# Novel Anode Material for Lithium-ion Batteries: Carbon-Coated Silicon Prepared by Thermal Vapor Decomposition

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(Received August 24, 2001; CL-010828)

Carbon-coated Si has been prepared by thermal vapor decomposition technique. The electrochemical behaviors of carbon-coated Si together with Si have been investigated as anode materials for lithium-ion batteries. The good cycleability of carbon-coated Si under lithiation capacity of 1200 mA h/g has been correlated with ex situ XRD patterns as well as SEM graphs.

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Since silicon can react with lithium to form $Li_xSi$ alloy to a maximum uptake of $Li_{4.4}Si$ with the theoretical capacity as high as 4000 mAh/g (as compared with graphite, $LiC_6$, 372 mA h/g), some research efforts in the last few years have been directed towards utilizing Si-based materials as possible anode materials to replace graphite.[1–4] A major problem with $Li_xSi$-based anode materials lies in the large volume change during charge–discharge process, which inevitably introduces cracking or crumbling of anode materials and thus cause loss in capacity during cycling. Current attempts to overcome this problem aimed at dispersing fine Si particles within a solid, mixed conducting host matrix by mechanical milling. This technique improved the cycleability of Si-based anodes considerably, but also gave rise to very big surface area of the electrode material and thus caused very large irreversible capacity at the first cycle due to the huge decomposition of electrolyte.[1-4]

In our previous study,[5,6] thermal vapor decomposition (TVD) technique has been successfully used to coat carbon onto the surface of natural graphite particles in order to protect it from the electrolyte decomposition. It is expected that this technique is also applicable for providing carbon host matrix for Si powders. In this communication, the electrochemical behavior of TVD-carbon-coated Si as an anode material for lithium-ion batteries has been investigated.

Most experimental details, including the preparation of carbon-coated Si samples, electrode fabrications, electrolytes, glove box operation, cells etc, are similar to those described before.[5] Carbon-coated Si was prepared by the TVD technique in Mitsui Mining Co. Ltd. Benzene vapor and nitrogen gas were fed into a reaction tube (1000 °C) at flow rates of 2 mL/min and 1 L/min, respectively. At such a high temperature, the organic vapor decomposed and carbon deposited onto the surface of Si particles. The mean particle of carbon-coated silicon, tapping density, specific surface area, the thickness and the amount of coated carbon are founded to be 18 μm, 0.9 g/cm$^3$, 2.8 m$^2$/g, 1.25 μm, and 20 wt%, respectively. In the ex situ experiments, lithiated carbon-coated Si electrodes were sealed in the polyethylene bags under argon atmosphere.

Figure 1 compares the typical charge–discharge curves of carbon-coated Si and the original Si electrodes. Pure silicon electrodes demonstrates very poor electrochemical performances in the terms of both rechargeable capacity and cycleability due to cracks of the Li–Si alloy in the course of cycling, the same as illustrated in the previous report.[7] By contrast, the charge capacities (de-lithiation) of carbon-coated Si electrodes are much larger than those of the original Si electrodes for all the cycles. Moreover, there are few decreases of charge capacities between every two adjacent cycles after the first cycle for carbon-coated Si electrodes, which implies a satisfactory cycling performance. Thus the superiority of carbon-coated Si electrodes over the original Si electrodes as anode materials for lithium-ion batteries can be clearly seen.

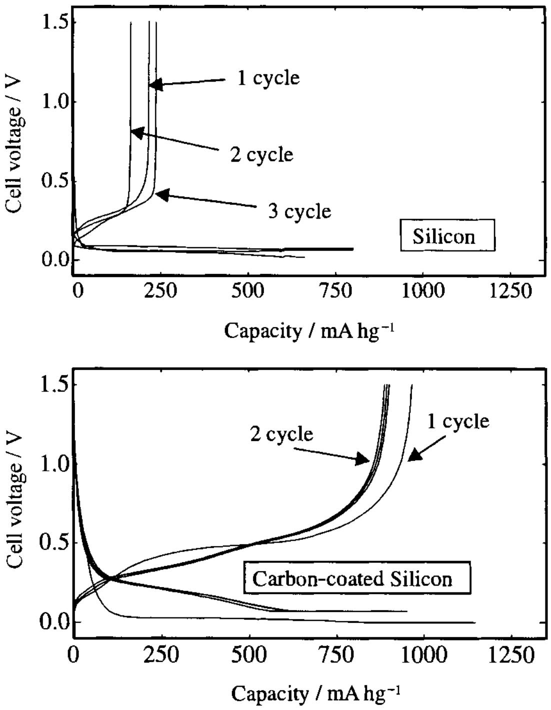

**Figure 1.** Typical charge–discharge curves of the original Si and carbon-coated Si electrodes.

Figure 2 shows the cycleability of carbon-coated Si electrodes. In this cycleability test, the cell was discharged at a constant current density of 0.3 mA/mg from open circuit voltage (ca. 3 V) to 3 mV and held at this voltage for 5 h in the first cycle, and then the cell was charged with the same constant current density (0.3 mA/mg) to 1.5 V in the first cycle; from the second cycle, the cell was discharged at 0.3 mA/mg to 100 mV and held at this voltage for 5 h, and then charged at 0.3 mA to 1.5 V. The cell subject to the above charge–discharge procedures demonstrates small capacity fading, from 900 mA h/g in the 2nd cycle to 750 mA h/g in the 20th cycle. Lithium can alloy with Si to the compositions of $Li_{1.71}Si$, $Li_{2.33}Si$, $Li_{3.25}Si$,

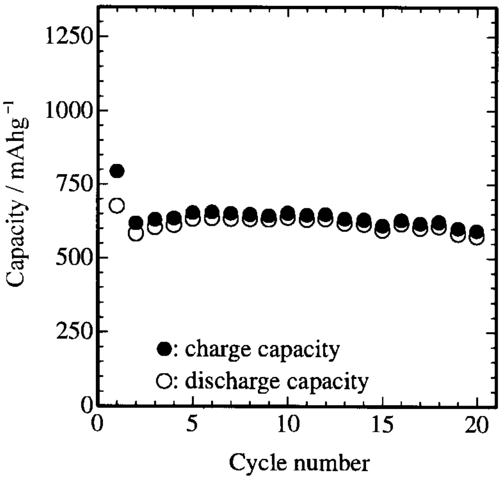

**Figure 2.** Charge–discharge capacities as a function of cycle number for carbon-coated Si electrodes.

and $Li_{4.4}Si$ at elevated temperature.[8] In our studies, the discharge capacity is restricted to less than the corresponding capacity of $Li_{1.71}Si$ (1640 mA h/g-Si). Thus the possible phase transition leading to big volume expansion can be eliminated. This may be parts of the reasons for the good cycleability.

To verify the above assumption, ex situ XRD measurements were performed on the carbon-coated Si electrodes discharged with various capacities as shown in Figure 3. Nickel powder was added into the composite electrode as an internal standard for correcting the diffraction angle in the XRD patterns. It can be observed that there is almost no noticeable shift of the diffraction peak corresponding to Si during the course of lithium doping until the discharge capacity reaches 1200 mA h/g. This indicates that the lattice expansion of Si is very small under the lithiation capacity of 1200 mA h/g. By contrast, it is noticed that the peak standing for carbon-coating shifts to lower angles, which implies that the graphitic layers of carbon-coating phase expands accompanying $Li^+$ intercalation. Thus we expects that the volume enlargement of carbon phase may have at least two effects: 1) suppress the crystal lattice expansion of carbon-surrounded Si particles; 2) fill the void space in the composite anode material and make more contact and adequate electric contact.

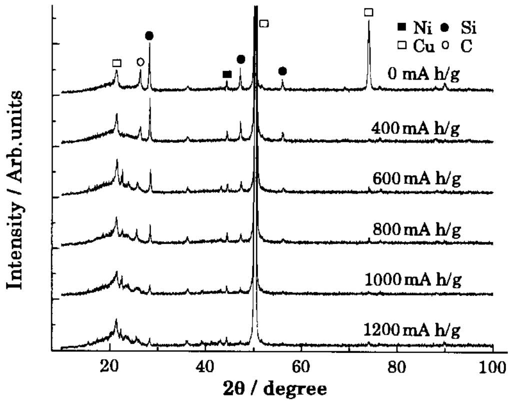

**Figure 3.** Ex situ XRD patterns of carbon-coated Si electrodes discharged with various capacities

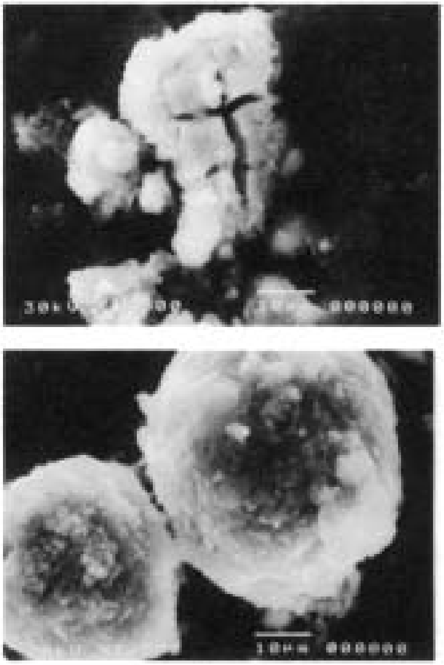

**Figure 4.** SEM images of the carbon-coated Si (down) and the uncoated Si (upper) after some cycle of charge–discharge

The superiority of carbon-coated Si anode materials can be further proved in SEM images of the carbon-coated Si and pure Si after some cycles of charge–discharge as shown in Figure 4. It can be seen clearly that the particle of uncoated Si cracks into several pieces only after several cycles, whereas the particle of carbon-coated Si still keep its integrity after fifty cycles of charge–discharge if the lithiation degree limited to the capacity of 800 mA h/g.

In conclusion, carbon-coated Si prepared by TVD technique shows superior electrochemical performance to Si as anode materials for lithium batteries. The TVD carbon coating can greatly prevent cracking and crumbling of Li–Si alloy in the cycling. If the lithiation capacity of carbon-coated Si is controlled under 1200 mA h/g, satisfactory cycleability can be obtained. The good cycleability might originate from the suppression of the lattice expansion for Si and better electric contact resulted from the volume increase of carbon-coating accompanying the lithiation.

**References and Notes**

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