

Supporting Information

Origin of Anomalous Large Reversible Capacity for SnO₂ conversion reaction

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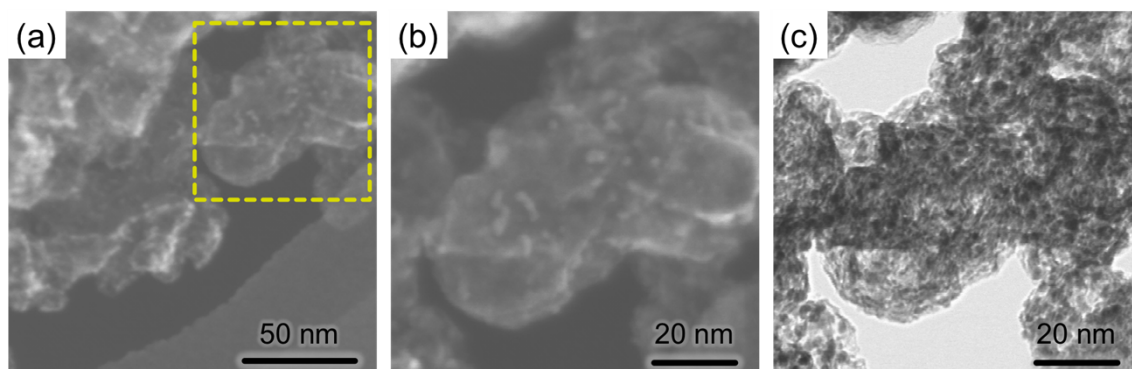


Figure S1. Bright-field ((a) and (b)) and dark-field (c) SEM images for the SnO₂/KB (45/55) composite.

In the bright-field image (a), one can see the agglomerated structure of KB spheres. A part of the agglomeration (the area surround by a yellow dotted square) was re-focused in higher resolution and shown in the image (b). With the closer view of KB structure (image (b)), only few SnO₂ particles can be seen on the outer surface of KB. (c) The dark-field SEM image of the same part of KB structure (image (b)) was pictured in order to verify the encapsulation of SnO₂ nanoparticles within the KB hollow structure. Contrary to the bright-field image (b), many small SnO₂ nanodots with a diameter of few nanometers can be seen in the image (c), which is consistent with the HRTEM image for SnO₂/KB (45/55) shown in Fig.2 (c).

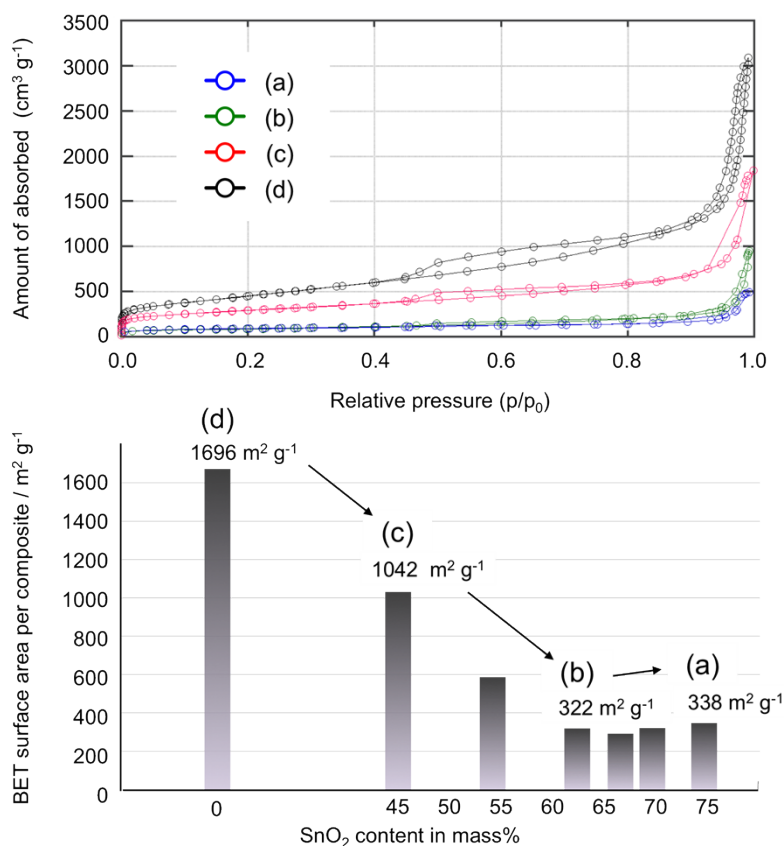


Figure S2 (TOP) Nitrogen adsorption–desorption isotherm curves for the (a) SnO₂/KB = 75/25, (b) SnO₂/KB = 63/37, (C) SnO₂/KB = 45/55, and (d) pure KB (UC-treated KB, denoted as UC-KB).

(BOTTOM) Relationship between the specific surface area (SSA) per SnO₂/KB composite mass and the SnO₂ content (0 to 75 wt%, 8 samples). In the figure, samples (a)-(c) correspond to the samples shown in Fig.2 (A)-(C), respectively. The SSA of the composites linearly decreases with a SnO₂ dosage increase from 0 wt% (UC-KB) up to 67 wt%, while the SSA slightly increases from 67 to 75 wt%. The slight increase of the SSA from 67 wt% can be due to the SnO₂ nanoparticles piled on the outer sphere of KB (see Fig. 2 (A)). Namely, the 8 samples can be divided into 2 groups; one is the high-dispersion composites with highly dispersed SnO₂ nanoparticles confined within the hollow structure of KB when the SnO₂ dosage is less than 67 wt%, and the other is the outer-deposition composites with the exposed SnO₂ nanoparticles outside of KB sphere when the SnO₂ dosage exceeds 67 wt%.

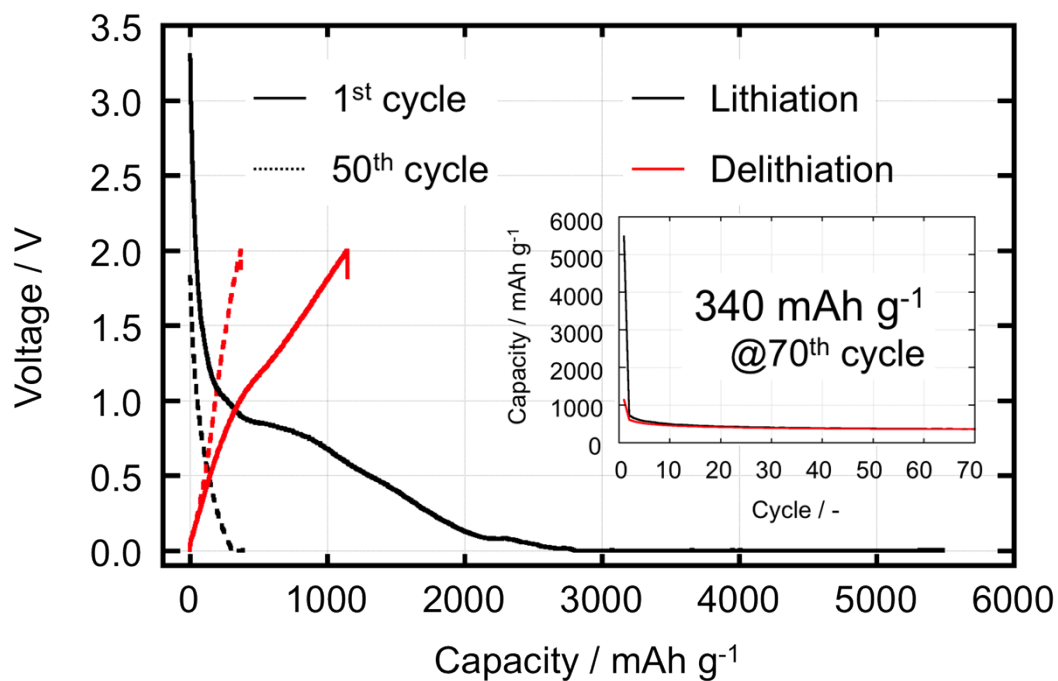


Figure S3. Charge discharge curves for the pure KB (UC-treated KB, denoted as UC-KB in the article) at 1st (heavy line) and 50th (broken line) cycle. The cycling test was performed on half cells consisting of Li/1 M LiPF₆ (EC+DEC)/UC-KB in the CC-CV (lithiation) and CC (delithiation) mode between 0.0 and 2.0 V at a current density of 300 mA g⁻¹ (the same current density as the data shown in Fig.3). Inset shows the specific capacity of the discharge (lithiation) and charge (delithiation). The stable charge-discharge capacity of UC-KB was 340 mAh g⁻¹ at 70th cycle.

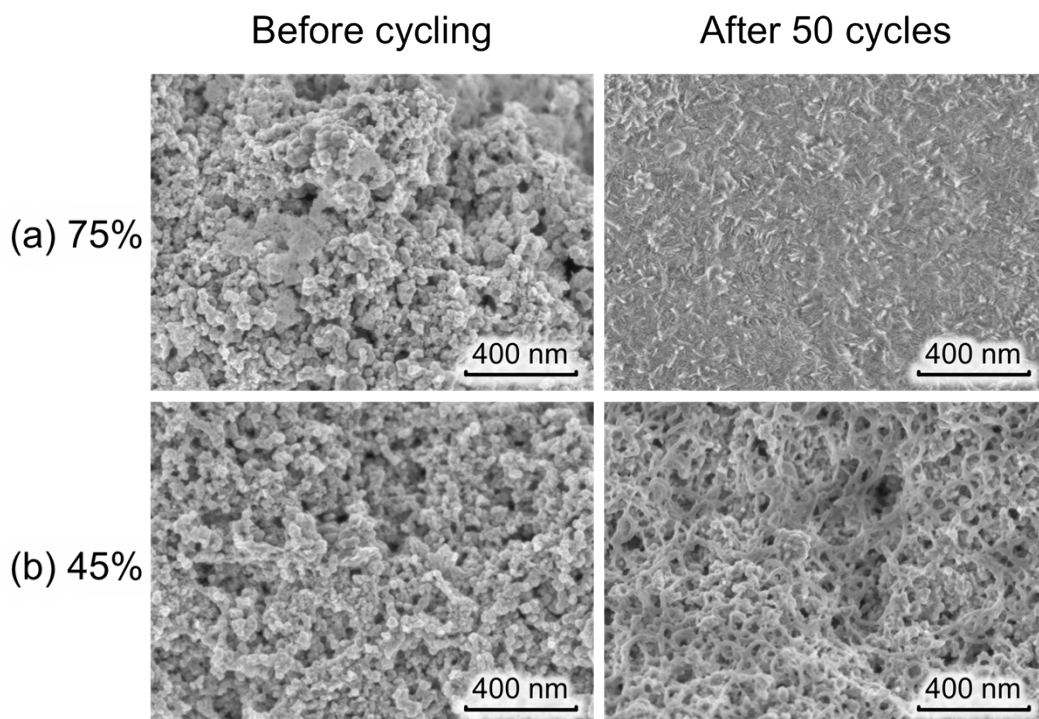


Figure S4. SEM images of the surface of SnO₂/KB composite electrodes with SnO₂ = (a) 75 and (b) 45 wt% before and after 50 cycles. These images (a) and (b) before cycling correspond to the electrode surface for Fig. 3 (A) and (C), respectively. As shown in (a) 75 wt% after 50 cycles (top right), the polymeric mixture (possibly consisting of SEI and Li₂O) uniformly covered the electrode surface and filled the pore of the composites, while the surface morphology of (b) 45wt% more or less unchanged (down right).

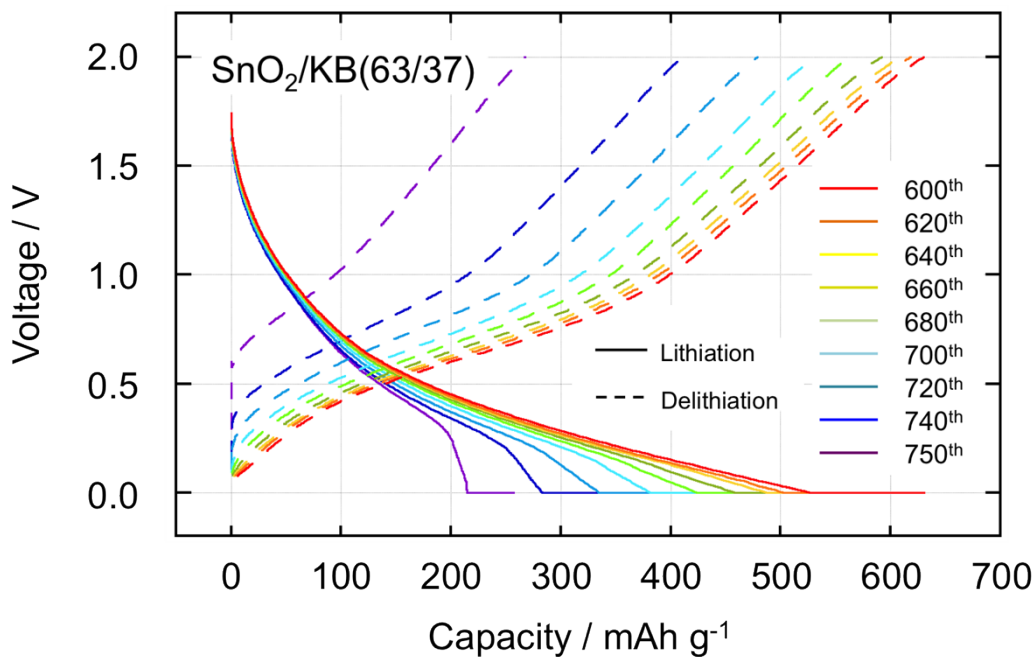


Figure S5. Charge-discharge curves for the SnO₂/KB (63/37) in the range of 600th and 750th cycle. The cycle tests of SnO₂/KB (63/37) are plotted in Fig.3 (B). The cycling test was performed on half cells consisting of Li/1 M LiPF₆ in EC+DEC/(SnO₂/KB = 63/37) in the CC-CV (lithiation) and CC (delithiation) mode between 0.0 and 2.0 V at a current density of 300 mA g⁻¹. From these curves, one can see two changes occurring within the 150 cycles; i) disappearance of the capacity at the voltage lower than 0.4 V during lithiation process, and ii) increase of internal resistance (IR) drops at the beginning of delithiation. Both phenomena suggest that the electrochemical reaction below 0.4V including Sn alloying, lithiation of KB, and SEI formation, became largely resistive after 600th cycle.

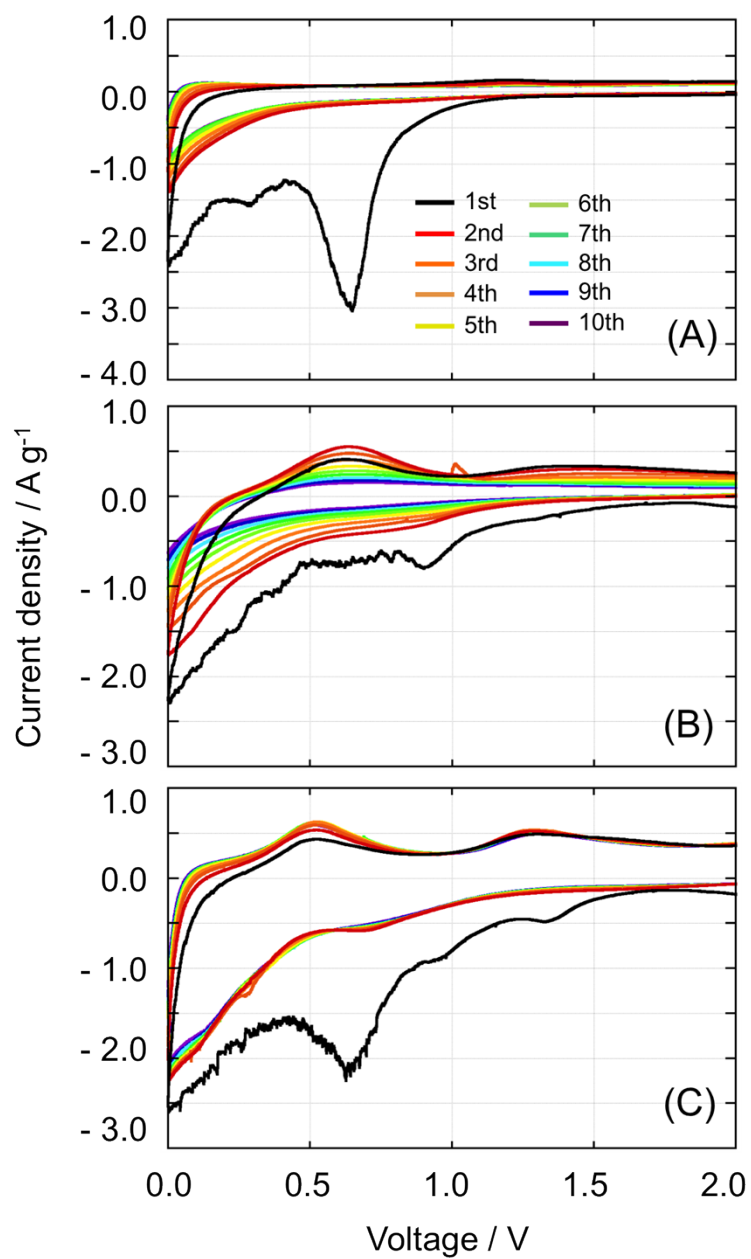


Figure S6. Cyclic voltammograms for the (A) pure KB (UC-treated KB (UC-KB)), (B) $\text{SnO}_2/\text{KB} = 75/25$, and (C) $\text{SnO}_2/\text{KB} = 45/55$. The cyclic voltammetry test was performed on laminate-type cells consisting of $\text{Li}/1 \text{ M LiPF}_6 \text{ (EC+DEC)}/\text{UC-SnO}_2/\text{KB}$ (or UC-KB) in the voltage range of 0.0–2.0 V at a scan rate of 0.2 mV s^{-1} .

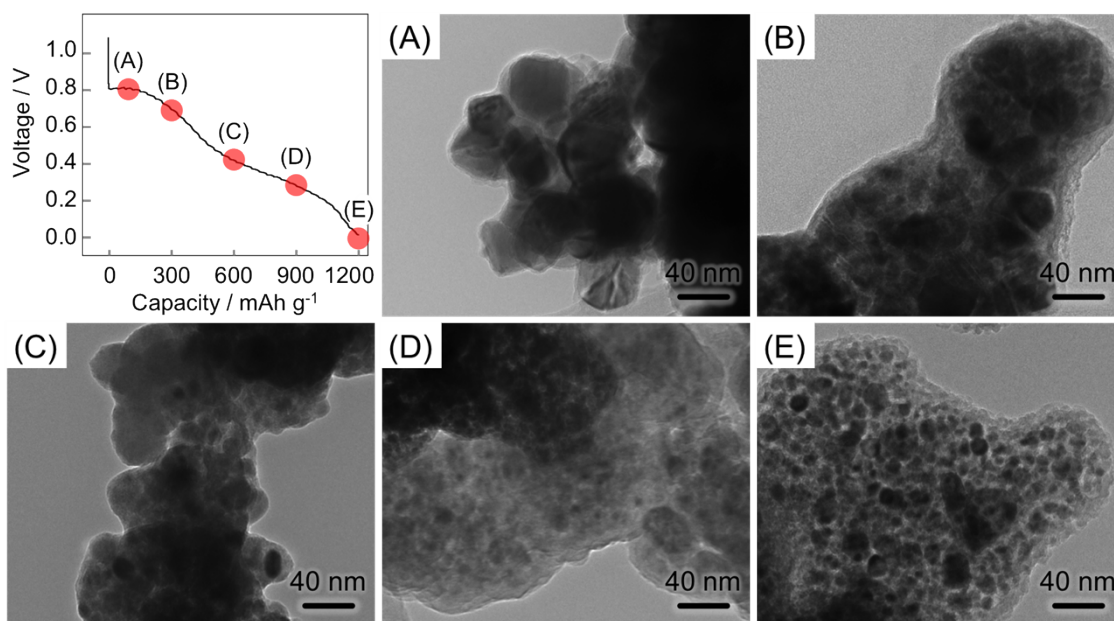


Figure S7. Lithiation profile curve (top left) and HRTEM images showing morphology changes of the bulk SnO₂ particles (purchased from Showa Kako Corp., 50-100 nm of the particle size) at different states of lithiation (A) 50 mAh g⁻¹, (B) 300 mAh g⁻¹, (C) 600 mAh g⁻¹, (D) 900 mAh g⁻¹, (E) 1200 mAh g⁻¹. Tested electrodes were composed of SnO₂ (90 wt%) and PVDF (10 wt%) without any conductive carbons. The electrochemical performance was performed on 2032 coin-type half cells consisting of Li/1 M LiPF₆ in EC+DEC/SnO₂ at a current density of 300 mAh g⁻¹. In the course of lithiation, the bulk SnO₂ particles are pulverized into small Sn particles. Each particle is surrounded by a large amount of polymeric mixture of SEI and Li₂O, thus isolated from other particles.