Thermal stability of silicon negative electrode for Li-ion batteries

Liwei Zhao[a], Seung-Hee Han[b], Shigeto Okada[a], Byung-Ki Na[c], Kazuhiko Takeno[d], Jun-ichi Yamaki[a,*]

[a] Institute of Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen, Kasuga 816-8580, Japan
[b] Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen, Kasuga 816-8580, Japan
[c] Department of Chemical Engineering, Chungbuk National University, 12 Gaeshin, Heungduk, Chungbuk 361-763, Republic of Korea
[d] DOCOMO R&D Center, NTT DOCOMO, Inc., 3-6 Hikarino-oka, Yokosuka, Kanagawa 239-8536, Japan

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ABSTRACT

A silicon/disordered-carbon powder was applied as the negative electrode material in Li ion batteries. The thermal characteristics of the Si/C electrode mixed with or without the electrolyte were investigated by DSC. Both lithiated (with capacity of 1120 mAh g^{-1}) and delithiated Si/C electrode powder showed exothermic peaks in DSC curves due to the reactions between the Li in the electrode and the SEI. The lithiated electrode caused much larger exothermic heat than the delithiated one, especially when they were mixed with the electrolyte. By changing the ratio between the lithiated Si/C electrode and the coexisting electrolyte, the thermal behavior of the mixture could be studied in detail. At about 290 °C, a mixture containing 0.5 mg lithiated Si/C electrode and 0.5 μl electrolyte showed the most drastic exothermic heat of 2.2 J among all mixtures due to a direct reaction between the residual lithiated electrode and the solvent of the electrolyte after the thermal breakdown of the SEI. Under this condition, the heat value based on the electrode weight was 4.4 J mg^{-1}, and that based on capacity was 5.1 J mA h^{-1}. These values of graphite were estimated to be 1.9 J mg^{-1} and 5.8 J mA h^{-1}, respectively. The generated heat was found to be very sensitive to the electrode/electrolyte ratio.

1. Introduction

Rechargeable Li-ion batteries have been extensively applied in various commercial applications, and seem to be an excellent candidate for the energy source of hybrid electric vehicles and electric vehicles. Graphitic carbon, which provides a theoretical capacity of 372 mAh g^{-1}, has been generally used as the negative-electrode material in current commercial Li-ion batteries. However, the increasing demands of advanced technologies make the need for power sources with higher energy density even more critical. Silicon is one of the most promising negative-electrode materials for Li-ion batteries because it has low Li-alloying potential (<0.5 V vs. Li/Li$^+$) [1] and the highest-known theoretical capacity of 4200 mAh g^{-1} [2,3], which is up to an order of magnitude higher than that of graphitic carbon. However, the practical application of silicon electrodes has been hindered because of its rapid capacity fading during electrochemical cycling. It has been demonstrated that a severe crystallographic volume change (order of 400%) [4] upon the electrochemical alloying process induced mechanical failure in Si electrodes, owing to the cracking and pulverization of the active material particles. Considerable efforts adopting different approaches have been made to solve this crucial problem. Reduction of the Si particles and crystallite size to the nm-range is supposed to have a positive influence on the cycling behavior, as the mechanical stress during the Li-alloying process would thereby be reduced. Nano-structure Si has been investigated as a negative-electrode material by many groups [5–12]. However, the nano-Si electrodes still have many problems, such as electrochemical sintering of particles, low cell capacity, high production cost. Therefore, more attention has been focused on the synthesis and application of Si composites, especially composites consisting of silicon and carbon materials, in which the Si particles are homogeneously dispersed within a soft and ductile carbon matrix [13–16] or coated with a carbon layer [17–21]. During the alloying process, the volume changes of silicon particles could be buffered to a certain extent. In addition, carbon is helpful in maintaining good electric contact in the electrode during cycling. Several synthetic methods and kinds of carbonaceous materials have been employed to obtain Si—C composites. This seems to be a promising way for the practical application of Si as a negative-electrode material in Li-ion batteries.

The negative electrode containing Li is thermodynamically unstable and reacts with the electrolyte, especially at an elevated temperature. The thermal characteristic of the negative electrode has a definite effect on the battery safety. As the Si-based negative electrode presents high specific capacity, its thermal properties,

* Corresponding author. Tel.: +81 92 583 7790; fax: +81 92 583 7790.
E-mail address: yamaki@cm.kyushu-u.ac.jp (J.-i. Yamaki).

especially when it coexists with the electrolyte, become a crucial concern for its practical application. However, very few comparative studies have been reported. Wang and Dahn [22,23] compared the thermal behaviors of lithiated Si and lithiated mesocarbon microbeads (MCMB) at high temperature using accelerating rate calorimetry (ARC). It was reported that the lithiated Si and lithiated MCMB showed similar ARC responses at an equal capacity, and lithiated Si was concluded to be safer than lithiated graphite at this state because a thicker LiF surface layer formed on the Si electrode. Recently, Park and Lee [24] investigated the effect of particle size on the thermal properties of the Si electrode with differential scanning calorimetry. A shift of the major exothermic peak to a lower temperature combined with a decrease of heat generation was obtained with smaller Si particles. However, the variation of irreversible Li loss with different Si particle sizes has not been clarified.

In order to study the safety of the Si-based electrode, especially that of the Si/C composite electrode, the thermal behavior of a Si/disordered-carbon composite in a $LiPF_6$-based electrolyte at different ratios of electrode to electrolyte was investigated in detail using thermogravimetry-differential scanning calorimetry (TG-DSC). The effect of the ratio between the Si/C electrode and electrolyte on the thermal stability of the system was clarified. Moreover, some mechanisms of the exothermic reactions between cycled Si/C composite and the electrolyte are also discussed here.

2. Experimental

The silicon/disordered-carbon (Si/C) composite was prepared from silicon powder (crystalline, −325 mesh, 99.999%, Alfa Aesar) and polyvinyl chloride (PVC, Aldrich) using the method reported by Liu et al. [25]. Silicon powder and PVC were mixed at a weight ratio of 3:7 by hand-milling. The mixture was heated at 900 °C for 1 h in an Ar atmosphere. After cooling down to room temperature, the products were further treated by a planetary milling system (premium line P-7, Fritsch) at 500 rpm for 2 h in an Ar atmosphere. The milled product was mixed with PVC again at a weight ratio of 3:7. Then the mixture was heated at 900 °C for 1 h again in an Ar atmosphere and cooled down to room temperature. After being ground by hand, the Brunauer–Emmett–Teller (BET) specific surface area of the Si/C composite samples was calculated to be 28.7 m² g⁻¹ (N₂ gas, BEL JAPAN, Inc.). The final product was characterized by XRD (RINT-2200, Rigaku) and SEM (JSM-6340F, JEOL).

The negative electrode was prepared by spreading a slurry of 85 wt.% Si/C composite, 5 wt.% acetylene black (DenkiKagaku Kogyo) and 10 wt.% poly(vinylidenefluoride) (PVdF)-binder (KF#9305, Kureha Chemical) dissolved in 1-methyl-2-pyrrolidinone onto a 0.1-mm-thick porous Cu-foil current collector. After being heated at 120 °C for 2 h and pressed by a rolling mill machine, circular electrodes (15-mm-diameter) with a typical loading of 9 mg cm⁻² Si/C were dried at 110 °C for 12 h in a vacuum oven.

Two-electrode coin cells were used in charge–discharge measurements to study the electrochemical properties of the Si/C composite. Each coin cell consisted of a working electrode, a polypropylene separator (Celgard 3501) and a lithium-foil (Honjo Metal Co., Ltd.) counter electrode. The electrolyte was 1 mol dm⁻³ $LiPF_6$/ethylene carbonate–dimethyl carbonate (EC-DMC, 1:1, v/v, Tomiyama Chemical). All cells were assembled in an Ar-filled glove box with a dew point below −70 °C. The charge–discharge cycling was performed between 0.05 and 1.5 V at a constant current density of 0.3 mA cm⁻², with a relaxation period of 1 min at the end of each charge/discharge process. All potentials reported in his work were referenced to the Li/Li⁺ redox couple.

After the second charge or discharge process, the coin cell was disassembled in an Ar-filled glove box. The test electrode was
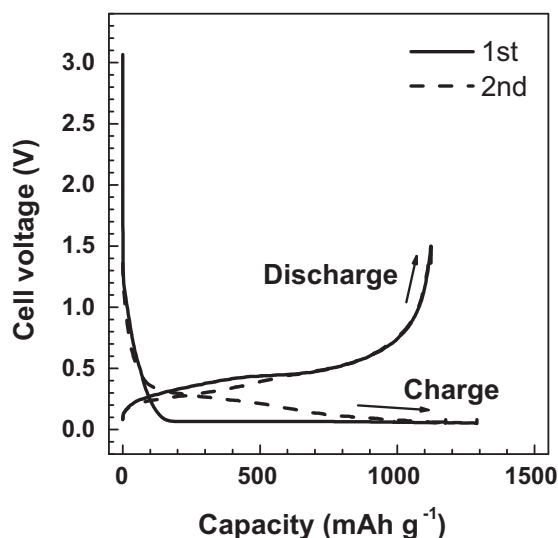

Fig. 1. Cycling profiles of silicon/disordered-carbon electrode in 1 mol dm⁻³ $LiPF_6$/EC-DMC (1:1, v/v) electrolyte.

rinsed and soaked in DMC for 4 h and vacuum-dried at room temperature for 12 h to remove the DMC. The thermal stabilities of Si/C electrode powder were investigated by differential scanning calorimetry combined with thermogravimetric analysis (TG-DSC, Thermo plus TG8110, Rigaku). Given amounts of the electrode powder and the electrolyte were packed in a crimp-sealed stainless pan. With alumina as a reference material, the pan was heated in air from room temperature to 450 °C at a rate of 5 °C min⁻¹. During measurements, both the exothermic and endothermic heat was monitored by DSC system, and the hermetization of the pan was verified by the absence of weight loss in the TG curves.

3. Results and discussion

The composition of the synthesized Si/C composite was studied first before it was applied to electrochemical measurement. A certain amount of Si/C composite was added to a mixture of 10 ml hydrogen fluoride and 2 ml nitric acid and heated up to 200 °C for 1 h. The Si of the Si/C composite was dissolved and then filtered out. By weighing the residue, the Si-to-C-ratio of the Si/C composite was determined to be 7:3 (w/w). XRD and SEM measurements were also carried out to characterize the Si/C composite. Only an inconspicuous peak related to SiC was observed in the XRD pattern besides the preponderant Si crystal signal, which indicated the Si crystal particles were well maintained in the synthesized Si/C composite. In SEM images, the Si/C composite showed uniform particles with diameters of 0.5–1.5 μm, which was much smaller than the 45-μm diameters of the precursor Si particles.

The charge/discharge profiles of the Si/C composite are shown in Fig. 1. The first cycling curves are shown by solid lines, and the second one are shown by dashed lines. The initial charge (lithiation of Si/C) and discharge (delithiation of Si/C) capacities were 1290 and 1120 mAh g⁻¹, respectively, and the irreversible capacity at the first cycle was 170 mAh g⁻¹. All capacities were calculated by the weight of Si/C. In the second cycle, the irreversible capacity abruptly decreased to 55 mAh g⁻¹, while the discharge capacity was maintained at 1120 mAh g⁻¹. The irreversible capacity was attributed to the formation of solid electrolyte interphase (SEI) [26,27] on the electrode surface. This result was consistent with that obtained by Liu et al. [25]. Since 30 wt.% disordered carbon was involved in the Si/C composite, the contribution of the disordered carbon on the specific capacity of the Si/C electrode was evaluated by using a disordered-carbon electrode that was fabricated from PVC using
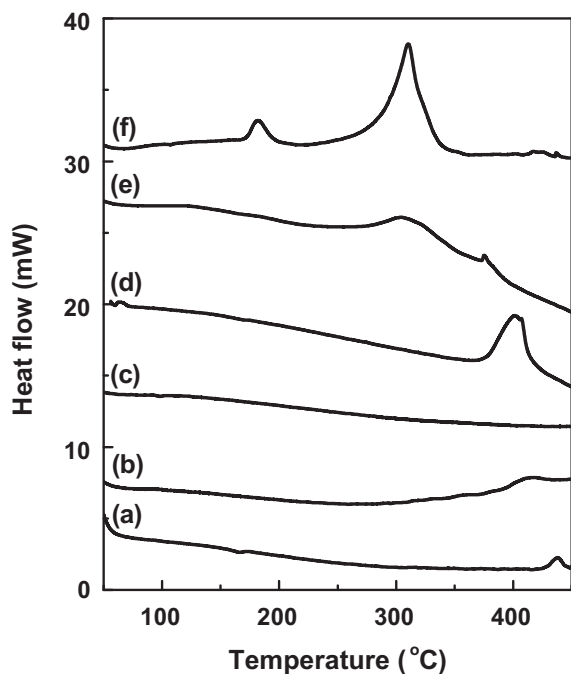
Fig. 2. DSC curves of (a) 0.4 mg PVdF binder, (b) 4 mg disordered-carbon pristine electrode, (c) 4 mg Si/C powder, (d) 4 mg pristine Si/C electrode, (e) 4 mg delithiated Si/C electrode, and (f) 4 mg lithiated Si/C electrode.

Fig. 3. DSC curves of (a) 0.5 μl, 1 mol dm^{-3} LiPF$_6$/EC-DMC (1:1, v/v) electrolyte and a mixture of 0.5 μl electrolyte and 0.5 mg of (b) pristine Si/C electrode, (c) delithiated Si/C electrode, and (d) lithiated Si/C electrode.

the same method as that for the Si/C electrode. A specific capacity of 250 mAh g^{-1} was obtained with the disordered-carbon electrode under the same cycling condition as that for Si/C composite. Accordingly, the specific capacity of the Si particle in the electrode was calculated to be 1493 mAh g^{-1} using a secondary discharge capacity of 1120 mAh g^{-1} based on the total weight of the Si/C electrode.

Fig. 2 shows the DSC curves of fresh Si/C powder, the initial electrode and the lithiated/delithiated electrodes. 4 mg sample was loaded in a pan for each measurement. For reference, 4 mg disordered-carbon electrode and a 0.4 mg pure PVdF were also analyzed by DSC, respectively. As expected, no thermal peak was observed in the DSC curve of fresh Si/C powder until 450 °C, due to the good thermal stability of the Si/C composite. As to the fresh electrode before the cell fabrication, an obvious exothermic heat at about 400 °C was obtained, which should be related to the PVdF binder in the electrode. However, in the DSC curve of either the 4 mg disordered-carbon electrode or the 0.4 mg PVdF binder, which contained the same amount of PVdF, only a much smaller exothermic peak at a temperature higher than 400 °C was observed. Therefore, the PVdF thermal decomposition should be accompanied by other exothermic reaction(s). As is well known, hydrogen fluoride (HF) is a thermal decomposition product of PVdF, so it was reasonable to attribute the large exothermic heat mainly to the reaction between HF and the Si particles in the electrode. The cycled Si/C electrodes showed completely different DSC curves compared with the initial one. For the delithiated electrode (charged to 1.5 V), only a mild exothermic heat at around 310 °C was obtained. For the lithiated electrode (discharged to 0.05 V), besides a small exothermic peak centered at 183 °C, a much stronger exothermic peak was observed at the same position as that of the delithiated electrode. It was reported that a solid electrolyte interphase (SEI) formed on a Si/C electrode surface consisting of compounds that were already known as SEI species to a carbon electrode [27]. Therefore, according to our previous studies on graphite [28] and disordered-carbon [29] electrodes, the exothermic heat around 310 °C of the lithiated Si/C electrode could be attributed to the reaction between Li in Si/C and the SEI. On the other hand, as the Si/C electrode showed rather
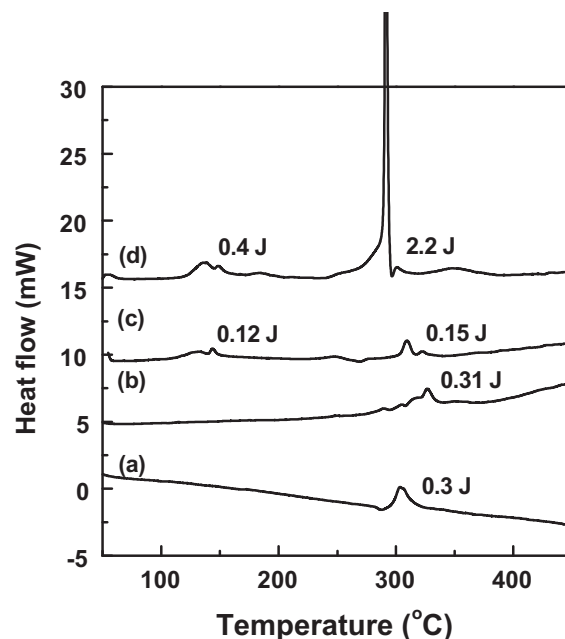
high irreversible capacity, some Li was supposed to have remained in the electrode even in the delithiated state. The irreversible Li reacted with the SEI at elevated temperature, just like the reversible Li did, and induced a mild exothermic heat at about 310 °C for the delithiated electrode. The peak at 180 °C was unique for the lithiated Si/C electrode as no relative peaks were obtained with lithiated graphite [28] and disordered-carbon [29] electrodes. This might be related to the unique siloxane species [27] in the SEI of the Si/C electrode.

From the point of application, heat generation caused by the reaction between the negative electrode and the electrolyte is crucial for Li-ion battery safety. Fig. 3 shows the DSC curves of 0.5-mg Si/C electrodes in different states mixed with 0.5 μl of electrolyte. For reference, the DSC curve of 0.5 μl electrolyte alone is also presented. For the fresh electrode, small exothermic peaks were obtained from 280 to 340 °C. Although some reactions between Si particles and PF$_5$ generated from the thermal decomposition of LiPF$_6$ might be involved, the heat value from the mixture of fresh electrodes and electrolyte was almost the same as that from the electrolyte only. The delithiated electrode-containing mixture showed two groups of small peaks at around 140 and 310 °C, respectively. A similar exothermic peak at 140 °C was also found with the mixture of lithiated electrode and electrolyte, but it had a higher intensity in the latter. It has been reported that a secondary SEI (s-SEI) was formed in the mixture of lithiated carbon and electrode during the DSC measurement [29] and induced exothermic heat at around 130 °C. When a lithiated electrode was heated up in the electrolyte, due to the increases of the diffusion constant of electrolyte molecules in SEI, the initial SEI formed during cycling could not prevent the contact between electrolyte molecules and Li in the electrode. When the electrolyte molecules and Li in the electrode came in contact, the SEI-formation reaction happened and a thicker passivation film was formed. The newly formed passivation film was defined as an s-SEI. According to the formation mechanism, the s-SEI was supposed to have similar components and function to the initial SEI. And with temperature ramping up further, the initial SEI and s-SEI could not be discriminated anymore, but worked together as a single SEI. It was reasonable to suppose that a
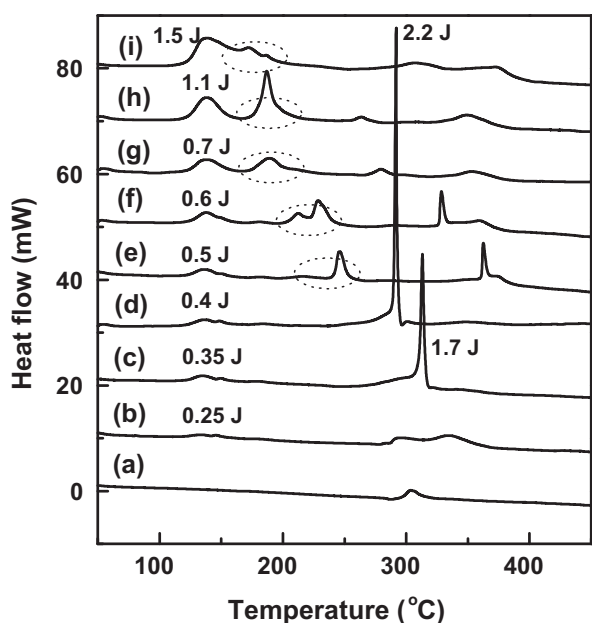
Fig. 4. DSC curves of mixtures of 0.5 μl electrolyte and (a) 0 mg, (b) 0.25 mg, (c) 0.37 mg, (d) 0.5 mg, (e) 0.65 mg, (f) 0.85 mg, (g) 1 mg, (h) 1.5 mg, and (i) 2 mg lithiated Si/C electrode.

Fig. 5. Dependence of the heat values of the peaks at 140 °C on the amount of electrode when mixed with 0.5 μl electrolyte.

similar phenomenon occurred during the DSC analysis of the mixture of Si/C electrode and electrolyte. Besides, the volume change of the Si fraction caused by Li consumption needed to be considered simultaneously because the s-SEI also could form on the new surface of the electrode when cracks occurred on the Si/C electrode. On the other hand, because of the abundance of Li in the lithiated electrode, more s-SEI was formed in its electrolyte mixture, which induced a larger exothermic heat at 140 °C than that from the mixture containing the delithiated electrode, just as shown in Fig. 3(c) and (d). The most remarkable information in Fig. 3 is the sharp peak at 290 °C obtained with the mixture of lithiated electrode and electrolyte. Obviously, this peak could be attributed to reaction(s) involving Li in Si/C. For the lithiated carbon electrode, similar phenomena have been obtained due to a drastic reaction between Li in carbon and the electrolyte induced by a breakdown of SEI [30]. And, with different kinds of carbon electrodes, the reaction temperature varied from 280 to 300 °C [28,29,31]. Taking into consideration the similar SEI compounds on the Si/C and carbon electrodes, it was reasonable to suppose that the dramatic exothermic heat at 290 °C was caused by similar reactions between lithiated Si/C electrode and the electrolyte after the SEI decomposition.

As the thermal risk of Si/C electrode is mainly related to the Li in the electrode, the thermal behaviors of the mixture of lithiated electrode (Si/C) and the electrolyte (1 mol dm^{-3} LiPF$_6$/EC-DMC) were studied in detail. Fig. 4 shows the variations in DSC curves to the amount of lithiated electrode while the amount of coexisting electrolyte was fixed at 0.5 μl. Although the DSC curves showed significant variation with regard to the amount of electrode, an exothermic peak at about 140 °C was observed in each DSC curve. Moreover, the peak intensity was found to have a direct relationship to the amount of electrode. So it was reasonable to attribute this peak to the formation of an s-SEI as discussed above. The peak appeared because a thicker s-SEI was formed and then the SEI formation was prevented. During the reaction, no limitation deriving from the amount of coexisting electrolyte was observed. Based on these data, the effect of Li in Si/C on the formation of s-SEI was investigated. Fig. 5 shows the variation of the heat value of peaks at 140 °C on the amount of lithiated Si/C electrode. Using a simple linear least-squares fit (R = 0.994), it was found that the heat value had
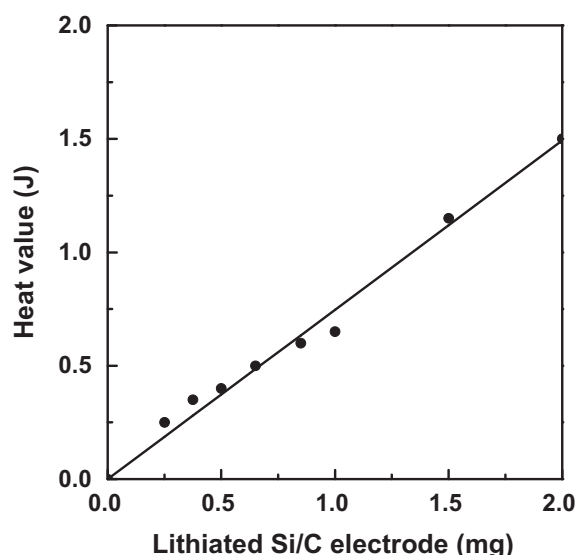
a proportional relationship with the amount of the electrode. The heat value was 0.73 J mg^{-1} based on the weight of the Si/C electrode. This result indicates that the exothermic heat at around 140 °C was limited by the amount of lithiated electrode.

Compared with the stable peak group at 140 °C, the peaks at higher temperature were more remarkable in Fig. 4 as shown by the dotted circles. The peak temperature became lower and the intensity became greater with the increase of the electrode amount. The most drastic peak was the exothermic one shown in Fig. 4d (same data as in Fig. 3d), which had been deduced to be caused by direct reactions between the lithiated electrode and the electrolyte because of the decomposition of SEI. From Fig. 4b–d, the development of this exothermic peak is clear. Based on these data, we could make some hypotheses about the reactions between the lithiated electrode and the electrolyte. The main peak at around 290 °C in Fig. 4d disappeared when the electrode amount was increased from 0.5 mg to 0.65 mg as shown in Fig. 4e. This was the first-ever discovery that a larger ratio of electrode/electrolyte could induce milder heat generation. In our previous researches about lithiated carbon electrode, we found that overabundant lithiated electrode induced much stronger exothermic heat. The mechanism of the special phenomenon of the Si/C electrode has not been clarified. One possible reason was that the Si/C electrode had a large specific capacity and could consume a large part of the coexisting electrolyte during s-SEI formation, so that the following drastic reactions between Li in the electrode and the electrolyte were depressed. In Fig. 4e, only a smaller peak (shown by dotted circle) was observed at around 250 °C. It was supposed that the amount of electrolyte was not sufficient and s-SEI formation stopped at around 250 °C in Fig. 4e. The thickness of the SEI was not enough to protect the Li in the electrode when the temperature became higher, in which case the Li in Si/C probably reacted with the solvent of the electrolyte and showed a peak at around 250 °C. The tendency of the peaks shown by dotted circles in Fig. 4f and e could be explained by the stopping of SEI formation.

Fig. 6 shows the DSC curves of a mixture of 0.5 mg lithiated Si/C electrodes and a given amount of electrolytes. It was expected that the DSC curves would be similar when the ratios of the electrode to electrolyte amount were the same. The values of the electrode (mg)/electrolyte (μl) ratio were 0, 0.5, 0.74, 1.0, 1.3, 1.7, 2.0, 3.0, and 4.0 mg μl^{-1} for Fig. 4a–i, respectively. And these values were ∞, 2.0, 1.0, 0.67, 0.5, 0.33, 0.25, 0.17 mg μl^{-1} for Fig. 6a–h. Comparing
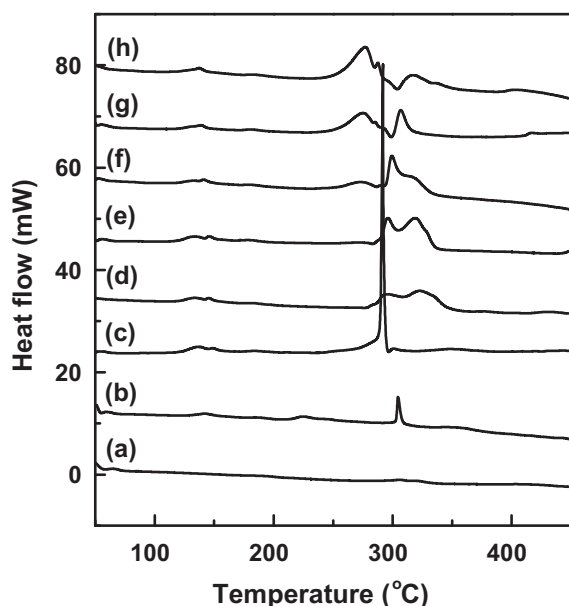
Fig. 6. DSC curves of mixtures of 0.5 mg lithiated Si/C electrode and (a) 0 μl, (b) 0.25 μl, (c) 0.5 μl, (d) 0.75 μl, (e) 1 μl, (f) 1.5 μl, (g) 2 μl, and (h) 3 μl electrolyte.

Fig. 7. Dependence of the heat values on the amount of electrolyte when mixed with 0.5 mg lithiated Si/C electrode.

Fig. 8. Comparison of the heat generation from a lithiated Si/C electrode and a natural graphite electrode with coexisting electrolyte.

the DSC curves in Figs. 4 and 6 with the same values for the electrode/electrolyte (mg/μl) ratio, a similar tendency was observed.

The vaporization of electrolyte solvent should also be taken into account to discuss the peaks at around 300 °C. It was supposed that both the gas-phase and liquid-phase electrolyte could react with the lithiated electrode, and the stronger peak might be caused by the gas-phase reactions. According to this supposition, the variation of the peaks at 300 °C in Fig. 6 with the electrolyte amount became reasonable. When only a small amount of electrolyte was mixed with the lithiated Si/C electrode, the electrode could not be completely covered by the liquid electrolyte. So the gas-phase solvent could be reduced on the electrode surface and could form the s-SEI. But when overabundant electrolyte was added, the electrode was covered with the liquid-phase electrolyte, and the reactions with the gas-phase solvent were reduced, which induced the fading of the former peak.

Fig. 7 shows the total heat value of DSC curves shown in Fig. 6. For reference, the heat generation from the electrolyte alone is also presented here with open circles (shown by line) [29]. Obviously, the heat generated from the mixture increased with the amount of electrolyte when the electrolyte was less than 0.5 μl. Then the heat value became almost constant because the amount of Li in the electrode limited the reaction.

No matter what the mechanisms of the reactions were in the battery, the decrease of heat generation is a key finding for battery researchers. We integrated the DSC curves in the range of 150–350 °C in Fig. 4 to show the dependence of the heat value generated from the electrode/electrolyte mixture on the amount of lithiated Si/C electrode in Fig. 8, together with the capacity of the coexisting electrode in each mixture. For comparison, corresponding results for a natural graphite electrode are also presented. It was supposed that the heat generated from the mixture of the graphite electrode and the electrolyte were proportional to the amount of mixture under the same electrode/electrolyte ratio. Therefore, the data for graphite could be estimated from the results obtained with given amounts of lithiated electrode mixed with 1 μl of the same electrolyte [32]. For the Si/C electrode, the variation of the mixture's heat generation with the electrode amount could be divided into two groups with a cutoff point of about 0.6 mg. When the electrode was less than 0.6 mg (the first group), ostensibly the Si/C
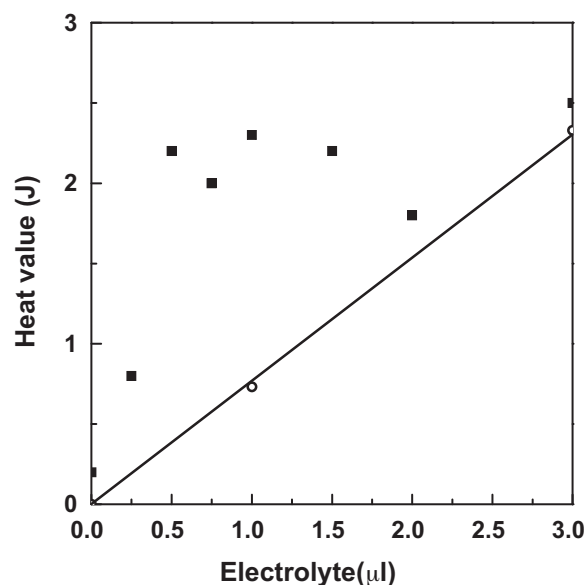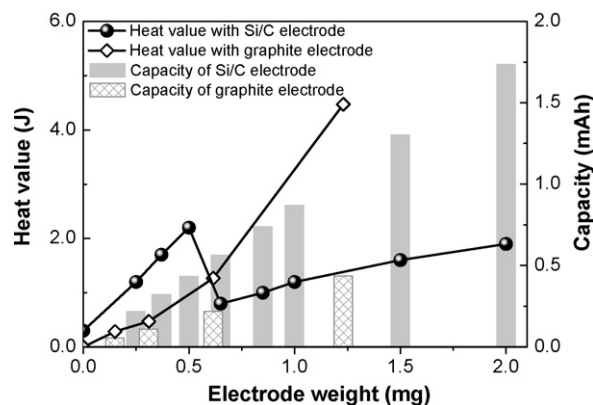
electrode gave larger exothermic heat (J mg^{-1}) than the graphite electrode in the electrolyte. But when the heat value was normalized by the electrode capacity (J mA h^{-1}), it was found that the Si/C electrode gave even less exothermic heat than the graphite electrode. When the added lithiated Si/C electrode was 0.5 mg, the heat value based on the electrode weight was 4.4 J mg^{-1}, and that based on capacity was 5.1 J mA h^{-1} (calculated by the discharge capacity of 1120 mAh g^{-1}). The respective values of graphite were about 1.9 J mg^{-1} and 5.8 J mA h^{-1}.

4. Conclusion

Silicon/disordered-carbon powder was applied as a negative-electrode material in Li-ion batteries. With 1 mol dm^{-3} LiPF$_6$/EC-DMC (1:1, v/v) as the electrolyte, an initial charge/discharge capacity of 1290/1120 mAh g^{-1} was obtained. The thermal characteristics of the Si/C electrode with or without the electrolyte were investigated by DSC measurements from room temperature to 450 °C at a heating rate of 5 °C min^{-1}. Exothermic peaks at about 310 °C were observed in DSC curves of both lithiated and delithiated electrode powder, and were supposed to be caused by reactions between the Li in the electrode and the SEI. The lithiated electrode caused much greater exothermic heat than the delithiated

electrode, especially when they were mixed with the electrolyte. By changing the ratio between the lithiated Si/C electrode and the coexisting electrolyte, the thermal behavior of the mixture became very complex. With the temperature ramp-up of the mixture, a secondary SEI was deduced to be formed on the electrode surface at about 140 °C by a reaction between lithiated electrode and the electrolyte. At about 290 °C, the mixture containing 0.5 mg lithiated Si/C electrode and 0.5 μl electrolyte showed the most drastic exothermic heat among all mixtures with different electrode/electrolyte ratios; this phenomenon was supposed to have been caused by a direct reaction between the electrolyte and residual Li in the electrode after the thermal breakdown of the SEI. But this peak was found to be very sensitive to the electrode/electrolyte ratio. When more electrode material was introduced, the drastic peak faded rapidly. This phenomenon could be partially attributed to the insufficient formation of a secondary SEI. When the added lithiated Si/C electrode was 0.5 mg, the heat value based on electrode weight was $4.4\,\mathrm{J\,mg^{-1}}$, and that based on capacity was $5.1\,\mathrm{J\,mA\,h^{-1}}$ (calculated by the discharge capacity of $1120\,\mathrm{mAh\,g^{-1}}$). The respective values for graphite were estimated to be $1.9\,\mathrm{J\,mg^{-1}}$ and $5.8\,\mathrm{J\,mA\,h^{-1}}$.

Acknowledgement

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