

# Supporting Information

## Effect of Sn Addition on the Anode Properties of SiO<sub>x</sub> for Lithium-Ion Batteries

Tomoki HIRONO,<sup>a,d,§</sup> Hiroyuki USUI,<sup>a,c,§</sup> Yasuhiro DOMI,<sup>a,c,§</sup> Takahiro NISHIDA,<sup>b,c,§§</sup>

Wataru IRIE,<sup>b,c,§§</sup> Toshiyuki SAWADA,<sup>d</sup> and Hiroki SAKAGUCHI<sup>a,c,§,\*</sup>

<sup>a</sup> *Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan*

<sup>b</sup> *Course of Chemistry and Biotechnology, Department of Engineering, Graduate School of Sustainability Science, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan*

<sup>c</sup> *Center for Research on Green Sustainable Chemistry, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan*

<sup>d</sup> *Sanyo Special Steel Co., Ltd., 3007, Nakashima, Shikama-ku, Himeji, Hyogo, 672-8677, Japan*

*\*Corresponding author. Tel./Fax: +81-857-31-5265, E-mail: sakaguch@tottori-u.ac.jp*

§ ECSJ Active Member

§§ ECSJ Student Member

ORCID

Hiroyuki USUI: 0000-0002-1156-0340

Yasuhiro DOMI: 0000-0003-3983-2202

Hiroki SAKAGUCHI: 0000-0002-4125-7182

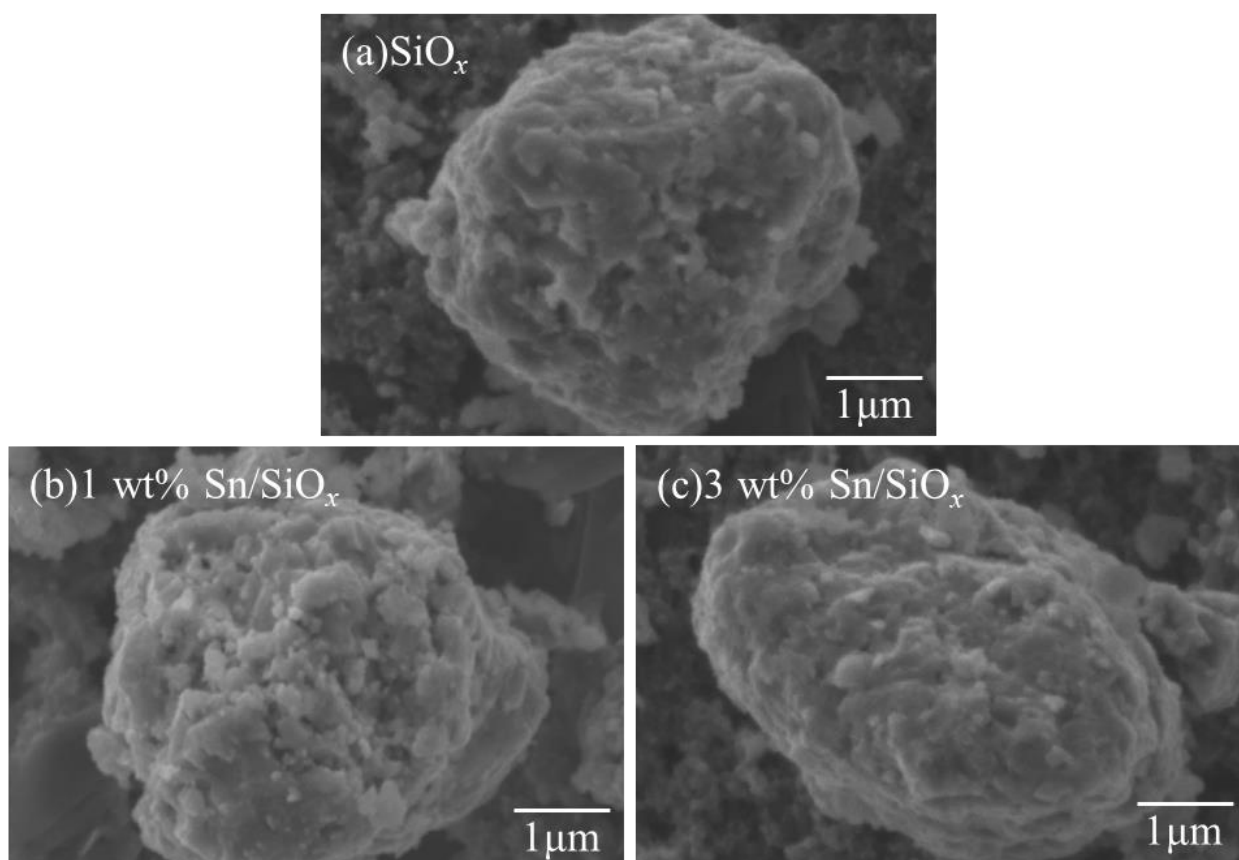


Fig. S1. SEM images of the milled (a) SiO<sub>x</sub>, (b) 1 wt% Sn/SiO<sub>x</sub>, and (c) 3 wt% Sn/SiO<sub>x</sub>. In each case, secondary particles with a size of approximately 5 μm were confirmed. Additionally, the secondary particles showed irregular shapes with irregularities. From these observation results, it can be considered that the effect on the size and shape of the secondary particles is small if the amount of Sn added is up to 3 wt%. Additionally, the shape of the primary particles could not be confirmed. Therefore, the primary particles were mixed on a scale smaller than several hundred nm.

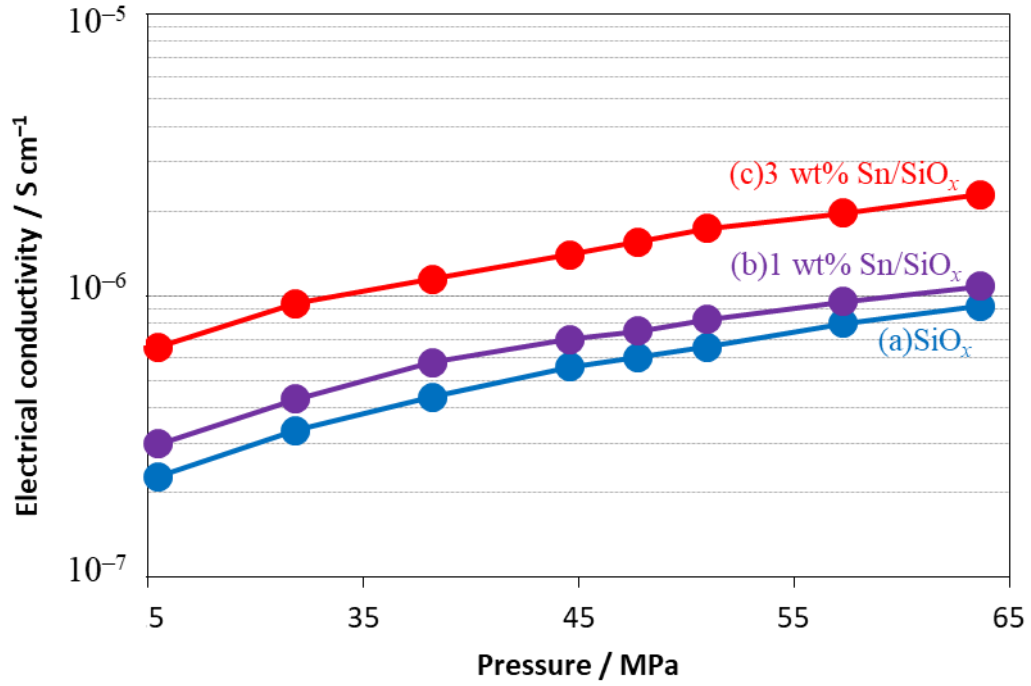


Fig. S2. Electronic conductivity of the milled (a) SiO<sub>x</sub>, (b) 1 wt% Sn/SiO<sub>x</sub>, and (c) 3 wt% Sn/SiO<sub>x</sub> particles under compression. When the powder pressure was measured at 64 MPa, the powder without Sn addition showed electron conductivity of  $9.2 \times 10^{-7} \text{ S cm}^{-1}$ . Contrarily, the 1 wt% Sn/SiO<sub>x</sub> and 3 wt% Sn/SiO<sub>x</sub> powders showed electron conductivities of  $11 \times 10^{-7} \text{ S cm}^{-1}$  and  $23 \times 10^{-7} \text{ S cm}^{-1}$ , respectively. In other words, it was confirmed that the electronic conductivity of SiO<sub>x</sub> improves as the number of Sn increases. Therefore, the addition of Sn increases the electronic conductivity of the material.

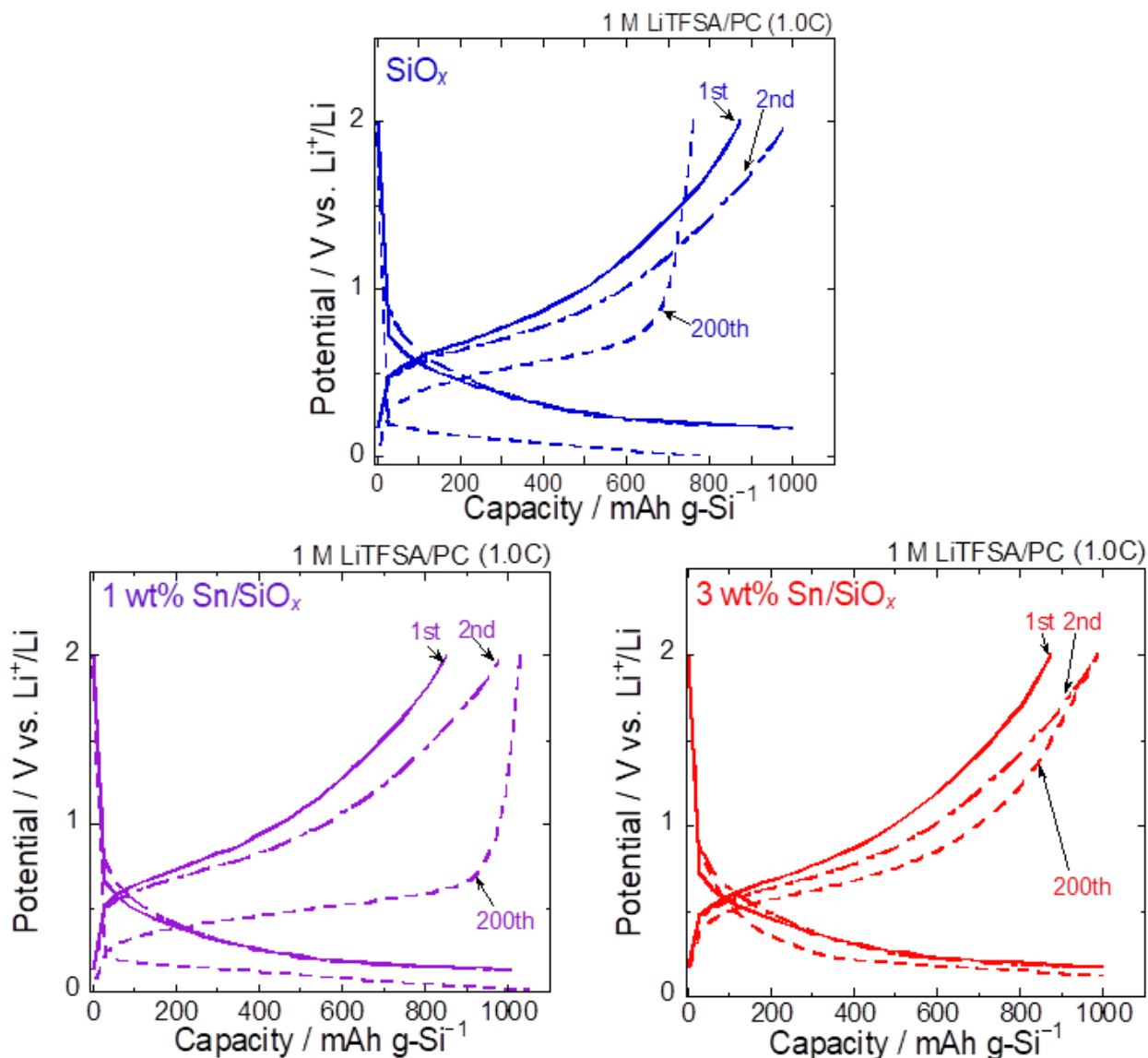


Fig. S3. Charge–discharge curve of the SiO<sub>x</sub>, 1 wt% Sn/SiO<sub>x</sub>, and 3 wt% Sn/SiO<sub>x</sub> electrodes in 1 M LiTFS/PC. Comparing the reaction potentials on the charge side and discharge side in the 1st and 2nd cycles and the 200th cycle of each electrode, the SiO<sub>x</sub> electrode was significantly shifted to the low potential side. Therefore, the authors created a differential capacity plot (dQ/dV curve) on the discharge side of each electrode and verified the mechanism of extending the life of the above cycle properties.

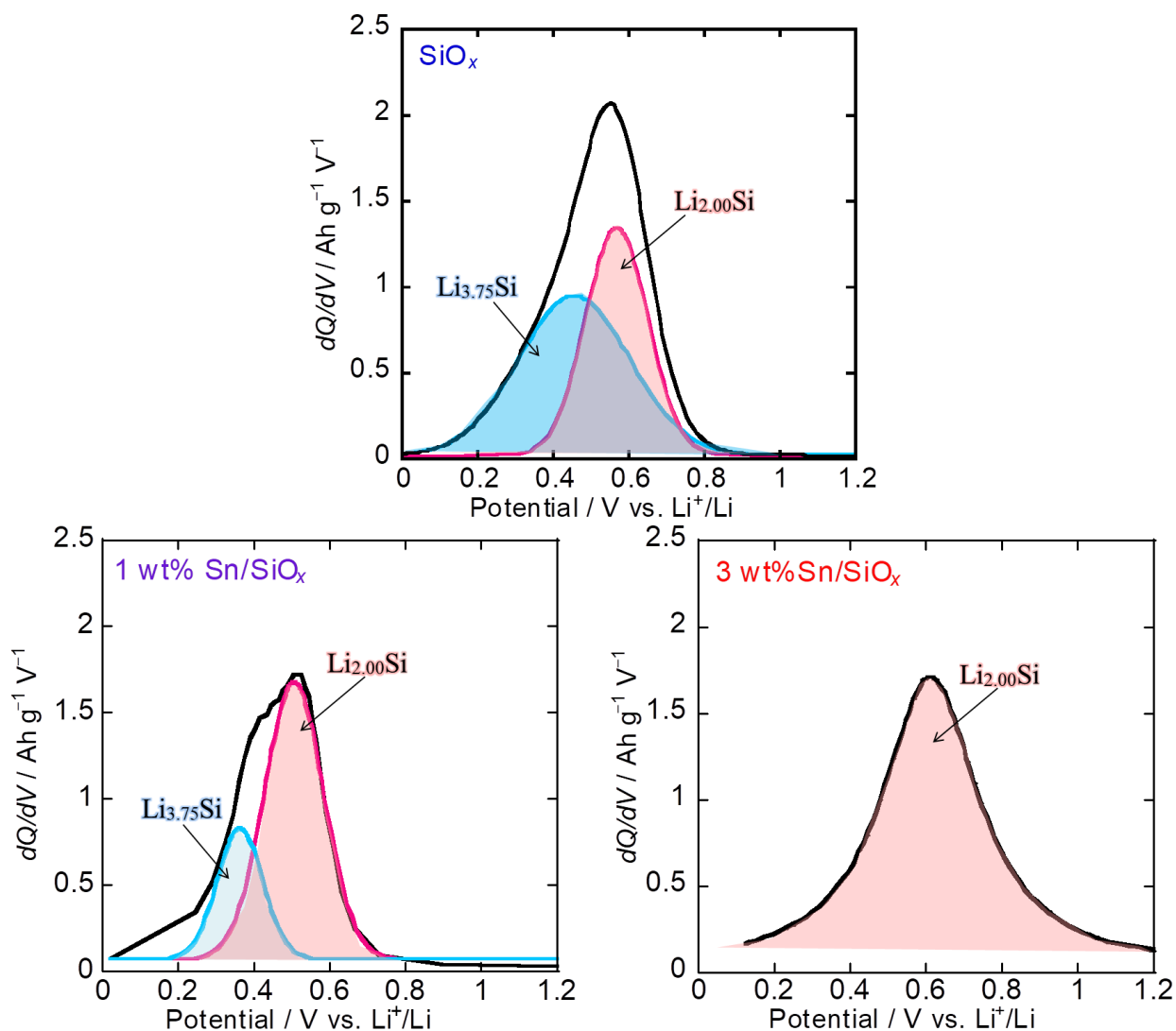


Fig. S4.  $dQ/dV$  plots of the  $\text{SiO}_x$ , 1 wt%  $\text{Sn/SiO}_x$ , and 3 wt%  $\text{Sn/SiO}_x$  electrodes in 1 M LiTFS/PC at 200 cycles. As a result of analyzing this  $dQ/dV$  curve, it was confirmed that  $\text{Li}_{3.75}\text{Si}$  with a large volume change was formed for an electrode without Sn addition or with a small amount (1 wt%) of Sn. Conversely, the formation of  $\text{Li}_{3.75}\text{Si}$  was not confirmed in the 3 wt%  $\text{Sn/SiO}_x$  electrode, and only the formation of  $\text{Li}_{2.00}\text{Si}$  with a small volume change was confirmed. Therefore, the authors were able to obtain data that support the results of the discussions in Figs. 6 and 7.

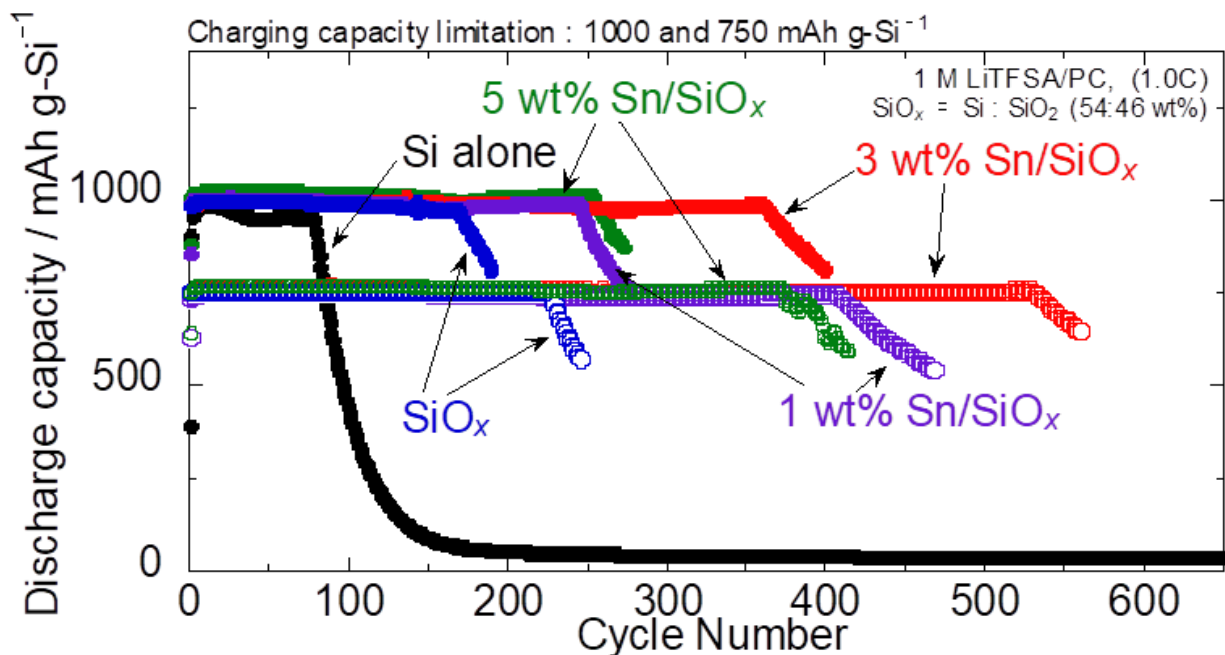


Fig. S5. Dependence of the discharge capacity of the  $\text{SiO}_x$ , 1 wt%  $\text{Sn/SiO}_x$ , 3 wt%  $\text{Sn/SiO}_x$ , and 5 wt%  $\text{Sn/SiO}_x$  electrodes on a cycle number in 1 M LiTFS/PC solution with a charge capacity limit of  $1000 \text{ mAh g}^{-1}$  and  $750 \text{ mAh g}^{-1}$ . Further, the result of the Si-alone electrode is shown. When the lithium-insertion amount was specified at  $1000 \text{ mAh g}^{-1}$ , this Si-alone electrode caused a rapid capacity fading loss by 100 cycles. Conversely, the  $\text{SiO}_x$  electrode suppressed the capacity decline up to 170 cycles. Furthermore, the capacity of the 5 wt%  $\text{Sn/SiO}_x$  electrode was maintained up to 260 cycles, which is equivalent to that of the electrode with 1 wt% of Sn. This is because the electronic conductivity of  $\text{SiO}_x$  was improved by adding 5 wt% of Sn, and the current collecting property of the electrode was improved. The electronic conductivity when measuring the powder pressure at 64 MPa was  $9.2 \times 10^{-7} \text{ S cm}^{-1}$  for the  $\text{SiO}_x$  powder without the addition of Sn. Additionally, when 5 wt% Sn was added, the value was  $36 \times 10^{-7} \text{ S cm}^{-1}$ .

Furthermore, the test was conducted by reducing the lithium-insertion amount from 1000 to  $750 \text{ mAh g}^{-1}$  to observe the effect of Sn addition. Resultantly, when the lithium-insertion amount was specified as  $750 \text{ mAh g}^{-1}$ , the difference in cycle life between the  $\text{SiO}_x$  electrode and 5 wt%  $\text{Sn/SiO}_x$  electrodes with Sn became more remarkable than the difference

in cycle life when specified at  $1000 \text{ mAh g}^{-1}$ . This is because the volume change of Si became smaller, and the electrode disintegration due to stress was reduced by reducing the amount of lithium inserted.

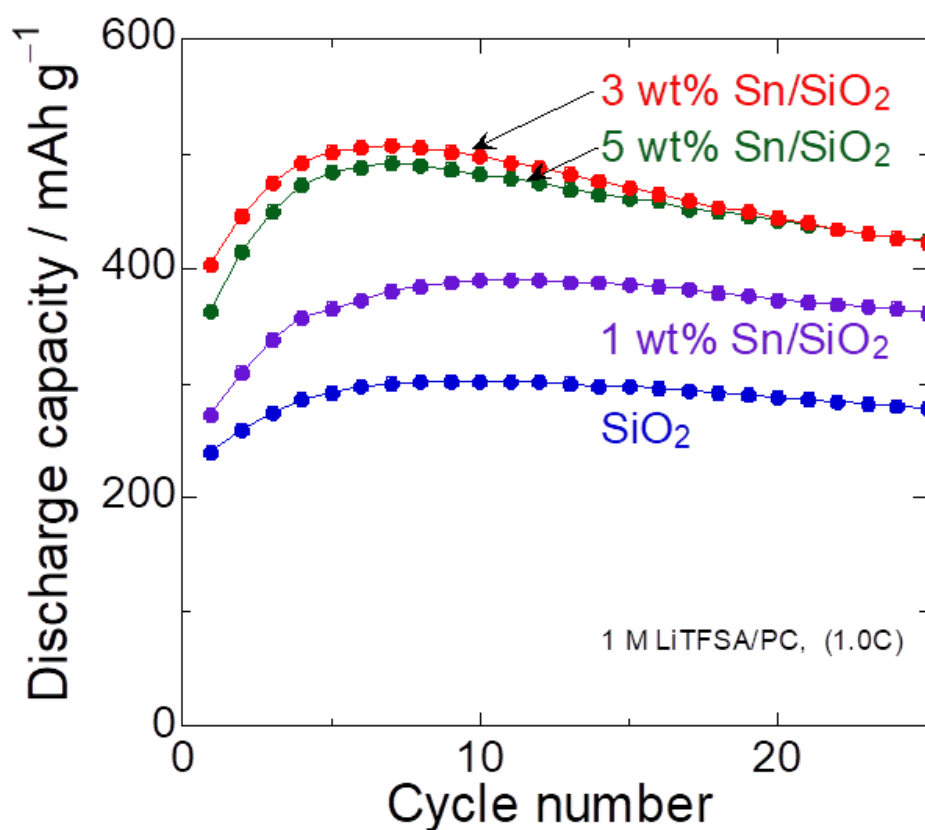


Fig. S6. Dependence of the discharge capacity of the SiO<sub>2</sub>, 1 wt% Sn/SiO<sub>2</sub>, 3 wt% Sn/SiO<sub>2</sub>, and 5 wt% Sn/SiO<sub>2</sub> electrodes on a cycle number in 1 M LiTFS/PC (1C-rate). Temperature and potential range for the testing were set to 303 K and 0.005–2.000 V vs. Li<sup>+</sup>/Li, respectively. For the 5 wt% Sn addition, in which the same powder preparation as 1 or 3 wt% Sn addition was performed, the metallic Sn that was not dissolved in SiO<sub>2</sub> formed agglomerates. They showed a large electronic conductivity of  $36 \times 10^{-7} \text{ S cm}^{-1}$  because this aggregate contributes to the improvement of the electron conductivity of SiO<sub>x</sub>. However, focusing on the SiO<sub>2</sub> matrix, it was found that the discharge capacity of the electrode with 5 wt% Sn added was almost the same as that with 3 wt% Sn. Therefore, Sn aggregates did not contribute to the lithium-ion reactivity of the SiO<sub>2</sub> matrix. In other words, the electrode with 5 wt% of Sn added shows the same lithium-ion reactivity of the SiO<sub>2</sub> matrix as that with 3 wt% of Sn.



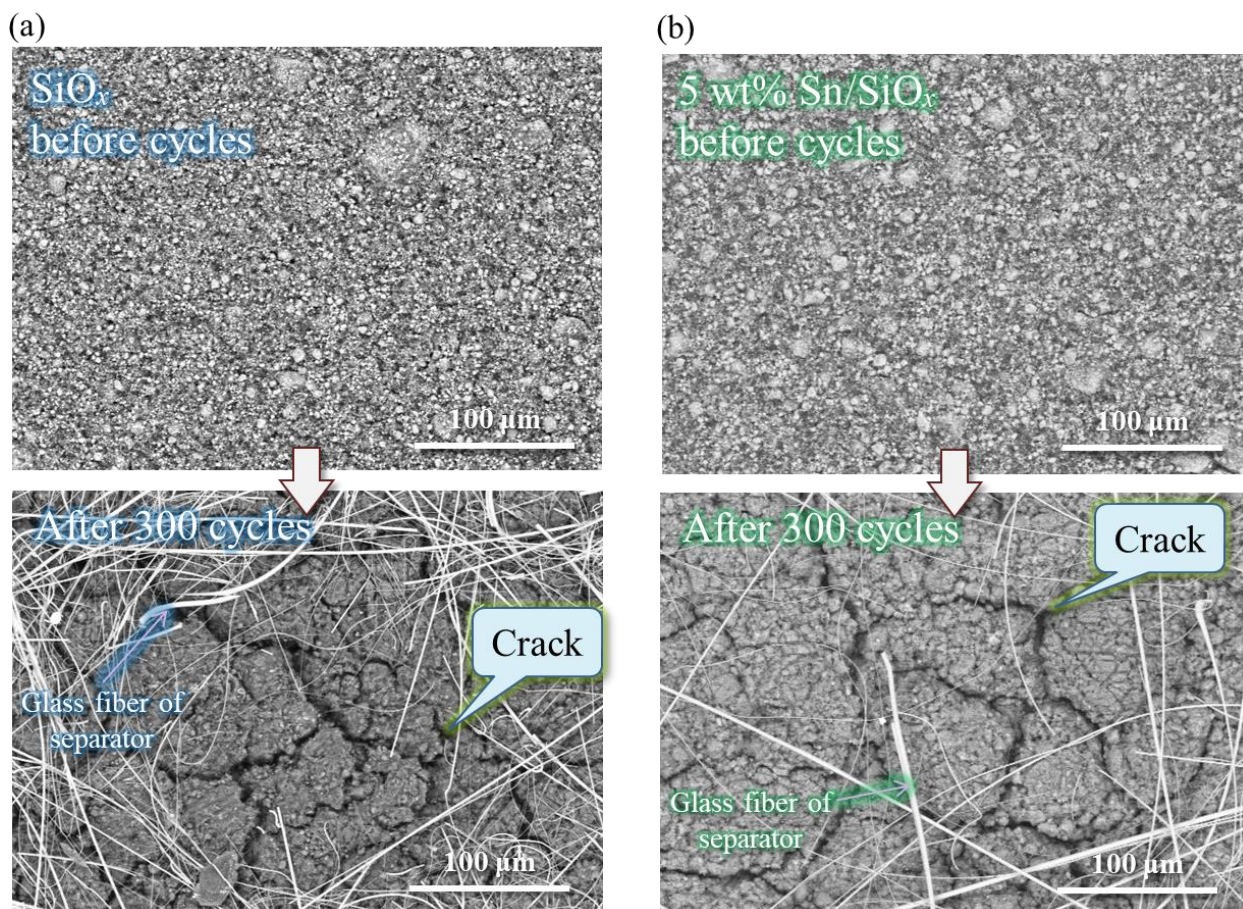


Fig. S7. SEM images of the (a)  $\text{SiO}_x$  and (b) 5 wt% Sn/ $\text{SiO}_x$  electrodes before cycling and after 300 cycles. Large cracks were confirmed in both electrodes after cycling. Conversely, as shown in Fig. 7 (a), no large cracks were found on the surface layer of the 3 wt% Sn/ $\text{SiO}_x$  electrode, which has the best cycling properties, after cycling.

For the electrode without Sn addition, lithium-ion occlusion of Si occurs locally because of the low reactivity of the  $\text{SiO}_2$  matrix with lithium-ion (Fig. 6 (b)). Resultantly,  $\text{Li}_{3.75}\text{Si}$  with a large volume change was formed, which is thought to have caused the disintegration of the electrode and a decline in capacity. This was supported by the results shown in Fig. S4. Furthermore, after cycling, the electrode could not remove part of the separator. This is because the electrode pressed the separator owing to the large volume change of Si and sank into the surface layer of the electrode, further supporting the above

consideration.

Conversely, when 5 wt% of Sn was added, even if the reactivity of the matrix with lithium-ion was equivalent to that of the 3 wt% Sn addition, the Sn aggregate reacted with lithium, albeit only slightly. Resultantly, it was speculated that the local volume change due to the expansion and contraction of Sn that reacted with lithium increased the formation of cracks.

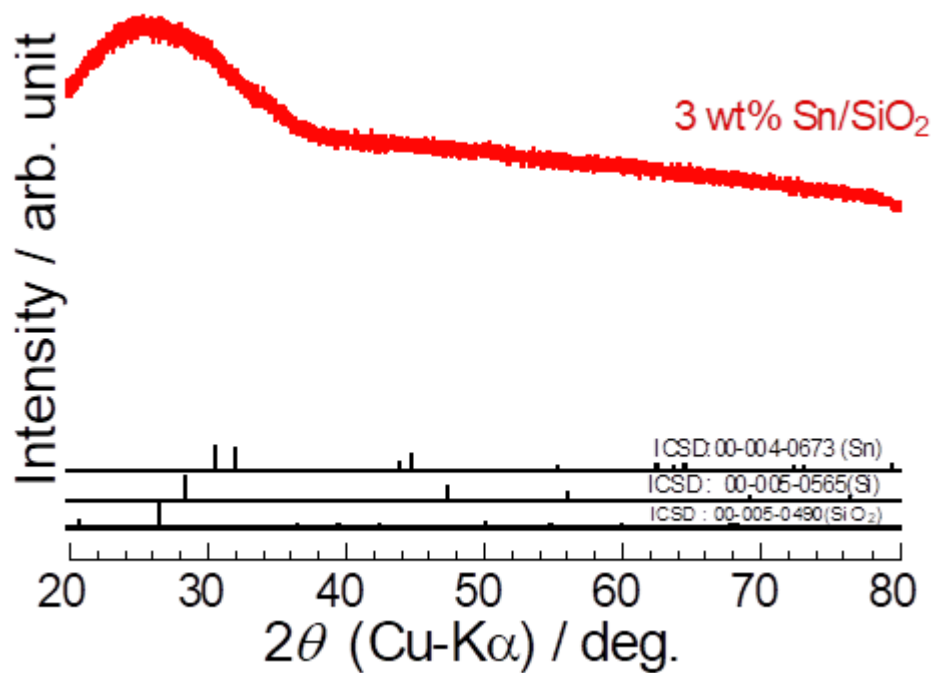


Fig. S8. XRD pattern of the milled 3 wt% Sn/SiO<sub>2</sub> powder in the angle ranges of 20°–80°. It was confirmed that the 3 wt% Sn/SiO<sub>2</sub> powder was amorphous. Also, other powders such as 1 wt% Sn/SiO<sub>2</sub> are considered amorphous because the manufacturing process and processing are the same as for 3 wt% Sn/SiO<sub>2</sub>.

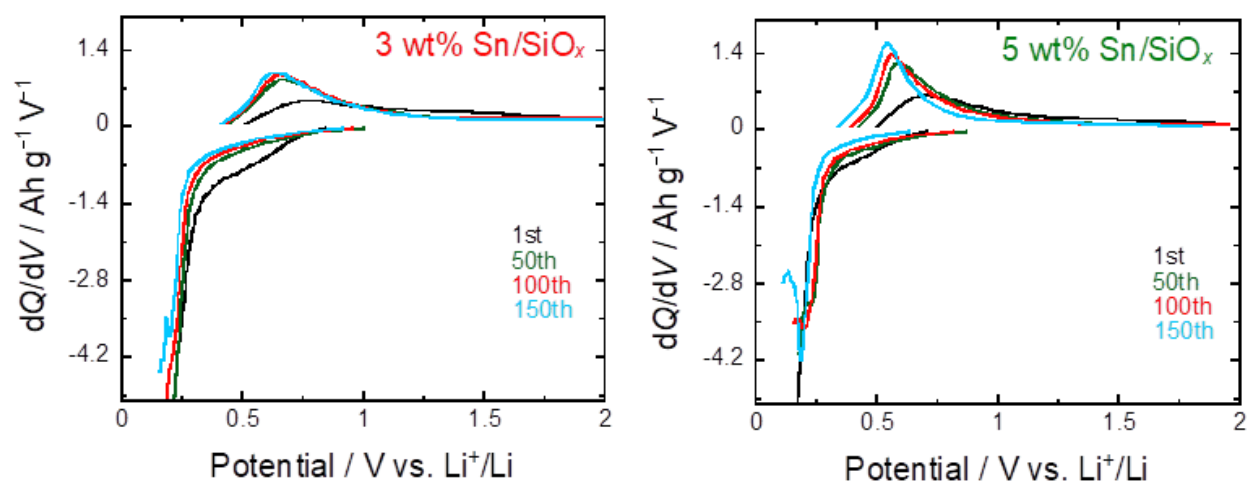


Fig. S9.  $dQ/dV$  plots of the 3 wt%  $\text{Sn}/\text{SiO}_x$  and 5 wt%  $\text{Sn}/\text{SiO}_x$  electrodes in 1 M LiTFS/PC at 1, 50, 100, 150 cycles.