

Short communication

Electrochemical behaviors of silicon based anode material

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Available online 21 July 2005

Abstract

Mixed silicon–graphite anode materials have been prepared by means of simple mechanical milling process. Research reveals that the microstructural changes, accompanying the electrochemical alloying/de-alloying operations, lead to a macrostructural deformation of the anodes. The key step for improving of such composites therefore could be sought in alternative electrode configurations or textures, preserving the electrodes from the detrimental effect of silicon hosts volume variations.

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Keywords: Silicon/graphite composites; Lithium-ion batteries; Alloying electrode; Electrode deformation

1. Introduction

Since the beginning of 1990s, we have witnessed the development of lithium-ion batteries, which are currently the power source of choice for most portable electronic devices, such as cell phones, digital cameras and laptop computers. During the last decade, the energy density of commercial lithium-ion batteries (LIBs) has considerably increased due to technological improvements. The first commercial cell employed different blends of hard carbon as anode material with a practical capacity of ca. 250 mAh g⁻¹. However, the introduction of new electrolyte additives in 1998 allowed the use of highly crystalline graphite anode materials, which as a result, increased the practical capacity of graphite anodes. This capacity recently reached ca. 350 mAh g⁻¹, which is close to the theoretical value of the composition LiC₆. Despite of these successes, the thirst for greater performance in portable devices continues to place greater demands on the storage capabilities of LIBs. Recently, many on-going research activities have focused on the development of second generation cathodes and anode materials with enhanced capacity and cycling life.

Among the most attractive candidate anodes are silicon and tin based alloying materials, which have recently

attracted much attention [1,2]. Lithium alloys have been more extensively studied than carbonaceous materials, such as LIB anodes. The first studies concerned Li–Al alloys in molten salt electrolytes [3], while later a number of other binary or ternary alloys [4–6] and inter-metallic [7] compounds were examined. Since pure silicon anodes have an extremely poor cycling life due to the large volume variations that occur during lithium alloying/de-alloying reactions, various forms of silicon containing composites have been studied. Elemental silicon powder can be used in combination with matrices, such as C and TiN, and it is also possible to use different silicides or SiO_x compounds as silicon containing starting materials. The thin film concept, which minimizes the volume change effect, is also well suited for lithium alloys. It was previously revealed that thin silicon film deposited directly on the current collector resulted in remarkable cycling performance [8,9].

A common feature of all silicon containing anodes is the vast difference between the first and subsequent cycles. During the first cycle, destruction of Si or the silicide crystal lattice takes place, followed by the formation of Li_xSi ($x = 1–4$). Since the specific volume of the amorphous Li–Si alloy is two to three times bigger than that of the parent Si solid phase, such materials are intrinsically unstable during these cycles, because the cycling results in microstructural anode changes. To increase the cycleability of Si based material, we previously mixed silicon powder with different blends of natural or artificial graphite and coated silicon–graphite composites

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by means of the CVD technique [10,11]. During this study, we found that the carbonaceous phase plays an important role in improving the cycling performance of these materials. The cycling performance of mixed active–inactive composite anodes containing alloying elements improved possibly as a result of the following reasons:

- (1) the stability of single metal particles;
- (2) the morphological stability of the electrode texture;
- (3) avoidance of direct Si–Si inter-particle interaction within the bulk of the electrode.

A theoretical study of particle fractures revealed that there should be a particle size under which fractures will not occur [12]. Our previous study showed that decreasing Si particle size allowed preparation of morphologically stable anodes [13]. Therefore, (1) and (2) are closely related, that is, the stability of single particles leads to morphological stability of the electrode texture. The present study describes further analyses of Si/C composites and examines additional reasons for electrode failure.

2. Experimental

Screening experiments revealed that the best results are obtained when the amount of silicon in the Si/C composite does not exceed 30 wt%. All samples were prepared as follows: first, silicon was milled until average particle grains of approximately $0.2\ \mu\text{m}$ were obtained ($\text{BET} \sim 50\ \text{m}^2\ \text{g}^{-1}$). The particles were then mixed with natural graphite (average flake size $15\ \mu\text{m}$, NG-7, Japan; weight ratio 3:7) and 10 wt% of commercial silver nano-powder (Fraunhofer Institut, Germany), which was added with respect to the weight of the Si/C mixture. The mixture was then milled for 5 h under Ar at 250 rpm by means of a rotary ball mill (Fritsch, Germany). The electrode preparation technique is the common method which is used in LIB industries. The dry Si/C composite was mixed with an appropriate amount of 9 wt% poly(vinylidene fluorides) (PVDF) in *N*-methyl-2-pyrrolidone (NMP) solution. It was then agitated and the resulting slurry was pasted on a copper foil current collector and dried at $120\ ^\circ\text{C}$. All electrode preparation steps were performed under an Ar atmosphere to minimize oxidation of the silicon powder. Circle-shaped electrodes were punched on the copper foil, then pressed and cycled in a coin cell versus Li metal.

3. Results and discussion

The importance of lower capacity buffering media mixed with the high capacity silicon phase can be demonstrated with the data presented in Fig. 1. It shows the first lithium insertion capacities of electrodes composed of silicon with variable BET surface area (particle size). Electrodes were prepared using silicon powder milled for different time intervals and

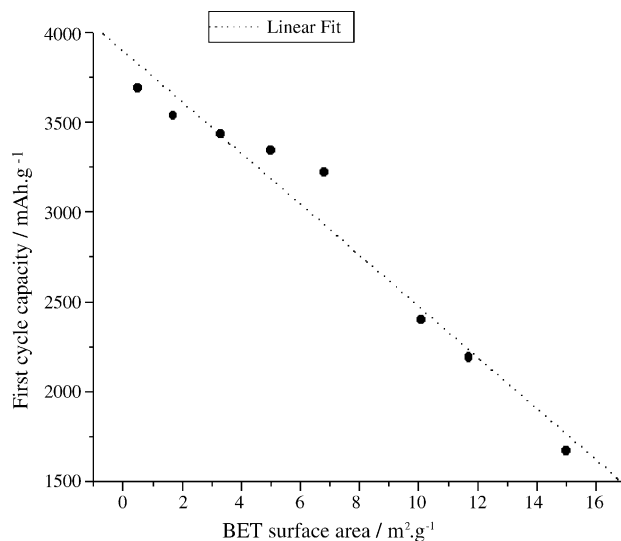


Fig. 1. First potentiostatic lithium insertion capacity of the pure silicon anode, prepared from silicon with gradually decreasing particle grain size.

PVDF. As BET surface area increased, the observed capacity decreased linearly.

A plausible reason for this behavior is that decreasing of silicon particle grain size leads to two effects that should be simultaneously considered (Fig. 2):

- (i) increase in the specific surface area of the silicon powder, which is proportional to $1/\rho r$, where ρ is the density of the silicon and r is the average grain size;
- (ii) limitation of particle crack during the initial alloying.

Our previous study revealed that Si particles with particle grain size of the order of few micrometers crack into smaller ones during the initial alloying, thus exposing fresh surfaces to the electrolyte [14]. However, smaller particles tend to expand without severe cracking. Having in mind these two effects the data presented in Fig. 1 could be logically explained. As the silicon particles become smaller, expansion of the single particles becomes more pronounced than their cracking. Since smaller particles have much higher contact area, their outer surfaces interact much stronger and form a layer of a Li-rich Li_xSi . It covers the fresh Si, which remains unavailable for the reaction due to kinetic reasons. Although the equilibrium attained under such conditions is not thermodynamic, the capacity that can be reached cannot, over a reasonable time, exceed the values presented in Fig. 1. Under a controlled potential mode, the current reaches values as small as several microamperes at 5 mV versus Li metal and the kinetics become very sluggish. Contrary to that, bigger particles crack easier and expose inner areas of the particles to the electrolyte. Moreover, cracking increases the porosity of the electrode which additionally enhances the electrochemical alloying. This result clearly shows the difference between the thin film approach, where the silicon is applied as a continuous film, and the composite electrode approach, where the particles interact with each other.

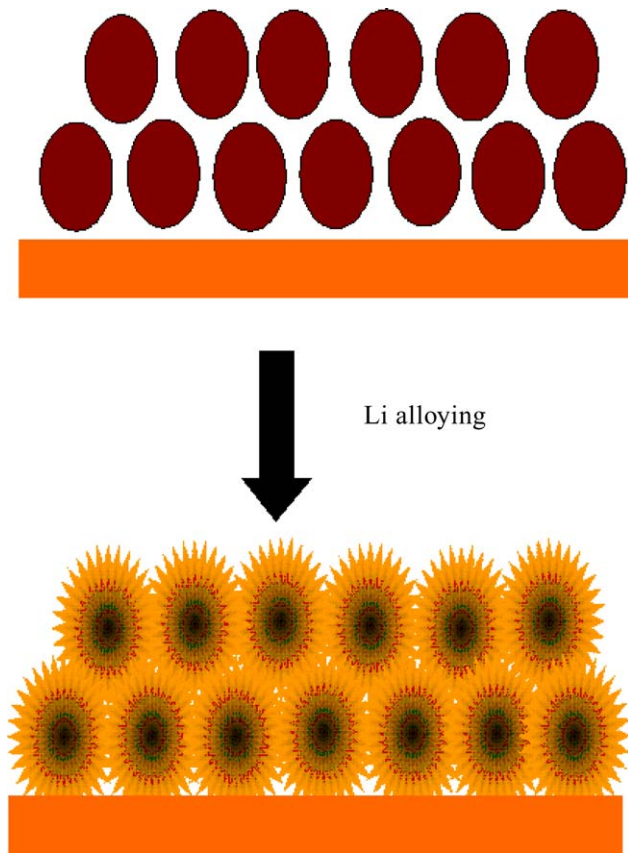


Fig. 2. Decreasing the average particle size increases the Si–Si contact area and reduces the cracking of single particles, which in the absence of supporting second solid phase lowers the observed initial alloying capacity as shown in Fig. 1 and discussed in the text.

In the presence of a graphite matrix, which is able to prevent silicon inter-particle interactions, most of the silicon is available for the electrochemical reaction at a reasonably high current density. These interfacial phenomena can be further

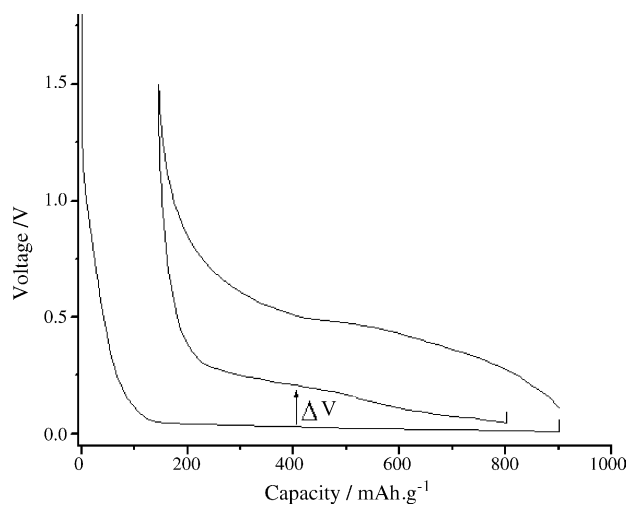


Fig. 3. Voltage profile of the composite Si/C electrode; note the large polarization between the first and the second cycle, which is due to silicon crystal lattice amorphization during the initial alloying with Li^+ .

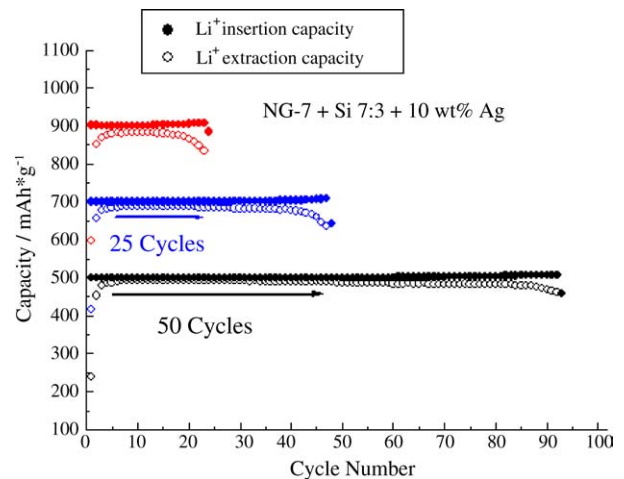


Fig. 4. CCCV test of Si/graphite/Ag composite. This kind of test was found to be useful for initial optimization of the composite electrodes processing conditions.

influenced by the presence of metal additives. Silver was chosen here because it was found to be an effective anode additive and many commercial cells contain up to 10 wt% Ag in their anode active materials.

It is interesting to note that the results obtained using such composites are sensitive to the mode of testing. Cycling life depends on the insertion capacity over the first cycle. Courtney and Dahn [15] proposed the idea of cycling lithium alloying anodes within a narrower potential window to improve the cycling performance of lithium alloying electrodes. However, with silicon carbon composites this approach is harder to apply. Even using the same composite, current density and cutoff voltages generally provides different initial charging capacities. The result is also sensitive to the electrode preparation technique, that is, the amount and type of binder used

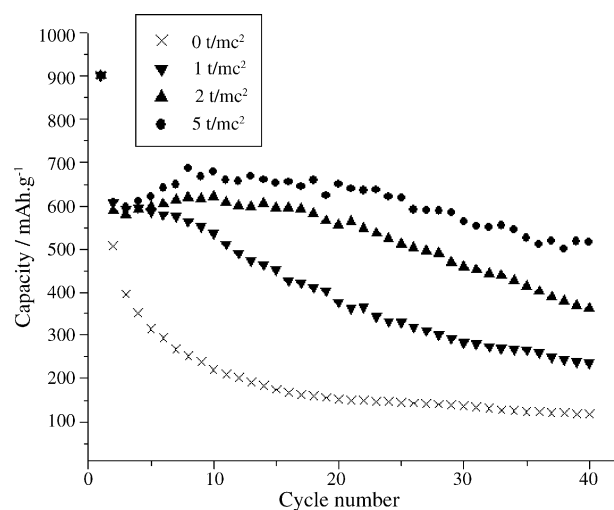


Fig. 5. Cycling test of the mixed Si/graphite composite containing Ag performed under CC mode. Electrodes punched from the same copper sheet were used. The variable parameter was only the pressing force. First cycle was performed as a constant capacity lithium insertion (900 mAh g^{-1}), next cycles performed under CC mode between 40 mV and 1.5 V.

as well as the viscosity of the slurry and drying conditions. Moreover, the voltage/capacity plots exhibit a large polarization between the first and subsequent cycles, which is shown in Fig. 3. Due to the above-mentioned obstacles, Si/C composite electrodes were tested in two complementary ways denoted CCCV (constant current constant voltage) and CC (constant current).

Under the CCCV mode the insertion capacity was limited to a given predefined value, as suggested by Jung et al. [16]. Thus the cycling could be performed at Δx in Li_xSi , which is clearly defined at least during the initial cycles. Another reason for working under such conditions is that in LIBs the insertion capacity is naturally limited by the materials balance ratio. Therefore, the cycling test in this mode was performed as follows: Li^+ insertion at a high current density (1.5 mA cm^{-2} or $\sim 0.35 \text{ mA mg}^{-1}$) until the required capacity was reached. If the capacity was not reached, the potential was held at 5 mV and current was decreased accordingly to keep the cell voltage at 5 mV versus Li. Exhaustion of the electrode occurs when the current approaches 0 mA without reaching the required capacity, and this was regarded as the last cycle of the test. Charging (Li^+ extraction) was performed at 1.5 mA cm^{-2} until 1.5 V, because the extraction of Li^+ under a CCCV mode does not improve lithium extraction efficiency and therefore extraction was performed in CC mode. This confirms that in this case, Li^+ extraction will correspond to the discharge (work) of real LIBs, which is normally performed under CC mode. A practical measure of electrode stability under CCCV conditions is the total number of cycles performed as well as the number performed with a high coulombic efficiency ($\approx 99\%$). The latter is indicated with an arrow below the corresponding data sets in Fig. 4. A clear trend was seen in all cases, that is, increased cutoff capacity lowered the number of cycles performed with high efficiency. The CCCV mode proved very useful for the initial optimization of the electrode compositions, because it allowed them to work at predefined lithium contents. This is particularly useful for alloying elements that behave unlike the intercalation hosts in which the lithium content is naturally determined only by the cutoff voltage.

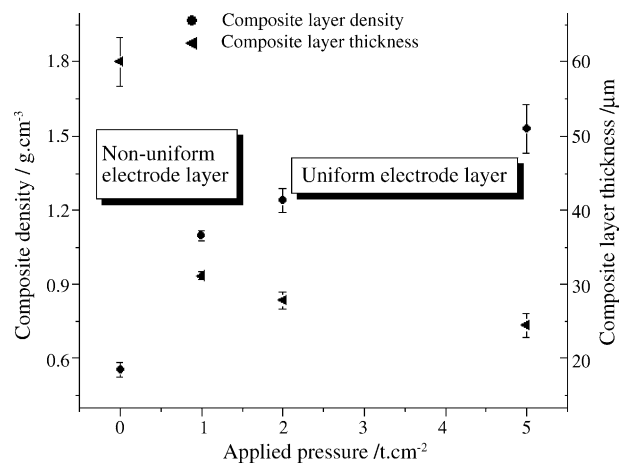


Fig. 6. Electrode density and composite layer thickness variation presented as a function of the applied pressure. Under lower pressures, there is a binding force gradient within the electrode thickness. After densification of the electrode, it becomes uniform and strongly attached to the current collector.

The complementary CC mode is given in Fig. 5. The variable in this case was only the pressing force. The first cycle in all cases was performed to a fixed capacity of 900 mAh g^{-1} after which cycling was performed in CC mode in a voltage window of 40 mV to 1.5 V, at 1.5 mA cm^{-2} /ca. 0.35 mA mg^{-1} . This potential window was chosen because it offered a reasonable compromise between high capacity and cycle life.

The data in Fig. 5 suggest the crucial role of pressing force on the cycle performance of composite electrodes such that the higher the pressure the longer the cycle life. To understand the reason for this, electrode density and binding force were measured after the application of various pressing forces. As shown in Fig. 6, electrode density sharply increases at lower pressures. Moreover, the standard peel-off test revealed that the binding force gradient within the electrode layer drastically changes with densification of the electrode. Electrodes that were not pressed with a thickness of ca. $55 \mu\text{m}$ typically peeled off in four or five layers with sequentially increasing

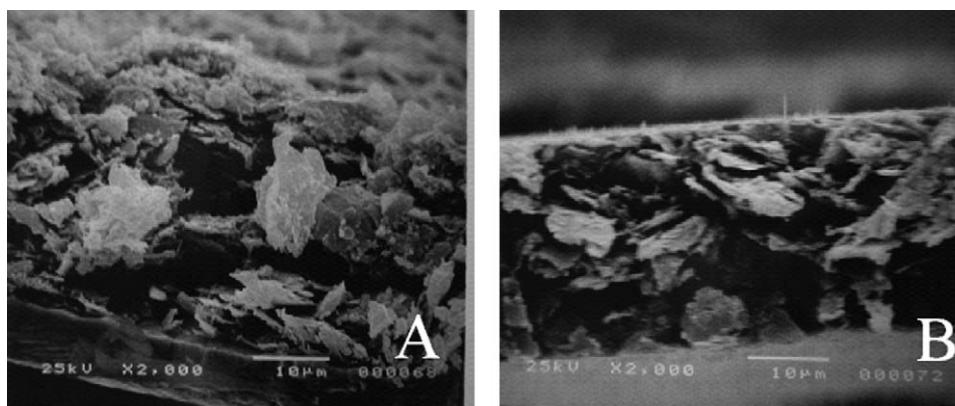


Fig. 7. Cross-sectional view of the composite Si/C/Ag electrode: (A) no pressure and (B) 5 t cm^{-2} .

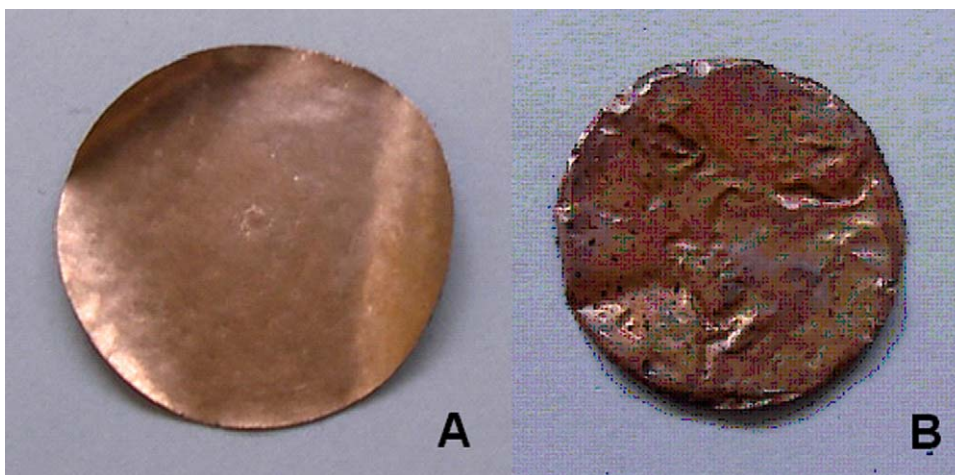


Fig. 8. Backside view of: (A) fresh and (B) cycled electrode composed by C/Si/Ag composite.

binding force. Binding force ranged from ca. 0.3 N cm^{-1} for the top layer to more than 5 N cm^{-1} for the layer adjacent to the copper current collector; 5 N cm^{-1} was the upper limit of measurable binding force with our equipment (Shimadzu EZ Test force meter, Japan). In contrast, electrodes pressed under pressure exceeding 3 t cm^{-2} showed uniform binding force distribution; entire layers did not peel off under the maximum measurable force of 5 N cm^{-1} . In addition, the electrode layer density increased by a factor of 2.5 due to the parallel ordering of the graphite flakes as seen in the SEM image presented in Fig. 7.

However, compared with pure graphite anodes, the cycling life of these electrodes remained unsatisfactory. Mechanically, the strongest electrodes became deformed after prolonged cycling as shown in Fig. 8. Moreover, despite the morphologically stable electrode texture, it seems that a large amount of the electrolyte was absorbed from the composite electrode layer, although this effect has not been estimated quantitatively.

4. Conclusions

Complementary cycling tests of mixed Si–C composites, containing silver powder were performed. It was revealed that the microstructural changes of the silicon-containing composite anodes lead to a macrostructural deformations of the electrode, possibly accompanied by accumulation of electrolytes within the active material layer. It therefore seems that further increase in cycle life could be expected with alternative electrode configurations like three-dimensional metal foam or metallized polymer woven fabrics. With the later, the electrode material is not situated in a single layer and therefore the mechanical deformation might be greatly reduced.

Acknowledgments

We gratefully acknowledge the New Energy and Industrial Technology Development Organization, NEDO, Japan (Grant No. 03001450) for partial financial support of this work.

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