Shape-controlled Silicon Particles for High-capacity Negative Electrode of Li-ion Batteries

Kenta Nakai, Ikuro Tsuchioka, Morihiro Saito, Akimasa Tsucha, Toshio Takenaka, Masato Hirota, Akika Kamei, and Minoru Inaba

Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, Doshisha University (Kyotanabe, Kyoto 610-0321, Japan)
Oike & Co., Ltd. (Kamitoba, Minami-ku, Kyoto 601-8121, Japan)

Received December 8, 2009; Accepted January 15, 2010

Pure Si platelets (Si-LP, thickness: 100 nm) and Ni layer-laminated Si platelets with different thicknesses (Si/Ni/Si-LP50 (50/50/50 nm) and Si/Ni/Si-LP30 (30/30/30 nm)) were prepared by a vapor deposition method, and their charge/discharge properties were investigated as alternative negative electrode materials to graphite for lithium-ion batteries. The shape of thin platelet effectively relieved the stress during the alloying and de-alloying processes, and improved the charge/discharge cycleability as compared with a commercially available Si powder. In particular, the laminated platelet samples showed very good cycleability, probably because of a shorter diffusion length of Li⁺ ions in the Si layers and an improved mechanical strength by the presence of the Ni layer.

Key Words: Li-Si Alloy Negative Electrode, Thin Platelets, High Capacity, Cycleability

1 Introduction

Silicon has attracted much interest as an alternative to graphite negative electrode for lithium-ion batteries (LIBs) due to its high theoretical capacity of ca. 4200 mAh g⁻¹. However, poor capacity retention is a major problem for its practical application in LIBs. It is widely known that large volume expansion and contraction on charging and discharging cause severe fracture and pulverization of Si particles, which results in a significant capacity loss on charge/discharge cycles. For large Si particles, the expansion proceeds from the surface to the bulk during the charging process, and mechanical stress due to the difference in expansion between the surface and the bulk of Si particles brings about crack formation and pulverization as shown in Fig. 1(a). The stress by the large volume change can be greatly relieved by the reduction at least of one dimension of metal materials. This concept has been realized by using thin metal films as shown in Fig. 1(b,c). However, the thickness of the thin film should be less than a few micrometers to obtain good cycleability, which limits the capacity of the batteries. Here we propose that thin metal platelets (Fig. 1(c)) are the most promising morphology for Li-M alloy materials to attain both high capacity and good cycleability. In addition, lamination with an inactive Ni layer would be very effective to improve the strength of nano-scale thin platelets, and can further reduce the diffusion length of Li⁺ ions.

In the present study, we prepared three kinds of Si thin platelets (Leaf Powder®, Oike & Co., Ltd.): one was simple Si platelets (Si-LP, thickness: 100 nm) and the others were Ni-laminated Si platelets with different thicknesses (Si/Ni/Si-LP50, thickness: 50/50/50 nm and

![Fig. 1](image1.png) Schematic images for morphology changes of Li-M alloy materials during charging. (a) particle, (b) thin film, and (c) platelet.

![Fig. 2](image2.png) Schematic illustrations of Si thin platelets (Leaf Powder®).
Si/Ni/Si-LP30, thickness: 30/30/30 nm) shown in Fig. 2. Charge and discharge characteristics of the Si platelets were investigated, and the effects of their structure such as shape, lamination and thickness of the platelets on the capacity and cycleability were discussed.

2 Experimental

Si-LP, Si/Ni/Si-LP50 and Si/Ni/Si-LP30 samples were prepared by a physical vapor deposition (PVD) method using vacuum evaporation. A commercially available Si powder (Aldrich, < 325 mesh) was also used for comparison. The active material was mixed with 15 wt% Ketjen black as a conductive agent and 10 wt% sodium carboxymethyl cellulose as a binder using water as a solvent. The slurry was coated on a copper foil current collector (0.785 cm²) with a thickness of 50 μm, and then dried overnight at 80°C under vacuum. A coin-type two-electrode half cell was constructed from the electrode, a separator (Celgard® 2326) and a lithium-foil counter electrode (Honjo Metal) in argon-filled glove box (Miwa, MDB-INKP-DS) with a dew point lower than –60°C. The electrolyte solution was 1 M LiClO₄ dissolved in a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Charge and discharge tests were carried out at C/6 rate between 1.5 and 0.02 V in the constant current-constant voltage (CC-CV) mode, using a battery test system (Hokuto Denko, HJ1001SM8). The surface morphology of the electrode before and after charge/discharge cycles was observed with a scanning electron microscope (SEM, JEOL, JSM7001FD).

3 Results and Discussion

Figure 3 shows SEM images of the Si platelet samples. They had platelet structure with an average size of 4-5 μm. The thicknesses of the Si-LP, Si/Ni/Si-LP50 and Si/Ni/Si-LP30 were 100, 150, and 90 nm, respectively. The presence of the Ni layer was confirmed for the laminated samples, especially clearly for the Si/Ni/Si-LP50.

XRD patterns of the platelets are shown in Fig. 4. For commercially available Si powder, sharp peaks assigned to Si(111), Si(220) and Si(311) were clearly observed. In contrast, no clear peaks assigned to Si were observed for all the platelet samples, which indicated that Si in the thin platelets was amorphous. On the pattern of the Si-LP, a small peak was found at around 38°, which is probably assigned to SiO₂. This indicates that a relatively large amount of SiO₂ covered the surface of the Si-LP as compared with those of the other laminated platelets.

Figure 5 shows charge and discharge curves in the initial cycles of the commercially available Si powder and the Si thin platelets. The Si powder and Si-LP exhibited high initial discharge capacities over 2000 mAh g⁻¹, while Si/Ni/Si-LP50 and Si/Ni/Si-LP30 exhibited lower initial capacities of ca. 1000 mAh g⁻¹. The lower capacities of the Si/Ni/Si-LP samples are partly owing to the presence of the inactive Ni layer. The theoretical capacity of the Si/Ni/Si-LP samples is 1440 mAh g⁻¹, when we assume the fully alloyed composition as Li₄Si. The Si utilization in the first cycle is therefore around 75% for the Si/Ni/Si-LP samples, while the Si powder and Si-LP showed ca. 60% (theoretical capacity: ca. 4200 mAh g⁻¹). This implies that the lamination with the inactive Ni layer is clearly effective to improve the Si utilization, which is probably attributable to enhancement of the mechanical strength against crack formation and pulverization, and further reduction of the diffusion length of Li⁺ ions. Each electrode showed a large irreversible capacity in the first cycle, which indicates that solid electrolyte interphase (SEI) was formed on the surface through the reductive decomposition of the electrolyte. It should be noted that the shape of the charge/discharge curves of the Si thin platelet samples was different from that of the Si powder. For example, the discharge curves of the platelet samples started at ca. 0.25 V, and the potential increased with discharging, which is typical of amorphous Si materials. In contrast, the discharge curve of the Si powder showed a plateau at ca. 0.5 V, which is typical of crystalline Si samples.

The cycleability of the Si platelets and Si powder is shown in Fig. 6. In the case of the Si powder, the discharge capacity dropped drastically in several cycles and it became hard to charge and discharge after only 15 cycles. The Si-LP showed an improved cycleability.
This indicates that the reduction of one dimension of metal materials is effective to improve the cycleability. Though the initial discharge capacity was lower (ca. 1000 mAh g⁻¹) than the Si powder and Si-LP, the laminated Si platelets showed good capacity retention. This fact indicates that the lamination with a Ni layer is greatly effective to improve the mechanical strength against crack formation and pulverization of Li-Si alloy electrodes. The capacity retention of Si/Ni/Si-LP30 was slightly better than that of Si/Ni/Si-LP50. This is probably due to a shorter diffusion length of Li⁺ ions, i.e. a smaller mechanical stress, in the former sample.

Figure 7 shows SEM images of the Si platelets and the Si powder before and after 50 cycles. The initially large particles of the commercially available Si powder were pulverized to fine particles after repeated charging and discharging cycles. For Si-LP, agglomeration of thin platelets was observed at the surface, but platelets remained inside the composite electrode. The shape of thin platelets almost completely remained after 50 cycles for Si/Ni/Si-LP50 and Si/Ni/Si-LP30, which indicates that the presence of the inert Ni layer suppressed the agglomeration of the thin platelets. Surprisingly, almost no change was observed for the Si/Ni/Si-LP30 after 50 cycles. It is therefore considered that a shorter diffusion length of Li⁺ ions in Si layers and an improved mechanical strength by the Ni layer brought about the good cycleability of the laminated thin platelet samples shown in Fig. 6.

4 Conclusions

Thin Si platelets (Si-LP, thickness: 100 nm) and Ni layer-laminated Si platelets of different thicknesses (Si/Ni/Si-LP50 and Si/Ni/Si-LP30) were prepared, and their charge/discharge properties were investigated. The shape of thin platelets effectively relieved the stress by volume expansion and contraction during the alloying and de-alloying with Li⁺ ions, and successfully improved the charge/discharge cycleability. In particular, the laminated platelet samples showed very good cycleability. This is probably because lamination with an inactive Ni layer further decreased the diffusion length of Li⁺ ions in Si layers and increased the mechanical strength against crack formation and pulverization. From these results, it was shown that thin Si platelets are promising as negative electrode materials with high capacity and good cycleability in LIBs. Further optimization of the structure, thickness, etc. of Si platelets is now in progress.
Fig. 7  SEM images of (a) Si-LP, (b) Si/Ni/Si-LP50, (c) Si/Ni/Si-LP30, and (d) Si powder before and after 50 cycles at C/6 rate.

References