

## Novel MnO/carbon composite anode material with multi-modal pore structure for high performance lithium-ion batteries

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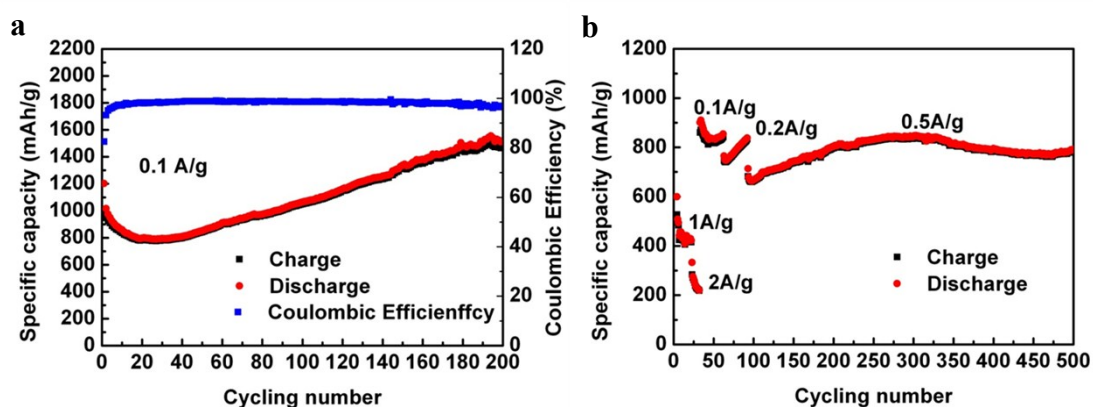
In this work, the BET specific surface area of the nanoporous MnO/carbon composite particles was measured to be about 223.2 m<sup>2</sup> g<sup>-1</sup>, higher than those reported about MnO-based electrodes (Table S1). The Quench Solid Density Functional Theory (QSDFT) pore size distribution (shown as inset of Fig. 7) revealed the multimodal mesopore distribution of the MnO/Carbon composite particles with two main peaks: 5.01nm and 48.5nm. Such a multi-modal pore structure would be beneficial to adjust the volume change of electrode materials during the lithiation/delithiation process, resulting in a relatively high capacity and excellent cycling stability [25, 29].

**Table S1** The comparison of BET specific surface area and pore size distribution of various MnO-based anode materials

Sample	BET specific surface area (m <sup>2</sup> g <sup>-1</sup> )	pore size distribution (nm)	Reference
Hollow porous MnO/C microspheres	76.9	11/87	19
MnO/C mesoporous networks	82.7	2.8/7.6	31
Heterostructured MnO/C nanopeapods	103	3.5/11/40	27
MnO@1-D Carbon	64	24.6	S1
Porous C-MnO disks	75.3	20	S2
Hierarchical Micro/Nanostructured MnO	52.5	20/60	S3
Nanoporous MnO/Carbon composite particles	223.2	5.0/48.5	This work

In Fig. S1a, conforming to the reported MnO/carbon anode materials [21], the capacity of the porous MnO/Carbon composite anode materials in this study dropped rapidly at first, and then gradually increased up to 1464.9 mA g<sup>-1</sup> at a current density of 0.1 A g<sup>-1</sup> after 200 cycles and subsequently remained the steady value.

Fig. S1b shows the rate performance of the porous MnO/carbon composite anode materials. Different from the previous studies, the test program in this study was set to: first high current density, and then low current density for abundant cycles, in order to evaluate the capability of the anode materials at high current density, the recover capability after the surge of high current density, and the stability after such a drastic rate change. To avoid the affects of high initial current density, the electrode was discharged and charged at 0.1 A g<sup>-1</sup> in the first 2 cycles, then high current density of 1.0 A g<sup>-1</sup> for 20 cycles, 2.0 A g<sup>-1</sup> for 10 cycles, as shown in Fig. S1b. The corresponding reversible specific capacity was 425.2 mA h g<sup>-1</sup> and 218.8 mA h g<sup>-1</sup> at 1.0 A g<sup>-1</sup> and 2.0 A g<sup>-1</sup>. It showed a fast capacity fading in the first dozens of cycles according with the cycling performance in Fig. 5c. When turned the current density back to 0.1 A g<sup>-1</sup> after 32 cycles, the specific capacity recovered to 910.4 mA h g<sup>-1</sup>. After 30 cycles at 0.1 A g<sup>-1</sup>, a reversible specific capacity of 841.6 mA h g<sup>-1</sup> was obtained. When the current density was turned to 0.2 A g<sup>-1</sup> for 30 cycles, the reversible capacity raised from 745.7 to 833.2 mA h g<sup>-1</sup>. After the 92 cycles, the current density was turned to 0.5 A g<sup>-1</sup> and then kept running till 500 cycles, during which the MnO/carbon composite anode materials exhibited an excellent rate performance with a maximum reversible specific capacity value of 842.5 mA h g<sup>-1</sup>, which showed a good cycling performance after cycles under high current densities.



**Fig. S1** Cycling performance and coulombic efficiency of the porous MnO/C composite anode materials at 0.1 A/g (a) and capacity of the porous MnO/C composite anode materials at different current densities (b).

The electrochemical impedance spectra of the porous MnO/carbon composite electrode before and after 500 discharge/charge cycles at different current densities were also measured as showed in Fig. S2. The Nyquist plots of the samples before and after 500 cycles are generally similar. But the charge-transfer resistance after 500 cycles was obviously smaller than that before cycling, which indicated the improved kinetics of conversion reaction upon cycling<sup>[36]</sup> and thus allowed better contact between the active material and electrolyte.<sup>[19]</sup> The improvement of the conversion reaction kinetics can lead to the oxidation of  $Mn^{2+}$  to a higher oxidation state and the phenomenon that the capacity curve firstly dropped and then increased gradually.<sup>[26]</sup>

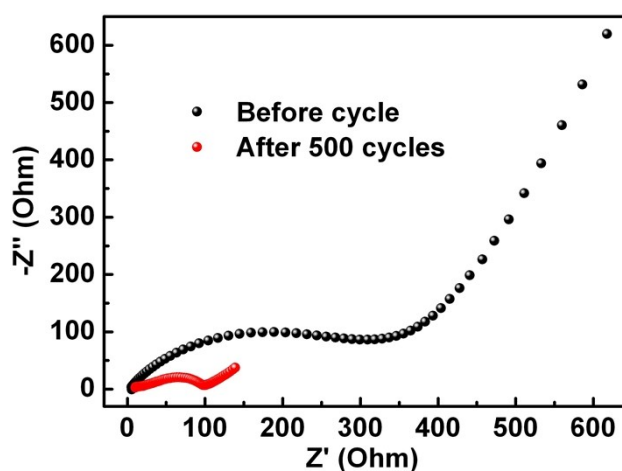


Fig. S2 Electrochemical impedance spectra of the MnO/carbon composite electrode before and after 500 discharge/charge cycles.

As discussed in the research, the carbon content of the MnO/carbon composite materials with excellent electrochemical performance was about 8 wt%. The influence of carbon content of the anode materials to the electrochemical performance was also studied in the paper. A higher content of carbon of about 13 wt% in the MnO/carbon composites was obtained by changing the material input ratio in the preparation process, as shown in Fig. S3a. Fig. S3b shows the charge capacity of the porous MnO/C composite anode materials with different carbon content at  $0.1A\ g^{-1}$ . Compared to the MnO/carbon samples involving 8% carbon content, the MnO/carbon composite anode materials with carbon content of 13% exhibited relatively low reversible capacity: firstly degraded to  $623.2\ mA\ h\ g^{-1}$ , and then increased to  $870.8\ mA\ h\ g^{-1}$  after 100 cycles. This is because the proportion of MnO crystal grains declined with the increase of carbon content, which would lead to the reduced specific capacity and more irreversible capacity loss.

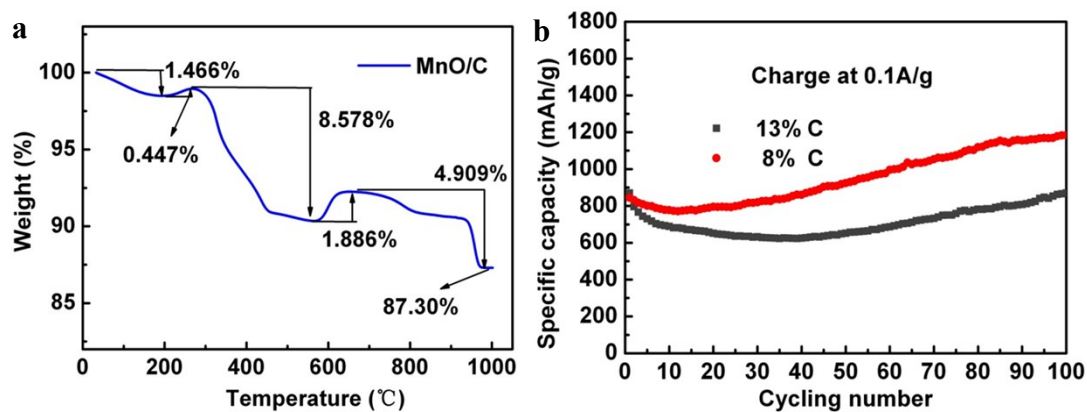


Fig. S3 (a) TGA curves for the MnO/carbon composite particles with higher carbon content; (b) Charge capacity of the porous MnO/C composite anode materials with different carbon content at  $0.1\text{ A g}^{-1}$ .

In addition, the introduction of carbon materials in the composite anode material can enhance conductivity and separate the MnO nanoparticles, as well as relieve the volume expansion/contraction during the lithiation/delithiation process, consequently improving the cycling stability. If the content of carbon was lower than the critical value, the special multi-modal pore structure and structure integrity of MnO/carbon composites would not be maintained. Therefore, the 8 wt% content of carbon was appropriate for the porous MnO/carbon composite anode materials.

## References

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