Investigation of the irreversible reaction mechanism and the reactive trigger on SiO anode material for lithium-ion battery

Hideyuki YAMAMURA, Kunihiro NOBUHARA, Shinji NAKANISHI, Hideki IBA and Shigeto OKADA

Battery Research Division, Higashifuuji Technical Center, Toyota Motor Corporation, Susono, Shizuoka 410–1193
*Institute of Advanced Material Study, Kyushu University, 6–1 Kasuga Koen, Kasuga, Fukuoka 816–8500

To clarify the reaction mechanism of SiO anode, the chemical and the electrochemical reactions of SiO and SiO2 with Li-metal and first principles calculations were investigated. In the chemical reactions, SiO and amorphous SiO2 formed lithium silicide (Li4Si) and lithium silicate (Li2SiO3, Li4SiO4) by reacting with Li. In the electrochemical reactions, crystalline SiO2 did not react with Li though amorphous SiO2 did do so. These results indicated that both Si area and amorphous SiO2 area in SiO matrix play an important part in SiO charge. Li easily. This finding was also confirmed by first principles calculations using VASP code.

Key-words : SiO, Irreversible reaction, Amorphous and crystalline SiO2, Anode material, Lithium-ion battery

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have a larger energy density than other secondary batteries, and are therefore used as power sources for various types of portable equipment (e.g., laptop computers, cellular phones) and are expected to be applied to electric vehicles (EVs) and hybrid electric vehicles (HEVs) as well. However, commercial LIBs have insufficient energy density to satisfy the demands for long distance driving. In recent years, many researchers have studied LIBs in an effort to increase their energy density. Graphite has commonly been used as an anode material, because the cycle performance is better than that of graphite. Nevertheless, the irreversibility is as high as 25%.12) However, the theoretical capacity is restricted to 372 mAh g\(^{-1}\). On the other hand, alloy-type anode active materials have a larger capacity than that of graphite. Among them, silicon is regarded as one of the most attractive anode active materials for LIB, because the theoretical capacity of Li4Si (4199 mAh g\(^{-1}\)) is 10 times larger than that of graphite.13) However, the cyclability of Si is poor, owing to the drastic volume change during the charge-discharge process.13) Recently, silicon monoxide (SiO) consisting of nano-sized Si and amorphous SiO2 matrix has become attractive as a new anode material, because the cycle performance is better than that of pure Si and the theoretical capacity (2100 mAh g\(^{-1}\)) is 5 times larger than that of graphite.13) Amorphous SiO2 component in SiO matrix may release a large volume change of Si component effectively during charge (Li-insertion)-discharge (Li-extraction) cycling.9)–12) Nevertheless, the irreversibility is as high as 25% of the first charge capacity, because amorphous SiO2 component in SiO matrix irreversibly changes to lithium silicate.13)–16) According to Yamada’s presentation,17) the reaction mechanism of SiO can be summarized as follows:

\[
\begin{align*}
4\text{SiO} + 17.2\text{Li} & \rightarrow 3\text{Li}_{4.4}\text{Si} + \text{Li}_4\text{SiO}_4 & (1) \\
\text{Li}_4\text{Si}_2\text{O}_4 & \text{is the reaction product of amorphous SiO}_2\text{component in SiO matrix with Li at the first charge process. Some of the Si-O bonds in SiO}_2\text{are broken by Li, but the other Si-O bonds still remain to form the Li}_2\text{SiO}_4. Based on X-ray photoelectron spectroscopy (XPS), Miyachi et al. concluded that lithium silicate, formed after the first charge, can be partially delithiated on the next discharge process.15)–20) This means that a reversible part and an irreversible part coexist in the amorphous silicon oxide matrix. In addition, Sun et al. reported that crystalline SiO2 (Tridemite; ICDD #00-089-3608) deposited by RF-sputtering became Li2Si2O5 after cycling, and Tridemite SiO2 was possible to charge-discharge with Li reversibly.21) In this instance, the Si-O bonds in silicon oxide do not seem to be broken by Li irreversibly.

In this study, we investigated the activity of silicon oxide against Li by chemical and electrochemical reactions. In addition, the formation energy was calculated by first principles calculations to confirm the possibility of the reaction of silicon dioxide and Li.

2. Experimental

Heat-treated SiO at 800°C, Li4SiO4 (Alfa Aesar; 99.9%), and amorphous and crystalline SiO2 (Kojyundo Chemical Laboratory Co., Ltd.) were characterized by X-ray diffraction (XRD) (Rigaku RINT-2000 diffractometer) with Cu/K\(\alpha\) radiation at a scan rate of 10° min\(^{-1}\) over a 2\(\theta\) range from 10 to 80°.

The chemical reactions: Each SiO2 was reacted with Li-metal (Honjyo Metal Co., Ltd.) in a crucible which was made from iron in order not to react with Li under an argon atmosphere. Figure 1 shows an image of the experimental setup used for the chemical reactions. In a glove box filled with argon gas, each silicate was enclosed in a bag-shaped Li-metal sheet (ca. 2 cm \times 3 cm) and set in an electric furnace at 200°C for 10 min. The structures of the reaction products were characterized by XRD under an argon atmosphere.

The electrochemical reactions: Slurry for the working electrode was prepared by mixing with the crystalline and amorphous SiO2 as an active material with acetylene black as an electronic conductor and polyimide as a binder in a weight ratio of 76.5:13.5:10 in N-methylpyrrolidone (NMP) solution. Then, the slurry was coated onto a Cu foil (15 \(\mu\)m in thickness), pressed,
and dried. The working electrodes were packed in a 2032 type coin cell (Hohsen Corp.) with separator, lithium counter electrode, and spring that induced a packing pressure on both electrodes to reduce the internal impedance. The electrolyte was 1 M LiPF$_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 3:7. The half cells were assembled in an argon-filled glove box and the electrochemical reaction was measured in the voltage range from 0.01 to 1.2 V vs. Li$^+$/Li.

First principles calculations: The total energies of all the compounds under investigation were calculated using the Projector Augmented Wave (PAW) method as implemented in the Vienna ab initio Simulation Package (VASP). The exchange and correlation energies were approximated in the Generalized Gradient Approximation (GGA). The energy cut-off for the plane wave basis set was kept fixed at a constant value of 2548 and 1791 mAh g$^{-1}$ for amorphous SiO$_2$ and Li$_4$SiO$_4$ after the chemical reaction with Li. Furthermore, Li-Si alloy was also produced by the reaction of Si in SiO with Li. Figure 3 shows XRD profiles of silicon dioxide and reaction products after the chemical reactions. Figure 3(a) shows amorphous SiO$_2$ and the reaction products. Before the reaction, XRD profile had no clear diffraction peaks to indicate the crystal structures. After the reaction with Li, sharp peaks belonging to Li$_2$Si alloy and lithium silicates such as Li$_2$SiO$_3$ and Li$_4$SiO$_4$ appeared. This result indicates an irreversible reaction of SiO similar to that of Eq. (1). Li$_2$SiO$_4$ must be formed by a reaction of amorphous SiO$_2$ component in SiO matrix with Li. Figure 3(b) shows crystalline SiO$_2$ and the reaction products. Crystalline SiO$_2$ was a quartz structure with P3121 space group, and the original structure was maintained even after the reaction with Li. Figure 4 shows Li$_2$SiO$_3$ before and after the reaction. Li$_2$SiO$_3$ did not react with Li. Based on the fact that crystalline SiO$_2$ and Li$_2$SiO$_3$ did not react with Li, chemically, we can conclude that the Si-O bonds in the SiO tetrahedrons, which are basically units in silicon dioxide, were not easily broken by Li.

3. Results and discussion

3.1 The chemical reactions

Figure 2 shows XRD patterns of heat treated SiO at 800°C before and after the chemical reaction with Li. Figure 6 shows charge–discharge curves of (a) amorphous SiO$_2$ and (b) crystalline SiO$_2$. A voltage plateau was observed at 0.05 V vs. Li/Li$^+$, as shown in Fig. 6(a). This plateau indicated the reaction of amorphous SiO$_2$ with Li. The first charge and the next discharge capacity of amorphous SiO$_2$ were 2548 and 1791 mAh g$^{-1}$, respectively. Although amorphous SiO$_2$ can reversibly react with Li, crystall-
line SiO₂ cannot react with Li, as shown in Fig. 6(b). This result is consistent with the results of the chemical reactions with Li. If the structure of silicon oxide was amorphous, it would be able to react with Li, chemically and electrochemically. Table 2 shows the estimated capacity of SiO compared with the experimental results of the charge–discharge tests. In this estimation, we used the following data: the capacity of Si was 4215 and 3962 mAh g⁻¹ for Li-insertion and Li-extraction, respectively. And the capacity of amorphous SiO₂ was 2013 and 950 mAh g⁻¹ for Li-insertion and Li-extraction, respectively. If SiO consisted of Si and amorphous SiO₂, 0.319 g Si and 0.681 g amorphous SiO₂ must have been included in 1 g SiO. In this calculation, SiO (Si + amorphous SiO₂) should have 2718 mAh g⁻¹ for Li-

Table 2. Estimated the capacity of SiO from the results of electrochemical tests and compared with SiO measurement capacity

<table>
<thead>
<tr>
<th>Weight (g)</th>
<th>Li-insertion capacity (mAh g⁻¹)</th>
<th>Li-extraction capacity (mAh g⁻¹)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1</td>
<td>4215</td>
<td>3962</td>
</tr>
<tr>
<td>Amorphous SiO₂</td>
<td>1</td>
<td>2013</td>
<td>950</td>
</tr>
<tr>
<td>SiO</td>
<td>1</td>
<td>2548</td>
<td>1791</td>
</tr>
<tr>
<td>Si + amorphous SiO₂</td>
<td>0.319 + 0.681</td>
<td>2718</td>
<td>1911</td>
</tr>
</tbody>
</table>

Fig. 3. XRD patterns of (a) amorphous and (b) crystalline SiO₂ before and after the chemical reactions with Li.

Fig. 4. XRD patterns of Li₄SiO₄ before and after the chemical reactions with Li.

Fig. 5. (Color online) The initial charge–discharge profiles of SiO in lithium cells at 0.025 mA cm⁻² in voltage range from 0.01–1.2 V at 60°C.

Fig. 6. (Color online) The charge–discharge profiles of (a) amorphous and (b) crystalline SiO₂ in lithium cells at 0.025 mA cm⁻² in voltage range from 0.01–1.2 V at 60°C.
insertion (Si capacity, 1348 mAh g⁻¹; amorphous SiO₂ capacity, 1370 mAh g⁻¹) and 1911 mAh g⁻¹ for Li-extraction (Si capacity, 1264 mAh g⁻¹; amorphous SiO₂ capacity, 647 mAh g⁻¹). On the other hand, the actual capacities of SiO in the charge-discharge tests were 2548 mAh g⁻¹ for Li-insertion and 1791 mAh g⁻¹ for Li-extraction, respectively. These results were close to the calculated values. This means that both nano-sized Si and amorphous SiO₂ show reactivity against Li. However, crystalline SiO₂ did not show any voltage plateau and specific capacity (100 mAh g⁻¹) capacity in Fig. 6(b) was the capacity for acetylene black) on Li-insertion process, despite the use of conditions identical to those in Fig. 6(a). This result of the electrochemical reactions corresponds with the chemical reactions. It suggests that Si–O bonds in the SiO₄ tetrahedrons could not be broken by Li, not only chemically, but also electrochemically.

Figure 7 shows that Li can not removed from Li₄SiO₄ by charging. Li₄SiO₄ is produced by the reaction of amorphous SiO₂ with Li. However, crystalline SiO₂ did not show any voltage plateau and specific capacity (100 mAh g⁻¹) capacity in Fig. 6(b) was the capacity for acetylene black) on Li-insertion process, despite the use of conditions identical to those in Fig. 6(a). This result of the electrochemical reactions corresponds with the chemical reactions. It suggests that Si–O bonds in the SiO₄ tetrahedrons could not be broken by Li, not only chemically, but also electrochemically.

Figure 7 shows that Li can not removed from Li₄SiO₄ by charging. Li₄SiO₄ is produced by the reaction of amorphous SiO₂ with Li and it is chemically stable and electrochemically inactive in the matrix. These results suggest that the origin of the irreversibility of silicate anodes is Li₄SiO₄.

Fig. 7. (Color online) The charge-discharge profiles of Li₄SiO₄ in lithium cells at 0.025 mA cm⁻² in voltage range from 3.0–14.0 V at 60°C.

### 3.3 First principles calculations

The lattice constant of the calculated structure of SiO₂ with P3121 space group was \( a = b = 4.91300, c = 5.40520 \), which consistent with the reference value \( a = b = 4.921, c = 5.4163 \) well.\(^{25}\) Figure 8 shows the possible empty sites in crystalline SiO₂, which belong to the quartz structure with P3121 space group. These were calculated in SiO₂ basic units using the find empty space tool of MedeA.\(^{25}\) In crystalline SiO₂, two kinds of the high symmetrical empty sites shown in Figs. 8(i) and 8(ii) were existed, and the formation energy (\( E_f \)) of Li-insertion was calculated for each site by Eq. (2).

\[
E_f = E_{tot}(\text{LiSi}_3\text{O}_6) - E_{tot}(\text{Si}_3\text{O}_6) - \mu_\text{Li} \tag{2}
\]

\( E_{tot}(\text{LiSi}_3\text{O}_6) \) is the total energy of the electron state that inserts Li into the empty sites of Si₃O₆. \( E_{tot}(\text{Si}_3\text{O}_6) \) is the total energy of the electron state of Si₃O₆, and \( \mu_\text{Li} \) is the chemical potential of Li. The formation energy was an endothermic reaction (positive value) in all case, and it was indicated that crystalline SiO₂ can not react with Li.

It is known that the difference of amorphous and crystalline SiO₂ is the ring structure (Si–O–Si valence angle) and the Si–O–Si bond length.\(^{26,27}\) While crystalline SiO₂ formed only with a six-membered ring, amorphous SiO₂ formed with 2, 3, 4, 6 and 8-membered ring of the SiO₄ tetrahedrons and the distortion energy of these ring structure is different.\(^{28}\) It was calculated the formation energy when Li was in 2, 3, 4 and 6-membered ring, but it was an endothermic reaction in all cases. It shows that the activity of Li and the ring structure (Si–O–Si valence angle) was not related. In Si–O–Si bond length, a decrease in the Si–O–Si valence angle by process of forming the ring structure brings the change in Si–O bond length, and the polarized Oxygen to \( \delta^- \) and the polarized Silicon to \( \delta^+ \) existed.\(^{27}\) However, it is not easy to calculate these electronic structure of the amorphous material. Therefore the formation energy of Li insertion was calculated in the case of Si⁺ and O⁻ by Eq. (3).

\[
E_f = E_{tot}(\text{Si}_3\text{O}_6) - E_{tot}(\text{Si}_3\text{O}_6) - \mu_\text{Li} \tag{3}
\]

\( E_{tot}(\text{Si}_3\text{O}_6) \) is the formation energy in the case of Si⁺ and O⁻ by Eq. (3).

![The formation energy](image)

**Fig. 8.** (Color online) Crystal structure of SiO₂ drawn by VESTA.\(^{28}\) Empty sites in crystalline SiO₂ and the calculated formation energy by Eq. (2) when Li was in (i) or (ii).
Li is the distorted SiO$_4$ tetrahedrons. Before, and the reactive trigger on amorphous silicon oxide and amorphous silicon oxide had the large capacity as discussed alloy is formed via the charge transfer. Therefore, we thought that reduced to Si in the electrochemical reaction. In addition, Si

When a vacancy of Si for making O$^-$ or O for making Si$^+$ exists in crystalline SiO$_2$, the values of (x,y) in Eq. (3) are (1,0) and (0,1). $E_{el}(LiSi_{1-x}O_{x-y})$ is the total energy of the electron state that inserts Li into the vacant sites of LiSi$_{1-x}$O$_{x-y}$, and $E_{el}(Si_{1-x}O_{y-x})$ is the total energy of the electron state of Si$_{1-x}$O$_{y-x}$. Figure 9 shows the structure of crystalline SiO$_2$ with the vacancy site of (a) Si and (b) O, and the formation energy when Li was in the vacancy sites. The formation energy was an exothermic reaction (negative value) when Li was in the vacancy site of Si which indicated that Li reacted with O$^-$. It is suggested that Li can not react with the SiO$_4$ tetrahedrons when each Si-O bond length is equivalent, but Li can react with the SiO$_4$ tetrahedrons when any Si-O bond length is inequivalent. In this calculation, O$^-$ and Li$^+$ react between diatomics by electrostatic force, which does not cause the specific capacity. However, in polarized states of O$^-$-Si$^+$ bond, Si-O bond is separated by the reaction with Li$^+$, producing Si$^+$. The transfer of the electric charge happens to compensate for this charge, when Si$^+$ is reduced to Si in the electrochemical reaction. In addition, Si-Li alloy is formed via the charge transfer. Therefore, we thought that amorphous silicon oxide had the large capacity as discussed before, and the reactive trigger on amorphous silicon oxide and Li is the distorted SiO$_4$ tetrahedrons.

4. Conclusions

The charge-discharge mechanism of SiO was investigated by chemical and electrochemical reactions against Li. These tests showed consistent results. Amorphous silicon dioxide can be reactive with Li, but Li$_2$SiO$_3$ which was the reaction product was inactive and Li ion could not be removed from Li$_4$SiO$_4$. We conclude that the discharge mechanism of SiO can be written as 4SiO + 17.2Li → 3Li$_2$SiO$_3$ + Li$_4$SiO$_4$, just as shown in Eq. (1). However, it was found that amorphous state of silicon dioxide is more reactive with Li. Furthermore, the Si-O bond of the SiO$_2$ tetrahedrons in crystalline SiO$_2$ could not be reduced by Li and the reaction products of amorphous SiO$_2$ consisted of the SiO$_2$ tetrahedrons units. According to the experimental results and calculations, one of the triggers of the irreversible reaction on SiO$_2$ was the distorted SiO$_4$ tetrahedrons in amorphous SiO$_2$, because it is possible to reduce the inequivalent Si-O bond length of the SiO$_4$ tetrahedrons in silicon oxide by Li.

Fig. 9. (Color online) Making O$^-$ and Si$^+$ in crystalline SiO$_2$ and the calculated formation energy by Eq. (3) when Li was in the each vacancy site; (a) O vacancy for making Si$^+$ and (b) Si vacancy for making O$^-$. When a vacancy of Si for making O$^-$ or O for making Si$^+$ exists in crystalline SiO$_2$, the values of (x,y) in Eq. (3) are (1,0) and (0,1). $E_{el}(LiSi_{1-x}O_{x-y})$ is the total energy of the electron state that inserts Li into the vacant sites of LiSi$_{1-x}O_{x-y}$, and $E_{el}(Si_{1-x}O_{y-x})$ is the total energy of the electron state of Si$_{1-x}O_{y-x}$.

<table>
<thead>
<tr>
<th>Site</th>
<th>Fractional coordinate</th>
<th>$E_f$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O vacancy(Si$^+$)</td>
<td>x=0.2676, y=0.4136, z=0.7859</td>
<td>0.44</td>
</tr>
<tr>
<td>Si vacancy(O$^-$)</td>
<td>x=0.5299, y=0.5299, z=0.0000</td>
<td>-3.66</td>
</tr>
</tbody>
</table>

References

16) T. Tabuchi, H. Yasuda and M. Yamachi, J. Power Sources,