

Supporting Information

Anomalous lithium storage in a novel nanonet composed by SnO₂ nanoparticles and poly(ethylene glycol) chains

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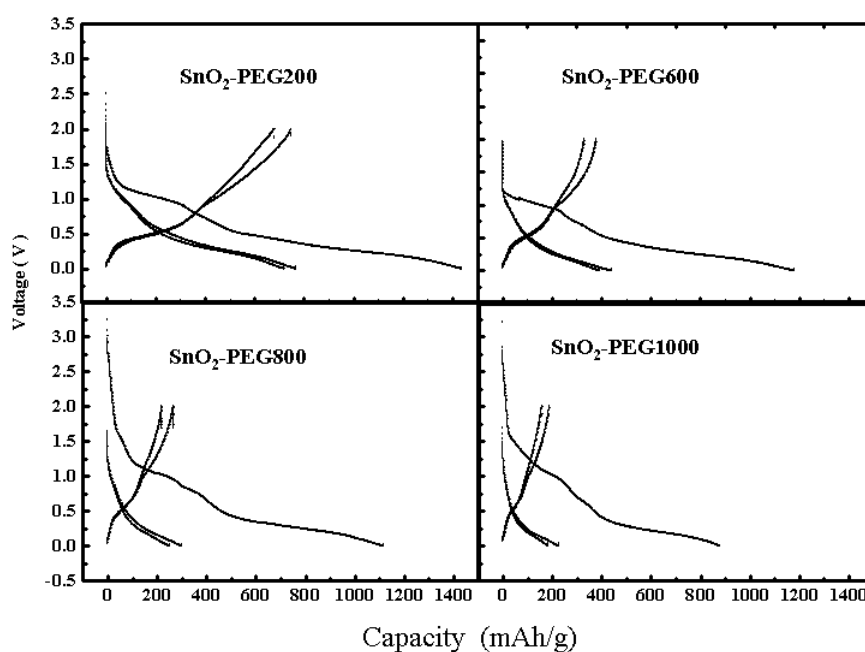


Figure S1 Typical charge/discharge curves of PEG/SnO₂ nanocomposites with different molecular weight of PEGs: a) PEG200, b) PEG600, c) PEG800, and d) PEG1000.

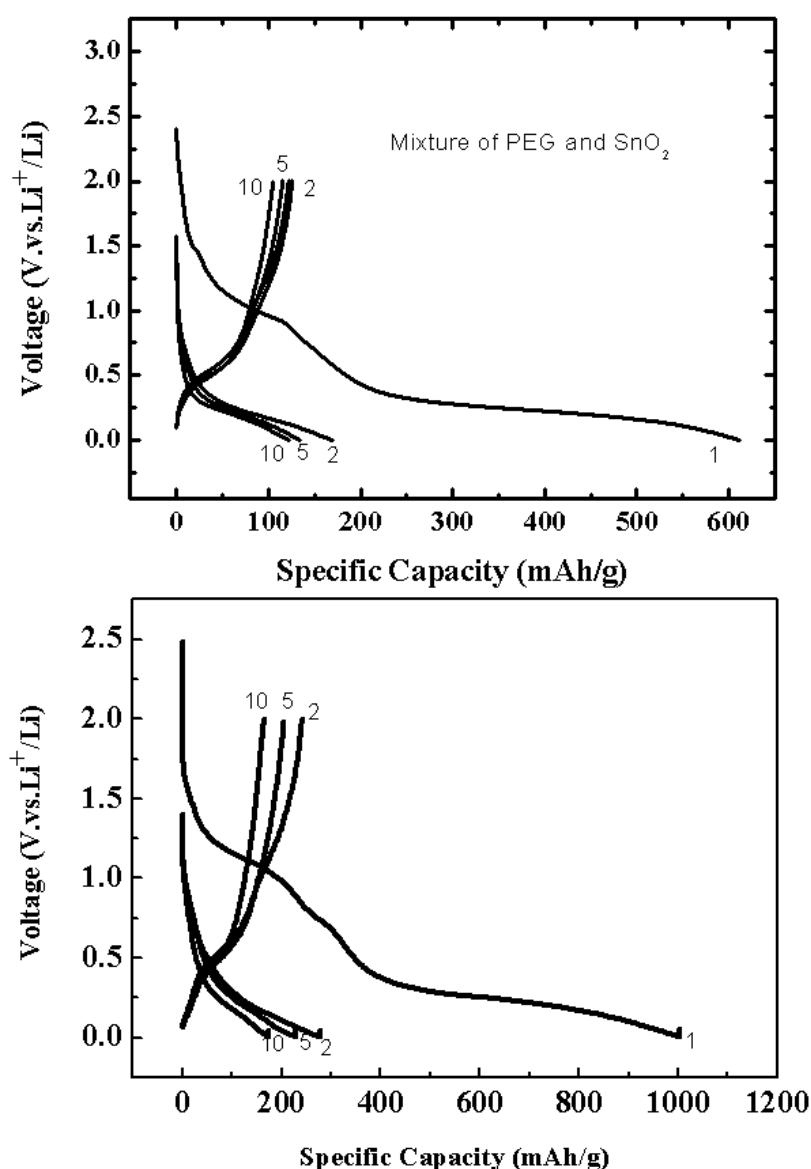


Figure S2 Typical charge/discharge curves of a) a simple mixture of PEG400 and SnO_2 (71%: 29% in weight ratio); b) PEGME- SnO_2 (PEGME Mw = 350 g/mol, in PEGME- SnO_2 the SnO_2 content is 30 wt %).

The simple mixture of PEG400 and SnO_2 delivers a first discharge capacity of 600 mAh/g, and a reversible capacity of 175 mAh/g which is smaller than the estimated reversible $\text{Li}_{4.4}\text{Sn}$ capacity of 234 mAh/g. For PEGME- SnO_2 nanocomposite shows a first discharge capacity of 1100 mAh/g, and a reversible capacity of 270 mAh/g, which is a little larger than that estimated reversible capacity of 234 mAh/g. Both samples do not show the extra capacities.

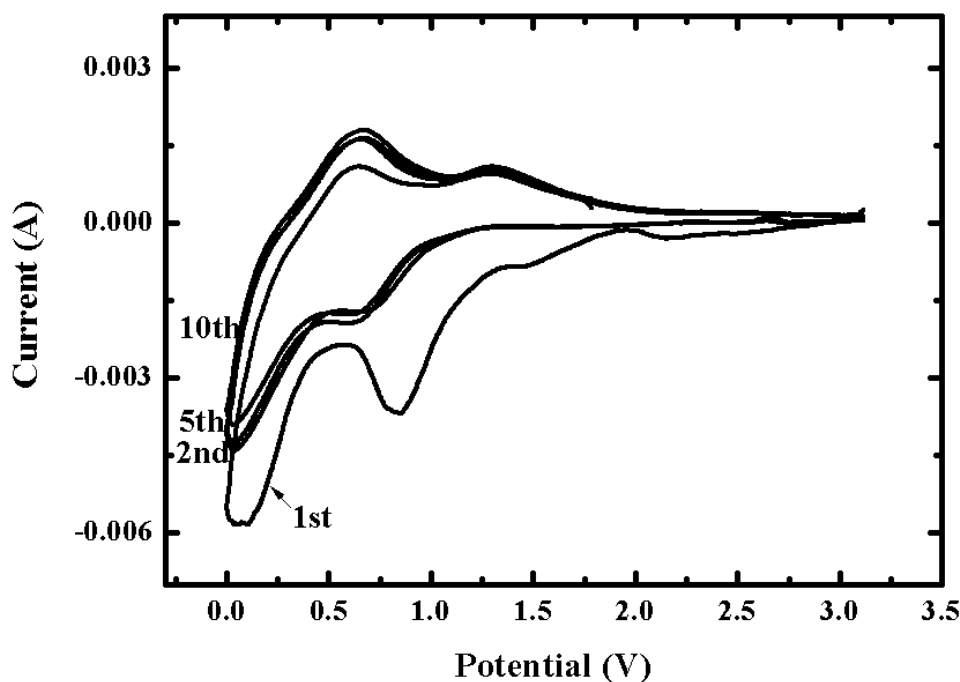


Figure S3 Cyclic voltammograms of the PEG400-SnO₂ composites at a rate of 0.5 mV/s in a voltage window of 3.2–0.0 V.

An irreversible reduction peak with a maximum at 0.8 V during the first cycle is observed, corresponding to the formation of SEI film on the surface of the composite. It is known that the reaction of SnO₂ involves a two step process: (1) reduction of SnO₂ to Sn; (2) alloying of Sn with Li to form a series of alloys. These reactions should contribute to the reduction peaks appearing below 0.6 V and oxidation peaks appearing at 0.6 V and 1.2V. According to the reference, (Angew. Chem. Int. Ed. 2007, 46, 750), the redox reaction of SnO₂ to Sn is partly reversible which indicates the peak at 1.2V should disappear after the first cycle. However, in Figure S3, this peak still exists in all cycles. Herein, we suggest that this peak is an overlap peak consisting of reaction (1) and the reaction that Li⁺ ions coordinate with EO segments which occurs also at *ca.* 1.2V according to the reference, (Nat. Mater. 2009, 8, 120).

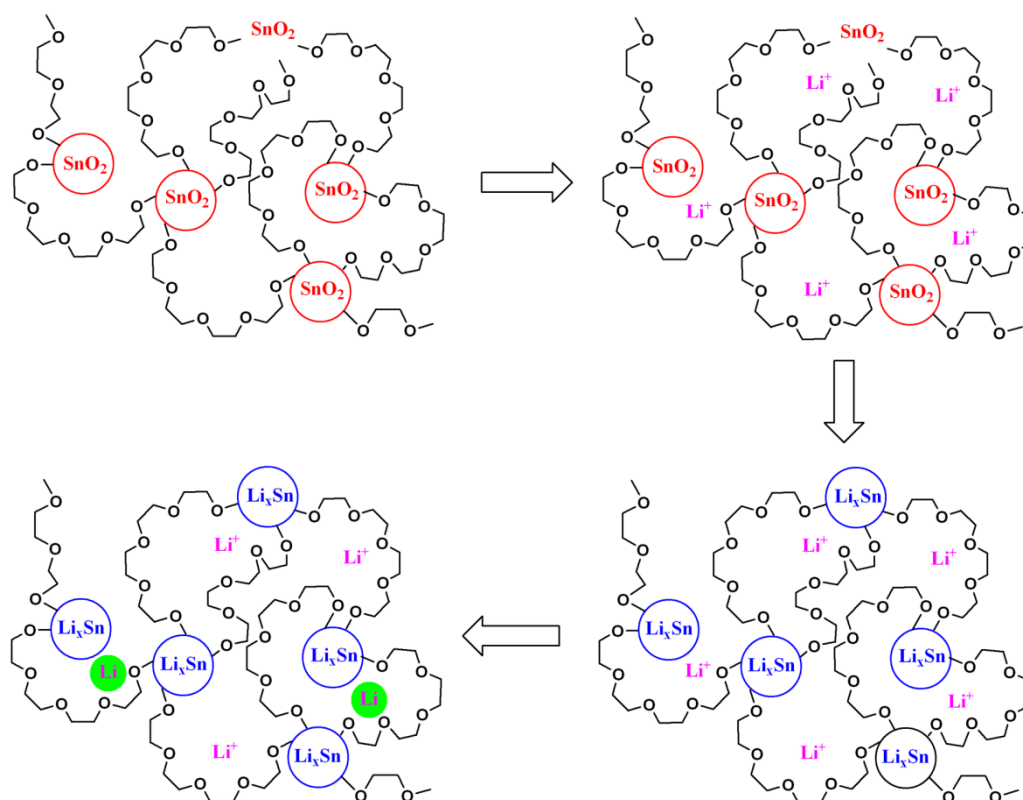


Figure S4 A possible mechanism for lithium storage in the PEG-SnO₂ nanonets.

On one hand, Table 1 confirms that the unexpected capacity is strongly influenced by the PEG molecular weight and the PEG/SnO₂ weight ratio. On the other, the control experiments prove that both the PEGME-SnO₂ nanocomposite and the simple physical mixture of PEG400 and SnO₂ do not show any unexpected capacity. Therefore, we suggest that the ethylene oxide units on the PEG could form coordination centers for lithium storage through reversibly forming/breaking Li-O bonds, just like those small lithium organic compounds which can store a large amount of lithium atoms. In general, electrochemical lithium storage needs effective transport of both electrons and ions. PEG is known as a lithium ion conductor when it is mixed with lithium salt, while the crosslinked SnO₂ particles may act as the electron path. When the PEG chains contact with SnO₂ particles, electron may tunnel or hop from SnO₂ or lithiated SnO₂ phase to the coordination centers revolved by ethylene oxide units. And thus, lithium ions are turned into lithium atom clusters and stored in the electrolyte phase. Due to poor electronic conductivity of PEG molecules, the PEG-SnO₂ samples containing more SnO₂ are favorable for achieving higher lithium storage activity, as shown in Table 1. In the meantime, more ethylene oxide units are favorable for forming coordination centers. As a result, PEG400-SnO₂ composite exhibit the highest extra capacity.