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Carbon-Coated Si as a Lithium-Ion Battery Anode Material

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Carbon-coated Si has been prepared by a thermal vapor decomposition method. Its electrochemical performance has been investigated by charge/discharge tests, cyclic voltammetric experiments, differential scanning calorimetry, and ^{7}Li-nuclear magnetic resonance, etc. This kind of material demonstrates good electrochemical performance as an anode material for lithium-ion batteries. The improvement in the electrochemical performance of Si is mainly attributed to the effect of carbon coating.
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Graphite has been commonly used as the anode material for lithium-ion batteries by virtue of its low and flat working voltage, good cyclability in compatible electrolytes, etc. However, its theoretical capacity is limited to 370 mAh/g or volumetric capacity of 830 Ah/L. To increase the specific energy of lithium-ion batteries, alternative anode materials with higher capacity are needed.

Besenhard *et al.* have evaluated different lithium alloys as anode materials for lithium-ion batteries.[1] Among so many matrices for lithium alloying, Si stands out because of its high capacity to accommodate lithium (with the maximum uptake of $Li_{4.4}Si$, corresponding to 4200 mAh/g Si). Unfortunately, there is one severe problem with the application of Si anode, *i.e.*, the big volume change during lithium intercalation/deintercalation, which inevitably causes great stress in Si lattice and thus leads to cracking and crumbling of the Si particle. As a result, capacity for alloying lithium fades abruptly only after several cycles of charge/discharge.

To circumvent this problem, several research efforts have been carried out to disperse fine Si particles within a solid, mixed conducting host matrix by mechanical milling.[2-5] Considerable improvements in cyclability have been obtained. Nevertheless, mechanical milling makes the specific surface area of the composite anode materials very big. Consequently, the decomposition of the electrolytes to build up solid electrolyte interface (SEI) films covering the surface of the composite anodes at low voltage will become drastic, and thus give rise to large irreversible capacities at the initial several cycles. This problem can still preclude further use of Si-based anodes in lithium-ion batteries.

In our previous studies,[6-7] a thermal vapor decomposition (TVD) technique has been applied to coat carbon onto the surface of natural graphite particles so as to protect the graphite ''core'' from the contact with PC-based electrolytes. It was found that the TVD carbon coating can suppress the decomposition of most electrolytes to a very small extent at low voltage. So it is assumed that the TVD technique is also applicable to the case of Si.

In this study, carbon-coated Si has been prepared by TVD. The excellent electrochemical performance of carbon-coated Si as an anode material for lithium-ion batteries has been demonstrated.

Experimental

Prior to the TVD carbon-coating process, Si powder (Wako, average particle size 8 μm) was ground in a disk mill for 1 h and then sieved. Si powder with particle size smaller than 53 μm was used for TVD carbon-coating treatment. 10 g of the obtained Si powder was put into a quartz tube furnace purged with a N_2 stream carried with benzene vapor (flow rate, 1 L/min). The temperature of the furnace was kept at 1000°C. At such a high temperature, the benzene vapor decomposed and deposited onto the surface of Si particles as a carbon coating. After a certain time of carbon coating, the furnace was switched off and cooled down slowly. The collected sample was softly ground by a pestle and mortar, and then fed into the tube furnace subject to TVD treatment again. After several cycles repeat of the above procedure, the resultant carbon-coated Si as well as the original Si was tested as the anode material for lithium-ion batteries. Some physical properties of the carbon-coated Si sample are listed in Table I.

Si-based electrodes were prepared by spreading the carbon-coated Si powder (or the original Si powder) slurry (90 wt %) and poly(vinylidene fluoride) (PVDF, 10 wt %) dissolved in 1-methyl-2-pyrrolidinone onto a copper foil substrate. The electrodes were then dried overnight at 105°C under vacuum and pressed between two flat stainless steel plates.

The electrolytes of 1 M $LiPF_6$-ethylene carbonate: dimethyl carbonate (EC:DMC) (1:2 by volume) and 1 M $LiPF_6$-PC were used in our studies. The water contents in these electrolytes were <20 ppm.

The electrochemical measurements included charge/discharge and cyclic voltammetric (CV) tests on the Si-based electrodes. In the charge/discharge tests, two-electrode cells were used. The two-electrode cells generally included a lithium metal electrode and a Si-based electrode, held apart by a separator (Celgard 2400) and a glass fiber. For simulating the true situations in practical lithium-ion batteries, the lithium metal electrode in the two-electrode cells was replaced by $LiMn_2O_4$, $LiCoO_2$, or $LiNiO_2$ electrodes in some cases. The electrodes of $LiMn_2O_4$ were received from Tohso and the $LiCoO_2$ and $LiNiO_2$ electrodes were obtained from Nihon Chemical Industry.

The charge/discharge tests included two sets of procedures. In the first set, namely, constant capacity charge (Here ''charge'' corresponds to lithium intercalation into Si-based electrodes) modes, the procedures were as follows (*e.g.*, for carbon-coated Si/Li metal cell): (*i*) The cell was charged at a constant current density of 0.5 mA/cm^2 from open circuit voltage (OCV, *ca.* 3 V) until the desired capacity, say 800 mAh/g, was reached; (*ii*) the cell was

Table I. Some physical properties of the carbon-coated Si sample.

Weight percents of carbon coating	20%
Average particle size	18 μm
Tap density	0.9 g/cm^3
BET[a] specific surface area	2.8 m^2/g
Volume resistance[b]	95 mΩ cm

[a] Brunauer-Emmett-Teller.
[b] Volume resistance of the Si powder before TVD treatment is 1500 Ω cm.

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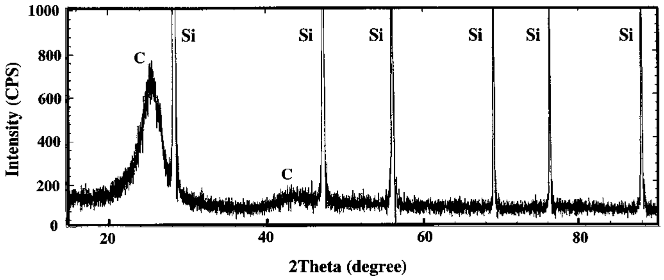


Figure 1. X-ray diffraction (XRD) pattern of carbon-coated Si powder.

rested for 10 min; (*iii*) the cell was discharged at a constant current density of 0.5 mA/cm^2 to 1.5 V; (*iv*) the cell was rested for 10 min; then the cycles were repeated. For carbon-coated Si/LiMn$_2$O$_4$, carbon-coated Si/LiCoO$_2$, and carbon-coated Si/LiNiO$_2$ cells, the cells were generally charged to 800 mAh/g *vs.* Si-based electrodes and then discharged to 2.5 V at the same current density (there was 10 min of rest after each cycle charge or discharge). By contrast, in the second set, namely, "constant voltage charge" mode, the procedures for carbon-coated Si/Li metal cell was as follows: (*i*) the cell was discharged/charged by the "constant capacity charge" mode in the first cycle; (*ii*) from the second cycle on, the cell was charged from 1.5 V to 100 mV at the constant current density of 0.5 mA/cm^2 and held at this voltage for 130 min; (*iii*) the cell was rested for 10

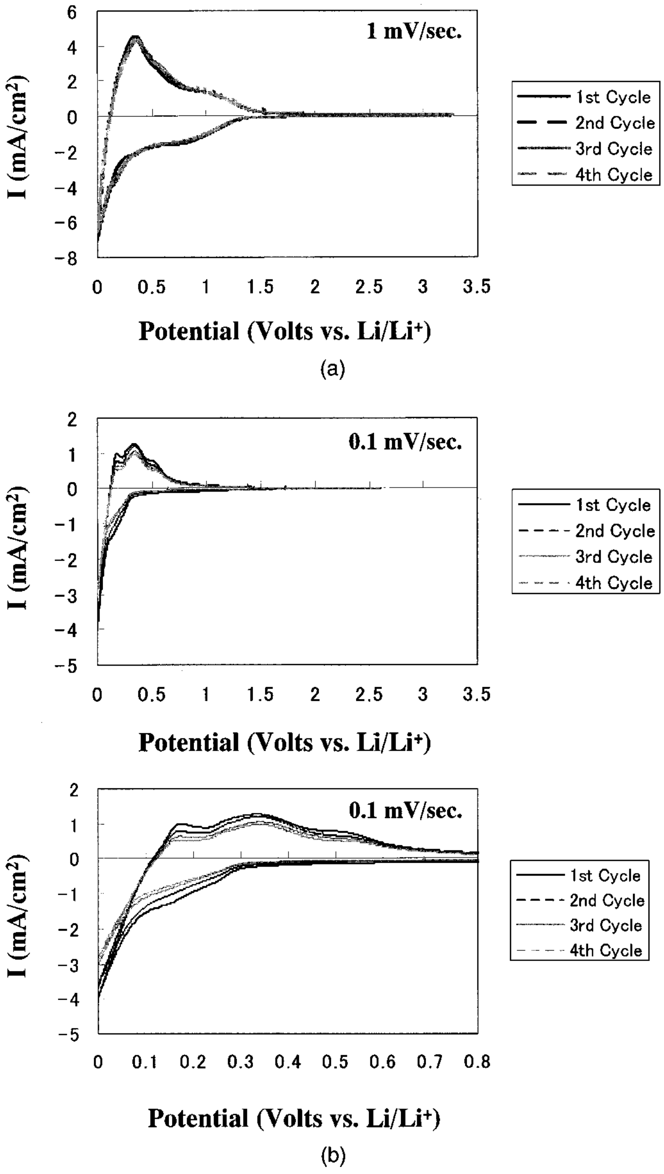


Figure 2. Typical CVs of carbon-coated Si in the electrolytes of 1 M LiPF$_6$-EC:DMC (1:2 by volume) at the scan rates of (a) 1 mV/s; and (b) 0.1 mV/s.

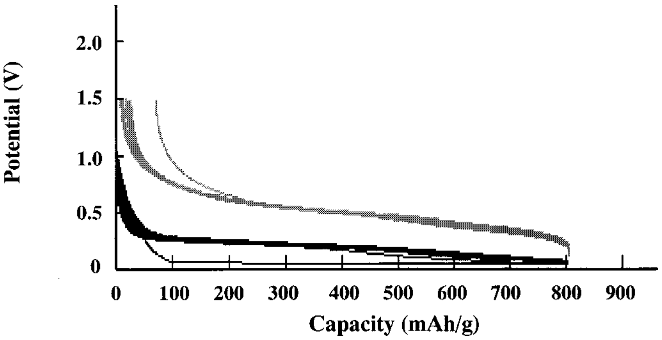


Figure 3. Typical charge/discharge curves of the carbon-coated Si/Li metal cells using the constant capacity charge mode in the electrolyte of 1 M LiPF$_6$-EC:DC (1:2 by volume).

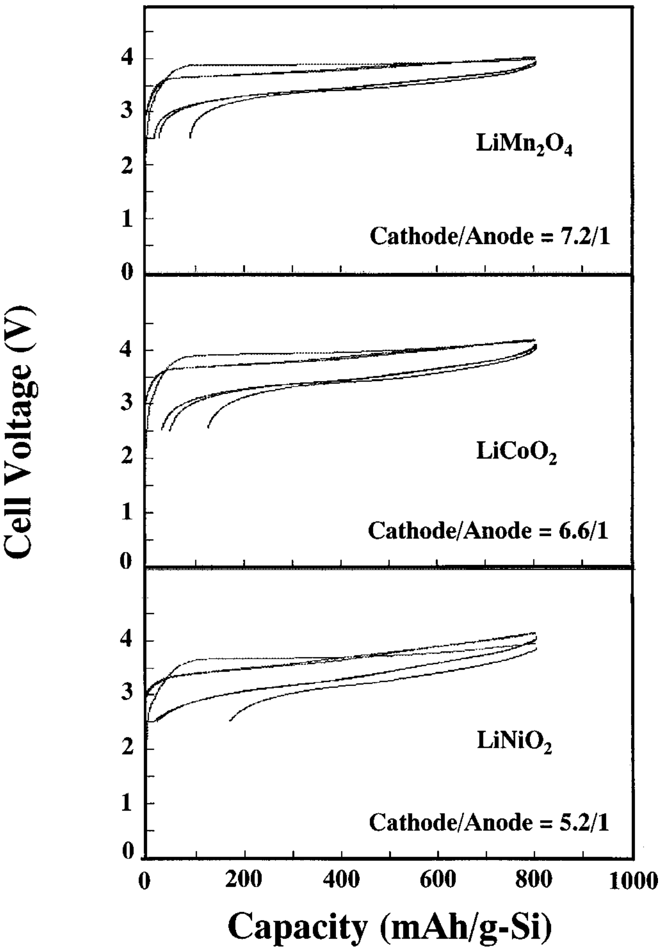
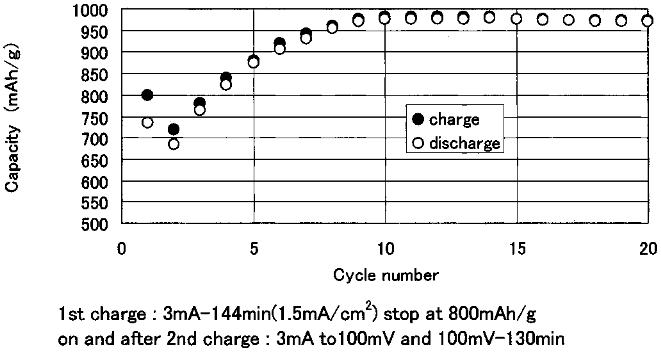


Figure 4. Typical charge/discharge curves of the carbon-coated Si/LiMn$_2$O$_4$, carbon-coated Si/LiCoO$_2$, and carbon-coated Si/LiNiO$_2$ cells using the constant capacity charge mode in the electrolytes of 1 M LiPF$_6$-EC:DMC (1:2 by volume).



1st charge : 3mA-144min(1.5mA/cm^2) stop at 800mAh/g
on and after 2nd charge : 3mA to100mV and 100mV-130min

Figure 5. Cycle life behavior of carbon-coated Si using the constant voltage charge mode in the electrolyte of 1 M $LiPF_6$-EC:DMC (1:2 by volume).

min; (*iv*) the cell was discharged with the constant current density of 0.5 mA/cm^2 to 1.5 V; then the cycles were repeated from steps ii to iv.

In the CV experiments, three-electrode cells were used. In these cells, lithium metal electrodes were used as both the counter and reference electrodes, and the Si-based electrodes were used as the working electrodes. The cells were cycled between OCV (*ca.* 3 V *vs.* Li/Li^+) and 0 V *vs.* Li/Li^+ at different scan rates.

In order to evaluate the thermal safety issue of carbon-coated Si as an anode material for lithium-ion batteries, we performed differential scanning calorimetry (DSC) studies on lithiated carbon-coated Si. DSC of lithiated MCMB-6-28 (Osaka Gas) is also investigated as a reference. The samples were washed with the solvent of DMC and dried over vacuum at room temperature prior to placement into DSC pans.

To gain more insights into our studies on carbon-coated Si, the Si-based electrodes were charged and discharged to different extents of lithiation and examined by ^{7}Li nuclear magnetic resonance (NMR) spectroscopy. The details are similar to those described in our previous paper.[6]

Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of carbon-coated Si powder. The peaks due to carbon and Si diffractions can be clearly observed, whereas no peak corresponding to SiC can be seen. In the previous study of Wilson *et al.*, SiC is formed in carbons containing nanodispersed Si atoms if the content of silicon exceeds 11 atom %.[8] SiC is electrochemically inactive toward lithium, which will decrease the overall capacity of the composite electrode material. Although both of the studies included gaseous sources for preparing the Si-C composite anode material, we only used organic vapor for the carbon-coating source but adopted Si powder as a starting material, whereas Wilson *et al.* utilized gases as all the starting materials. This may be one of the reasons in the difference of the products.

To get a rough estimation of the electrochemical behavior for the carbon-coated Si, cyclic voltammetric experiments were conducted at first. Figure 2 shows the typical cyclic voltammograms (CV) of carbon-coated Si at the scan rates of 1 and 0.1 mV/s, respectively. The three-electrode CV cells were cycled at high scan rate (1 mV/s) prior to slow scan rate (0.1 mV/s). In the first cycle of CV, the irreversible peak of electrolyte decomposition ranging from 0.5 to 1.5 V *vs.* Li/Li^+ can hardly be seen (all the CV curves in this potential range overlap with each other throughout the fifth cycles), which implies that the electrolyte decomposition on the surface of carbon coating can be suppressed to a very small extent, and thus ensure high reversibility of this material. Moreover, in the CV at high scan rate, say, 1 mV/s, the features due to lithium intercalation/deintercalation into or from the carbon coating are mainly demonstrated, as discussed in Ref. 7. It is expected that at high scan rates, most lithium ions only diffuse in the outer carbon-coating layer of

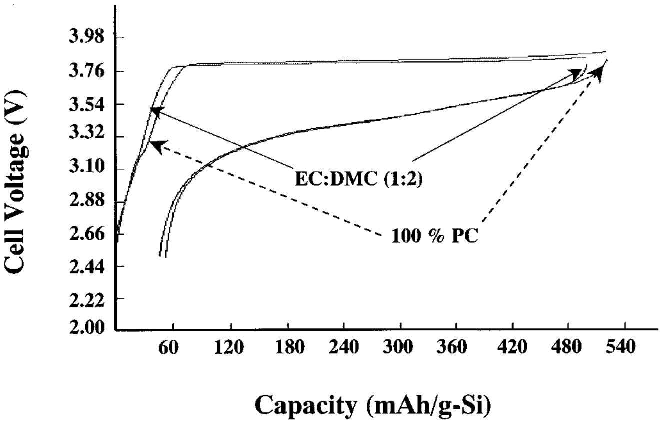


Figure 6. Initial charge/discharge curves of the carbon-coated Si/$LiCoO_2$ cell using constant capacity charge (520 Ah/g) mode in the electrolytes of 1 M $LiPF_6$-EC:DMC (1:2 by volume) and 1 M $LiPF_6$-PC.

every Si-based particle and few lithium ions can penetrate into the Si core since the diffusion rates in both the Si and carbon phases are too slow to catch up with the potential sweep. As the scan rate decreases to certain degree, like 0.1 mV/s, more and more lithium ions can follow up with the potential steps and enter the Si core. Thus the peaks due to Li-Si alloying/dealloying predominate in the CV. As shown in the CV at 0.1 mV/s, the humps range from 0.7 to 1.3 V *vs.* Li/Li^+. In the CV at 1 mV/s, the humps can hardly be seen in both cathodic and anodic directions. The humps are fingerprints of a carbon phase. By contrast, there are roughly three anodic peaks that can be clearly observed at about 0.20, 0.36, and 0.53 V *vs.* Li/Li^+, respectively. A shoulder at about 0.3 V *vs.* Li/Li^+ can also be watched at the negative-potential side of the anodic peak at 0.36 V *vs.* Li/Li^+. These delicate peaks originate from the phase transitions between $Li_{4.4}Si$, $Li_{3.25}Si$, $Li_{2.33}Si$, $Li_{1.71}Si$, and Si, respectively.[9] On the other hand, the corresponding delicate anodic peaks can barely be observed in the cathodic scans of the CV at 0.1 mV/s. Instead, the cathodic current begins to rise up slopingly from *ca.* 0.3 V *vs.* Li/Li^+ until the lowest potential of 0 V *vs.* Li/Li^+, which may come from the big polarization due to low diffusion of lithium ions in Si phase. Comparison of the CVs at 1 and 0.1 mV/s also indicates the difference in the cyclabilities of the carbon-coating and Si core in the potential range from OCV to 0 V *vs.* Li/Li^+. In the CV at 1 mV/s, there is little decrease of the currents with cycling, which implies the good cyclability of carbon coating phase. On the contrary, noticeable decreases can be seen in the currents during cycling in the CV at 0.1 mV/s. This means that the capacity is fading in Si phases along with cycling.

Figures 3 shows the typical charge/discharge curves of the carbon-coated Si/Li metal cells by using the "constant capacity charge" mode. In the first cycle, the charge capacity (intercalation of lithium into Si-based electrode) was 800 mAh/g while the discharge capacity (deintercalation from Si-based electrode) was 737 mAh/g. Thus the coulombic efficiency in the first cycle was 92.1%. From the second until the 50th cycle, the values of discharge and charge capacity are very near for every cycle, which implied very high coulombic efficiency (near 100%). It is well known that Li alloys with Si with the compositions of $Li_{1.71}Si$, $Li_{2.33}Si$, $Li_{3.25}Si$, and $Li_{4.4}Si$ at elevated temperature.[9] In our studies, it is anticipated that if the charge capacity is restricted less than the corresponding capacity of $Li_{1.71}Si$ (1640 mAh/g-Si), the big expansion of Si lattice due to phase transition can be considerably suppressed and thus the cyclability of Si-based electrode is improved.[10]

Figure 4 shows the typical charge/discharge curves of the carbon-coated Si/$LiMn_2O_4$, carbon-coated Si/$LiCoO_2$, and carbon-coated Si/$LiNiO_2$ cells using the constant capacity charge mode. The

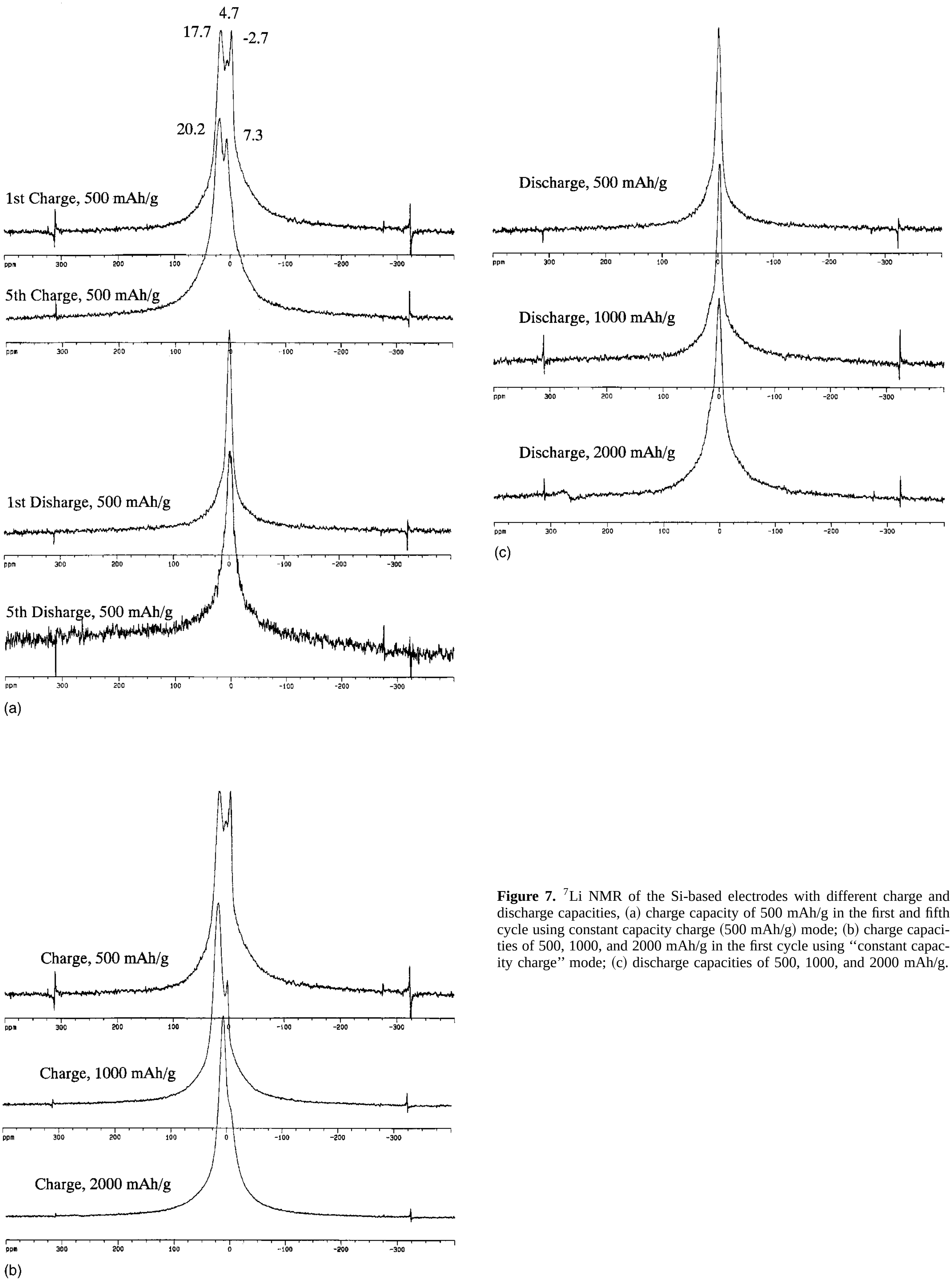


Figure 7. ^{7}Li NMR of the Si-based electrodes with different charge and discharge capacities, (a) charge capacity of 500 mAh/g in the first and fifth cycle using constant capacity charge (500 mAh/g) mode; (b) charge capacities of 500, 1000, and 2000 mAh/g in the first cycle using "constant capacity charge" mode; (c) discharge capacities of 500, 1000, and 2000 mAh/g.

weight ratios between the cathode materials ($LiMn_2O_4$, $LiCoO_2$, and $LiNiO_2$) and carbon-coated Si anode are indicated in the figure. In these cells, the high coulombic efficiency as in the carbon-coated Si/Li metal cell could not be obtained and the discharge capacities (deintercalation from Si-based anodes) were a little lower than 800 mAh/g. This may be due to some limitations in cathode materials. Moreover, the average working voltages of these cells were *ca.* 3.5 V (carbon-coated Si/$LiMn_2O_4$), 3.4 V (carbon-coated Si/$LiCoO_2$), and 3.25 V (carbon-coated Si/$LiNiO_2$), respectively. These values are *ca.* 0.3 V lower than the working voltages of the corresponding cells using graphite as anode material.

As demonstrated above, high reversible capacity of 800 mAh/g can be obtained by the constant capacity charge mode for carbon-coated Si. Figure 5 shows the cycle life behavior of carbon-coated Si using the constant voltage charge mode. After being charged to 800 mAh/g and discharged to 1.5 V in the first cycle, the cell was charged to 100 mV and held at this voltage for 130 min from the second cycle on. As a result, both the charge and discharge capacities in the second cycle are low, and from the third to the 10th cycle, both the charge and discharge capacities grow up until the saturation value of 980 mAh/g. From the 10th cycle, the capacities fade slowly with the cycles. Therefore it seems that charge (intercalation of lithium into Si-based electrode) mode plays a very important role in the cyclability of the carbon-coated Si electrode.

The above satisfactory electrochemical performance of carbon-coated Si was obtained in the EC-based electrolyte of 1 M $LiPF_6$-EC:DMC (1:2 by volume). To make carbon-coated Si a versatile anode material for lithium-ion batteries, the compatibility of carbon-coated Si with PC-based electrolyte was also tested. Figure 6 shows the initial charge/discharge curves of the carbon-coated Si/$LiCoO_2$ cell in the electrolytes of 1 M $LiPF_6$-EC:DMC (1:2 by volume) and 1 M $LiPF_6$-propylene carbonate (PC). It can be seen that there is almost no difference in the charge curves for both the EC and PC-based electrolytes, other than one small shoulder at 3.2 V in the charge curve for 1 M $LiPF_6$-PC electrolyte, which is due to the mild decomposition of the electrolyte on the surface of carbon-coated Si. This indicates that a Si-based electrode also is compatible with PC-based electrolytes.

To shed more light on the storage states of lithium in Si-based electrodes, ^7Li NMR was applied on the Si-based electrodes with different charge and discharge capacities as shown in Fig. 7. In the ^7Li NMR spectra (as shown in Fig. 7a) of the carbon-coated Si electrode being charged (intercalation of lithium) with 500 mAh/g in the first cycle, there are mainly three peaks at the chemical shifts of -2.7, 4.7, and 17.7 ppm, respectively. On the other hand, in the ^7Li NMR spectra of carbon-coated Si electrode charged with 500 mAh/g in the fifth cycle (after constant capacity charge of 500 mAh/g for 4 cycles), two peaks can be observed at the chemical shifts of 7.3 and 20.2 ppm, respectively. If we correct the chemical shift of the peak at -2.7 to 0 ppm in the former ^7Li NMR spectra, the peaks at 4.7 and 17.7 ppm can be modified to 7.4 and 20.4 ppm, repectively. The ^7Li NMR spectra of carbon-coated Si lithiated to 500 mAh/g at different cycles (first and fifth) demonstrate almost the same signals at *ca.* 7.3 and 20.2 ppm, except the peak at 0 ppm in the spectra at the first cycle. Moreover, the intensity ratios of the peaks at 7.3 and 20.2 ppm for both spectra are near. From the chemical shifts of the signals in the ^7Li NMR spectra of lithiated Si-based electrodes, the highly ionic states of lithium stored in the carbon-coated Si can be clarified. As for the peak at 0 ppm in the first cycle, it may originate from two sources: (1) the signal of the residue electrolyte on the surface of the Si-based electrode; (2) some response from lithium inserted into Si based electrodes. However, the signal from the residue electrolyte must be much weaker as compared with the response from lithium inserted into the electrode since the electrode material was tested by ^7Li NMR after being rinsed with DMC solvent and dried. In the ^7Li NMR spectra of the carbon-coated Si electrodes in fully discharged (deintercalation of lithium from 500 mAh/g lithiated carbon-coated Si states, as shown in Fig. 7c, only the signal at 0 ppm can be observed. The intensities of this signal are very high. So it seems more likely the peak at 0 ppm originates from the Li^+ irreversibly bonded with Si-based material. With increasing lithiation extent (charge capacities of 500, 1000, and 2000 mAh/g), as shown in Fig. 7b, the intensities of the peaks at 7.3 and 20.2 ppm increase whereas that at 0 ppm decreases relatively, and becomes a shoulder of the former peaks. In the ^7Li NMR spectra of carbon-coated Si electrodes fully delithiated from the charged capacities of 500, 1000, and 2000 mAh/g, respectively, as shown in Fig. 7c, the signal at 0 ppm is always very large, and the signal at 7.3 ppm becomes a very small shoulder of the peak at 0 ppm in the cases of charge capacities of 1000 and 2000 mAh/g. The signal at 20.2 ppm cannot be seen in all the spectra of fully delithiated Si-based electrodes. Therefore, the signal at 0 ppm can be mainly attributed to Li^+ irreversibly bonded with carbon-coated Si, whereas the signal at 20.2 ppm originates from lithium reversibly alloyed with Si.

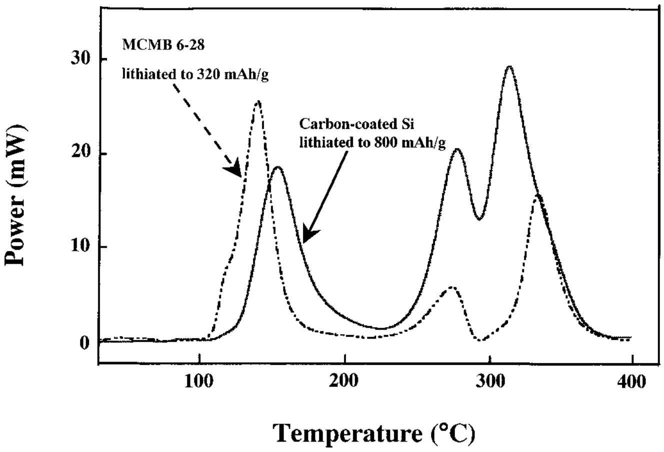


Figure 8. DSC thermal profiles of carbon-coated Si lithiated to 800 mAh/g and MCMB 6-28 lithiated to 330 mAh/g.

To evaluate the thermal stability of carbon-coated Si electrodes, DSC experiments were carried out on lithiated carbon-coated Si and mesocarbon microbeads (MCMB) 6-28. Figure 8 shows the DSC thermal profiles of carbon-coated Si lithiated to 800 mAh/g and MCMB 6-28 lithiated to 330 mAh/g. The exothermic peaks lower than 150°C can be observed for both lithiated Si-based material and MCMB, which originate from the breakdown of the SEI layer.[11,12] These peaks demonstrate close intensities. This implies similar exothermic heat generations. Moreover, the onset temperature of the exothermic peak corresponding to lithiated carbon-coated Si is a little higher than that of the lithiated MCMB. In addition, two exothermic peaks appear at temperatures higher than 250°C for each DSC thermal profile. These peaks may be due to the reaction of intercalated lithium (into Si or C) with PVDF binder.[12] The exothermic heat generation corresponding to the peaks of lithiated carbon-coated Si higher than 250°C amount to almost three times of that of lithiated MCMB. This seems in accord with their relative capacities to accommodate lithium. Thus, carbon-coated Si is a little thermally safer than the conventional anode material, graphitic carbon, at temperatures lower than 150°C.

Conclusion

So far we have showed the excellent electrochemical performance of carbon-coated Si as anode materials for lithium-ion batteries in terms of high reversible capacity over 800 mAh/g, high coulombic efficiency, good cyclability, satisfactory compatibility with both the EC and PC-based electrolytes, and better thermal stability than that of graphite, etc. Carbon-coating in the outer layer plays a very important role in the improvement of the electrochemical behavior. It could not only considerably suppress the big decomposition of electrolytes on the surface of Si-based electrodes, but also provide integral and continuous electric contact networks around Si particles even they are a little expanded after lithium insertion. ^{7}Li NMR spectra of lithiated/delithiated Si based electrodes demonstrates three kinds of storage sites for lithium in carbon-coated Si, corresponding to the signals at 0, 7.3, and 20.2 ppm, respectively. The signals at 0 and 20.2 ppm can be ascribed to lithium irreversibly bound with and reversibly alloyed with Si, respectively. Lithium-ion batteries using carbon-coated Si as anode materials have average working voltages about 0.3 V lower than those using graphite.

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