Supporting Information for

Silicon Oxycarbide-Antimony Nanocomposites for High-Performance Li-Ion Battery Anodes

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Experimental Details.

TEM samples preparation. SiOC/Sb was dispersed in ethanol and a few drops of the suspension were deposited onto a perforated carbon foil supported on a copper grid. STEM investigations were performed on an aberration-corrected, dedicated STEM microscope, a HD2700CS (Hitachi) operated at an acceleration potential of 200 kV (cold field emitter). A probe corrector (CEOS) that is incorporated in the microscope column between the condenser lens and the probe-forming objective lens provides a resolution below 0.1 nm. Images were recorded with a high-angle annular dark field (HAADF) detector with incoherently scattered electrons resulting in an intensity strongly increasing with the atomic number (Z-contrast). The images (1024 × 1024 pixels) were recorded with frame times between 10 and 20 s. Analytical investigations were done with an energy-dispersive X-ray spectrometer (EDXS, EDAX) attached to the microscope column.

***Ex-situ* Samples Preparation.** NMR and STEM-imaging experiments were performed *ex-situ* on a series of samples of SiOC and SiOC/Sb after electrochemical cycling. All samples were investigated after the described washing treatment designed to remove electrolyte from the surface of the particles while preventing any change to their state of charge. Samples are denoted as: **"Lithiated" SiOC** or **SiOC/Sb**: electrochemically cycled (one single discharge down to 5 mV at 18.6 mA g^{-1}), collected from four coin cells, washed with three portions of EC/DMC (1:1 by weight) (1 mL each), collected after centrifugation at 8000 rpm for 3 min after each washing, and finally dried overnight under vacuum. **"Delithiated": SiOC** or **SiOC/Sb**: electrochemically cycled (one single discharge and charge at 18.6 mA g^{-1}), collected from four coin cells, washed with three portions of EC/DMC (1:1 by weight) (1 mL each), collected after centrifugation at 8000 rpm for 3 min after each washing, and finally dried overnight under vacuum. **"Cycled 10 times"**: SiOC/Sb electrochemically cycled (1 cycle at 18.6 mA g^{-1}, followed by 9 cycles at 372 mA g^{-1}, collected from two coin cells, washed with

two portions of EC/DMC (1:1 by weight) and one portion of THF (anhydrous, degassed) (1 mL each), collected after centrifugation at 8000 rpm for 3 min after each washing, and finally dried overnight under vacuum.

Table S1. Elemental analysis of SiOC/Sb-50 nanocomposite. The explanation of the calculations of C_{free} and SiOC contents is given in the experimental section.

Sample	Elemental Content [wt%]				Formula (normalized)	$SiC_xO_{2(1-x)}$	C_{free}	C_{free}	SiOC
	Si	C	O	Sb				[wt%]	
SiOC/Sb-50	26.05	21.45	22.20	30.30	$SiC_{1.92}O_{1.49}Sb_{0.27}$	$SiC_{0.25}O_{1.49}$	1.67	18.61	51.09

Table S2. ^{29}Si CP MAS NMR analysis of SiOC and SiOC/Sb with their respective relative areas. Due to the nature of the CP experiment, the intensity of the SiO_4 peak might be underestimated.

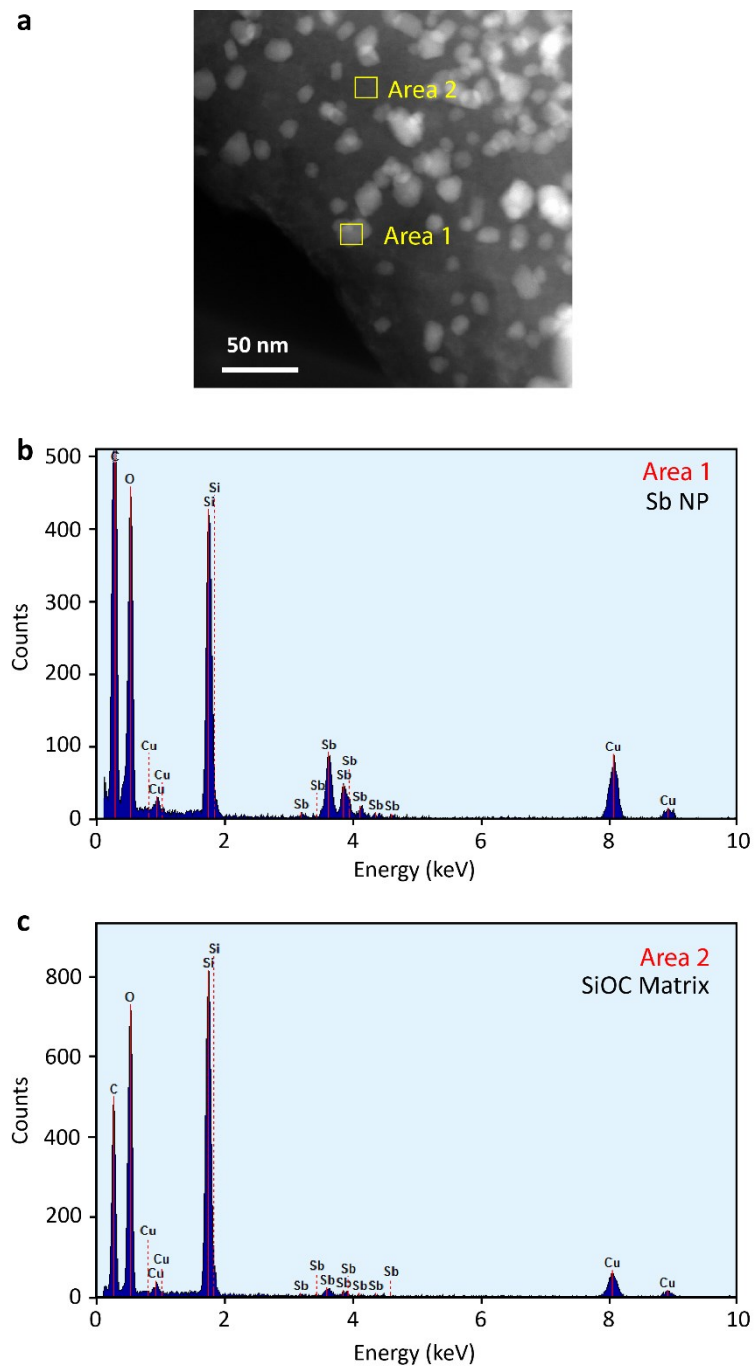| ^{29}Si CP MAS	SiO_4		SiO_3C		SiO_2C_2		$SiOC_3$		SiC_4	
	δ / ppm	Area	δ / ppm	Area	δ / ppm	Area	δ / ppm	Area	δ / ppm	Area
Literature	-108	-	-70	-	-35	-	-5	-	-16	-
SiOC	-103	0.10	-70	0.31	-36	0.26	-4	0.16	-17	0.17
SiOC/Sb	-104	0.21	-69	0.45	-31	0.18	-4	0.02	-19	0.15

Figure S1. (a) HAADF STEM image of pristine SiOC/Sb. The areas 1 and 2 of EDXS mapping are shown in yellow squares, representing an Sb NP and SiOC matrix, accordingly. (b) EDXS histogram of an Sb NP (area 1). (c) EDXS histogram of the SiOC matrix (area 2).
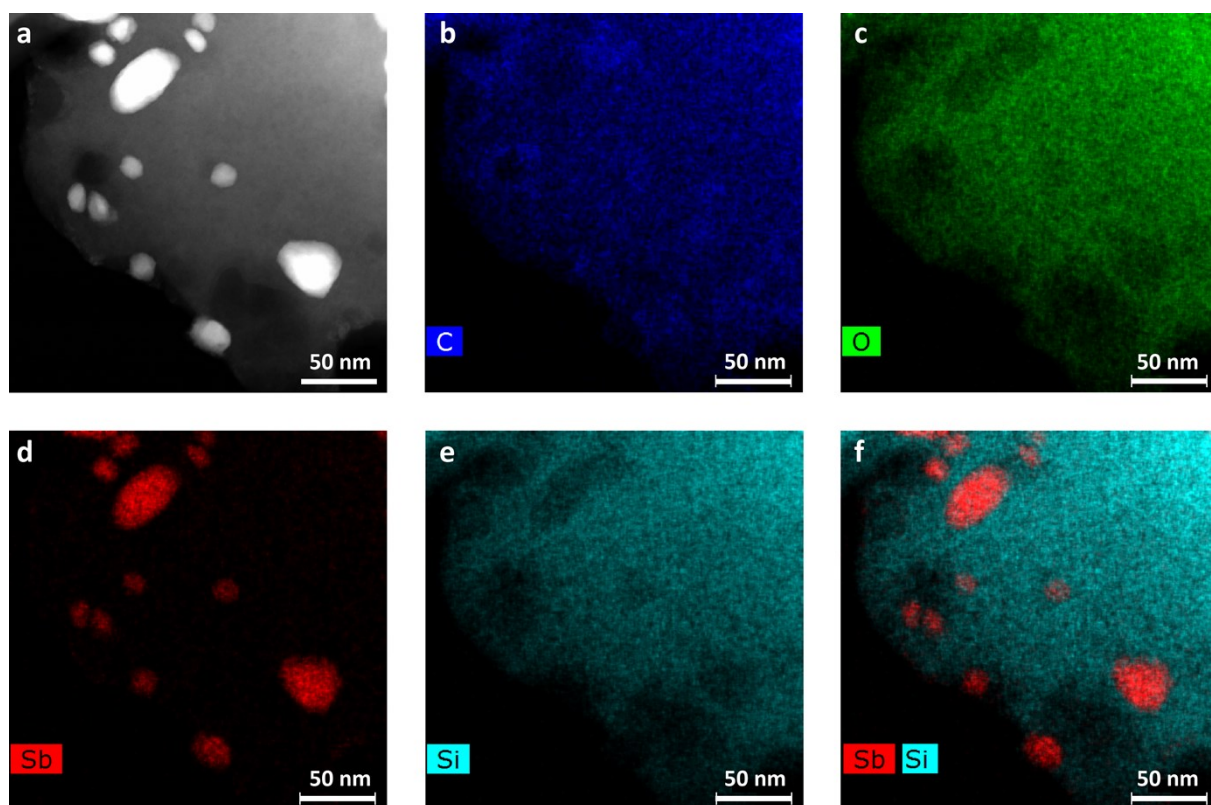
Figure S2. (a) High-resolution HAADF STEM image of pristine SiOC/Sb. (b-e) C, O, Sb and Si elemental STEM-EDXS maps of pristine SiOC/Sb. (f) Reconstructed overlay image of the elemental maps shown in (d-e).
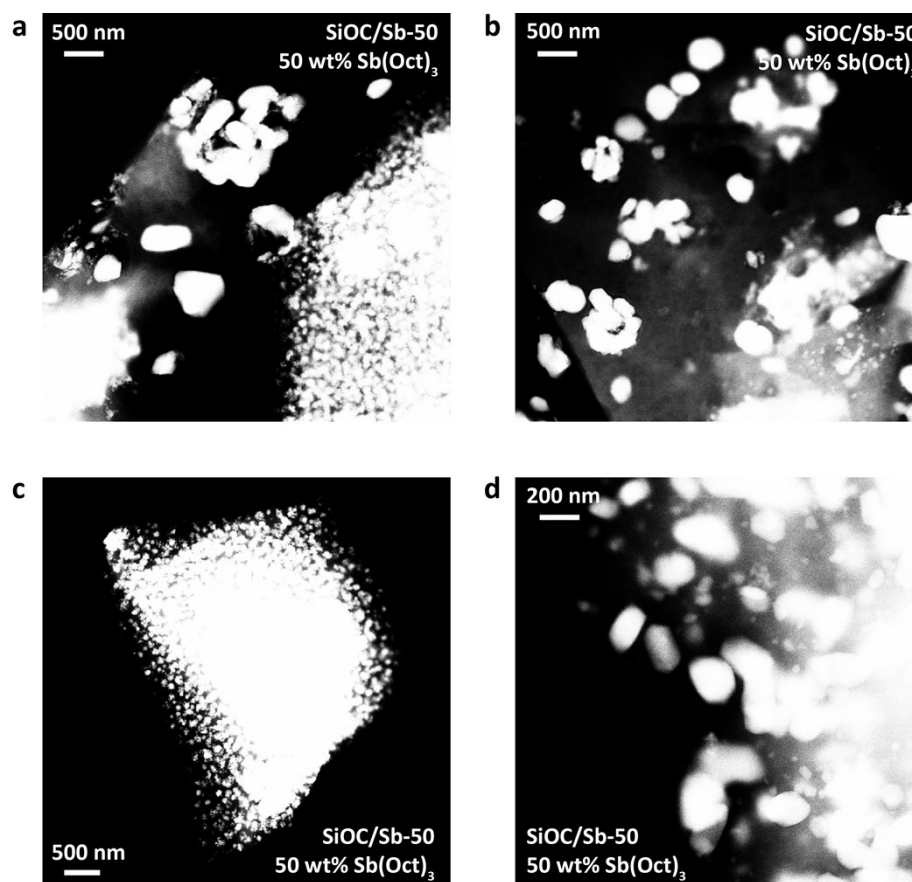
Figure S3. HAADF-STEM images of SiOC/Sb nanocomposite synthesized with 50 wt% Sb(Oct)$_3$ precursor (denoted as SiOC/Sb-50).
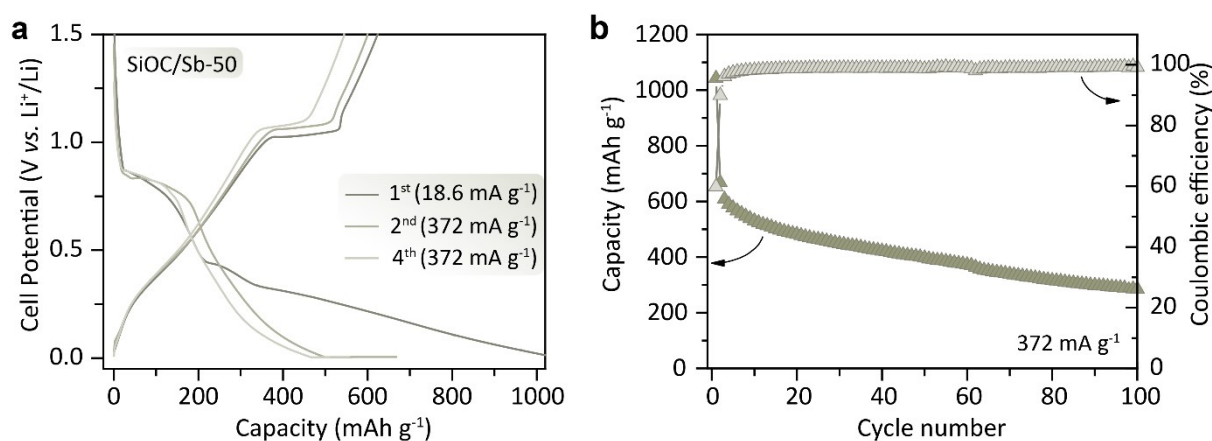

Figure S4. (a) Galvanostatic charge-discharge curves of SiOC/Sb nanocomposite synthesized with 50 wt% Sb(Oct)$_3$ precursor (denoted as SiOC/Sb-50). The first cycle is measured at a current density of 18.6 mA g^{-1}, and the plotted curves correspond to the 1st, 2nd and 4th cycles. (b) Cyclic performance of SiOC/Sb-50 tested at a current density of 372 mA g^{-1}.
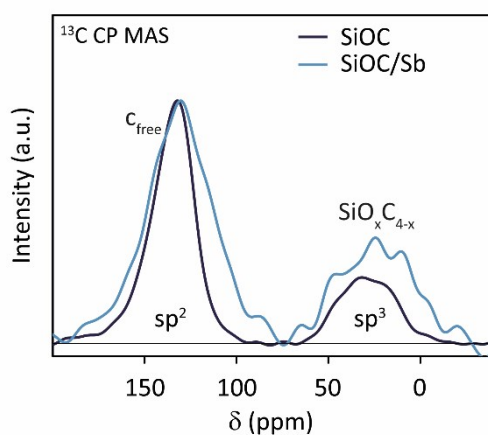
Figure S5. ^{13}C CP MAS NMR comparison between SiOC and SiOC/Sb. The intensities are scaled to the intensity of the sp^2 hybridized "graphitized" carbon (C_{free}).
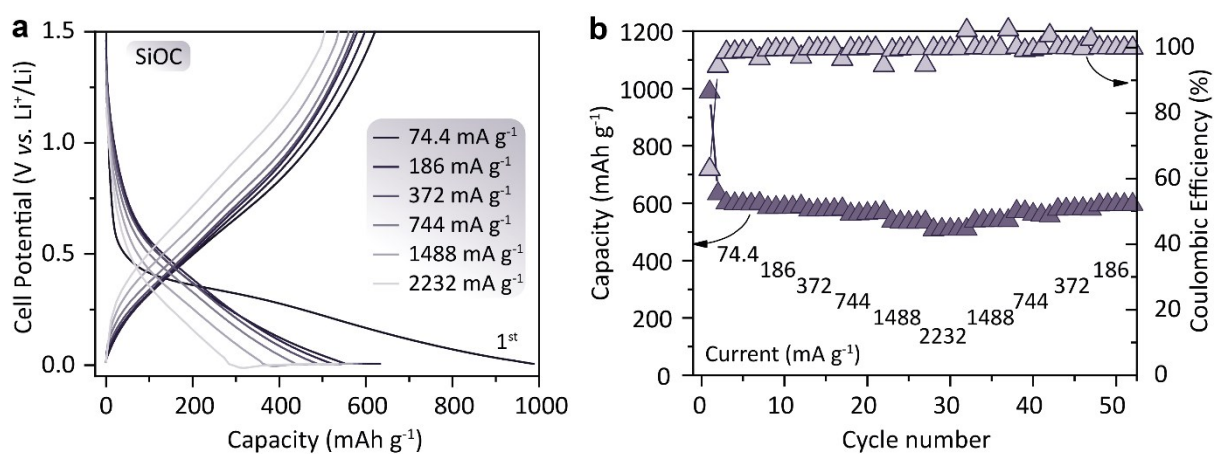

Figure S6. (a) Galvanostatic charge-discharge curves and (b) corresponding discharge capacities of SiOC measured in a half cell at different current densities ranging from 74.4 to 2232 mA g^{-1}.
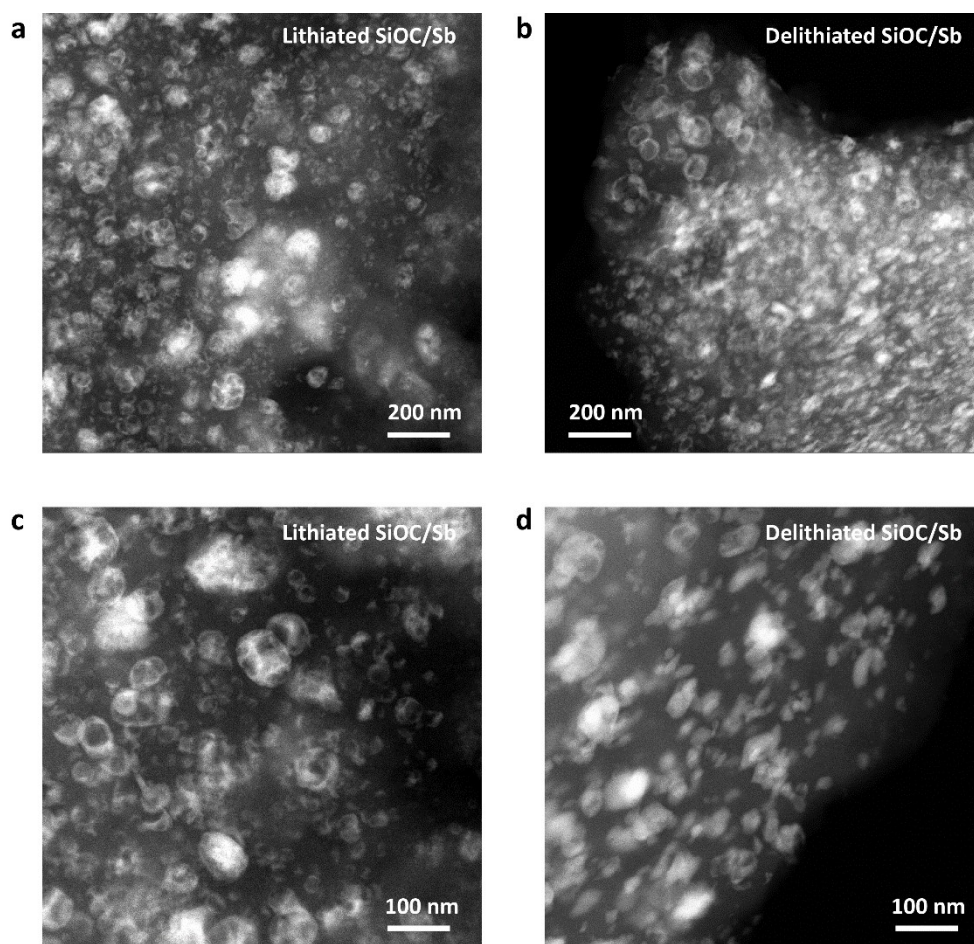
Figure S7. HAADF STEM images of SiOC/Sb after lithiation (a, c) and delithiation (b, d).
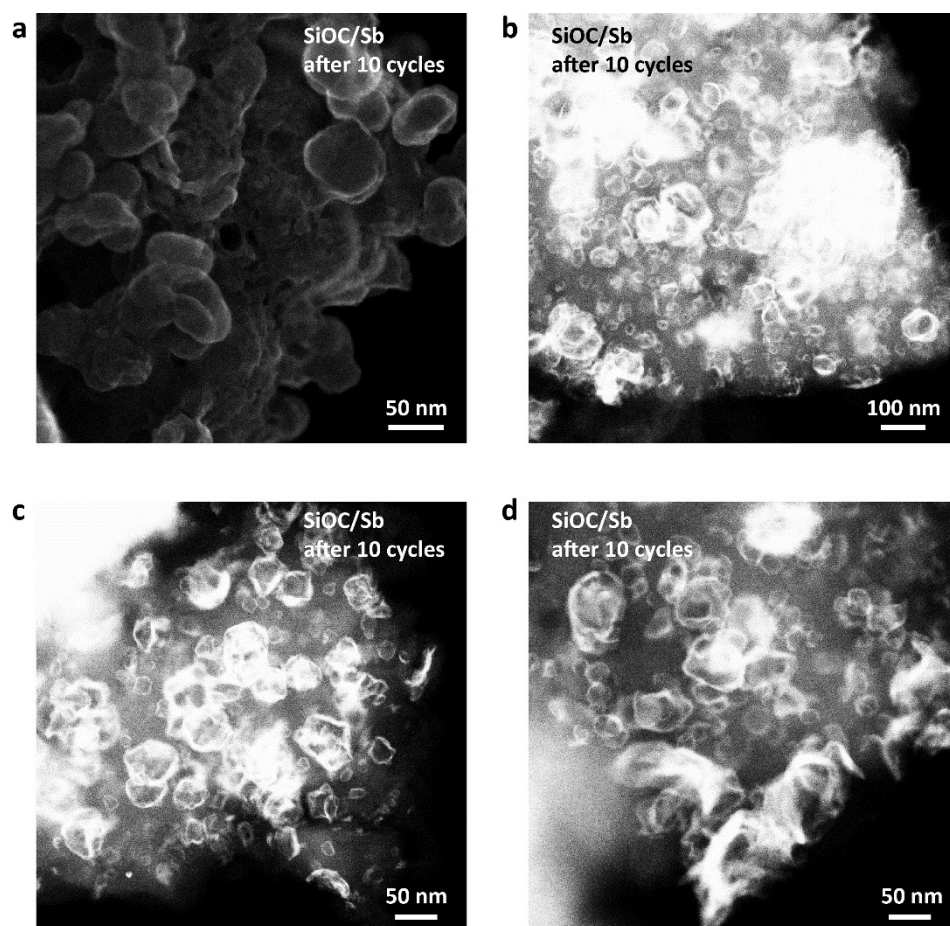
Figure S8. (a) Secondary electron imaging of SiOC/Sb recovered after 10 cycles of lithiation and delithiation. (b,c,d) HAADF STEM images of SiOC/Sb recovered after 10 cycles.