



Short communication

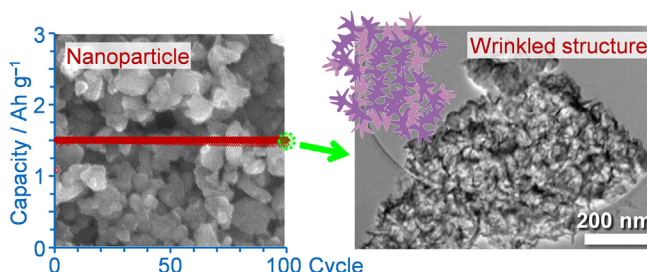
Remarkable performance improvement of inexpensive ball-milled Si nanoparticles by carbon-coating for Li-ion batteries

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HIGHLIGHTS

- Inexpensive ball-milled Si nanoparticles (BM-Si) are investigated for LIBs.
- BM-Si is much worse than expensive CVD-derived Si-nanoparticles (CVD-Si).
- The key factor is found to be the physical contact between each of Si nanoparticles.
- Carbon-coating and capacity restriction remarkably improve the performance of BM-Si.
- A specific 'wrinkled' structure is formed not only in CVD-Si but also in BM-Si.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 March 2016

Received in revised form

8 April 2016

Accepted 9 April 2016

Available online 16 April 2016

Keywords:

Si/C composites

Si anodes

LIBs

Structure change

Transmission electron microscopy

ABSTRACT

Si nanoparticles prepared by ball-milling (BM-Si) are expected as practical negative-electrode materials for lithium-ion batteries, but their performance is much lower than those of more expensive Si nano-materials, such as chemical-vapor-deposition derived Si nanoparticles (CVD-Si) having a tight network structure. It is found that carbon-coating of aggregations of BM-Si forms a quasi-network structure, thereby making the performance comparable to that of CVD-Si under capacity restriction (to 1500 mAh g⁻¹). In this case, the structural transition of BM-Si during charge/discharge cycling is characterized by the formation of a specific 'wrinkled structure', which is very similar to that formed in CVD-Si.

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Towards the development of high-capacity lithium-ion batteries (LIBs), silicon (Si) has attracted significant attention as a new

negative-electrode material from its high theoretical capacity (3572 mAh g⁻¹) [1], which is 10 times as large as that of conventional graphite (372 mAh g⁻¹). However, Si has disadvantages of low rate-capability and poor cyclability due to its low electric conductivity and significant volume change upon lithiation/delithiation, respectively. To overcome these problems, the use of nano-sized Si is essential. A variety of nano-sized Si materials have

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been reported thus far, such as Si nanoparticles [2,3], Si nanowires [4–6], Si nanotube [7,8], and Si thin films [9]. As the second strategy, the combination with conductive materials, such as carbon, is of importance. Thus, high-performance Si/C composites have been reported, e.g., Si/C inverse opal [10], Si/C core-shell nanoparticles [11], C/Si core-shell nanowires [12], carbon-coated 3D porous Si particles [13]. However, their high production costs do not allow their practical use, and it is therefore highly desirable to develop high-performance Si-based materials which can be mass-produced at a reasonable cost.

One of the solutions for this challenge is the use of ball-milled Si nanoparticles (BM-Si) [14,15]. About 7700 thousand tons of Si was produced in the world in 2014 for a variety of applications including computers and solar cells [16]. Among them, silicon metal is generally produced in a form of ingot, and it is cut by a wire saw to produce silicon wafers. But at this cutting step, ca. 40% of Si is lost as swarf (sawdust) [17,18], which at present is industrial waste [19]. Consequently, it would be ideal if the Si swarf is reused as a high-performance negative-electrode for LIBs. To prepare nano-sized Si from such raw materials, ball-milling is the most facile and practical method. Thus, the preparation of BM-Si from Si swarf and its feasible performance have been reported recently [15]. However, the structure change of BM-Si during charge/discharge cycling has not been fully investigated thus far. Herein, we report the drastic structural transition of BM-Si in detail, and propose an effective way to control the deterioration process to achieve high performance and cycle stability.

We have previously revealed that Si nanoparticles produced by plasma chemical vapor deposition (denoted as CVD-Si) exhibit an interesting structural transition during their lithiation/delithiation cycles [20]. The behavior of CVD-Si can be a good reference to understand the structural change of BM-Si. Moreover, the performance of CVD-Si is much better than that of BM-Si and can be regarded as a target for the latter. Thus we first explain the charge/discharge property of CVD-Si for 100 cycles in Fig. 1a and b, together with its structural change (Fig. 1c–e). A transmission electron microscope (TEM) image of CVD-Si shows that its primary particles (ca. 80 nm in size) are tightly connected each other to form a network like the 'structure' of carbon blacks (Fig. 1c). With lithiation/delithiation, CVD-Si is transformed into an intermediate and metastable state, 'wrinkled structure' (Fig. 1d and S1), which still retains a good charge/discharge performance. Afterward, the structure is further changed into an aggregated lump (Fig. 1e), and the performance of CVD-Si is getting worse at this final stage (Fig. 1a). In addition, capacity restriction (up to 1500 mAh g⁻¹) is found to be very effective to improve its cyclability and rate capability (Fig. 1b), and the wrinkled structure is kept even after the 100th cycle in this case [20]. Thus, the formation of the wrinkled structure and its retention are responsible for keeping a good performance over many cycles. We have examined also the effect of carbon-coating (CVD-Si/C in Fig. 1a and b), but the coating does not change the structural transition process so much and the improvement effect is therefore not remarkable [20].

One of the purposes of this work is to achieve a high performance in BM-Si: the concrete target is to reach the performance of CVD-Si (Fig. 1a and b). BM-Si was prepared from commercial Si powder (99.9%, ca. 0.1–90 μm in particle size, Soekawa Rikagaku Co., Ltd.) by using a high-power planetary ball mill, followed by HF washing to remove a surface oxide layer. In addition, BM-Si thus obtained was coated with carbon by a pressure-pulsed CVD (P-CVD) technique [20] to prepare BM-Si/C. The details about experiments are shown in the Supporting Information. SEM images of BM-Si and BM-Si/C are shown in Fig. 2a and b, respectively. Most of BM-Si consists of finely crushed primary particles with sizes of less than 100 nm, and they are naturally aggregated to form secondary

particles. The size of the aggregates ranges from ca. 0.5–10 μm. The average primary particle size of BM-Si is calculated as 47 nm from its BET surface area (50 m² g⁻¹). There is an essential difference in morphology between CVD-Si and BM-Si, i.e., the former has the network structure consisting of tightly connected nanoparticles (Fig. 1c), and the latter is a weak aggregation of isolated primary particles. By P-CVD, the color of BM-Si is changed from dark brown to complete black, and the carbon content in BM-Si/C is estimated to be 15 wt%, from the result of elemental analysis. Nevertheless, the SEM image of BM-Si/C (Fig. 2b) looks almost the same as that of BM-Si (Fig. 2a) in terms of particle size and the state of aggregation, suggesting that BM-Si is uniformly covered with a very thin carbon layer. If an ideal Si sphere having a diameter of 47 nm is uniformly covered with 15 wt% of carbon, its thickness should be 1.7 nm. However, the actual thickness is 10–20 nm (Fig. 2d). This suggests that each of the individual Si nanoparticles is not covered with the carbon layer, but the outer surfaces of aggregates (secondary particles) containing the primary particles are tightly covered (Fig. 2c). For the carbon-coated sample, it is possible to roughly estimate the average secondary particle size, and the number of the primary particles included in one secondary particle can be estimated as ca. 220–1760 (Supporting Information S3). As is found in Fig. 2d, the carbon layer of BM-Si is not highly crystallized (Supporting information, S4).

The charge/discharge measurements of BM-Si and BM-Si/C were performed for 100 cycles by using a lithium foil as a counter electrode in a 2032-type coin cell (Hohsen Co.) at 25 °C. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume). In addition, several other cells were also assembled and individually charged/discharged for certain cycles, and then the cells were disassembled to observe the structure of the sample after the charge/discharge cycles. See the Supporting Information about more details of the experimental method.

The charge/discharge capacities and coulombic efficiencies during 100 cycles are shown in Fig. 3a (note that the current density is changed during the cycling, as in the case of CVD-Si). The charge/discharge curves are presented in the Supporting Information. The discharge (lithiation) capacity of BM-Si in the 1st cycle is 3388 mAh g⁻¹, and the 1st coulombic efficiency is 74%. These values are lower than those of CVD-Si (Fig. 1a) [20]. In the following cycles, BM-Si shows much lower rate-capability and cyclability than those of CVD-Si [20]. Since the sizes of the primary particles in these two samples are almost the same, this remarkable difference is ascribed to the presence of the network structure in CVD-Si. In BM-Si, individual Si nanoparticles are loosely aggregated and therefore they could be easily isolated by the large volume change upon lithiation/delithiation cycles. Once isolated and then surrounded by electrolyte under 0.7 V (vs. Li/Li⁺), the Si nanoparticles are immediately covered by solid-electrolyte interface, which is an electrically insulative layer, and lose the capacity.

On the other hand, the carbon-coated sample (BM-Si/C) exhibits much better performance than BM-Si (Fig. 3a). In the 1st cycle, the discharge capacity and the coulombic efficiency are 3528 mAh g⁻¹ and 84%, respectively. During the 36–65th cycle at the highest current density of 5 A g⁻¹, the discharge capacity of BM-Si/C is higher than that of BM-Si. At the 100th cycle, BM-Si/C retains a discharge capacity of 1045 mAh g⁻¹, which is higher than that of BM-Si (855 mAh g⁻¹). In the case of CVD-Si, the carbon-coating is not very effective under the same conditions as shown in Fig. 1a [20]. The big difference in the effect of the carbon-coating between CVD-Si and BM-Si should be ascribed to their different initial structures: the network structure and the weak aggregation, respectively. As shown in the TEM observation (Fig. 2c and d), the carbon-layer covers the aggregates of BM-Si. In other words, the carbon-layer accommodates a large number of primary particles to

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