Adsorbed Water on Nano-Silicon Powder and Its Effects on Charge and Discharge Characteristics as Anode in Lithium-Ion Batteries

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The amounts of adsorbed water on several kinds of carbon and silicon materials including Si nano-flake powder (Si LeafPowder, Si-LP) were determined at 250°C. It was found that nano-sized Si materials adsorb a large amount of water even after being dried at 120°C because of the hydrophilicity of the surface and the high specific surface area. The adsorbed water on Si-LP can be removed, but not completely, after drying at a 180°C. The charge and discharge characteristics of Si-LP, especially the initial irreversible capacity and the coulombic efficiencies upon repeated cycling, were significantly improved by removal of the adsorbed water at 180°C. The 180°C-dried sample also suppressed gas evolution during the initial charging and discharging cycle. From the results of gas analysis, it was found that gases evolved from the Si-LP electrodes were mainly H2 and CO2. From the results of charge and discharge tests and gas analysis, the effect of the adsorbed water on the irreversible decomposition of the electrolyte solution was discussed.

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Electrochemical Li alloying and de-alloying reactions of Si anodes in lithium-ion batteries (LIBs) are accompanied by large volume changes, which results in fracture and pulverization of Si particles and leads to poor cyclability by a loss of electrical contacts. To reduce the physical stress originating from the large volume changes and to improve the poor cycleability, nano-sized silicon anodes of different morphologies have been proposed.1-6 We have also developed Si LeafPowder (Si-LP, OIKE & Co., Ltd.), which is an amorphous Si nano-flake powder with a thickness of 100 nm, and have reported that it exhibited a good cyclability as an anode in LIBs.7-9

Another serious problem of nano-sized Si anodes, including Si-LP, is the substantial irreversibility owing to severe decomposition of the electrolyte solution compared with that for graphite anodes. The resulting large irreversible capacity in the initial cycles and continuous low coulombic efficiencies in repeated cycling remain to be solved for practical use. In previous studies, we have developed Li pre-doping methods, which effectively compensated the large irreversible capacity in the initial cycles.10,11 However, the irreversible decomposition of the electrolyte solution continued ceaselessly upon repeated cycling and hence the coulombic efficiency was hovered at around 98-99% and did not reach 100% even after repeated cycles. The continuous irreversibility originates from the decomposition of the electrolyte solution and leads to the growth of solid electrolyte interface (SEI) on the surface of Si anodes. It is widely known that a trace amount of water in a cell causes many problems in SEI formation and decomposition on graphite anodes.12-16 The moisture generates H2 and LiOH, and decomposes LiPF6 into LiF, HF and POF3, which deteriorates SEI and accelerates the decomposition of electrolyte solution.

The surface of Si is more hydrophilic than that of graphite, and hence water is more strongly adsorbed on Si surface. However there have been no reports on the effects of adsorbed water on the charge and discharge characteristics of Si anodes. In the present study, the amounts of adsorbed water on Si nano-sized powder samples and electrodes were evaluated using a moisture vaporizing system coupled with a Karl-Fischer titration system. Charge and discharge characteristics of Si-LP electrodes were investigated after being dried at different temperatures, and the effects of the adsorbed water on the irreversible decomposition of the electrolyte solution was discussed based on the analytical results of the gas evolved during charging and discharging.

Experimental

The amorphous nano-flake powder (Si LeafPowder, Si-LP, OIKE & Co., Ltd.) was prepared by an electron beam evaporation method. The thickness and the average in-plane size of Si-LP were 100 nm and 4 μm, respectively. The specific surface area of Si-LP was 20.7 m2 g−1. For comparison, natural graphite powder (Alfa Aesar, < 200 mesh, 3.8 m2 g−1), acetylene black powder (DENKA, HS-100, 36 m2 g−1), carbon black powder (TIMCAL, Super P, 74 m2 g−1), micro-sized Si powder (Wako Pure Chemical Industries, 99.9%, 0.6 m2 g−1) and nano-sized Si powder (Aldrich, < 100 nm, > 98%, 35.8 m2 g−1).

The amount of water adsorbed on these powder samples was evaluated using a moisture vaporizing system (Kyoto Electronics Manufacturing, ADP-611) coupled with a Karl-Fischer titration system (Kyoto Electronics Manufacturing, MKC-610). The powder sample (100–150 mg) was set in a glass tube, and was pre-dried at 120°C for 1 h under N2 flow at 150 mL/min. The glass tube was then transferred to an electric oven pre-heated at 250°C for 40 min under N2 flow. The effluent gas was bubbled in the solution for the Karl-Fischer system to monitor continuously the moisture in the effluent gas. The water collected for 40 min were integrated to estimate the adsorbed water on the sample. In some experiments, the adsorbed water was measured for Si-LP composite electrodes described below in a similar manner.

Si-LP composite electrodes for charge and discharge measurements were prepared with a doctor-blade method. A slurry was prepared by mixing Si-LP, Ketjen Black (KB) as a conductor and carboxymethyl cellulose sodium salt (NaCMC) as a binder with a weight ratio of 83.3:5.6:11.1. The Si-LP electrode was fabricated by coating the slurry on a copper foil (18 μm) as a current collector. The loading of the active material and the electrode density were typically 0.8 mg cm−2 and 1.6 g cm−3, respectively. Electrochemical measurements were carried out using CR2031 coin-type two-electrode half-cells. Prior to cell assembly, the Si-LP electrode was dried at 120 or 180°C for 8 h under vacuum of 3 Pa, and subsequently transferred to an Ar glove box without any atmospheric exposure. Test cells were assembled with the dried Si-LP electrode, a separator (Celgard 2400) and a Li foil counter electrode. The electrolyte solution was 1 M LiPF6 / EC+DEC (3:7 by volume). The charge and discharge characteristics were measured at 30°C in the constant current-constant voltage (CC-CC) mode between 1.5 and 0.02 V at 1/10 C (1 C = 3.580 mA h g−1) using a battery test system (HOKUTO DENKO, HJ1001SMB). Gas generation from the Si-LP electrodes dried at 120 and 180°C for 8 h under a vacuum of 3 Pa was measured in the first charge and discharge.
specific surface areas are also shown in Fig. 2. The values of the adsorbed water on (a) Si and (b) carbon fell on clear two lines. The adsorbed water on Si powder drastically increased with an increase in specific surface area. In contrast, the adsorbed water on carbon powder depended less on the specific surface area. These results can be explained by a difference in the affinity of the surface between Si and carbon to water; that is, the carbon surface is hydrophobic, while Si surface is hydrophilic. These results also suggest that the water molecules are strongly adsorbed on the surface of nano-sized Si materials and cannot be removed in a typical drying process at around 100°C, which is commonly employed as an electrode pre-treatment before cell assembling. Si-LP has a specific surface area (20.7 m² g⁻¹) lower than nano-sized Si (35.8 m² g⁻¹) because of its unique nano-flake shape, and hence the adsorbed water was lower than nano-sized Si powder.

For electrode preparation, CMC (or CMC and styrene-butadiene rubber (SBR) in industry), which is also hydrophilic, is commonly used as a binder for graphite and Si electrodes. The graphite and Si-LP electrodes prepared with a CMC binder were dried at 120°C and 180°C for 8 h under vacuum of 3 Pa before water content measurements. The adsorbed water on as-prepared and 120°C-dried samples was measured in a similar manner, and the results are summarized in Table 1. The adsorbed water of the graphite electrode drastically decreased from 2,852 to 974 ppm after being dried at 120°C. In contrast, the adsorbed water of the Si-LP electrode was surprisingly high (ca. 20,000 ppm) and changed little after being dried at 120°C. The water content of the Si-LP electrode decreased to 4,930 ppm after being dried at 120°C; however, it was five times higher than that of the graphite electrode after being dried at 120°C. Unfortunately the drying temperature of 180°C was practically the highest in the present study because the thermal degradation of CMC begins at around 200°C.

### Results and Discussion

**Adsorbed water on graphite and Si powders.**—Both anode and cathode electrodes are usually dried at ~100°C before being assembled into a cell. The graphite, micro-sized Si, nano-sized Si, and Si-LP particles were dried at 120°C for 1 h under N₂ flow, and the amounts of adsorbed water on these samples were measured by heating them at 250°C for 40 min. The variations of water released from the four samples (in ppm of sample mass) with time are shown in Fig. 1. The amount of released water was very small for graphite and micro-sized Si powder; however, a large amount of water was released immediately after heating at 250°C for nano-sized Si and Si-LP powder. The amount of released water declined with time, but did not decrease completely to zero even at 40 min. The cumulative amount of released water at 250°C for 40 min can be considered as adsorbed water on these samples after dried at 120°C, though a small amount of adsorbed water was present for nano-sized Si and Si-LP powder after 40 min.

Figure 2 shows the relationships between the content of adsorbed water and the specific surface areas of the samples. The results for a few kinds of commercially available carbon powders of different specific surface areas are also shown in Fig. 2. The values of the adsorbed water on (a) Si and (b) carbon fell on clear two lines. The adsorbed water on Si powder drastically increased with an increase in specific surface area. In contrast, the adsorbed water on carbon powder depended less on the specific surface area. These results can be explained by a difference in the affinity of the surface between Si and carbon to water; that is, the carbon surface is hydrophobic, while Si surface is hydrophilic. These results also suggest that the water molecules are strongly adsorbed on the surface of nano-sized Si materials and cannot be removed in a typical drying process at around 100°C, which is commonly employed as an electrode pre-treatment before cell assembling. Si-LP has a specific surface area (20.7 m² g⁻¹) lower than nano-sized Si (35.8 m² g⁻¹) because of its unique nano-flake shape, and hence the adsorbed water was lower than nano-sized Si powder.

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### Charge and discharge characteristics of dried Si-LP electrodes.—The Si-LP electrodes were dried at 120°C and 180°C under vacuum for 8 h, and their charge and discharge characteristics were measured at a C/6 rate in 1 M LiPF₆/ EC+DEC (3:7). The charge and discharge curves, and variations of the discharge capacity and coulombic efficiency with cycle number are shown in Figs. 3 and 4, respectively. Both Si-LP electrodes showed charge and discharge curves typical of amorphous Si anodes.17,18 Both electrodes exhibited large irreversible capacity (Qir) in the first cycle; however, Qir of 180°C-dried Si-LP (790 mAh g⁻¹) was smaller than that of 120°C-dried one (1,160 mAh g⁻¹), which resulted in a higher coulombic efficiency (80.2%) for the former. On the other hand, the discharge capacity of the 180°C-dried electrode was 2,910 mAh g⁻¹ in the first cycle, which was slightly higher than that of the 120°C-dried one (2,690 mAh g⁻¹). After a rapid drop during the initial 4 cycles, the discharge capacity was kept stably high (2,200–2,300 mAh g⁻¹) to the 30th cycle for both electrodes (Fig. 4a). The effect of adsorbed water on coulombic efficiency was surprising. The coulombic efficiency of the 180°C-dried electrode increased to 90.2% in the second cycle and 97.7% in the third cycle, and reached almost 100% (99.7%) at the tenth cycle, whereas that of 120°C-dried electrode reached 97.0% at the tenth cycle (Fig. 4b) and kept at around 97% to the thirtieth cycle. It is clear that removal of adsorbed water at 180°C effectively suppressed the decomposition of the electrolyte solution, which gave very high coulombic efficiencies of nearly 100% upon repeated cycling.

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**Figure 1.** Variation of water released from (a, blue) nano-sized Si, (b, red) Si-LP, (c, azure) micro-sized Si and (d, gray) graphite particles at 250°C for 40 min under N₂ flow. The samples are pre-dried at 120°C for 1 h. Released water was measured by Karl Fischer titration.

**Figure 2.** Relationships between the content of adsorbed water and the specific surface areas of various (a) Si and (b) carbon powder materials.

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**Table 1.** Water contents for graphite and as-prepared, 120°C-dried and 180°C-dried Si-LP electrodes measured at 250°C for 40 min.*

| Graphite | Si-LP |
|----------|-------|
| Pre-dried temperature / °C | 120 | 120 | 180 |
| Water content / ppm | 2,852 | 974 | 20,357 | 21,029 | 4,930 |

*Measured by a Karl-Fischer titration method after pre-drying at 120°C for 1 hour. The electrodes pre-dried at 120°C and 180°C for 8 hours under vacuum of 3 Pa.
Gas analysis during charging and discharging from Si-LP electrodes.—Variations of gas volume evolved from 120°C- and 180°C-dried Si-LP electrodes during the first charge and discharge cycle are shown in Fig. 5. Their charge and discharge curves are superposed in Fig. 5. The gas generated mainly in the charging process and the amount of gas generation from the 180°C-dried electrode was reduced by approximately half from the 120°C-dried electrode. This fact clearly indicates that adsorbed water was involved in the gas evolution processes. The results for the gas compositional analysis after the first charge and discharge cycle are summarized in Table II. The main components of the evolved gases from Si-LP electrodes and lithium metal electrodes were H₂ and CO₂ with minor hydrocarbon components. Here again the amounts of H₂ and CO₂ were reduced by raising the drying temperature from 120 to 180°C.

Reductive decomposition of the EC+DEC electrolyte solutions on lithium metal and graphite anodes have been intensively studied, and the following reactions have been proposed[19–22]:

\[
\text{EC} + \text{Li}^+ + e^- \rightarrow \text{CH}_3\text{OCO}_2\text{Li} + \bullet \text{CH}_3 \quad [5]
\]

\[
\text{DEC} + 2\text{Li}^+ + 2e^- \rightarrow \text{CH}_3\text{CH}_2\text{OLi} + \text{CO} \uparrow \quad [6]
\]

Reactions 1, 2, 4, and 6 are accompanied by gas evolution of CO and C₂H₄. However, in this study, CO and C₂H₄ evolution were hardly observed from the 120°C- and 180°C-dried Si-LP electrode. This fact

![Figure 3](image-url) Charge and discharge curves of Si-LP electrodes after dried at (a) 120 and (b) 180°C for 8 h under vacuum of 3 Pa in 1 M LiPF₆/EC+DEC (3:7 by volume).

![Figure 4](image-url) Variations of (a) discharge capacity and (b) coulombic efficiency of Si-LP electrodes after dried at (in black) 120°C and (in red) 180°C for 8 h under vacuum of 3 Pa in 1 M LiPF₆/EC+DEC (3:7 by volume).

![Figure 5](image-url) Variations of gas volume evolved from (a) 120°C and (b) 180°C-dried Si-LP electrodes during the 1ˢᵗ charge and discharge cycle in 1 M LiPF₆/EC+DEC (3:7 by volume). Respective charge and discharge curves are superposed in the figure.
implies that these gases were not generated simply by solvent reduction in the present study. Aurbach et al. reported that reaction products between LiPF₆ and trace impurities (H₂O and HF) in electrolyte solution deteriorates SEI and generates CO₂.12,13,21

Based on these reactions reported in the literature,12-16,19-22 the mechanisms for H₂ and CO₂ generation observed in the present study are considered to be

\[ \text{H}_2\text{O} + \text{Si} \rightarrow \text{SiO}_2 + \text{H}_2 \uparrow \]  
[7]

\[ \text{H}_2\text{O} + \text{Li}^+ + e^- \rightarrow \text{LiOH} + 1/2\text{H}_2 \uparrow \]  
[8]

\[ \text{LiOH} + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{O} + 1/2\text{H}_2 \uparrow \]  
[9]

\[ \text{H}_2\text{O} + (\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow \text{Li}_2\text{CO}_3 + (\text{CH}_2\text{OH})_2 + \text{CO}_2 \uparrow \]  
[10]

\[ \text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_3 \]  
[11]

\[ \text{PF}_5 + \text{Li}_2\text{CO}_3 \rightarrow 2\text{LiF} + \text{POF}_3 + \text{CO}_2 \uparrow \]  
[12]

\[ \text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + 2\text{HF} + \text{POF}_3 \]  
[13]

\[ \text{HF} + (\text{CH}_2\text{OCO}_2\text{Li})_2 + \text{Li}_2\text{CO}_3 \rightarrow \text{LiF} + (\text{CH}_2\text{OCO}_2\text{H})_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow \]  
[14]

\[ \text{HF} + \text{CH}_3\text{CO}_2\text{OLi} \rightarrow \text{LiF} + \text{CH}_3\text{OH} + \text{CO}_2 \uparrow \]  
[15]

H₂ is generated via direct chemical and electrochemical reductions of H₂O as shown in Reactions 7-9, and CO₂ is generated via a reaction of H₂O with lithium alky carbonate (CH₂OCO₂Li₂), which is a main component of SEI, as shown in Reaction 10. Moreover, PF₅, which is formed from LiPF₆, reacts with Li₂CO₃ to generate CO₂ as shown in Reactions 11 and 12. In addition, HF formed by a reaction of H₂O and LiPF₆ plays a role in assisting in CO₂ generation as shown in Reactions 13-15. Note that the reaction of HF with lithium alkyl carbonate (CH₂OCO₂Li₂) not only generates CO₂ gas, but also re-generates H₂O (Reaction 14). Hence H₂O may works as a shuttle and continuously deteriorates SEI with gas generation (H₂ and CO₂), by which the decomposition of the electrolyte solution continues ceaselessly. As mentioned earlier, a large amount of water remains on the surface of nano-sized Si materials after dried at around 100°C because of the hydrophilicity of the surface and the high specific surface area. It is therefore important to remove adsorbed water as much as possible for suppressing the decomposition of the electrolyte solution and improving the coulombic efficiency for nano-sized Si materials.

**Table II. Gas compositions after first charge and discharge cycle for 120°C-dried and 180°C-dried Si-LP electrodes in 1 M LiPF₆/EC+DEC (3:7 by volume).**

|     | H₂  | CO  | CO₂ | CH₄ | C₂H₄ | C₂H₆ |
|-----|-----|-----|-----|-----|------|------|
| 120°C dried / 10⁻³ mL | 1.08 | 0.00 | 1.08 | 0.00 | 0.04 | 0.00 |
| 180°C-dried / 10⁻³ mL | 0.67 | 0.00 | 0.41 | 0.05 | 0.00 | 0.00 |

**Conclusions**

The results in the present study revealed that nano-sized Si materials strongly adsorb a large amount of water even after being dried at ~100°C because of the hydrophilicity of the surface and the high specific surface area. The adsorbed water on Si-LP can be removed, but not completely, after drying at a higher temperature of 180°C. The charge and discharge characteristics of Si-LP, especially the initial irreversible capacity and the coulombic efficiencies upon repeated cycling, were improved significantly by removal of the adsorbed water at 180°C. The 180°C-dried sample also suppressed gas evolution during the initial charging and discharging cycle. From the results of gas analysis, it was found that gases evolved from the Si-LP electrodes were mainly H₂ and CO₂, which might be produced via the direct reactions of adsorbed water and the deterioration of SEI by water, respectively. All of these results suggest that removal of the adsorbed water as much as possible is effective for suppressing the decomposition of the electrolyte solution and improving the coulombic efficiency for nano-sized Si materials. Unfortunately, the drying temperature of 180°C was the highest practical temperature in the present study because of the thermal degradation of the CMC binder. The use of a binder with a high thermal durability may be preferable for removing the adsorbed water completely.

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