Supporting Information

Effect of Sn Addition on Anode Properties of SiO_x in Sodium-Ion Batteries

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Keywords : Sn-added SiO_x; Na-ion battery; Anode material; Na^+ conductivity

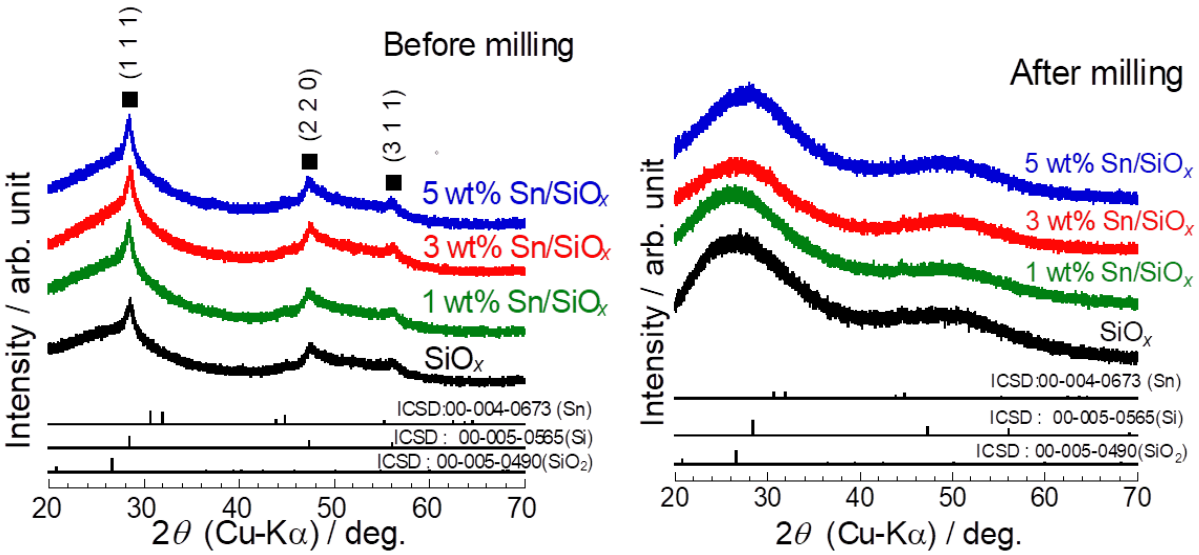

Figure S1. XRD patterns of SiO_x, 1 wt% Sn/SiO_x, 3 wt% Sn/SiO_x, and 5 wt% Sn/SiO_x powders before and after mechanical milling.

Si-derived diffraction peaks are observed for all the samples before mechanical milling. The crystallite sizes of Si in SiO_x, 1 wt% Sn/SiO_x, 3 wt% Sn/SiO_x, and 5 wt% Sn/SiO_x powders were 3.2 nm, 3.5 nm, 3.8 nm, and 3.5 nm, respectively. It was confirmed that the Si-derived diffraction peaks disappeared and broadened after further mechanical milling of the samples for 20 h.

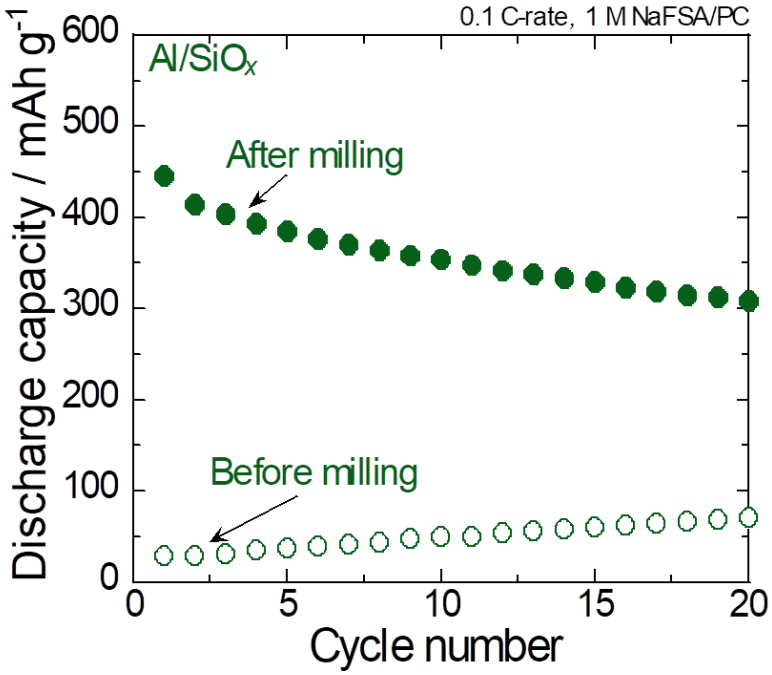

Figure S2. Dependence of the discharge capacity of Al/SiO_x electrodes before and after mechanical milling on the cycle number in a 1 M NaFSA/PC as the electrolyte.

The Al/SiO_x powder was largely similar to the Sn/SiO_x powder before mechanical milling, in which Si microcrystals were confirmed by TEM. The Si crystallite size decreased after mechanical milling. The finer the Si crystal is, the higher are the discharge capacity and reactivity with Na.

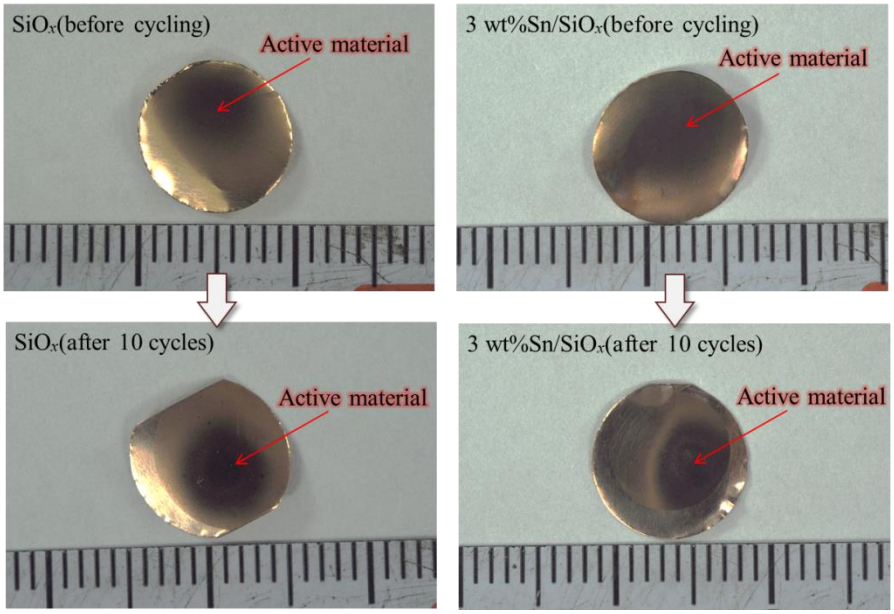

Figure S3. Photographs of the external appearance of SiO_x and 3 wt% Sn/SiO_x electrodes before and after 10 cycles.

The electrode surfaces of SiO_x and 3 wt% Sn/SiO_x electrodes were observed before cycling and after 10 cycles to study the electrode conditions. The examined electrodes were prepared using the same amount of active material and current density. The color of the portion where the active material adhered to both electrodes became darker after 10 cycles than before cycling. It was confirmed that the electrodes did not completely return to the initial state but remained expanded than the initial state after repeated expansion and contraction of the entire active material during the repeated charge–discharge cycles. No large cracks or delamination were visually confirmed for either electrode, and there was no significant macroscopic difference.

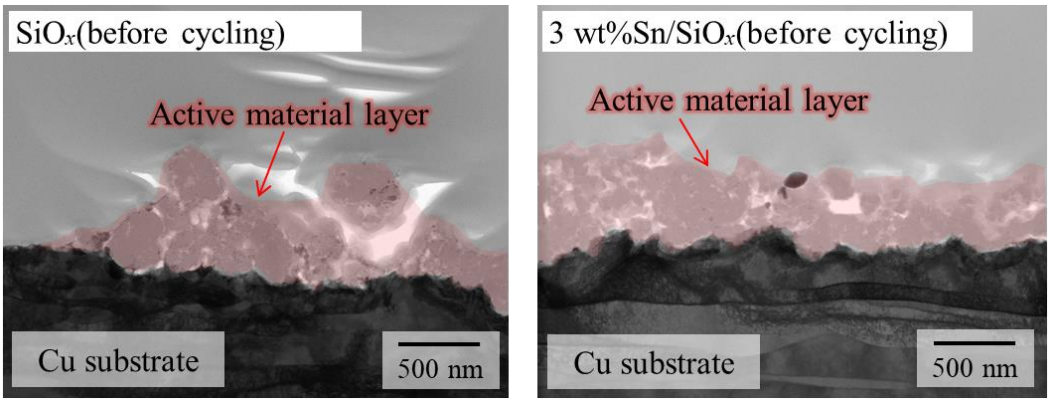

Figure S4. Cross-sectional TEM images of SiO_x and 3 wt% Sn/SiO_x electrodes before cycling.

TEM observations of SiO_x and 3 wt% Sn/SiO_x electrodes revealed clear boundaries between the active material particles before cycling.

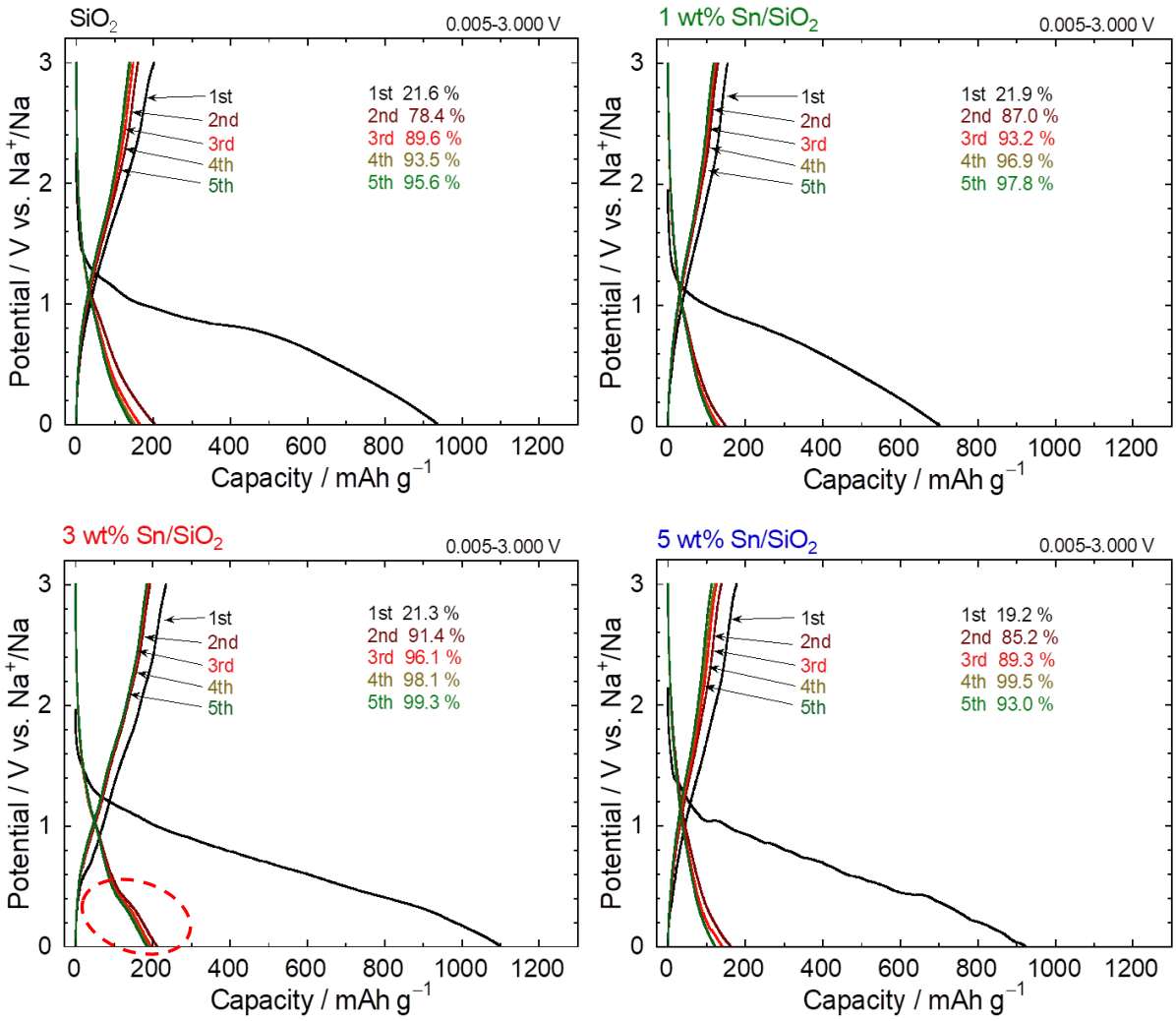

Figure S5. Charge–discharge curves of SiO_2, 1 wt% Sn/SiO_2, 3 wt% Sn/SiO_2, and 5 wt% Sn/SiO_2 mechanically milled electrodes on the cycle number in a 1 M NaFSA/PC as the electrolyte.

The initial charge curves for the 3 wt% Sn/SiO_2 electrode had the highest discharge capacity, indicating a clear plateau around 0.5 V after the second cycle compared to other electrodes. The addition of Sn improves the Na^+ conductivity of amorphous SiO_2, and SiO_2 reacts with Na^+ to form $Na_2Si_2O_5$, which is active with Na^+.

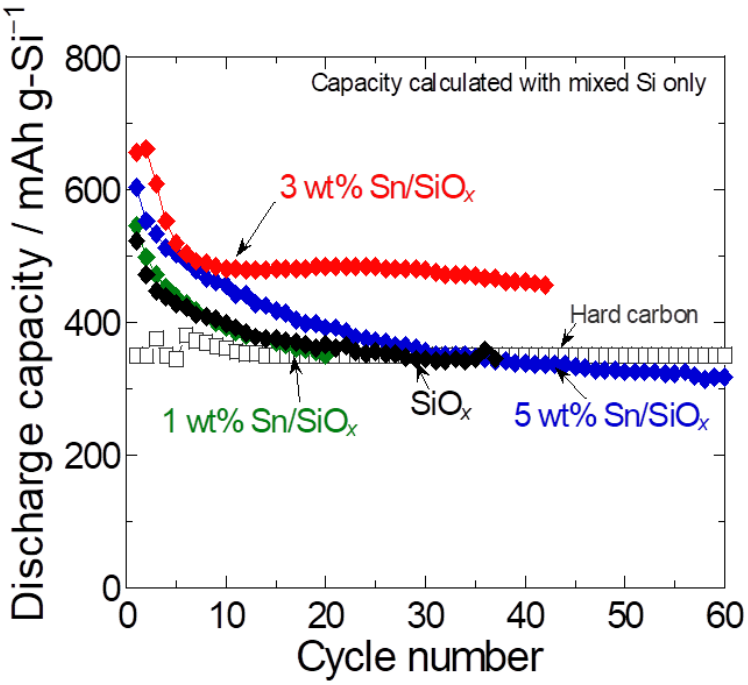

Figure S6. The dependence of the discharge capacity of hard carbon, SiO_x, 1 wt% Sn/SiO_x, 3 wt% Sn/SiO_x, and 5 wt% Sn/SiO_x after mechanical milling electrodes on the cycle number in a 1 M NaFSA/PC as the electrolyte.

Figure S6 shows the transition of the discharge (Na desorption) capacity of the Sn-doped SiO_x electrode. The matrix capacity was excluded and the investigation was also conducted from the viewpoint of Si utilization. The capacity of the SiO_x electrode decreased sharply up to 5 cycles, then decreased gradually and converged to 350 mAh g-Si^{-1}. Electrodes doped with 1 wt% and 5 wt% Sn showed similar charge–discharge behavior. In contrast, the 3 wt% Sn-doped SiO_x electrode decreased its capacity during the initial 10 cycles, followed by a high capacity of 480 mAh g-Si^{-1} up to 40 cycles. The initial discharge capacity of this electrode had an extremely high value of 660 mAh g-Si^{-1}. This capacity accounted for 69 % of the theoretical capacity of Si [954 mAh g^{-1} composition of NaSi]. Furthermore, this value was 15 % higher than that of SiO_x without Sn addition.

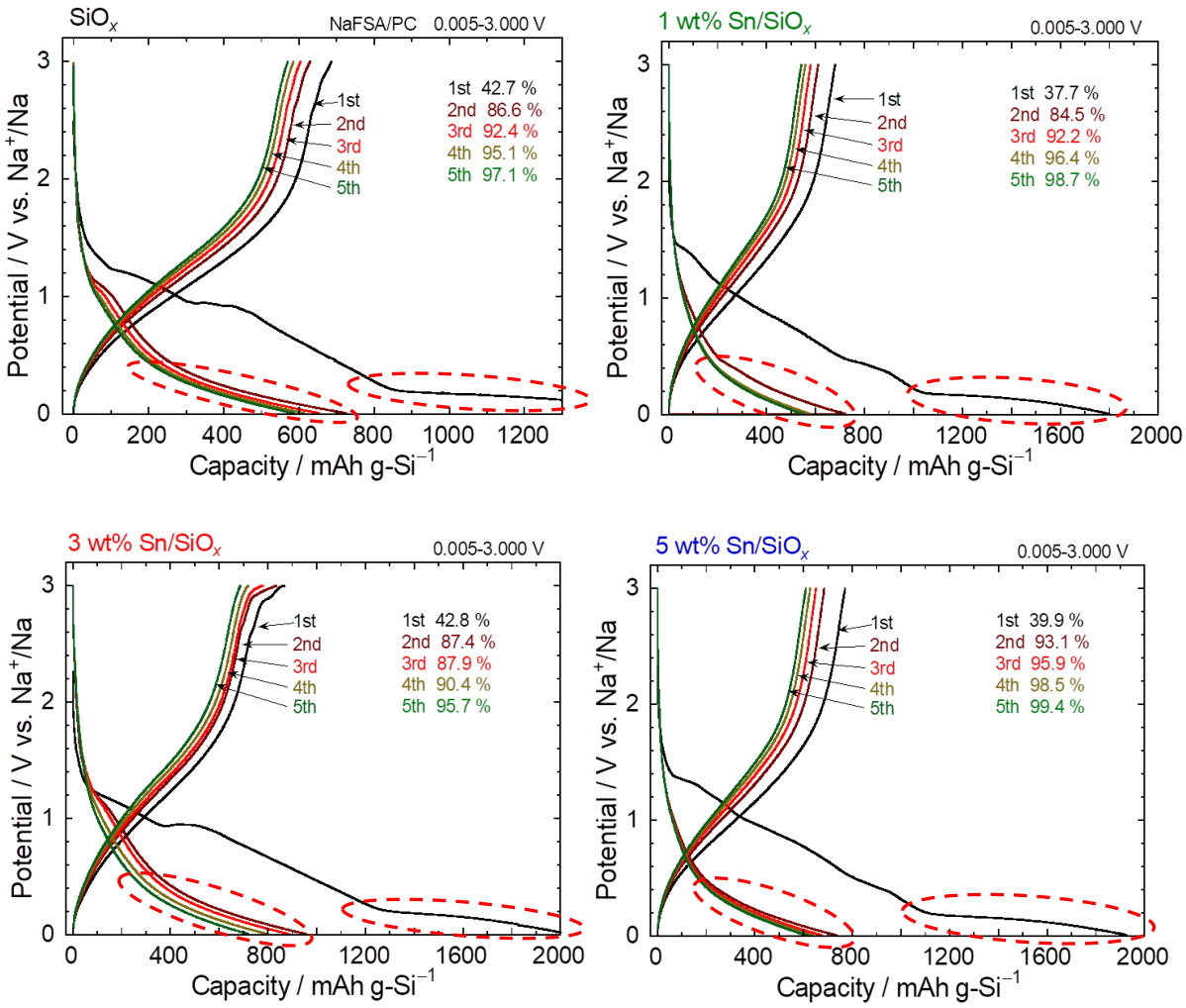

Figure S7. Charge–discharge curves of SiO_x, 1 wt% Sn/SiO_x, 3 wt% Sn/SiO_x, and 5 wt% Sn/SiO_x mechanically milled electrodes on the cycle number in a 1 M NaFSA/PC as the electrolyte.

As a supplement to Fig. 2, we also describe the charge-discharge behavior plotted with the capacity per Si.

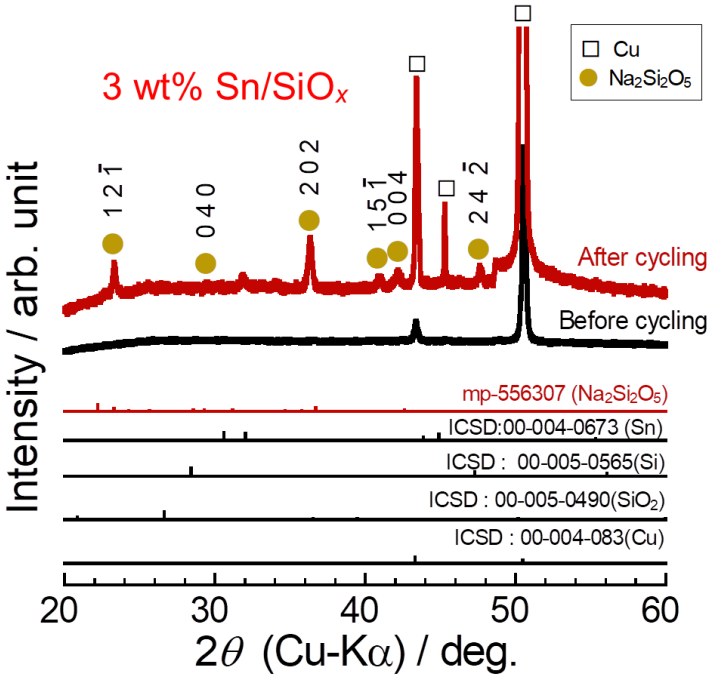

Figure S8. XRD patterns of the 3 wt% Sn/SiO_x electrode in a 1 M NaFSA/PC as the electrolyte before and after initial cycles. XRD measurements were carried out for the cycled electrode after post-annealing treatment at 500 °C in a vacuum.

The 3 wt% Sn/SiO_x electrode did not show the presence of the $Na_2Si_2O_5$ phase before cycling, but it appeared after initial cycling. $Na_2Si_2O_5$ is a Na^+-conductive material. Amorphous SiO_2 reacts with Na^+ to form a Na^+-conductive phase. The discharge capacity increased due to the facile transfer of Na^+ to Si *via* this phase.

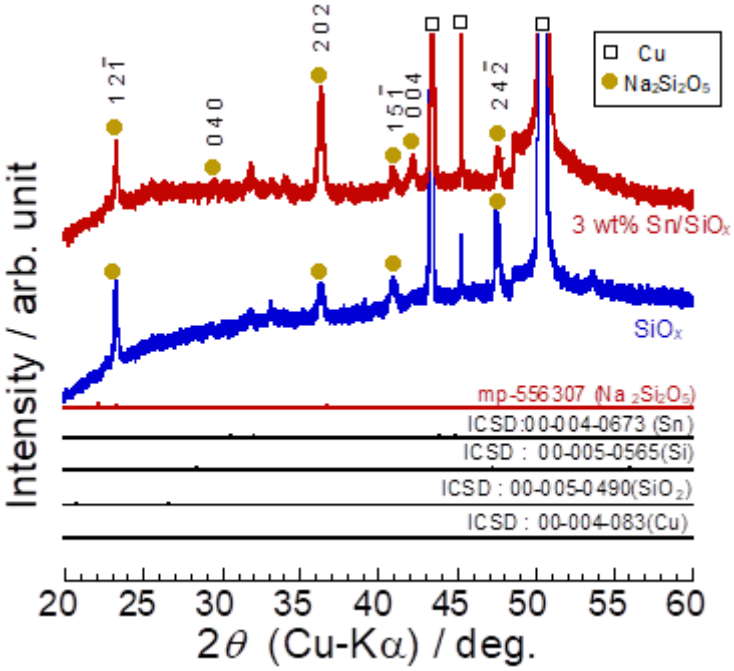

Figure S9. XRD patterns of SiO_x and 3 wt% Sn/SiO_x electrodes in 1 M NaFSA/PC as the electrolyte after initial cycles. XRD measurements were carried out for the cycled electrodes after post-annealing treatment at 500 °C in a vacuum.

The $Na_2Si_2O_5$ phase was formed even after the initial cycle in the SiO_x electrode.