Si is one of the most promising candidates as a next generation negative-electrode active material with high capacity Li-ion batteries (LIBs). Si has a theoretical capacity of 3578 mAh/g\(^{1}\) which is much higher than that of graphite of 372 mAh/g currently used in standard LIBs. Si nanopowder fabricated by expensive methods such as laser ablation\(^{2}\) and plasma-enhanced chemical vapor deposition\(^{3}\) has been investigated to moderate the stress of Si caused by the size change during lithiation and delithiation,\(^{4,5}\) and reduce the internal resistance.\(^{6,7}\)

Si nanopowder still has many problems to use as LIB electrode active material; volume expansion up to four times during lithiation, and shrinkage during delithiation, resulting in formation of cracks in Si nanopowder,\(^{8}\) electrical isolation of Si nanopowder from an electrode,\(^{9}\) and peeling-off of a part of Si nanopowder,\(^{8}\) all of which lead to an increase in internal resistance, poor cyclability and low coulombic efficiency.

To suppress the size change of Si nanopowder, the lithiation capacity is limited at e.g., 1500 mAh/g\(^{10}\) and 1200 mAh/g\(^{11}\) after deep lithiation at 0.01 V on the cell performance is investigated. This limitation of the delithiation capacity after deep lithiation at 0.01 V is the most effective to achieve a constant high capacity for long cycles. The delithiation capacity keeps constant at 1500 mAh/g until the 200th cycle, and it slightly decreases to 1480 mAh/g at the 300th cycle. However, without limitation of the lithiation and delithiation capacities in the voltage range between 1.5 and 0.01 V, the delithiation capacity monotonically decreases with the cycle number, and it becomes 950 mAh/g at the 300th cycle. With limitation of the lithiation capacity at 1500 mAh/g after deep delithiation at 1.5 V, the delithiation capacity keeps 1470 mAh/g until the 137th cycle, and then decreases monotonically with the cycles to 860 mAh/g at the 300th cycle. With limitation of the delithiation capacity, the overvoltage estimated from the lithiation and delithiation curves is the lowest, and peeling-off of Si nanopowder from the Si electrode is suppressed because of limited size changes of Si nanopowder during lithiation and delithiation of Si nanopowder.

In this study, LIB half cells are fabricated using Si nanopowder produced from Si swarf, and the effect of limitation of the delithiation capacity after deep lithiation at 0.01 V on the cell performance is investigated. This limitation of the delithiation capacity at 1500 mAh/g is found to greatly improve the cyclability.

Experimental

Si swarf generated during slicing of solar cell grade n-type Si ingots (1 ~ 2 Ω·cm) by use of the fixed abrasive machining technology was used as the starting material. After cleaning Si swarf, it was milled in acetone using the ball milling method. Si nanopowder was annealed at 1000°C under H\(_2\) atmosphere, followed by annealing at 1000°C under C\(_3\)H\(_4\) (99.5%) atmosphere to coat Si nanopowder with a ~10 nm carbon layer (C-coated Si nanopowder).

C-coated Si nanopowder was mixed with Ketjen Black (KB, EC-300J, Lion Co. Ltd.), binder polymers carboxymethylcellulose ammonium (CMC) and poly(vinyl alcohol) (PVA) dissolved in pure water with the weight ratio of 50:25:20:5. Copper foil was coated with the slurry, and dried at 120°C under vacuum for 3 h. The copper foil was cut with a diameter of 11.3 mm (1 cm\(^2\)) and dried at 120°C under vacuum for 6 h. The mass of active materials on the electrodes was adjusted to be ~0.65 mg.

The C-coated Si nanopowder electrode was packed as a working electrode in a coin cell (CR 2032-type) with a lithium foil (battery grade) as a counter electrode, a polyethylene separator, and an electrolyte. The electrolyte consisted of 1 M LiPF\(_6\) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) (battery grade, Kishida Chemicals Co. Ltd.) with 10 wt% fluoroethylene carbonate (FEC).

The cells were cycled in the cell voltage range between 0.01 and 1.5 V during 300 cycles using a battery charge/discharge unit (SD8, Hokuto Denko Co). The lithiation and delithiation current densities were set at 180 mA/g for the first 5 cycles and at 1800 mA/g for the subsequent 295 cycles.

TEM micrographs were obtained using a JEOL JEM-2100 microscope with the 200 kV incident electron energy. Before the TEM observation, the C-coated Si nanopowder electrodes were washed in DEC to remove LiPF\(_6\).

Results and Discussion

Fig. 1 shows the TEM micrographs of Si nanopowder fabricated from Si swarf with the ball milling method with (Fig. 1c) and without C-coating (Figs. 1a and 1b). Si nanopowder consisted of flake-shaped aggregates with two largely different sizes, i.e., several hundred nm size (Fig. 1a) and size less than 30 nm (Fig. 1b). The selected-area electron diffraction (SAED) pattern of large nano-flake shaped Si nanopowder showed sharp spots due to a single crystal nature and dim rings due to Si crystals stacked on large nano-flakes. Fig. 1c clearly shows that aggregated Si nanopowder was uniformly covered with a 9~13 nm thick C layer. The C/Si ratio determined by weight increases after C-coating and the theoretical capacity were 14 wt% and 3190 mAh/g, respectively, assuming that the theoretical capacities of Si and graphite were 3578 mAh/g\(^{10}\) and 372 mAh/g, respectively.

Fig. 2 shows the delithiation capacities for the C-coated Si nanopowder electrode vs. the cycle number. During the initial 5 cycles, all cells were run between 0.01 and 1.5 V to cause phase transition from crystalline Si to amorphous Si. Table I summarizes the delithiation capacity at the 300th cycle and the cycle numbers for the last delithiation and lithiation equal to or higher than 1500 mAh/g. Si nanopowder anode with mass of active materials at 1.7 mg/cm\(^2\) showed the performance at the lithiation/delithiation rate of...
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Figure 1. TEM micrographs for Si nanopowder without C-coating at low magnification (a) and high magnification (b), and that with C-coating (c). The inserted diffraction pattern was observed at the area indicated by the circle.

600 mAh/g during cycles in the cell voltage range between 0.01 V and 1.5 V, which is similar to that shown in Fig. 2. Without limitation of the lithiation and delithiation capacities (no limited case) after the 6th cycle, the maximum delithiation capacity of 2160 mAh/g was obtained at the 300th cycle, but thereafter, the delithiation capacity monotonically decreased to 950 mAh/g at the 300th cycle. With limitation of the lithiation capacity at 1500 mAh/g (lithiation limited case), the lithiation capacity from the 6th cycle to the 137th cycle kept 1500 mAh/g. The delithiation capacity largely decreased from the 137th cycle and that at the 300th cycle was only 860 mAh/g, which was lower than that without limitation of the lithiation and delithiation capacities. With limitation of the delithiation capacity at 1500 mAh/g (delithiation limited case), the delithiation capacity at the 300th cycle was 1480 mAh/g. It was found that delithiation limited case was more effective to improve the cyclability than lithiation limited case. Average coulombic efficiencies in the 1st, 2~4th and 6~300th cycles were 78.2%, 97.7% and 99.3~99.1%, respectively, for all cases. These coulombic efficiencies are higher than those reported for C-coated Si nanoparticle anode.12–14 C-coating on the stacked Si nanopowder and fusion of Si nanopowder in the 1st cycle can decrease the surface area of Si nanopowder (as discussed in Fig. 3 later) and moderate side reactions.

Fig. 3 shows the TEM micrographs of C-coated Si nanopowder observed after the 100th cycle. For no limited (Fig. 3a) and delithiation limited (Fig. 3b) cases, C-coated Si nanopowder was fused, and became a wrinkle structure after the 100th cycle. It has been reported that wrinkle structures with dark frameworks are formed after a few ten cycles.10,15 An energy dispersive X-ray spectrometry (EDS) mapping shows that the frameworks are composed of high density of carbon, and they are thought to increase the electrical conductivity and suppress peeling-off of Si nanopowder.10,15 Therefore, Figs. 3a and 3b show that Si nanopowder was lithiated and delithiated homogeneously. For lithiation limited case, (Figs. 3c and 3d), a wrinkle structure was formed on most of C-coated Si nanopowder (Fig. 3c), but on some part, it wasn’t formed (Fig. 3d), probably resulting in inhomogeneous lithiation of Si nanopowder. In addition, peeling-off of crystalline Si from the C-coated Si nanopowder electrode was observed after the 100th cycle (Fig. 3d) due to the stress at the boundaries between lithiated parts and unlithiated parts of Si nanopowder.

Fig. 4 shows the cell voltage at the 1500 mAh/g delithiation capacity, i.e., charging overpotential with the current density of 1800 mAh/g in the delithiated state, vs. the cycle number. For delithiation

| Table I. Delithiation capacity measured at the 300th cycle and the last cycle numbers for delithiation and lithiation equal to or higher than 1500 mAh/g. |
| delithiation capacity at the 300th cycle | last cycle number for delithiation equal to or higher than 1500 mAh/g | last cycle number for lithiation equal to or higher than 1500 mAh/g |
| delithiation | lithiation |
| none | 1480 mAh/g | 290 | 127 |
| lithiumation | 950 mAh/g | 125 | 137 |
| | 860 mAh/g | | |
Figure 3. TEM micrographs for C-coated Si nanopowder observed after the 100th cycle without limitation of the lithiation and delithiation capacities (a), with delithiation capacities at 1500 mAh/g (b), and with limitation of the lithiation capacity at 1500 mAh/g (c and d).

limited case, the cell voltage at the 1500 mAh/g delithiation capacity decreased from ~0.65 V and kept almost constant at ~0.55 V until the ~100th cycle. This decrease in the cell voltage at the 1500 mAh/g delithiation capacity probably results from a decrease in the overvoltage because of the improved inter-particle contact during fusion of Si nanopowder. After the ~100th cycle, the cell voltage at the 1500 mAh/g delithiation capacity monotonically increased with the cycles due to destruction of inter-particle contact with Si nanopowder size change.

Fig. 4 shows the cell voltage at the 1500 mAh/g delithiation capacity, i.e., charging overpotential with the current density of 1800 mA/g in the lithiated state, vs. the cycle number. For no limited case, the cell voltage at the 1500 mAh/g delithiation capacity kept almost constant at 0.10~0.11 V until the 38th cycle, and decreased monotonically thereafter due to electrical isolation of Si nanopowder as explained later. For lithiation limited case, however, the cell voltage at the 1500 mAh/g lithiation capacity drastically decreased from 0.09 to 0.06 V between the 7th and 30th cycles, probably because of peeling-off of Si nanopowder and inhomogeneous lithiation (Figs. 3c and 3d).

Figs. 5 shows the cell voltage at the 1500 mAh/g lithiation capacity, i.e., charging overpotential with the current density of 1800 mA/g in the lithiated state, vs. the cycle number. For no limited case, the cell voltage at the 1500 mAh/g lithiation capacity kept almost constant at 0.10~0.11 V until the 38th cycle, and decreased monotonically thereafter due to electrical isolation of Si nanopowder as explained later. For lithiation limited case, however, the cell voltage at the 1500 mAh/g lithiation capacity drastically decreased from 0.09 to 0.06 V between the 7th and 30th cycles, probably because of peeling-off of Si nanopowder and inhomogeneous lithiation (Figs. 3c and 3d).

Figs. 6a and 6d show the cell voltage vs. the lithiation and delithiation capacities, respectively, at the 100th cycle for the C-coated Si nanopowder electrode for no limited case. The curve in Fig. 6b (or Fig. 6e) was divided into regions (ii) ~ (iv) (or (vi) ~ (viii)) in which difference between the cell voltage and the tangent line was less than 0.003 V of the cell voltage. The voltages of the peak minima (or maxima) of the $\frac{dQ}{dV}$ curves in Fig. 6c (or Fig. 6f) correspond to the tangential contact points.

Regions (i)~(ix) in Fig. 6 are often categorized into the five regions in which the reaction formulae of Si with Li are given in Table II and Fig. 7. In region (A), i.e., (i) ~ (iii), a-Si is lithiated to a-Li2.5Si.16 In region (B), i.e., (iv), a-Li2.5Si is lithiated further to c-Li15Si4 and a-Li2Si (2.5 < x < 3.75).16~20 An outermost c-Li15Si4 layer is formed as

Figure 4. Cell voltage at the 1500 mAh/g delithiation capacity vs. the cycle number with and without limitation of the delithiation capacity at 1500 mAh/g.

Figure 5. Cell voltage at the 1500 mAh/g lithiation capacity vs. the cycle number with and without limitation of lithiation capacity at 1500 mAh/g.
Figure 6. Lithiation (a) and delithiation (d) curves for the C-coated Si nanopowder electrode at the 100th cycle without limitation of the lithiation and delithiation capacities. Magnified view of figures (a) and (d) are shown in figures (b) and (e), respectively. The $\frac{dQ}{dV}$ curves of the curves in figures (a) and (d) are shown in figures (c) and (f), respectively. The curves in figure (b) and (e) were divided into regions (ii)$\sim$(viii) in which difference between the cell voltage and the tangent line was less than 0.003 V of the cell voltage. The voltages of the peak maxima or minima of the $\frac{dQ}{dV}$ curves correspond to the tangential contact points.

Figure 7 suggests that the internal resistance in the following three regions increases. In region (C), i.e., (v) and (vi), a-Li$_x$Si ($2.5 < x < 3.75$) is delithiated to a-Li$_2$Si, and then in region (D), i.e., (vii) and (viii), c-Li$_{15}$Si$_4$ is delithiated to a-Li$_2$Si, because of higher stability of c-Li$_{15}$Si$_4$ than a-Li$_{15}$Si$_4$. In region (E), i.e., (ix), a-Li$_2$Si and a-Li$_x$Si ($0 < x < 2$) are delithiated to a-Si. Table II shows the reaction formulae of lithiation and delithiation of Si nanopowder.

**Table II. Reaction formulae of for lithiation and delithiation of Si nanopowder.**

| Categorized region | Region   | Reactions                                                                 | References |
|--------------------|----------|--------------------------------------------------------------------------|------------|
| (A)                | (i)$\sim$(iii) | a-Si $\rightarrow$ a-Li$_{2.5}$Si                                           | 16         |
| (B)                | (iv)     | a-Li$_{2.5}$Si $\rightarrow$ c-Li$_{15}$Si$_4$ + a-Li$_{4.5}$Si ($2.5 < x < 3.75$) | 16,19      |
| (C)                | (v)$\sim$(vi) | a-Li$_{4.5}$Si ($2.5 < x < 3.75$) $\rightarrow$ a-Li$_2$Si                 | 16         |
| (D)                | (vii)$\sim$(viii) | c-Li$_{15}$Si$_4$+ a-Li$_2$Si $\rightarrow$ a-Li$_x$Si ($0 < x < 2$)       | 16,19      |
| (E)                | (ix)     | a-Li$_2$Si + a-Li$_x$Si ($0 < x < 2$) $\rightarrow$ a-Si                   | 16         |
Figure 7. Schematics of structure changes of Si nanopowder during lithiation and delithiation.

outermost c-Li\textsubscript{15}Si\textsubscript{4} layer. In region (D), the inter-particle resistance increases with a decrease in the thickness of the c-Li\textsubscript{15}Si\textsubscript{4} layer. In region (E), due to shrinkage of Si nanopowder, the inter-particle resistance increases as explained later.

Fig. 8 shows the cell voltage at the end of region (A) (figure a), and regions (C) and (D) (figure b). A lower cell voltage during lithiation and a higher cell voltage during delithiation result from a higher over-voltage due to the poor inter-particle contact. For delithiation limited case, the overvoltage was the lowest among all cases, indicating the good inter-particle contact. It should also be noted that the lithiation capacity in region (B) largely increases with a decrease in the overvoltage. For example, the overvoltage of 0.01 V decreases the lithiation capacity of 100 mAh/g (cf. Fig. 6b). Therefore, delithiation limited case is effective to increase the lithiation capacity at a high Li concentration because of the low overvoltage. For lithiation limited case, on the other hand, the overvoltage was higher than those for delithiation limited case. It was indicated that the inter-particle contact was destroyed by deep delithiation and did not recover after lithiation to 1500 mAh/g. For no limited case, the overvoltage at the end of region (A) was close to that for lithiation limited case, while those at the ends of regions (C) and (D) were close to that for lithiation limited case. These results indicate that deep lithiation can recover only a part of the inter-particle contact destroyed by deep delithiation.

Fig. 9 shows the lithiation and delithiation capacities for regions (A)∼(E). For delithiation limited case, the capacity was the highest in regions (B)∼(D). The capacities in regions (B)∼(D) increased or slightly decreased until the 100th cycle. Between the 50th and 100th cycles, the delithiation finished in region (D), indicating that Si nanopowder size changed slightly. The capacity in regions (B)∼(D) decreased after the 100th cycle, and it was compensated by the capacity in regions (A) and (E). The high capacity in regions (B)∼(D) and increase in the capacity in regions (A) and (E) after the 100th cycle can be explained by the good inter-particle contact, which agrees...
Figure 9. Lithiation and delithiation capacities in regions (A) ∼ (E) vs. the cycle number.

with the low overvoltage (cf. Fig. 8) and homogeneous lithiation and delithiation of Si nanopowder, leading to a homogeneous wrinkle structure (Fig. 3b). For no limited case, the capacities in all the regions decreased with the cycles after the 50th cycle due to electrical isolation of Si nanopowder. For lithiation limited case, the capacities in all the regions decreased with the cycles except for those in regions (B) and (C) until the 150th cycles. It is suggested that electrical isolation and peeling-off of Si nanopowder in the 7th ∼ 30th cycles (Figs. 3c, 3d and 5) led to inhomogeneous deep lithiation of Si nanopowder in region (B), causing electrical isolation of Si nanopowder occurring with the cycles.

The mechanism of structural changes of Si nanopowder by lithiation and delithiation capacities is summarized in Fig. 7. The best cyclability was achieved for delithiation limited case. The overvoltage was the lowest (Fig. 8) because the good inter-particle contact remained for long cycles. The lowest overvoltage is explained by the model that an energetically stable outermost c-Li15Si4 layer is formed in regions (B)∼(D) (Fig. 7) and it suppresses shrinkage of the outermost layer. On the other hand, for lithiation limited case, a part of Si nanopowder is isolated in the C-coated Si nanopowder electrode, peeled off from the C-coated Si nanopowder electrode (Fig. 3d) and fused only locally during the 7 ∼ 30th cycles (Fig. 5). The overvoltage further increases with the cycles (Figs. 4 and 8) because lithiation and delithiation in regions (A') and (E) drastically change the size of Si nanopowder (Fig. 7). For no limited case, the overvoltage is relatively high during lithiation, and relatively low during delithiation (Fig. 8). A part of destroyed inter-particle contact during delithiation recovers during deep lithiation (Fig. 7B), but the
lithiation capacity decreases with the cycles due to unrecovered electrical isolation of Si nanopowder (Figs. 7E−7B').

Conclusions

Si nanopowder electrodes for LIBs are fabricated from Si swarf using the ball milling method, and the effect of limitation of the delithiation capacity on the cyclability is investigated. The following results and conclusion have been obtained from the present study:

1) Si nanopowder fabricated by ball milling is mainly composed of aggregates of Si flakes with two largely different sizes, i.e., several hundred nm size and size less than 30 nm.

2) Limitation of delithiation capacity at 1500 mAh/g results in the best cyclability. The delithiation capacity keeps constant at 1500 mAh/g until the 290th cycle, and slightly decreases to 1480 mAh/g at the 300th cycle.

3) The overvoltage for delithiation limited case is lower than that for lithiation limited case. The low overvoltage and good cyclability result from suppression of electrical isolation of Si nanopowder because of limited shrinkage of Si nanopowder in the high Li concentration regions.

4) With limitation of lithiation capacity at 1500 mAh/g, the delithiation capacity keeps 1470 mAh/g until the 137th cycle, and decreases to 860 mAh/g at the 300th cycle. The overvoltage during lithiation is close to that for lithiation limited case, while the overvoltage during delithiation is close to that for delithiation limited case. Deep lithiation recovers a part of the inter-particle contact destroyed during deep delithiation.

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