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Improved Initial Performance of Si Nanoparticles by Surface Oxide Reduction for Lithium-Ion Battery Application

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Improved Initial Performance of Si Nanoparticles in Lithium-ion Batteries by Surface Oxide Reduction

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1

Abstract

This study characterizes the native oxide layer of Si nanoparticles and evaluates its effect on their performance in Li-ion batteries. X-ray photoelectron spectroscopy and transmission electron microscopy were applied to identify the chemical state and morphology of the native oxide layer. Elemental and thermogravimetric analysis were used to estimate the oxide content for the Si samples. Hydrofluoric acid was used to reduce the oxide layer. A correlation between etching time and oxide content was established. The initial electrochemical performances indicate that the reversible capacity of etched Si nanoparticles was enhanced significantly compared with that of the as-received Si sample.

Compared with conventional graphite negative electrode materials, Si has a superior theoretical specific capacity of 3759 mAh/g at the $Li_{15}Si_4$ lithiation stage,[1, 2] and is regarded as a promising candidate to replace or combine with graphite for the next generation of high-energy lithium-ion batteries. The size effect of Si particles during cycling has been extensively investigated recently. It has been generally accepted that nanosizing of Si particles is important to enable high capacity and stable cycling.[3-10] Commercial Si nanoparticles in the range of 10 to 100 nm have also been used as a capacity booster with graphite particles in lithium-ion cells. However, an important aspect that has not been well studied is the surface of the Si nanoparticles and its impacts on the initial cell performance. Nanomaterials, including spherical particles, wires or sponge structures, tend to have enhanced surface area compared to micron-sized particles. Surface impurities play a significant role in the performance of the nano-material; the initial performance of Si nanoparticles with similar size distribution can vary significantly from batch to batch even if they are from the same supplier. In this letter, we demonstrate that the performance variation is due to variations in the native oxide surface layer on Si nanoparticles, and that the removal of this layer can significantly improve the Si nanoparticles' initial performance.

Experimental

Materials and process Si nanoparticles (aver. 50 nm diam.) were purchased from Nanostructured & Amorphous Materials Inc. Hydrofluoric acid (HF, 47% - 51%) and anhydrous *N*-methylpyrrolidone (NMP) were purchased from Sigma-Aldrich. Hydrofluoric acid (HF) was diluted to 2% before use. The procedure for reduction of the

oxide layer is as follows: 0.5 g of Si nanoparticles and 30 mL of 2% HF were introduced into a 50 mL centrifuge tube. The mixture was sonicated at 50 - 60 Hz for different periods of time in a tabletop ultrasonic cleaner (Branson 2510). The Si powder was collected by centrifugation and washed by ethanol 5 times to remove the residual HF. This etched Si powder was dried under vacuum at room temperature for 1 h and under vacuum at 130°C for 16 h.

Instrumentation X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5400 XPS system. The pass energy was set to 35 eV for Si $2p$ region scans. All spectra were fit with a Voight profile and the thickness of the oxide layer was determined by comparing the relative areas of the peak at 99.8 eV (assigned to Si^0) and the peak at 103.8 – 104.5 eV (assigned to Si^{4+}). Thermogravimetric analysis (TGA) was performed using the THERAL TA Instruments SDT Q600 from room temperature to 1450°C with a heating rate of 10°C min^{-1} in an Al_2O_3 crucible, under 100 mL min^{-1} O_2 flow. Transmission electron microscopy (TEM) images were acquired using Phillips CM200 at 200kV operating voltage. Elemental analysis was conducted by Columbia Analytical in Tucson Arizona.

Laminate and cell The composition of Si/acetylene black (AB)/polyvinylidene difluoride (PVDF) (1:2:1 weight ratio) was used in this study. The laminates and coin cell assembly were prepared according to a previously reported method.[11] Lithium metal was used as the counter electrode. The coin cell performance was evaluated with a Maccor Series 4000 Battery Test System in a thermal chamber at 30°C. The coin cells were cycled at C/10 current density between 1V and 0.01 V.

Results & Discussion

To study the effect of surface oxide thickness on cell performance, surface oxide was systematically removed by dissolving in HF solution. TEM images of Si nanoparticles before and after etching for 30 min. are shown in Fig. 1. Besides the large size distribution of the as-received sample, a core-shell structure was observed for most particles in Fig. 1a,b. Shell thickness is around 4 -10 nm, with thicker shells on bigger particles. This amorphous shell layer is believed to be the native oxide layer from the manufacturing process. We have investigated different samples from various sources, and the thickness of this glassy amorphous layer varies significantly. After HF etching, this amorphous oxide layer was reduced to 1-2 nm (Fig. 1c,d). Another noticeable difference is the separation among the particles. Although the primary particle size is only slightly reduced after etching, the morphology is very different. The particles are aggregated into branches in the as-received sample (Fig. 1a) but separated after HF etching (Fig. 1c). The particle aggregation in the as-received sample may result from the manufacturing process, in which the oxides that formed on the surface of the Si core connected the particles together into branched structures. The etching process dissolves away the oxide layer, thereby separating the Si nanoparticles.

Since Si can have different oxidation states and the corresponding oxides (SiO_x) have different electrochemical behaviors, XPS was used to characterize the oxide layer before and after etching. In acquired Si $2p$ spectra (96 - 107 eV binding energy region), two peaks were observed, shown in Fig. 2a. The peaks at 100 eV and 104 eV are assigned to elemental silicon $2p$ (Si^0) and the stoichiometric Si dioxide (Si^{4+}) component, respectively.[12, 13] There is no additional Si oxide components observed. A slight shift of

the Si^{4+} peak can be observed in these samples, which depends on the thickness and quality of the oxide layer. By comparing the relative areas of the two peaks, the thickness of SiO_2 layer in the as-received sample is estimated at about 6 nm (Fig. 2b), which is in the range of observed results based on TEM. The smaller Si^{4+} peak after etching confirms that the surface oxide is being reduced; the estimated oxide thickness of 1.3 nm after 30 min. of etching (Fig. 2b) is consistent with TEM measurements.

The SiO_2 content as a function of different etching times was investigated using TGA.[14] As shown in Fig. 3 SiO_2 content decreases from 26.5 % before etching to 18.9 % after 5 min. and 12.9% after 10 min. of etching. A simple calculation based on elemental analysis assuming 50-nm Si nanoparticles yields an initial surface SiO_2 layer of 4 nm, which is at the lower limit of the TEM observations for the as-received sample. The SiO_2 content reaches an equilibrium of 6.6% between 25 min. and 30 min. of etching. Note that the etching and sampling process is performed under ambient conditions. These results demonstrate that HF etching provides a facile process for generating Si nanoparticles with different SiO_2 content by controlling the etching time.

The as-received Si nanoparticles and those after 10 min. and 30 min. of etching were used as negative electrodes in coin cells with Li metal as the counter electrodes, and their initial electrochemical performance was evaluated for 10 cycles (Fig. 4). The specific capacities in Fig. 4a,b,c are based on the overall weight of the Si nanoparticles, whereas those in Fig. 4a-1,b-1,c-1 are after discounting the weight of the SiO_2. Comparing the specific capacities based on Si powder weight in Fig. 4a,b,c, there is a clear correlation between the SiO_2 surface layer thickness and measured reversible capacity. The reversible capacity of the as-received Si nanoparticles is less than 970

mAh/g (Fig. 4a), and even after discounting SiO_2, it is 1320 mAh/g (Fig. 4a-1), which is still far short of the 3750 mAh/g expected from Si materials. The limited reversible specific capacity of the as-received sample indicates that SiO_2 does not significantly contribute to the reversible capacity in the 0.01 V to 1 V range.[15, 16] The specific capacities improve steadily after 10 min. (Fig. 4b, b-1) and 30 min. (Fig. 4c, c-1) of etching to reach the theoretical capacity limit for Si. Therefore, the SiO_2 layer has an insulating effect on the Si cores, preventing some of the Si from reacting with lithium-ion, and removal of this layer via an HF etch significantly improves the reversible capacity.

Conclusions

The surface oxide layer on Si nanoparticles adversely affects their initial performance as electrodes by reducing the reversible capacity. Since thicker oxide layers result in lower reversible capacity, the surface oxide needs to be reduced to achieve better initial cycling performance. HF etching of commercial Si nanoparticles allows them to reach the theoretical specific capacity for the first few cycles. This study provides a clear interpretation of the origins of the performance variability for the Si nanoparticles on the market, and develops a general strategy to modify the surface chemistry and morphology of Si materials to achieve better performance for Li-ion battery applications.

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Figure Captions

Figure 1. TEM images of Si nanoparticles (a,b) as-received and (c,d) after 30 min. of HF etching.

Figure 2. (a) Si 2p XPS spectra of Si particles for samples as-received and after 10 and 30 min. of etching. (b) Estimated SiO_2 thickness of the Si particles based on XPS measurements.

Figure 3. SiO_2 content in the samples, determined using TGA, as a function of etching time.

Figure 4. Specific capacity vs. potential of the first 10 cycles of Si electrode. (a, a-1) As-received Si, (b, b-1) Si after 10 min. of etching, (c, c-1) Si after 30 min. of etching. (Specific capacities in a, b, and c are based on gross Si particle weight; specific capacities in a-1, b-1 and c-1 are based on pure Si weight after discounting SiO_2.)

(a) Si 2p spectra showing Si⁴⁺ and Si⁰ peaks for 0 min (As-received), 10 min, and 30 min etching. (b) SiO₂ thickness versus etching time.