Supporting Information

Si/MnOOH composite with superior lithium storage property

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1. γ -MnOOH synthesis

 γ -MnOOH was synthesized by the hydrothermal method, Potassium permanganate (1.5 g) and manganese sulfate monohydrate (0.66 g) was dissolved in distill water (20 mL). After stirring for an hour, the solution was transferred into a 100 mL Teflon-line stainless steel autoclave and iso-propanol (20 mL) was added in it. Then the autoclave was sealed and heated at 150 °C for 10 h. After cooling down to the room temperature, the brown precipitate was collected and washed with distilled water and iso-propanol for several times. The final product was dried in vacuum at 80 °C overnight.

2. Si/MnOOH composite preparation

The as-synthesized γ -MnOOH was thoroughly mixed with silicon powder (Alfa Aesar, 50 nm) by high-energy ball-milling (Fritsch pulverisette 7) for 2 hours. The product was used without further treatment.

3. Electrochemical measurements

The Si/MnOOH electrodes consisted of the active material (60 wt.%), acetylene black (30 wt.%) and lithium poly-acrylic acid binder (10 wt.%). The mixture slurry was well-stirred and then coated onto a copper foil. Typical mass loading of the electrodes was about 1.0 mg cm⁻².

The 2016 coin cell was fabricated by separating Li anode and Si/MnOOH cathode with a Celgard 2300 separator. The electrolyte was 1 M LiPF₆ dissolving in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) with 10% fluoro-ethylene carbonate (FEC) addition. The cell was assembled in Ar-filled M. Braun glove box.

The charging/discharging tests were conducted on Land battery cycler (Land Co. Ltd., China). For Si/MnOOH and bare silicon electrode, a low current of 0.1 A g⁻¹ was applied in the first two cycles, and then increased to higher current in the subsequent cycles, and the voltage range was kept between 1.5-0.01 V. γ -MnOOH electrode was tested at 50 mA g⁻¹ between 0.01-2.0 V. AC impedance measurements were performed on an Autolab electrochemical analyzer (Autolab PGSTAT30, Eco Chemie) in the frequency range of 10 kHz–10 mHz at an amplitude of 5 mV. The spectra were all collected at the OCV.

4. Characterization

X-ray diffraction (XRD) analysis was conducted with a XRD-6000 diffractometer (Shimadzu, Japan), using Cu K α 1 radiation and a scan rate of 3° min⁻¹. The

morphology was observed on a Quanta 200 scanning electron microscope (SEM, FEI company, Holland).

Fig. S1 a) Cycling stability of γ -MnOOH electrode at a current density of 50 mA g⁻¹; b) Voltage *vs.* capacity plot of γ -MnOOH electrode; c) dQ/dV curve of γ -MnOOH electrode at the 3rd cycle.





Fig. S1a shows the capacity/coulombic efficiency vs. cycles plot of MnOOH electrode. In the 1st cycle, the discharge and charge capacity was 1508 mAh g⁻¹ and 587 mAh g⁻¹ respectively, corresponding to a very low coulombic efficiency of 38.9%. After the 1st cycle, the coulombic efficiency increased gradually until finally stabilized at around 98%. The voltage-capacity profile of the initial three cycles is compared in Fig. S2b. A long plateau around 0.2-0.3 V could be observed in the 1st discharging, but disappeared in the subsequent cycles, and it well explains the big irreversible capacity in the 1st cycle. Further comparison revealed that the 2nd and 3rd voltage profiles almost overlapped to each other and were very similar to that of MnO anode^[15,16]. In addition, a much higher discharging voltage could be noticed in the 2nd and 3rd cycle than the 1st cycle. Differential dQ/dV plot of the 3th charge/discharge curve is displayed in Figure S2c. Interestingly, the redox pair around 1.2/0.7 V is similar to that of MnO anode, except the higher reducing potential than MnO (usually blow 0.5 V). Similar observation has also been obtained on Ni(OH)₂ anode which showed a higher reducing voltage than NiO^[18,19]. The results in Fig S1 suggest that γ -MnOOH

first decomposes into MnO in the 1st discharge with the LiOH formation and generates the irreversible capacity (equation 1), and then the reaction will follow the route in Equation 2. The higher reducing potential of MnOOH than MnO should be ascribed to LiOH, which may promote the conversion reaction of MnO.

$$\gamma-MnOOH+Li^++e\leftrightarrow MnO+LiOH$$
Equation 1
MnO+2Li^++2e\leftrightarrow Mn+Li_2O
Equation 2

Fig. S2 The cycling performance of the Si/MnOOH composite electrode with different γ -MnOOH content in 1 M LiPF₆ EC: DMC (1:1, v/v) with 5% FEC addition.



Fig. S3 SEM images of a) the Si/MnOOH composite electrode with 5% γ-MnOOH;Corresponding EDX mapping of b) Si, c) Mn and d) O in the composite electrode.



Fig. S4 a) Long-term cycling of Si/MnOOH electrode (0.1 A g⁻¹ in the first two cycles, 2 A g⁻¹ in the rest of cycles).



Fig. S5 Discharging curves for Si electrode and Si/MnOOH electrode at the current density of 0.5, 1, 4, 8 A g⁻¹. (Mass loading is 3 mg cm⁻²)



The rate capability of the "thick electrode" is shown in Fig S5. We tried to increase the loading by 3 times, namely 3 mg cm⁻². We can see, though the improvement after MnOOH addition is not as striking as in Figure 3, Si/MnOOH still definitely has much better rate performance than Si. For example, 2490 mAh g⁻¹ for Si/MnOOH and 1770 mAh g⁻¹ for Si at 1 A g⁻¹, 1580 mAh g⁻¹ for Si/MnOOH and 900 mAh g⁻¹ for Si at 4 A g⁻¹, 790 mAh g⁻¹ for Si/MnOOH and 350 mAh g⁻¹ for Si at 8 A g⁻¹. However, it should be noted that when the mass loading increased to 3 mg cm⁻², the specific area capacity of 4.5 mAh cm⁻² was achieved at 1 A g⁻¹, this high capacity has seldom been reported. In the other hand, one fact has to be pointed out is that it was very difficult to coat such loading on Cu foil with the same binder and the same ratio of Si: acetylene black: PAA binder, and cracks was found in the electrode and even powder came off during the electrode drying. In addition, the electrode started to peel off from Cu foil even after dozens of cycles. Consequently, the capacity of this "super thick" Si/MnOOH anode dropped more rapidly than in Figure 2. This fact indicates that when a high loading is required, binder optimization and electrode fabrication optimization may be as same important as the material itself. A recent paper proposed some work on the binder for Si anode, and the importance of binder in "thick electrode" has been illustrated and investigated^[1].

[R(RQ)(RQ)W]	R _{SEI}	R _{ct}	σ(Warburg factor)
Si	91.67	52.49	8.92
Si-MnOOH	22.54	3.216	8.94

Table S1 Fitting result of the impedance spectrum collected after 100 cycles.