Lithiation and Delithiation Properties of Silicide/Si Composite Alloy Electrodes Prepared by Rapid Quenching Method

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ABSTRACT

Rapid quenching is one of the methods for preparing silicide/Si composite alloy as an active material for negative electrode in lithium-ion batteries. In this study, we focused on the method's control over the positional relation between the Si and silicide phase by changing the additive elements. Various Si-alloys and the relationship between their lithiation and delithiation properties and their arrangement was investigated.

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Keywords : Lithium-ion Battery, Negative Electrode, Si Alloy, Silicide

1. Introduction

Silicon (Si) is very attractive as a high capacity active material for negative electrode in lithium-ion batteries (LIBs) because of its theoretical capacity value of 3600 mA h g⁻¹ (Li₁₅Si₄).^{1–3} However, Si expands and contracts largely during lithiation (charge) and delithiation (discharge), respectively.⁴ The expansion ratio per Si atom corresponds to 380%, which generates high stress and large strain in the active materials. The strain that accumulates during repeated charge–discharge cycling causes collapse and pulverization. Consequently, Si electrode cannot exhibit sufficient cyclic stability.

Compositing transition metal silicide and Si is one of the effective methods for improving the cyclic stability of the Si electrode.⁵ We have previously reported that the following four kinds of properties are essential for compositing phases with Si:^{5–10}

- 1) Mechanical properties suitable for the relaxation of the stress from Si
- 2) High electronic conductivity
- 3) Moderate reactivity with Li⁺
- 4) High thermodynamic stability

Many studies utilizing a mechanical alloying method with planetary ball mill have been reported for preparing silicide/Si composite alloys.^{6,11–13} Conversely, rapid quenching method can also be used for producing Si-alloys.^{14,15} We focused on this method's control over the arrangement of Si and silicide phases, by changing the additive elements. Figure 1 presents a schematic illustration of the structural formation of Si-alloy by rapid quenching. While the crystallizing of Si is the initial phase from the molten Si-alloy (Fig. 1, Pattern 1), silicide phase forms around the Si phase. In contrast, in the case of crystallizing silicide phase as the initial phase (Fig. 1, Pattern 2), Si phase forms around the silicide phase. Formation of Pattern 1 or Pattern 2 is dependent on the elements and the amount of the additives present. In this study, we prepared various binary Si-alloys, and evaluated the influence of the arrangements between the Si phase and silicide phase on the electrochemical performance of LIBs.

Figure 1. Schematic illustration of the phase-structure formation by rapid quenching method.

2. Experimental Method

2.1 Selection of additive element

Iron (Fe), Copper (Cu), and Cobalt (Co) were selected as the additives for making Si in the initial phase (Pattern 1) with reference to binary phase diagrams. Further, Zirconium (Zr) and Titanium (Ti) were selected for making silicide in the initial phase (Pattern 2). The corresponding amount of additives was determined by the ratio of the Si phase to silicide phase as 33:67 mass%. Table 1 lists the contents and the silicide phase of synthesized Si-alloys.

2.2 Preparation of Si-alloy ribbon by rapid quenching

Si-alloys were prepared by rapid quenching. First, Si-alloy ingots were prepared in a button arc furnace. Next, the ingot was melted at approximately 1773 K in an induction furnace. After melting, the molten Si-alloy was dropped on a Cu roll at a rotating speed of 40 m/s. The molten Si-alloy was thus quenched and Si-alloy ribbons

Table 1. Contents and silicide phase of synthesized Si-alloys.

Alloy type	Silicide phase	Contents (mass%)		Phase ratio (mass%)		Initial phase
		Si	X	Si	Silicide	
Si-Fe	[FeSi ₂]	66.5	33.5			[Si]
Si-Cu	[Cu ₃ Si]	41.0	59.0			[Si]
Si-Co	[CoSi ₂]	65.8	34.2	33	67	[Si]
Si-Zr	[ZrSi ₂]	58.6	41.4			[ZrSi ₂]
Si-Ti	[TiSi ₂]	69.2	30.8			[TiSi ₂]

were prepared. The thickness of these ribbons was approximately 20 μm .

2.3 Cross-sectional observation and FE-EPMA analysis of Si-alloy ribbons

Si-alloy ribbons were placed in a Bakelite resin. Samples for the cross-sectional observation were prepared using mechanical polishing. The cross-sectional observation was performed using a field-emission scanning electron microscope (FE-SEM, SU6600, Hitachi High-Technologies Corporation). The accelerating voltage was set at 15 kV and the magnification was 5000 $\times$. Field emission-electron probe microanalysis (FE-EPMA, JXA-8500F, JEOL, Co., Ltd.) was used for detecting the position of Si and additive elements. The accelerating voltage was 15 kV, irradiation current was 50 nA, and magnification was 5000 $\times$.

2.4 Cell assembly and electrochemical measurement

Si-alloys were pulverized by hand milling and classified as <25 μm . Active material (Si-alloy powders), conductive agent (Ketjen black), and polyamic acid binder (Dreambond, I. S. T. Corporation) were mixed in the ratio of 85:5:10 (wt%). The mixture was diluted using 1-methyl-2-pyrrolidone for preparing slurry. We painted the slurry on a SUS316L foil (thickness: 20 μm) using a doctor blade with a thickness of 50 μm . SUS316L foil was used as current collector to suppress deformation during charge-discharge cycle. The electrode was then dried at 343 K for >30 min. We heated the electrode in vacuum at 573 K for 1 h for polyimidation. The electrode thickness after heating was approximately 30 μm .

A 2032-type coin cell was used for evaluating the electrochemical performance of the Si-alloy electrode. The coin cell comprised of a Si-alloy electrode as its working electrode, a glass fiber filter as the separator, and a Li metal sheet (thickness: 1 mm, diameter: 12 mm) as the counter electrode. 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) (EC: DEC = 1:1 vol%) was employed as the electrolyte. The

cell was assembled in an open dry chamber (HWR-60AR, DAIKIN INDUSTRIES Ltd.) maintaining its dew point at <−70°C.

The charge-discharge cycle test was performed with an electrochemical measurement system (TOSCAT3100, TOYO SYSTEM Co., LTD.) in the potential range of 0.002–1.000 V vs. Li⁺/Li at 298 K. The current was set at 0.2 mA in the first cycle to measure accurate initial discharge capacity. After the second cycle, the current density was set to about 0.3 A g (Si+silicide)^{−1}.

3. Results and Discussion

3.1 Characterization

We confirmed that the Si-alloys composed only of Si and silicide phases using X-ray diffraction (XRD) technique. Figure 2 shows the FE-EPMA analysis results of the cross-section of Si-Fe alloy and Si-Zr alloy ribbons. The elemental mapping result (Fig. 2(a)) confirmed that the black phase is Si and the white phase is Iron-silicide (FeSi₂). Hence, the silicide phase surrounded the Si phase in Si-Fe alloy. Furthermore, the black phase formed around the white phase in Si-Zr alloy (Fig. 2(b)), that is, Si-Zr alloy is that Si phase surrounded silicide phase (ZrSi₂).

Figure 3 shows the cross-sectional SEM images of Si-alloy ribbons. From the positional relation of black phase (Si phase) and white phase (silicide phase) of Si-Fe, Si-Cu and Si-Co alloys, we can see that Si crystallized as the initial phase and silicide phase formed around the Si phase. For Si-Zr and Si-Ti alloys, silicide phase crystallized as the initial phase and Si phase formed around the silicide phase. Thus, by varying the additives, we could prepare various Si-alloys that differ in the positional relationship with respect to Si and silicide phases.

3.2 Charge-discharge cycle test of Si-alloy electrodes

Figure 4 shows the results of the cycle test of Si-alloy electrodes. The discharge capacity of all Si-alloys decreased significantly during the first and second cycles. This is because of the current density in the first cycle (0.2 mA c.c., 0.075 A g (Si+silicide)^{−1}) is lower than that in the second cycle (0.8 mA c.c., 0.3 A g (Si+silicide)^{−1}) to measure the accurate initial discharge capacity of Si-alloy electrode. A decrease in the discharge capacity of Si-Fe and Si-Zr alloy electrodes from the first to second cycle was smaller than that of other Si-Cu, Si-Co, and Si-Ti electrodes, which indicates that the rate capability of the former two electrodes is superior to others. Additionally, initial discharge capacity of Si-Zr, Si-Co, and Si-Ti electrodes was higher than that of others.

After the second cycle, discharge capacity gradually decreased with a progressing cycle. We infer that the reduction of capacity is due to the gradual collapse of Si-alloy because of repeated charge-discharge and the loss of conduction path of Li-ion/electron. We can

Figure 2. Results of FE-EPMA of prepared (a) Si-Fe alloy and (b) Si-Zr alloy on a 5 μm scale bar.

Figure 3. Cross-sectional SEM images of prepared Si-alloy on a 1 μm scale bar.

Figure 4. Charge–discharge cycling performances of Si-alloys.

Figure 5. Cross-sectional SEM images of Si-alloy electrodes before and after the 50th cycle on a 10 μm scale bar.

confirm that Si–Zr and Si–Ti alloy electrodes exhibit high initial capacity and good cycle stability. It is considered that four properties of silicide (electrical resistivity, reactivity with Li^+ , thermodynamic stability, and mechanical properties) influence on the electrochemical performance of the silicide/Si composite electrodes.^{5–10} In this study we founded that the arrangement of Si and silicide phases is likely to influence on the electrochemical performance of Si-alloy in addition to above silicide properties.

3.3 Effect of the arrangement of Si and silicide phase on cycle stability

Figure 5 shows the cross-sectional SEM images of Si-alloy electrodes before and after the 50th cycles. In Si–Cu and Si–Co alloys, there was a small electrode layer on the current collector because the electrode layer of those alloys reduced during rinsing of the electrode. Active material particles collapsed during the charge–discharge cycle and were exfoliated from the current collector. As the result, it was considering that the collapsed particles removed from the electrode during rinsing and the electrode layer became small. There was a space between electrode layer and current collector in Si–Cu alloy. This space may be generated during polishing for sample preparation. Further, Si–Fe alloy collapsed and was pulverized. Electrode thickness of Si–Fe alloy after the 50th cycle increased by a factor of approximately three compared to before charging. Si–Zr and Si–Ti alloys maintained their particle shape. The expanding of electrode thickness was approximately 1.5 times, which was considerably smaller than that of Si–Fe alloy. These results indicate that collapse of Si–Zr and Si–Ti alloys was suppressed during the charge–discharge cycle. We believe that the positional relation between the Si phase and the silicide phase was influential in this regard. In the Si–Fe, Si–Cu, and Si–Co alloys (Fig. 1, Pattern 1), the silicide phase was subject to large stress due to the Li storage in the Si phase, which causes electrode expansion. As a result, Si-alloy collapsed and the electrode thickness increased. In the Si–Zr and Si–Ti alloys (Fig. 1, Pattern 2), the stress which the silicide phase received is small because Si phase can expand

outward during Li storage. Consequently, the collapse of Si-alloy particle was suppressed and the cycle stability of Si-alloy improved.

4. Conclusion

We prepared various Si-alloys, whose structures were controlled by rapid quenching, and evaluated their electrochemical properties. Our results determined that the collapse of Si-alloy was suppressed and the cycle stability was improved by selecting additive elements (like Zr or Ti) to locate the Si phase around the silicide phase.

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