Synthesis and performance of Ti₂O₃/LiTiO₂ decorated micro-scale Si-based composite anode materials for Li-ion batteries

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The process involved in synthesizing Ti₂O₃/LiTiO₂ is described below. Firstly, TBOT is hydrolyzed in ethanol solvent to obtain Ti(OH)₄ (S1), which generates TiO₂ under high temperature treatment (S2). Secondly, TiO₂ interacts with carbon source to generate Ti₂O₃ (S3). And finally, Ti₂O₃ interacts with LiOH to generate LiTiO₂ (S4).The specific reaction equations is as follows[1,2]:
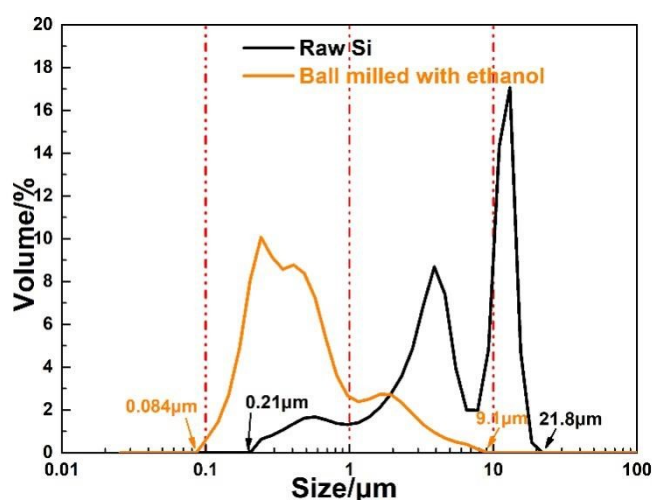
$$Ti(OC_4H_9)_4 + 4C_2H_5OH \rightarrow Ti(OH)_4 + 4C_4H_9OH \qquad \text{(S1)}$$

$$Ti(OH)_4 \underset{900°C}{\rightarrow} TiO_2 + 2H_2O\uparrow \qquad \text{(S2)}$$

$$TiO_2 + C \rightarrow Ti_2O_3 + CO\uparrow \qquad \text{(S3)}$$

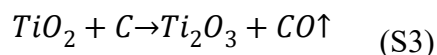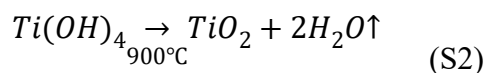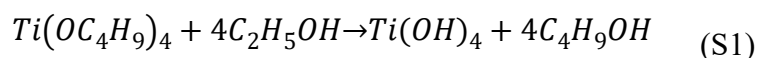$$Ti_2O_3 + 2LiOH \rightarrow 2LiTiO_2 + H_2O\uparrow \qquad \text{(S4)}$$
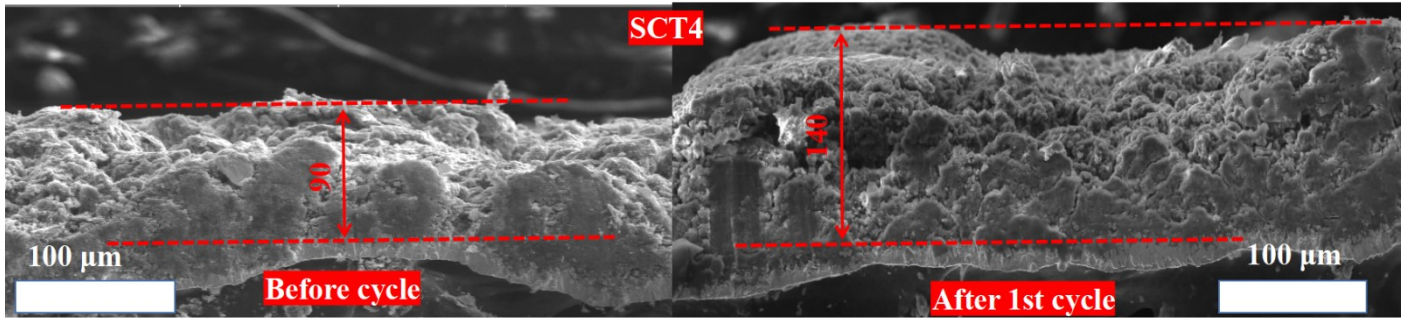

Fig.S1 Particle size distribution curve.

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Fig.S2 SEM images of the thickness of the electrodes before and after cycling

According to Fick's second law of lithium ion diffusion[3,4]:

$$D_{Li+} = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma_\omega^2) \quad (S5)$$

$$Z' = R_e + R_{ct} + \sigma_\omega * \omega^{-0.5} \quad (S6)$$

Where T is the absolute temperature, R is the gas constant 8.314J (mol/K), A is the surface area of the electrode, n is the number of electrons transferred during the reaction, F is the Faraday constant (96500 C/mol), C is the concentration of Li+ in the electrode (C = n/Vm, Vm is the molar volume of the substance), D_{Li+} is the diffusion coefficient of the lithium ions, and σ is the Warburg coefficient, with slopes in the graphs of the linear relationships between Z′ and $\omega^{-1/2}$ corresponding to σ. From Eq. S6, D_{Li+} is inversely proportional to the square of σ. It is apparent that the D_{Li+} is only related to the Warburg coefficients (ω), which were determined from a linear fit to the low-frequency region:

The calculation of Li+ diffusion coefficient (D_{Li+}) using the galvanostatic intermittent titration technique (GITT)is based on the following equation S7[5]:

$$D_{Li+} = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \quad (S7)$$

Where D represents the D_{Li+} (cm²/s), τ represents the duration of the current pulse (s), n_m represents the number of moles of the active material (mol), Vm represents the molar volume of the electrode (cm³/mol), A is the contact area between the electrode and electrolyte (cm²), in this case, the surface area is the actual area of the collector, ΔEs is the steady-state voltage change caused by the current pulse (V), ΔEτ corresponds to the voltage change during a constant current pulse that ignores the IR decrease（V）.

To obtain a better understanding of the Li-storage mechanism in the material, cyclic voltammetry (CV) curves were further analyzed for the initial three cycles of SC-T6 at a scan rate of 0.1 mV/s over the potential

range of 0.01 to 3 V. As depicted in Figure S3 (a), during the first cathodic scan, a prominent reduction peak emerges around 1.0 V, attributed to irreversible reactions occurring during the electrolyte-electrode surface interaction and SEI film formation. Interestingly, this peak was not observed after the second cycle, thus illustrating this point more fully. An additional reduction peak near 0 V is typically associated with an internal alloying reaction between Si and Li-ions. In contrast, two anodic peaks at 0.34 and 0.51 V are observed, primarily due to the de-lithiation process of the Li-Si alloy, resulting in the conversion of crystalline-Si to amorphous-Si. The intensity of both oxidation and reduction peaks progressively increased with scanning time, indicating the gradual activation of the composite material and enhancement of electrode reaction kinetics. Furthermore, a subtle broadening peak appears around 1.2 V in the second scan, mainly corresponding to the embedded lithium potentials of $Ti_2O_3/LiTiO_2$ within the composite. The peaks at 1.0 and 2.0 V in the reverse scan signify the removal of Li-ions from the composite. Potentially due to its low content, an SEI film initially forms on the electrode surface during the initial lithiation process, impeding peak observation in the first cycle. For further illustration, an enlarged view of the CV curves of SC-T6 is attached (Fig. S3 (b))), where the position of the delithiation corresponding to $Ti_2O_3/LiTiO_2$ is determined to be at 2.0 V.
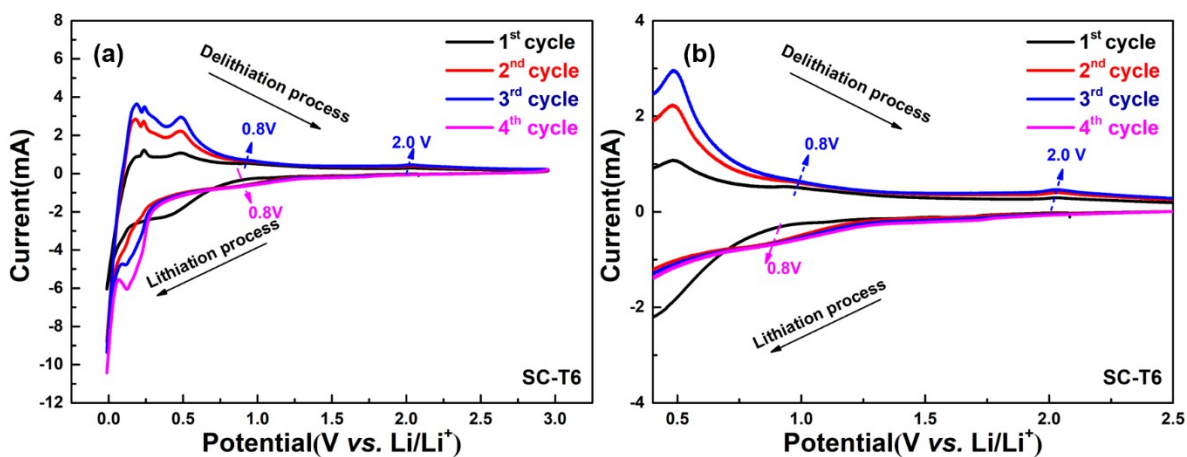
Fig.S3 CV curves of SC-T6.

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