## **Supplementary Information for**

## Nickel-doped δ-MnO<sub>2</sub> abundant in oxygen vacancies as cathode for aqueous Zn-ion batteries with superior performance

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Fig. S1. SEM images of (a) 3%Ni-δ-MnO<sub>2</sub>, (b) 4%Ni-δ-MnO<sub>2</sub> and (c) 6%Ni-δ-MnO<sub>2</sub>;.



Fig. S2. (a) GCD profiles at 0.1 A  $g^{-1}$  in the initial five cycles, and (b) GCD profiles of the  $\delta$ -MnO<sub>2</sub> cathode across different current densities.



Fig. S3. EDS mapping of the 5%Ni- $\delta$ -MnO<sub>2</sub> cathode when discharged to 0.8 V.

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Samples	SSA (m <sup>2</sup> g <sup><math>-1</math></sup> )	TPV (cm <sup>3</sup> g <sup>-1</sup> )	APD (nm)	
δ-MnO <sub>2</sub>	24.02	0.053428	3.5135	
5%Ni-δ-MnO <sub>2</sub>	84.28	0.143309	3.7450	

Table S1. SSA, TPV and APD of  $\delta$ -MnO<sub>2</sub> and 5%Ni- $\delta$ -MnO<sub>2</sub>.

Table S2 Summary of the electrochemical performance of various heteroatom-doped manganese-based cathodes in ZIBs.

Cathode	Electrolyte	Voltage	Specific	Cycling stability	Ref.
		window	capacity		
5%Ni-ð-MnO <sub>2</sub>	2 M ZnSO <sub>4</sub> +	0.8-1.8 V	401 ( 41]	75.50/ material and them	This
	0.25 M		401.6 mAn g <sup>1</sup>	/5.5% retention after	1 n1s
	MnSO <sub>4</sub>		at 0.1 A g <sup>-1</sup>	1000 cycles at 1 A $g^{-1}$	work
Ce-MnO <sub>2</sub> @CC	PAM/ZnSO <sub>4</sub> -	0.8-1.8 V	311 mAh g <sup>-1</sup>	65.0% retention after	1
	MnSO <sub>4</sub>		at 0.1 A g <sup>-1</sup>	450 cycles at 0.1 A $g^{-1}$	1
K- $\delta$ -MnO <sub>2</sub>	2 M ZnSO <sub>4</sub> +	1-1.9 V	$270.5 \text{ mAh } \text{g}^{-1}$	$\sim 50\%$ retention after	2
	0.1 M MnSO <sub>4</sub>		at 0.1 A g <sup>-1</sup>	1000 cycles at 2 A g <sup>-1</sup>	Z

V-doped	1 M ZnSO <sub>4</sub>	1-1.8 V	$266 \text{ mAh } \text{g}^{-1}$	49.2% retention after	3
$MnO_2$			at 0.1 A g <sup>-1</sup>	100 cycles at 0.1 A $g^{-1}$	
Zn-doped	2 M ZnSO <sub>4</sub> +	1 1 9 37	${\sim}320 \text{ mAh } g^{-1}$	66% retention after	4
$MnO_2$	0.2 M MnSO <sub>4</sub>	1-1.0 V	at 0.1 A g <sup>-1</sup>	100 cycles at 0.2 A $g^{-1}$	
La–Ca co-	2 M ZnSO <sub>4</sub> +	0.8-1.9 V	297 mAh g <sup>-1</sup>	76% retention after	5
doped ε-MnO <sub>2</sub>	0.4 M MnSO <sub>4</sub>		at 0.2 A g <sup>-1</sup>	100 cycles at 0.2 A $g^{-1}$	
Co-Mn <sub>3</sub> O <sub>4</sub>	2 M ZnSO <sub>4</sub> +	0 2 2 2 V	220 mAh g <sup>-1</sup>	72.5% retention after	6
	0.2 M MnSO <sub>4</sub>	0.2-2.2 V	at 0.1 A g <sup>-1</sup>	1100 cycles at 2 A $g^{-1}$	
Mo-MnO <sub>2</sub>	2 M ZnSO <sub>4</sub> +	0018V	327 mAh g <sup>-1</sup>	76.8% retention after	7
	0.9-1 0.1 M MnSO <sub>4</sub>	0.9-1.8 V	at 0.2 A g <sup>-1</sup>	1000 cycles at 1 A $g^{-1}$	

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