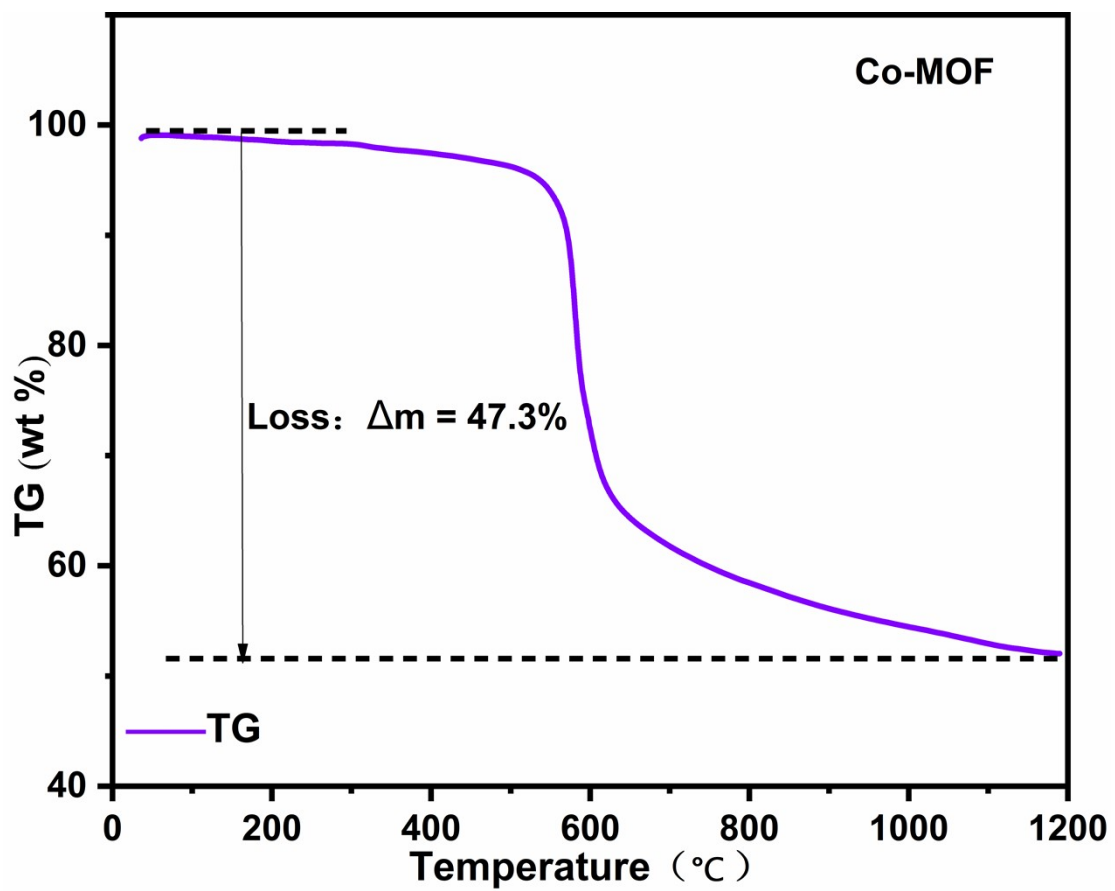


Figure S1 The thermogravimetric curve of Co-MOF

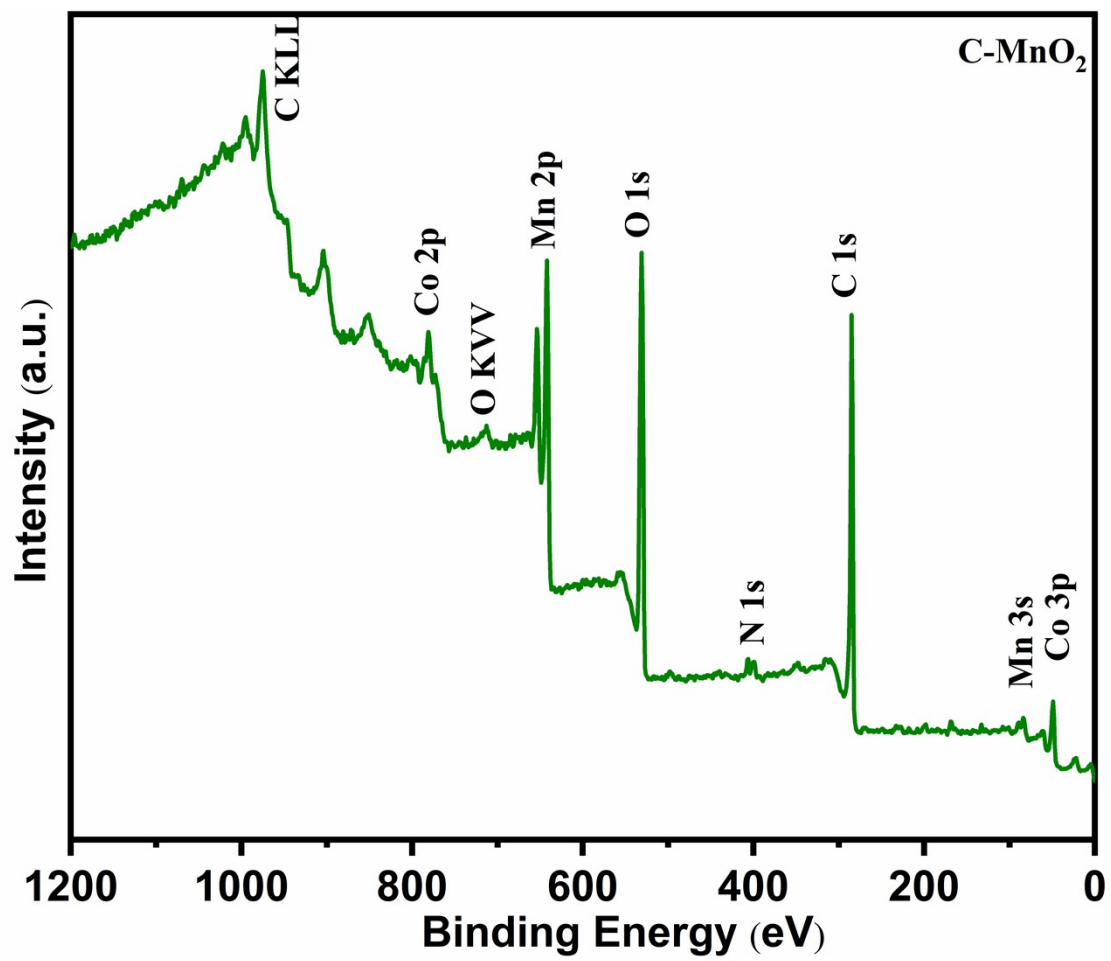


Figure S2 XPS survey spectra of C-MnO₂

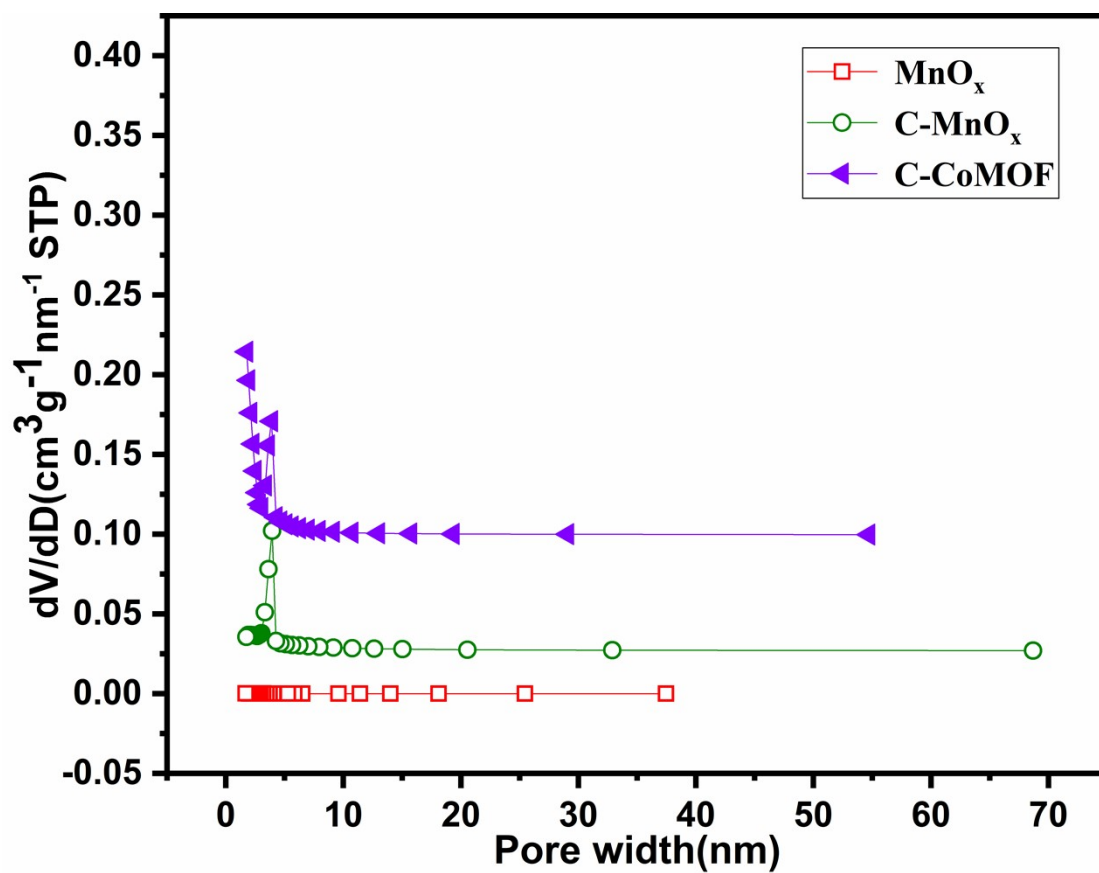


Figure S3 Pore size distribution of C-MnO₂

Table S1 Specific surface area of different electrodes

Cathode	C-CoMOF	C-MnO₂	MnO₂
Surface area (m² g⁻¹)	502	136	0.4

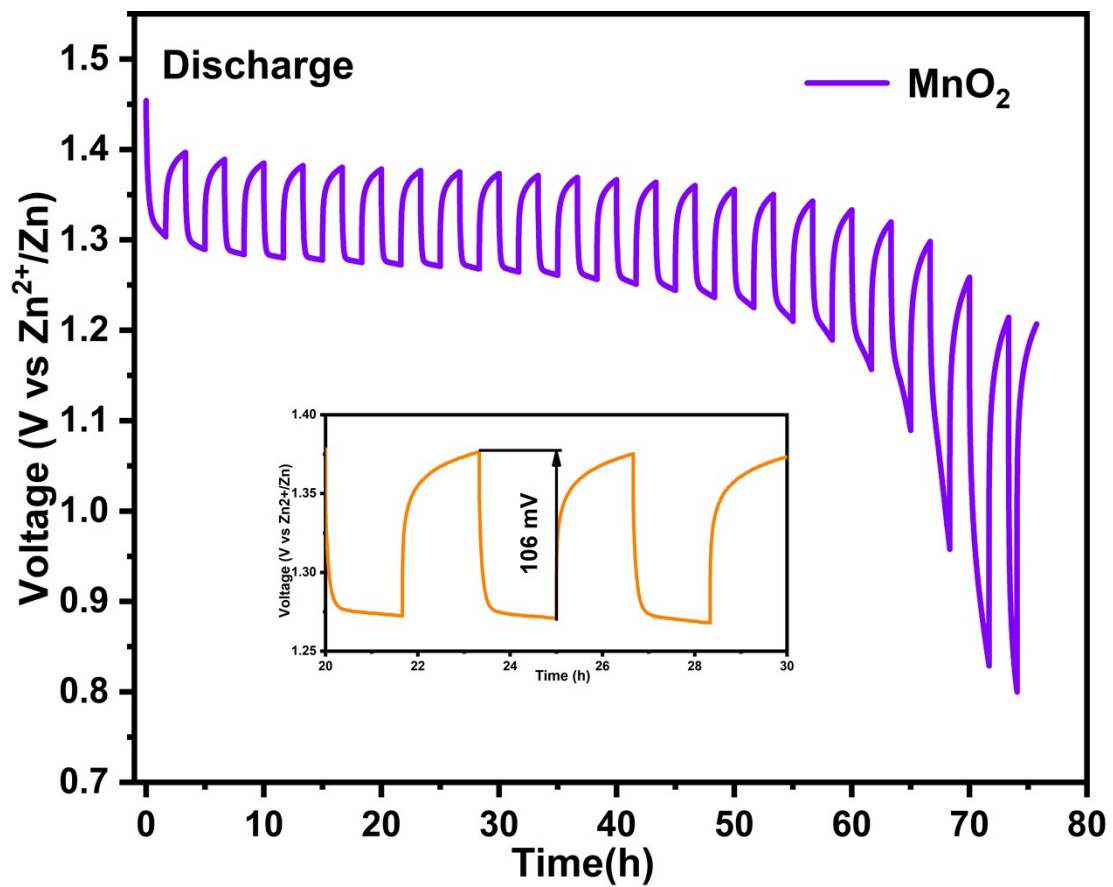


Figure S4 GITT curve of MnO₂

Table S2 Overpotential of ohmic impedance and charge transfer impedance & ion diffusion

Cathode	C-MnO₂			MnO₂
	I	II	III	
IR drop / mV	25	90	40	50
ΔE_t / mV	33	0	230	56
Total	58	90	270	106

Table S3 Passivation and broadening of peaks at different scanning rates for C-MnO₂ and MnO₂

Cathode	C-MnO₂		MnO₂	
Scan rate	Angle	Width	Angle	Width
(mV s⁻¹)	(Peak 1)	(Peak 4)	(Peak 1)	(Peak 4)
0.2	43 °	210 mV	34 °	150 mV
0.4	50 °	189 mV	36 °	152 mV
0.8	>90 °	175 mV	50 °	134 mV

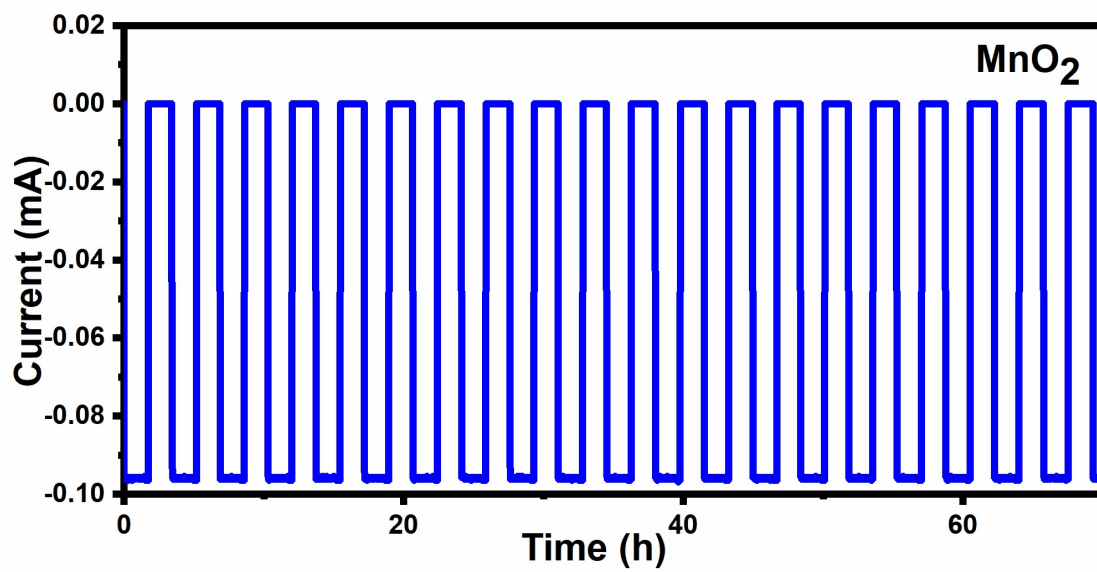


Figure S5 Current of GITT at 1st discharge (MnO₂)

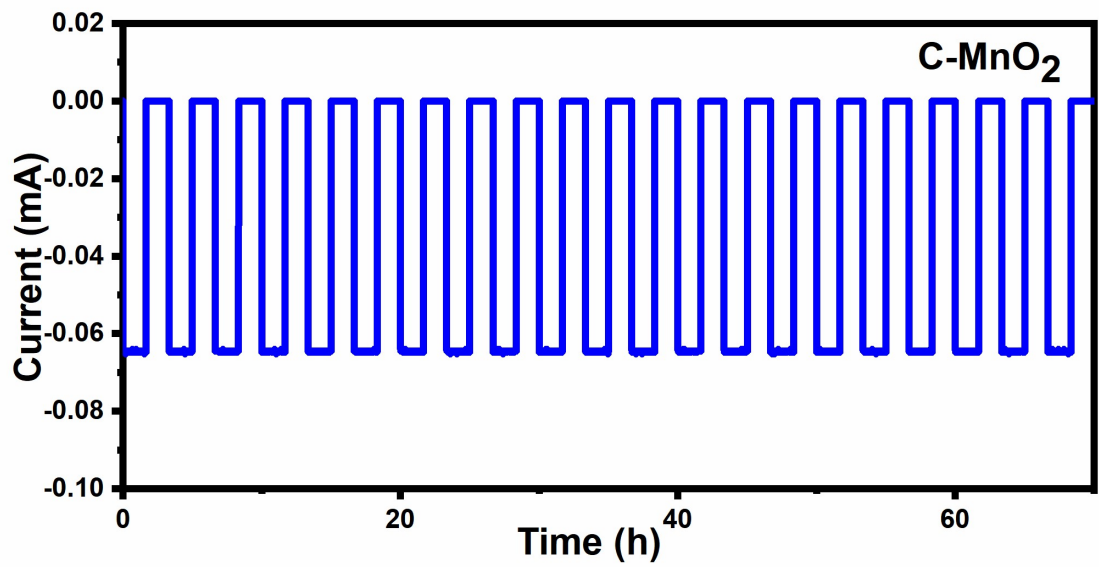


Figure S6 Current of GITT at 1st discharge (C-MnO₂)

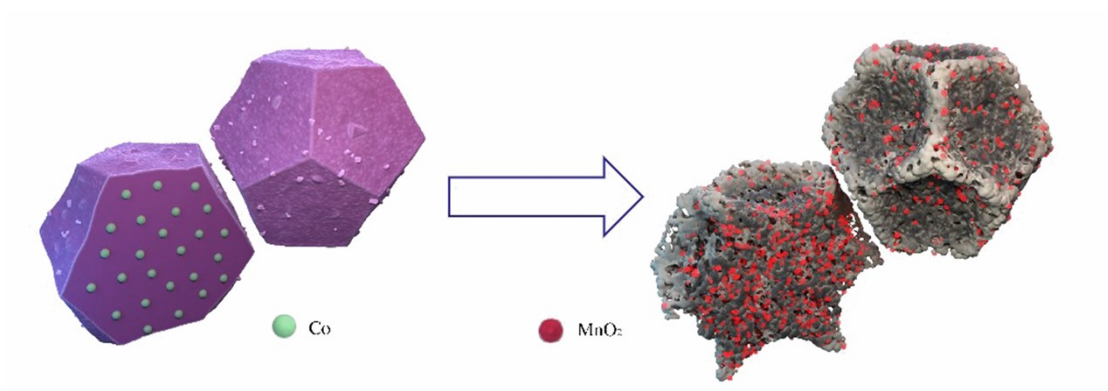


Figure S7 Schematic diagram of the preparation of C-MnO₂

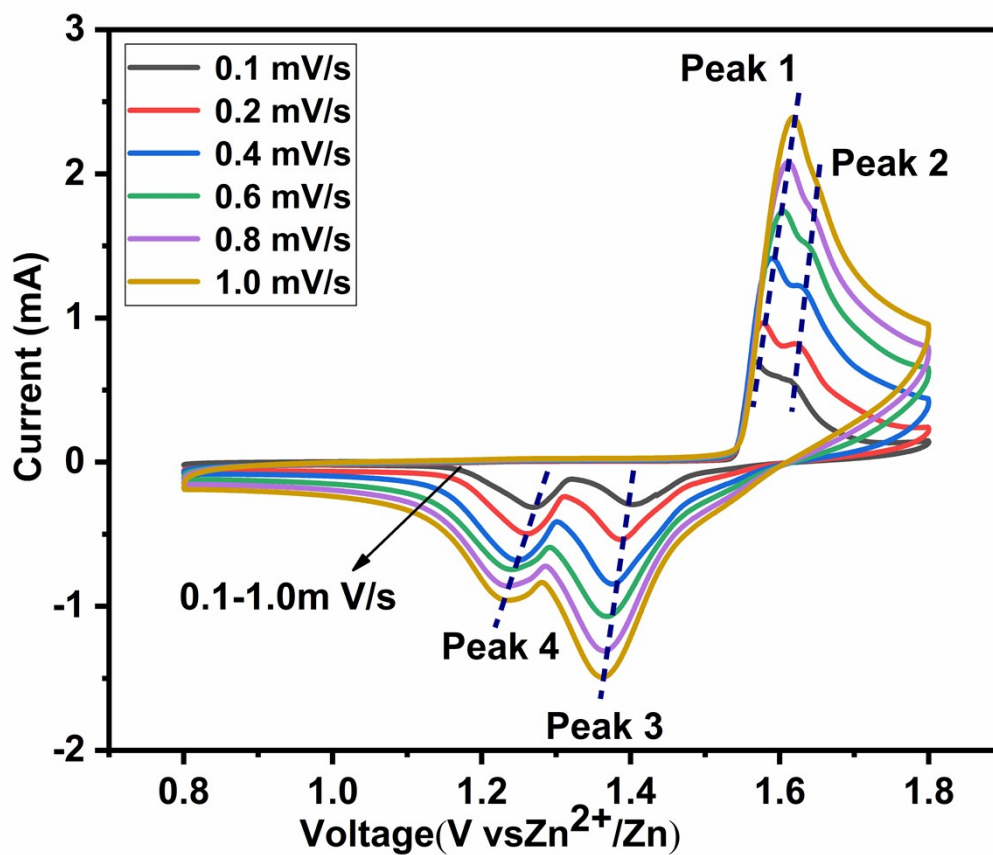


Figure S8 CV curves of MnO₂ at different scanning rates.

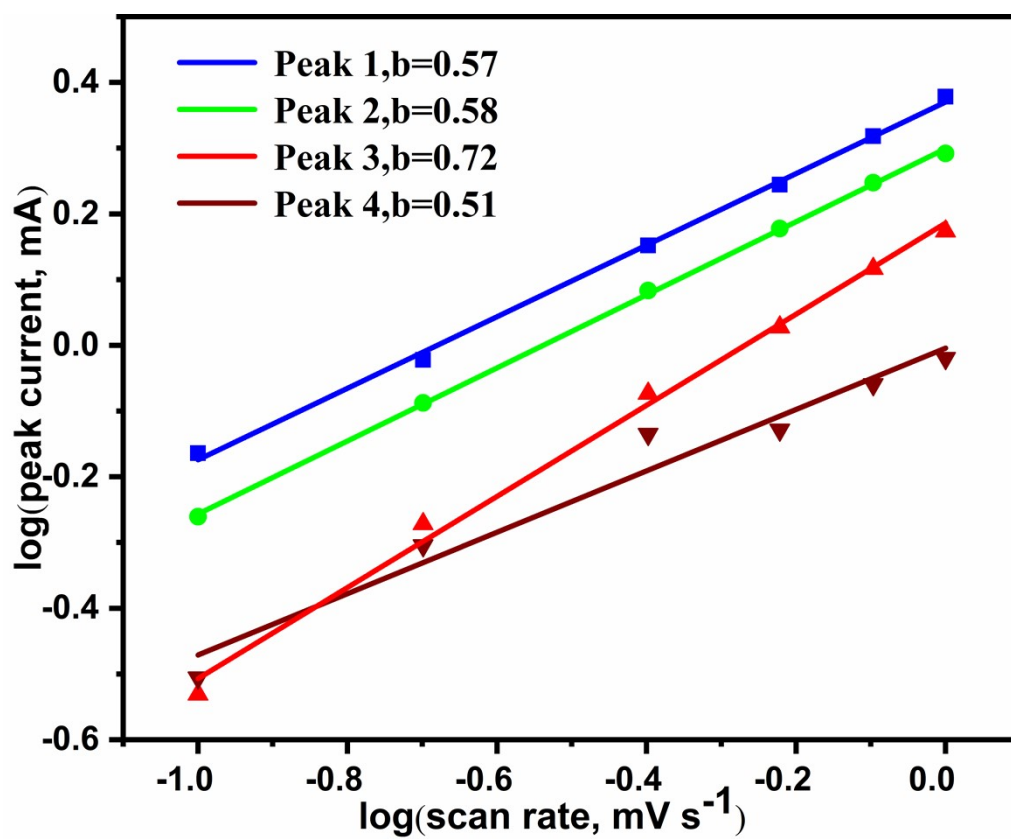


Figure S9 Corresponding $\log(i)$ vs. $\log(v)$ curves and b values.

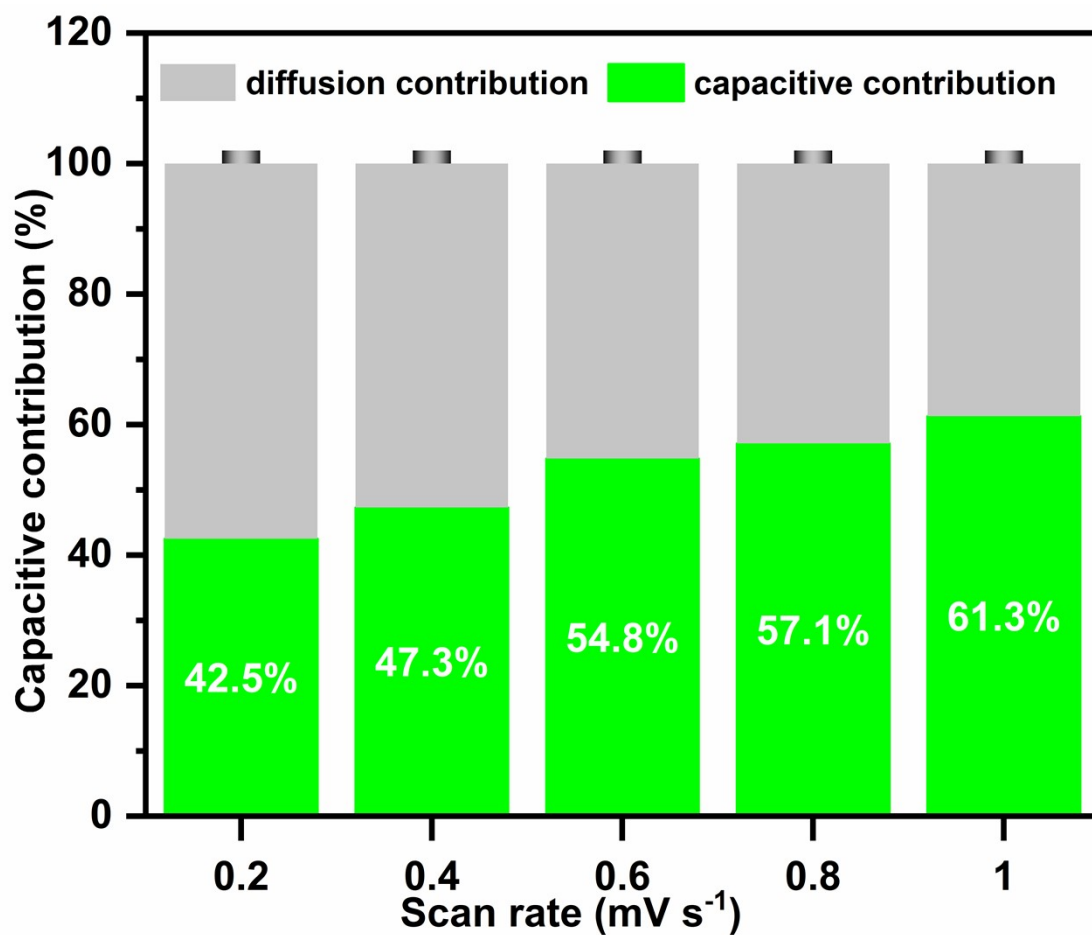


Figure S10 Capacitance contribution (electrical double layer capacitance + pseudocapacitance) at different at different scan rates

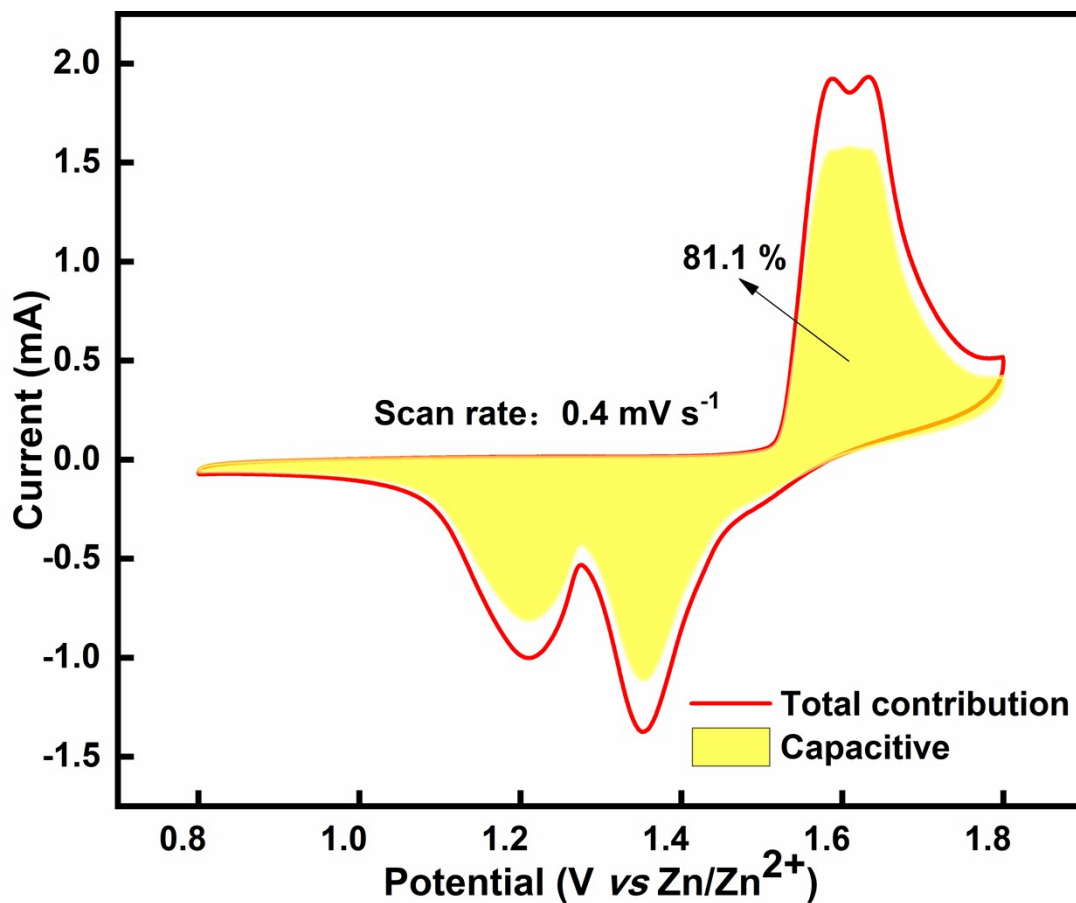


Figure S11 Ratio of capacitance contribution at 0.4 mV s⁻¹.

Table S4 Electrochemical performances of manganese-based cathode materials of AZIBs

Cathodes	Electrolyte	Specific capacity (mAh g ⁻¹)	Capacity retention (%)	Ref.
ZnMn ₂ O ₄	1 M ZnSO ₄ + 0.05 M MnSO ₄	106.5 (0.1 A g ⁻¹)	84 % (300 cycles, 0.1 A g ⁻¹)	[38]
Na _{0.95} MnO ₂	0.5 M Zn(CH ₃ COO) ₂ + 0.5 M CH ₃ COONa	60 (0.05 A g ⁻¹)	92 % (2000 cycles, 0.2 A g ⁻¹)	[39]
δ-MnO ₂	1 M ZnSO ₄	252 (0.08 A g ⁻¹)	44 % (100 cycles, 0.08 A g ⁻¹)	[40]
β-MnO ₂	1 M ZnSO ₄	180 (0.2 A g ⁻¹)	75 % (200 cycles, 0.2 A g ⁻¹)	[41]
β-MnO ₂	3 M Zn(CF ₃ SO ₃) ₂ + 0.1 M Mn(CF ₃ SO ₃) ₂	225 (0.2 A g ⁻¹)	94 % (2000 cycles, 2 A g ⁻¹)	[42]
This work ε-MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	234 (0.2 A g ⁻¹)	91 % (1000 cycles, 1 A g ⁻¹)	/