Supplementary Information

Reduced Expansion and Improved Full-Cell Cycling of SnO$_x$#C Embedded Structure for Lithium Ion Battery

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**Note S1. Calculation method for SEI area of SnO$_x$/C composite**

In our work, SnO$_x$ nanoparticles are randomly embedded in carbon matrix. Moreover, the morphology of the SnO$_x$#C is irregular. To simplify the calculation model, we set up a model assuming that the SnO$_x$ particles arrange periodically in cubic clusters, as shown in Fig. 1a. For dispersed SnO$_x$@C, SEI is formed on the outer surface of every individual SnO$_x$@C particles, meaning that the SEI area nearly equals the total outer surface area of all the SnO$_x$@C particles. Since the outer surface area keeps the same whether the SnO$_x$@C particles arrange randomly or periodically, the periodically arranged cubic cluster model in Fig. 1a is applicable for dispersed SnO$_x$@C to calculate the SEI area. In this model, $r$ is the average radius of SnO$_x$ nanoparticles; $t$ is the thickness of the carbon layer; $n$ is the number of SnO$_x$ nanoparticles in each dimension of the cubic clusters. The SEI area (SA) of SnO$_x$@C is

$$SA_d = n^3 \cdot 4\pi (r+t)^2$$

where $n^3$ represents the total number of SnO$_x$@C particles; $4\pi (r+t)^2$ is the SEI area of single SnO$_x$@C particle.

For embedded SnO$_x$#C, the SEI formation is limited on the outer surface of the carbon matrix, because electrolyte molecules, except lithium ions, can’t seep into the carbon matrix. Herein, the SEI area of SnO$_x$#C equals the outer surface area of the carbon matrix. During carbon-coating process, the arrangement and size of SnO$_x$ particles in SnO$_x$#C nearly keep unchanged compared with that of dispersed SnO$_x$@C, so a periodically arranged cubic SnO$_x$ cluster embedded in carbon matrix model is established for SnO$_x$#C as shown in Fig. 1a. In this model, $r$ is the average radius of SnO$_x$ nanoparticles; $t$ is half of the average distance between adjacent particles, which amounts to the carbon layer thickness in SnO$_x$@C; $n$ is the number of SnO$_x$ nanoparticles in each dimension of the cubic clusters. The SEI area of SnO$_x$#C is

$$SA_e = 6(2n(r+t))^2$$

where $2n(r+t)$ equals the length of the cubic clusters.

In our experiment, $r$=35 nm; we got the curves in Fig. 1b by plotting $n^3$ (number of nanoparticles) and the calculated $SA_d$, $SA_e$ at $t$=10 nm, 40 nm and 80 nm, respectively. It can be seen that the SEI area of embedded SnO$_x$#C is much smaller (~ one third) than that of dispersed SnO$_x$@C even when the average distance between adjacent particles reaches $80 \times 2 = 160$ nm. This tendency gets much more obvious with increased number of SnO$_x$ nanoparticles.

**Fig. S1.** Structural and elemental analysis of SnO$_2$, SnO$_x$ and SnO$_x$#C. (a) SEM image of chestnut-like SnO$_2$ and reduction product-- dispersed SnO$_x$ particles; (b) TEM image of dispersed SnO$_x$ particles, scale bar: 200 nm; (c) Sn, O, and C elements mapping in SnO$_x$ particles, scale bar: 100 nm; (d) Sn, O and C elements mapping in the SnO$_x$#C composite, scale bar: 100 nm.
Fig. S2. (a) Average diameter of partially reduced SnO$_x$; (b) size distribution of SnO$_x$ particles embedded in SnO$_x$#C composite; (c) size evolution along the synthesis process. It can be seen that the size of SnO$_x$ is much smaller compared to Sn and SnO$_2$ particles.

Fig. S3. Thermally induced chemical reduction process of chestnut-like SnO$_2$. (a) TEM images of SnO$_x$. (from left to right) original state, partially reduced state, and completely reduced state of SnO$_x$, respectively; scale bar: 100 nm. (b) magnified TEM images of SnO$_x$ under different reduction states; scale bar: 50 nm. For unreduced SnO$_2$ (left), the particles contain randomly arranged SnO$_2$ nanosheets. After partially reduction (middle), a portion of the SnO$_2$ sheets turns to a spherical shape, which is triggered by surface tension of molten Sn. On complete reduction (right), all the SnO$_2$ sheets are reduced into Sn nanoparticles. (c) schematic illustration of the reduction process. During the reduction process, one single SnO$_2$ sheet is reduced to one SnO$_x$ particle. The carbon matrix isolates individual SnO$_x$ particles and prevents their agglomeration even at 450 °C which is much higher than the melting temperature of Sn (232 °C). (d) Line analysis of the elemental distribution within SnO$_x$ particles. It can be seen that the faceted particles (A) and the spherical particles (B) are all partially reduced, except that the faceted particles (A) contain more oxygen than the spherical particles (B).
Fig. S4. TG-DTG curve of pure PVDF powder (heated in Ar from room temperature to 900°C at a heating rate of 10°C/min). The carbon-coating process via CVD is conducted at 700 °C, during which, the PVDF powder decomposes completely into other carbon composites.

Fig. S5. (a) TEM image (left) of SnO$_x$#C composite and high resolution TEM image (right) of the dispersed ~8 nm particles. The d-spacing of 0.292 nm illustrates that the smaller particles are Sn nanoparticles; (b) high resolution TEM image of SnO$_x$ particles (~74 nm), the characteristic d-spacing of both Sn and SnO$_2$ suggests that the larger SnO$_x$ particles are composed of nanocrystalline Sn and SnO$_2$.

Note: Interdiffusion of Sn and O at the interface between Sn particles and Li$_2$O is considered to be the mechanism to form reversible SnO$_x$, which contribute to the extra specific capacity that exceeds the theoretical value of SnO$_2$. When the size get smaller than 10 nm, the volume ratio of the interdiffusion-induced SnO$_x$ layer in Sn particle can exceed 50%. For SnO$_x$#C, over 30% SnO$_x$ particles is smaller than 10 nm. For the other particles with larger diameters (~74 nm), they are composed of nanocrystalline Sn and SnO$_2$ (~10 nm, dashed white circle in Fig. S5b). Attributed to the characteristic of small size and embedded structure (preventing the particles from agglomeration) of SnO$_x$#C, the conversion reaction that Li$_2$O reacts with Sn to form SnO$_x$ exhibits excellent reversibility.
Fig. S6. Half-cell electrochemical performance of SnO$_2$#C. (a) Representative cyclic voltammograms (CV) of SnO$_2$#C composite at a scanning rate of 0.5 mV s$^{-1}$; (b) charge/discharge voltage profiles of SnO$_2$#C composite at various current densities (half cell); (c) cycling performance of SnO$_2$#C embedded structure at different voltage ranges (half cell); (d) rate capabilities of SnO$_2$#C composites (half cell); (e) cycling performance of SnO$_2$#C embedded structure at different current densities (half cell).
Fig. S7. (a) Weight ratio of carbon and initial coulombic efficiency (ICE) at various dwelling time; (b) ICE of partially reduced SnO$_x$, obtained at different H$_2$ concentrations with and without the carbon-coating treatment. It can be seen that the ICE values of all the materials with embedded structure (dwelling time: 20 minutes) are largely improved from ~40% (without carbon coating) to more than 80%.

Note: ICE increases with the dwelling time during carbon-coating process. However, the weight ratio of carbon in the electrode film increases with dwelling time as well, which means larger ratio of low specific capacity materials and naturally lower gravimetric and volumetric capacity. Herein, to get an enhanced comprehensive performance, the ICE and capacity should be balanced.

Fig. S8. Comparison of the lithium ion storage properties of different SnO$_x$/C anode materials.
Fig. S9. (a) Electrochemical impedance spectra (EIS) of SnO$_x$ and SnO$_x$#C anodes obtained between 0.1~100000 Hz; (b) resistance of $Z'$ versus minus square root of the scanning frequency, $\omega$, in the low frequency range of the EIS spectra.

Table S1 Comparison of resistance and ion diffusion coefficient between SnO$_x$ and SnO$_x$#C

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<tr>
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<th>SnO$_x$</th>
<th>SnO$_x$#C</th>
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<tbody>
<tr>
<td>Solution resistance $R_s$ ($\Omega$)</td>
<td>6.773</td>
<td>4.56</td>
</tr>
<tr>
<td>Charge transfer resistance $R_{ct}$ ($\Omega$)</td>
<td>61</td>
<td>5.32</td>
</tr>
<tr>
<td>Li ion diffusion coefficient $D_{Li}$ (cm$^2$ s$^{-1}$)</td>
<td>$3.43\times10^{-17}$</td>
<td>$2.00\times10^{-16}$</td>
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Note: The above $R_s$ and $R_{ct}$ are obtained by simulating EIS data using Zview software based on the equivalent circuit as shown in the inset in Fig. S9a. $D_{Li}$ is obtained according to the following equation:

$$D_{Li} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$

where $R$ is the gas constant, $T$ is the temperature, $A$ is the surface area of the electrode, $n$ is the number of electrons transferred in the reaction, $F$ is the Faraday constant, $C$ is the concentration of Li ions in the electrode material, and $\sigma$ is the Warburg factor which can be taken directly from the slope of the linear plot of the real impedance ($Z'$) against the minus square root of the frequency (Fig. S9b).
Fig. S10. Charge/discharge voltage profiles of SnO$_x$#C anode and LiCoO$_2$ cathode in half-cell test.

Fig. S11. SEM images showing the cross section of the electrode film after 100 cycles. (a) SnO$_x$ electrode without coating carbon; (b) SnO$_x$#C electrode. The layer with brighter contrast on the electrode film surface is the SEI layer. Note that SnO$_x$ has a thicker SEI coating than SnO$_x$#C. Scale bar : 2.5 μm.

Fig. S12. Schematic illustration of the proposed redox shuttle inside the electrolyte that leads to effect resembling self-discharge.$^{10}$

Note: During the shuttle process, soluble redox mediators ‘S’ get oxidized to its cation form ‘S$^+$’, which, via diffusion across the cell electrolyte, would be reduced back to its original or reduced state on the surface of the anode. The reduced form would then diffuse back to the cathode and oxidize again. The ‘oxidation-diffusion-reduction-diffusion’ cycle can be repeated continuously due to the reversible nature of the redox shuttle, which would cause self-discharge behavior and then leads to capacity loss and low CE in each cycle.
**Fig. S13.** Calculated hypothetical self-discharge current of full cell shown in Fig. 3d in the main text. Note: Based on the assumption that the coulombic inefficiency (CI=1-CE) is completely caused by self-discharge effect, then the hypothetical self-discharge current of each cycle is calculated by dividing the capacity loss with duration of charge/discharge process.

**Fig. S14.** Self-discharge test of SnO$_2$#C full cell. (a) self-discharge current of SnO$_2$#C full cell measured by detecting the stable current when the cell is charged at various constant voltages; (b) voltage profile of SnO$_2$#C full cell during and after 12 hours’ static duration. The calculated self-discharge current is 5.7 uA based on the loss of discharge capacity.
References