Supporting Information

Naphthalene Dianhydride Organic Anode for 'Rocking-Chair' Zinc-Proton Hybrid Ion Battery

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Table S1: Crystal structure information of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA).[1]

Space group	$P2_1/c$
Crystal system	Monoclinic
Cell parameters	a = 7.880 Å, b = 5.322 Å, c = 12.601 Å, α = 90°, β = 107.257°, γ = 90°

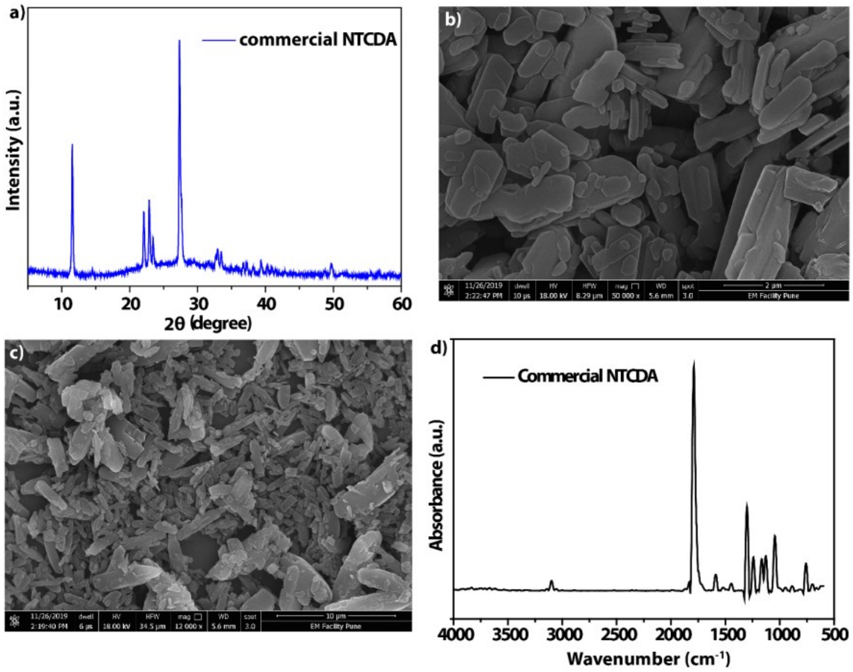

Figure S1. (a) XRD data and (b)-(c) FESEM images, (d) FTIR data of the commercial NTCDA.

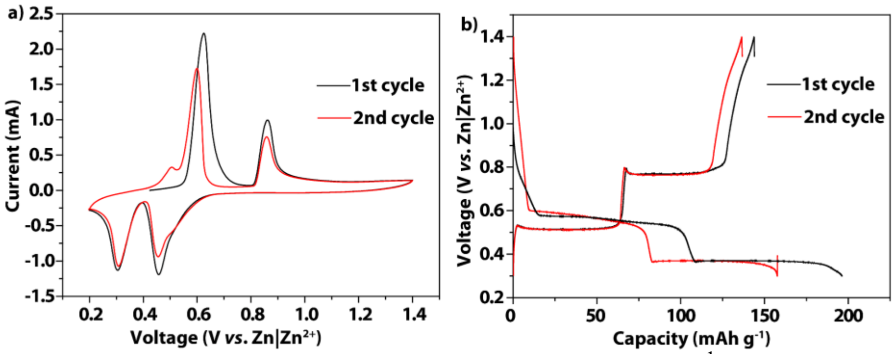

Figure S2. (a) CV profiles recorded at the scan rate of 1.0 mV s^{-1} and (b) GCD profiles recorded at the current rate of 0.1A g^{-1} for the NTCDA||Zn cell.

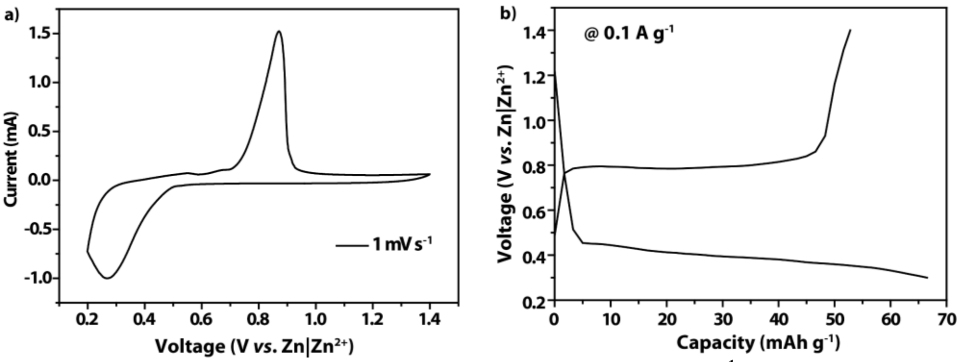

Figure S3. (a) CV profile recorded at the scan rate of 1.0 mV s^{-1} and (b) GCD profile recorded at the current rate of 0.1 A g^{-1} for the NTCDA||Zn-(O) cell in 0.5M ZnOTF/ACN electrolyte.

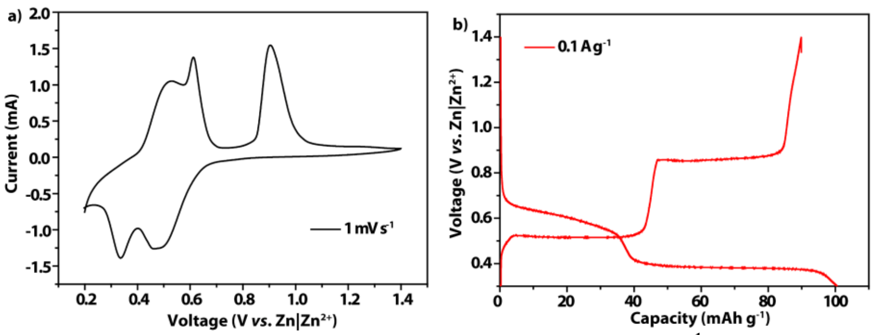

Figure S4. (a) CV profile recorded at the scan rate of 1.0 mV s^{-1} and (b) GCD profile recorded at the current rate of 0.1 A g^{-1} for the NTCDA||Zn-(A) cell in 0.01M H_2SO_4 electrolyte.

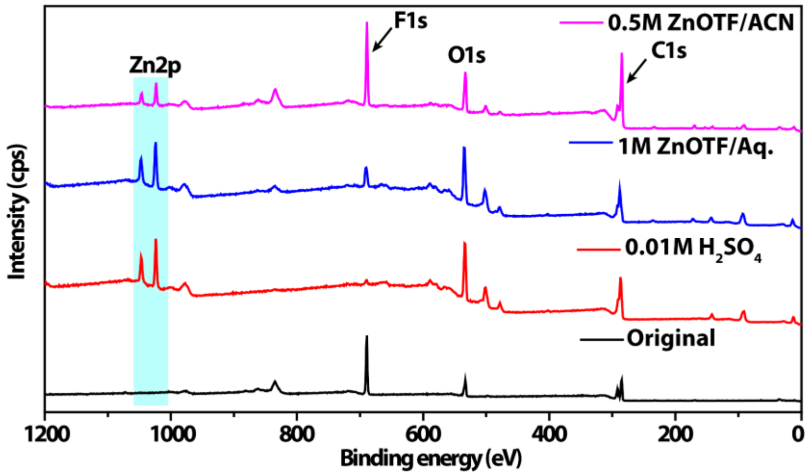

Figure S5. XPS survey spectra of the NTCDA electrodes at the original state and after recovering from the NTCDA||Zn-(N), NTCDA||Zn-(A), and NTCDA||Zn-(O) cells at the discharged state.

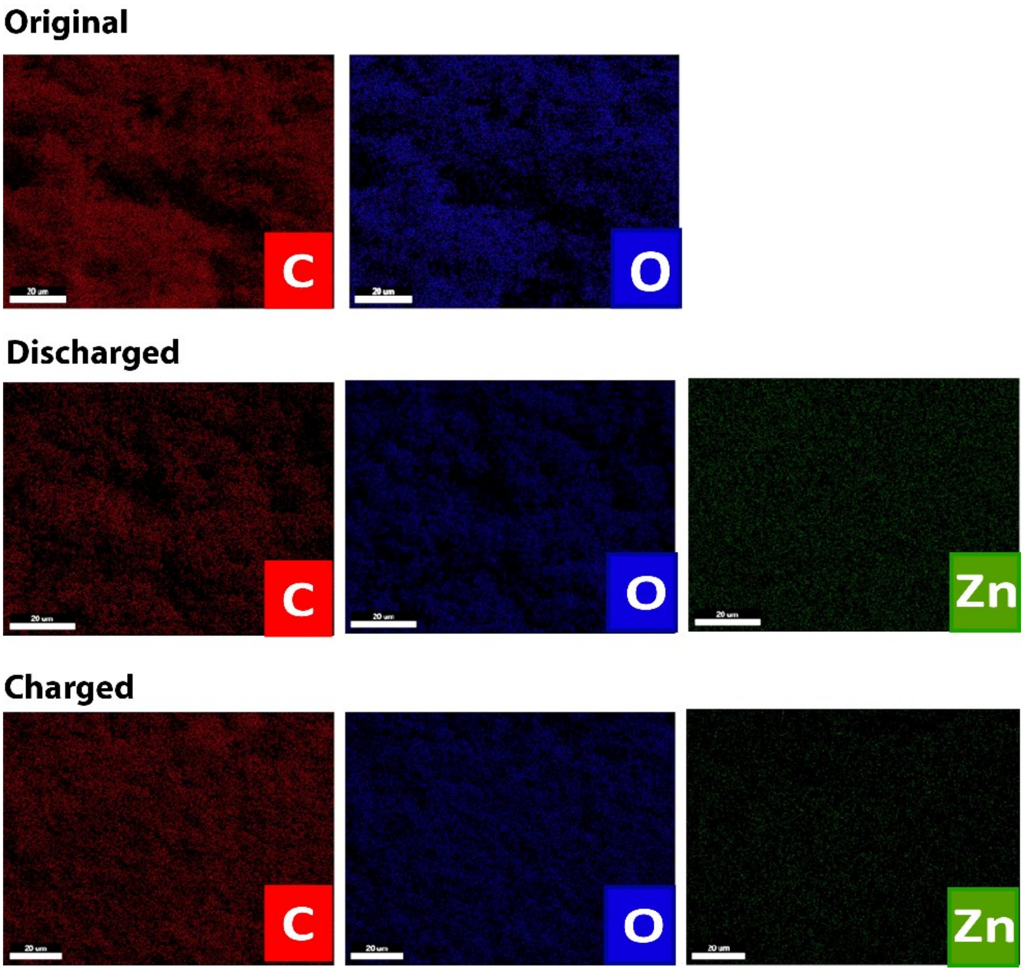

Figure S6. Elemental mapping of the NTCDA electrodes at the original state, and after recovering from the NTCDA||Zn-(N) half-cells at the discharged (0.30 V) and charged (1.4 V) states.

Table S2. Atomic percentage of the elements obtained from the EDAX analysis of the NTCDA electrodes recovered from the NTCDA||Zn-(N) half-cells.

	Carbon (Atomic %)	Oxygen (Atomic %)	Zinc (Atomic %)
Original	71.4	28.6	-
Discharged	52.6	39.4	7.9
Charged	58.4	39	2.5

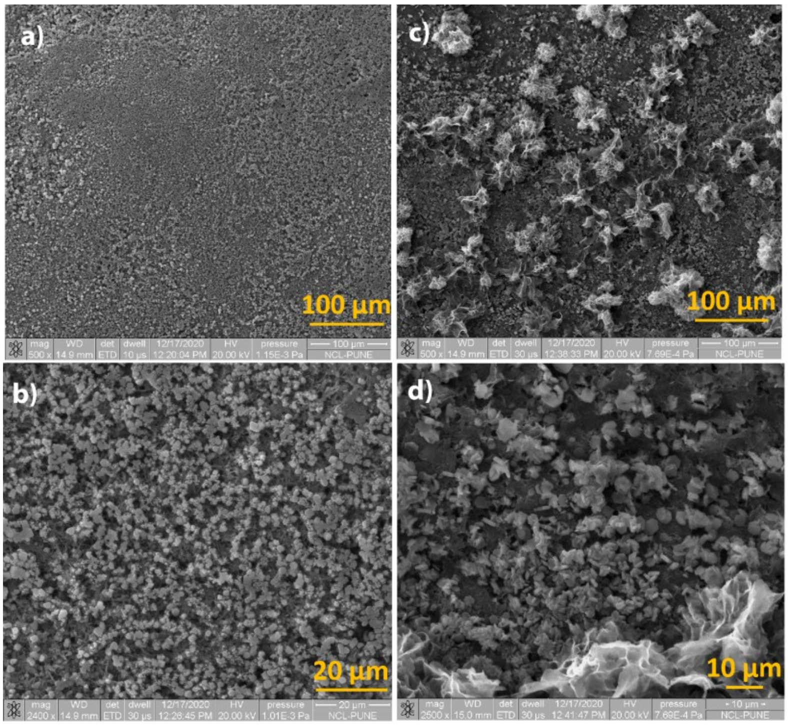

Figure S7. SEM image of NTCDA electrodes recovered from the NTCDA||Zn-(N) cell at the (a-b) discharged, and (c-d) charged states at different magnifications.

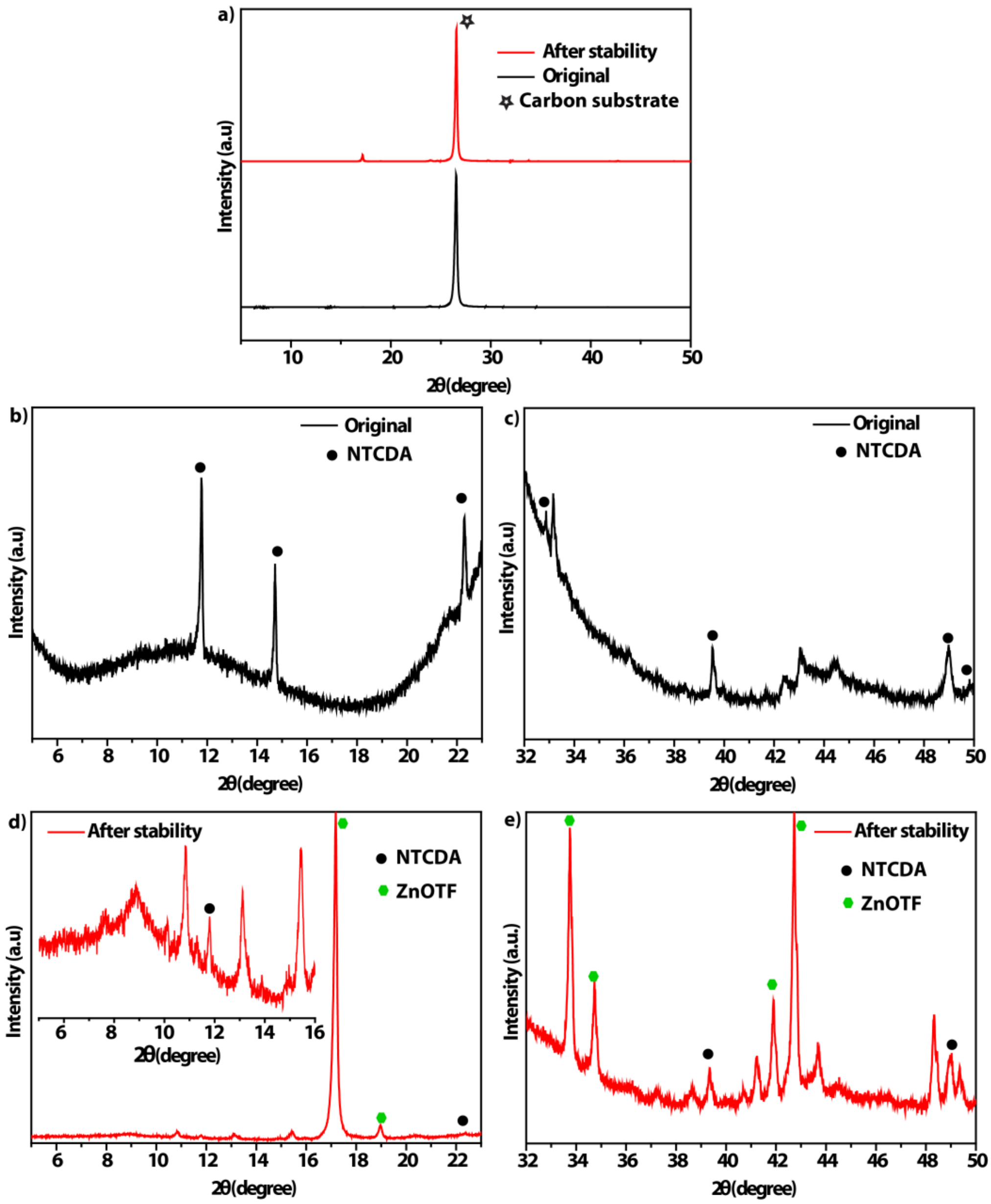

Figure S8. (a) XRD profiles of the NTCDA cathode recorded at the original state and after recovering from the post-cycled NTCDA||Zn-(N) half-cell; (b)-(c) and (d)-(e) show the zoomed view of the XRD data of the original electrode and the post stability electrode (the electrode was washed with water and dried before the XRD analysis), respectively.

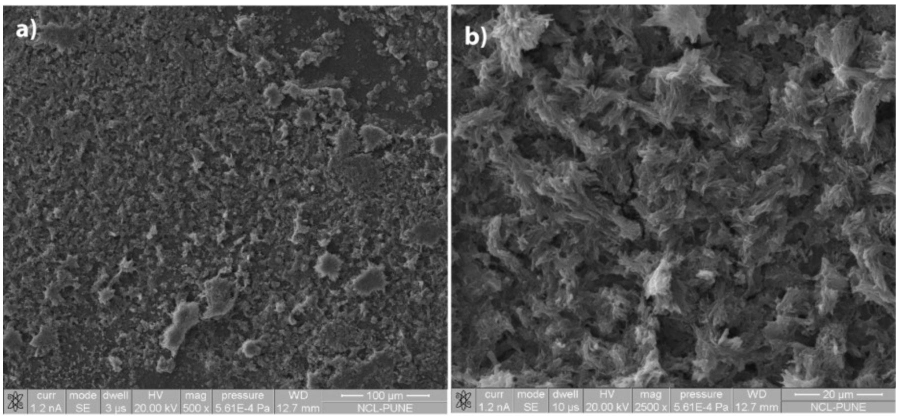

Figure S9. (a)-(b) SEM images of the NTCDA electrode recovered from the NTCDA||Zn-(N) half-cell after the cycling stability test (the electrode was washed with water and dried before the SEM analysis).

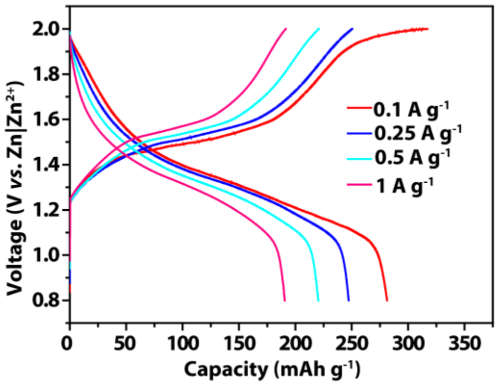

Figure S10. GCD profiles of the MnO_2||Zn-(N) half-cell recorded at different current rates.

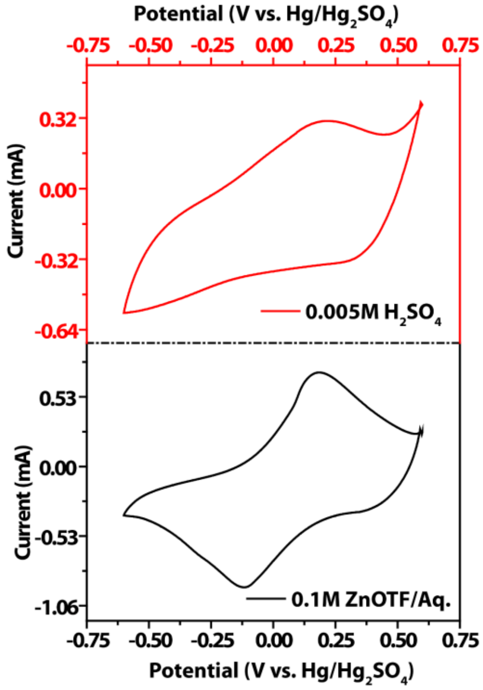

Figure S11. CV profiles for the MnO_2 electrode characterized in the three-electrode cell with respect to the Hg/Hg_2SO_4 reference electrode in 0.005M H_2SO_4 and 0.1M ZnOTF/Aq. electrolytes.

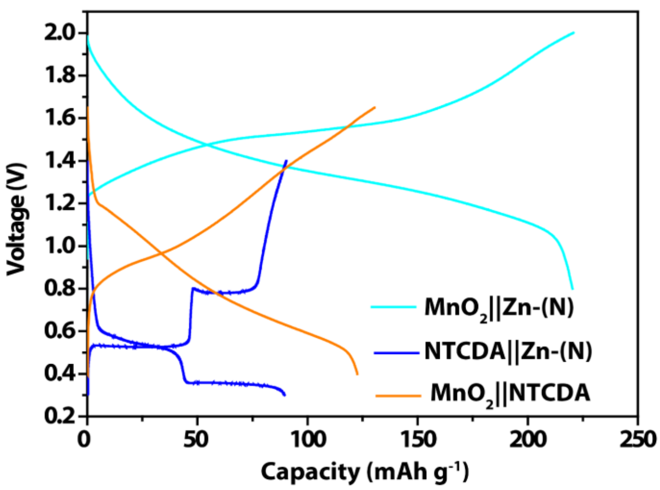

Figure S12. Charge/discharge capacities of the MnO_2||Zn-(N), NTCDA||Zn-(N), and MnO_2||NTCDA cells recorded at the current rate of 0.50 A g^{-1} (here, the capacity values and current rate are normalized with respect to the mass-loading of the electrode material in the positive electrode).

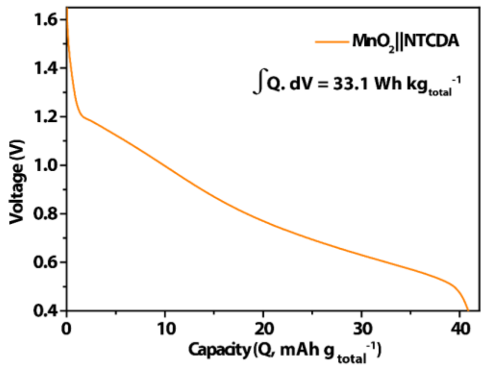

Figure S13. Voltage *vs.* discharge capacity plot of the MnO_2||NTCDA full-cell recorded at a current rate of 0.17 A g_{total}^{-1}.

The area under curve of the voltage *vs.* discharge capacity plot indicates the specific energy density based on the loading of the active material on cathode. The integrated area from Figure S13 is calculated to be 33.1 Wh kg_{total}^{-1} and the corresponding discharge capacity is 41 mAh g_{total}^{-1}. Therefore, the average voltage can be calculated from the following equation.

$$Average\ voltage = \frac{\text{Specific energy density}}{\text{Specific discharge capacity}} = \frac{33.1\ \text{Wh}\ kg_{total}^{-1}}{41\ \text{mAh}\ g_{total}^{-1}} = 0.80\ \text{V}... \ (\textbf{Equation S1})$$

Table S3. The electrochemical performance parameters of NTCDA in the NTCDA||Zn half-cell and MnO_2||NTCDA full-cell configurations are compared with the performance of some of the previously reported anode materials for ZIBs.

Cathode|| Anode	Performance in half-cell			Performance in full-cell			Ref. (Main Text)
	Capacity (current rate)	Voltage	Cycling stability	capacity	Voltage	Cycling stability	
PB|| PTCDI/rGO	141 mAh g^{-1} (0.5 A g^{-1})	0.38 V	95% (1200 cycles)	48 mAh g_{total}^{-1}	0.95 V	75% (150 cycles)	27
$ZnMn_2O_4$|| $Na_{0.14}TiS_2$	120 mAh g^{-1} (0.1 A g^{-1})	0.30 V	77% (5000 cycles)	38 mAh g_{total}^{-1}	0.95 V	74% (100 cycles)	11
PB|| $Zn_2Mo_6S_8$	~60 mAh g^{-1} (0.128 A g^{-1})	0.35 V	-	62 mAh g_{total}^{-1}	1.40 V	-	28
MnO_2|| PI-COF	92 mAh g^{-1} (0.7 A g^{-1})	-	85% (4000 cycles)	60 mAh g_{total}^{-1}	~0.90-0.80 V	82.5% (2000 cycles)	29
PB|| Ferrocene/C	106 mAh g^{-1} (1C)	-	70% (2000 cycles)	30 mAh g_{total}^{-1}	0.90 V	58% (1000 cycles)	30
MnO_2|| NTCDA	143 mAh g^{-1} (0.1 A g^{-1})	0.46 V	~75% (300 cycles)	41 mAh g_{total}^{-1}	0.80 V	~60% (100 cycles)	**This work**

References

1. https://www.ccdc.cam.ac.uk/structures/search?id=doi:10.5517/cc4bplq&sid=DataCite.