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Quantitative studies on the thermal stability of the interface between graphite electrode and electrolyte

Takayuki Doi [a,*], Liwei Zhao [a], Mingjiong Zhou [b], Shigeto Okada [a], Jun-ichi Yamaki [a]

[a] Institute for 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

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ABSTRACT

The thermal stability of a charged graphite electrode was studied quantitatively by differential scanning calorimetry (DSC). Charged electrode powder gave exothermic peaks at around 285 °C, and their heat values were proportional to the amount of charged electrode powder sealed in hermetic pans. These results suggest that a solid electrolyte interphase (SEI) that is formed on graphite during charging would react exothermally with charged graphite at around 285 °C. Mass spectrometry coupled with thermogravimetric analysis and differential thermal analysis (TG-DTA/MS) of the charged electrode powder indicated that the exothermic reactions at around 285 °C should be accompanied by the generation of methane. When charged electrode powders coexisted with electrolyte solution in a hermetic pan, the heat values at around 285 °C varied in an apparently complicated way depending on the ratio of charged electrode powder to an electrolyte. These phenomena are discussed quantitatively by considering the amount of lithium-ions in charged graphite powder and a coexisting electrolyte. These results suggest that the exothermic reactions at around 285 °C can be attributed to the reductive decomposition of SEI by charged graphite.

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1. Introduction

Lithium-ion batteries have been used in a wide variety of portable electronic devices. Due to their high energy densities, lithium-ion batteries have been considered as possible power sources in hybrid electric vehicles, artificial satellites, and load-leveling. However, before lithium-ion batteries can be used in large-scale applications, the performance of lithium-ion batteries still needs to be improved with regard to battery cycle life, rate capability, and safety. Among them, the safety issues should be alleviated to make lithium-ion batteries serve as reliable power sources. Commercially available lithium-ion batteries generally use graphitic carbon as a negative-electrode material, lithium 3d-transition metal oxides such as $LiCoO_2$ as a positive electrode material, and non-aqueous organic solvents containing lithium salts as an electrolyte solution. The safety of lithium-ion batteries is closely related to the thermal stability of their constituent materials at elevated temperatures since flammable organic solvents are used. Several exothermic reactions are known to occur in lithium-ion batteries at elevated temperatures [1,2].

Electrochemical lithium-ion intercalation and de-intercalation reactions at a graphite negative-electrode take place at extremely negative potentials close to lithium metal. At such potentials, most conventional electrolyte solutions should be thermodynamically unstable. In fact, considerable experimental evidence supports the notion that electrolytes are reductively decomposed to form a surface film on graphite, which is called the solid electrolyte interphase (SEI), particularly during the initial charging [3]. It is generally accepted that SEI is conductive for lithium-ion but electronically insulating, and the charge and discharge reactions proceed even after prolonged charge and discharge cycles. In practice, however, reductive decomposition of the electrolyte proceeds steadily at low potentials over repeated cycles, in particular at elevated temperatures, which results in the formation of thicker and/or denser SEI [4–6]. The thermal stability of graphite negative-electrode has been investigated by calorimetry methods such as differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) [7–17]. A charged graphite electrode is known to give a large amount of exothermic heat at temperatures above 250 °C in addition to a small exothermic heat at around 100–130 °C. Based on the literature, these exothermic reactions are closely related to the thermal stability of SEI that is formed on charged graphite [7–18]; exothermic reactions occur at around 100–130 °C by the transformation of SEI into more stable SEI and/or the further formation of SEI accompanied by the electrolyte decomposition. The SEI was believed to be

* Corresponding author. Tel.: +81 92 583 7657; fax: +81 92 583 7791.
E-mail address: doi@cm.kyushu-u.ac.jp (T. Doi).

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decomposed exothermally at temperatures above 250 °C. However, the mechanism of the exothermic reactions that occur at temperatures above 250 °C is still a matter for speculation. The exothermic behaviors as well as their heat values reported in the literature were not always consistent. These results may be due to the difference in the kind of graphite, the composition of graphite composite electrodes containing additives such as binder, and the methods for preparing samples for thermal measurements. In fact, exothermic behaviors varied depending on the quantitative ratio of electrolyte solution to coexisting charged graphite [19].

In this study, we systematically examined the thermal stability of electrochemically lithiated graphite in an electrolyte by DSC, and then quantitatively discussed the heat amount to clarify the mechanism of the exothermic reaction at elevated temperatures.

2. Experimental

Natural graphite powder (LF-18D, Chuestu Graphite) was used as an active material for a test electrode. The graphite powder (95 wt%) was mixed with a poly(vinylidenefluoride) binder (KF#9100, Kureha Chemical) (5 wt%) and dispersed in 1-methyl-2-pyrrolidinone. The slurry was applied to a current collector consisting of a porous Cu-foil with a thickness of 0.1 mm, and then dried at 120 °C for 12 h in a vacuum oven. The typical loading of the graphite powder was 6 mg cm^{-2}. The electrochemical properties of the graphite were studied by charge–discharge measurements using a two-electrode coin cell. The graphite test electrode was round with a diameter of 15 mm. A lithium-foil and a polypropylene film (Celgard 3501) were used as the counter electrode and separator, respectively. The electrolyte used was 1 mol dm^{-3} $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v, Tomiyama Chemical). Unless otherwise stated, the charge/discharge cycles were carried out at a constant current rate of 0.2 mA cm^{-2} with a relaxation period of 60 min at the end of each discharge/charge measurement. The charging and discharging processes ended at 10 mV and 2.0 V, respectively. After the charge/discharge cycles, the cells were disassembled in an Ar-filled glove box. The test electrode was rinsed and soaked with DMC for 8 h, and then dried under vacuum in the glove box at room temperature for 10 h to remove low-molecular weight compounds such as $LiPF_6$. The thermal stabilities of test electrode powder were investigated by differential scanning calorimetry combined with thermogravimetric analysis (TG-DSC, Thermo plus TG8110, Rigaku). A given amount of fresh electrolyte solution and test electrode powder, which was scraped from a Cu current collector in an Ar-filled glove box, was packed in a hermetically sealed pan. The pan was heated from room temperature to 400 °C at a rate of 5 °C min^{-1}. No leakage was verified by the absence of weight loss in TG curves during heating. After DSC measurement, sample powder in a hermetic pan was taken out in an Ar-filled glove box, and then sealed in an optical cell. Raman spectra were excited using the 514.5 nm line (100 mW) of an argon ion laser, and the scattered light was collected in a quasi-backscattering geometry. All spectra were recorded using a spectrometer (NRS-2100, Jasco) equipped with a multichannel charge coupled device detector. Each measurement was carried out at room temperature with an integration time of 60 s.

The gas generated from test electrodes with an increase in temperature was investigated by TG-DTA/MS (8210H/5050AW, Rigaku). A TG-DTA instrument was placed in an Ar-filled glove box and combined with an MS instrument using a heatable transfer tube. Hence, measurements could be performed without exposing measurement samples to the air. The test electrode powder was put in a hermetic pan or an open-type pan to be introduced into the furnace of the TG-DTA, and then heated to 550 °C at a rate of 5 °C min^{-1} under helium flow. Nearly equivalent amounts of alumina powder was used as reference materials. Gaseous products, which were generated by pyrolysis of the test electrode powder in an open-type pan, were identified with a mass spectrometer. Ionization for MS was carried out by electron impact in which the voltage and current for acceleration were set at 70 eV and 60 mA, respectively.

All of the experiments described so far were conducted under an argon atmosphere with a dew point below −70 °C.

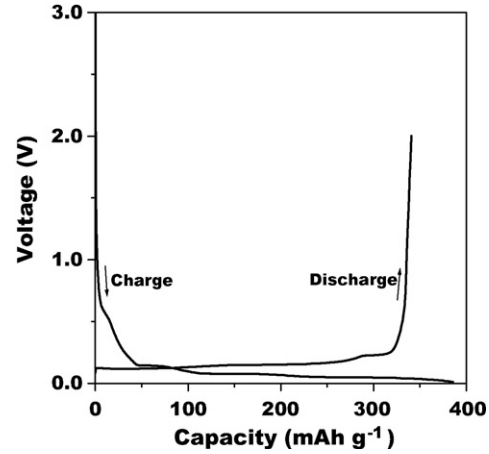

Fig. 1. Charge and discharge curves of a graphite electrode in 1 mol dm^{-3} $LiPF_6$/EC + DMC. The current density was 0.2 mA cm^{-2}.

3. Results and discussion

Fig. 1 shows charge and discharge curves in the 1st cycle. The initial charge (intercalation of lithium-ion into graphite) and discharge (de-intercalation of lithium-ion from graphite) capacities were 386 and 341 mAh g^{-1}, respectively, and hence the irreversible capacity in the 1st cycle was 45 mAh g^{-1}. After the 2nd cycle, charge and discharge reactions proceeded reversibly and the irreversible capacity was negligible small.

DSC curves of charged electrode powder obtained after the 2nd charge are shown in Fig. 2, together with that of discharged electrode powder after the 2nd discharge. No exothermic peak was seen at around 100–130 °C, which was often reported in the literature and identified as the conversion of meta-stable SEI into stable SEI or

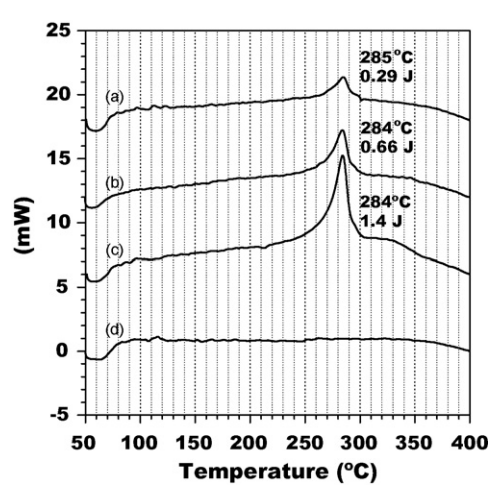

Fig. 2. DSC curves of (a–c) charged and (d) discharged graphite-electrode powder. The weight of the graphite-electrode powder in the pan was (a) 1 mg, (b) 2 mg, and (c, d) 4 mg.

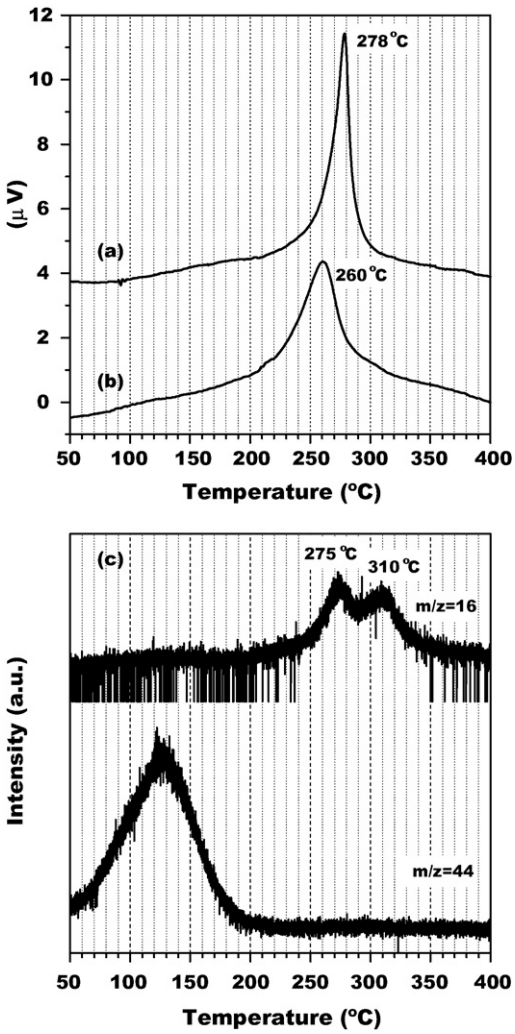

Fig. 3. DTA curves of 4 mg of charged graphite-electrode powder in (a) hermetic and (b) open-type pans. (c) Variation of mass signals of $m/z = 16$ and 44 with temperature for 4 mg of charged graphite-electrode powder, which was obtained concurrently with the DTA curve shown in (b).

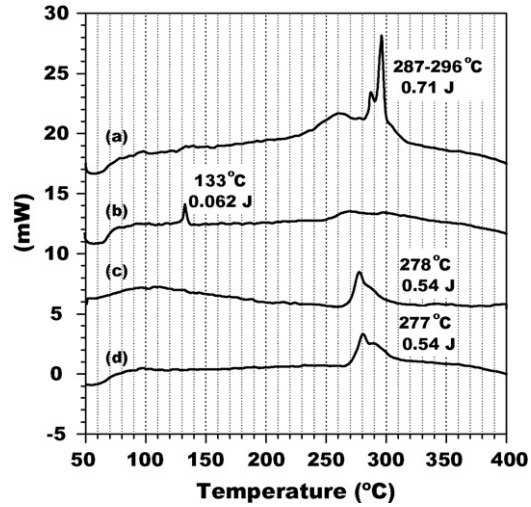

Fig. 4. DSC curves of a mixture of 1 μl of EC + DMC-based electrolyte solution and 1 mg of (a) charged, (b) discharged, and (c) pristine graphite-electrode powder. (d) DSC curve of EC + DMC-based electrolyte solution.

the further formation of SEI accompanied by the electrolyte decomposition [7,10,16]. Exothermic peaks appeared at around 285 °C for the charged electrode powder, while no peak was observed for discharged electrode powder. The heat values, which were evaluated by integrating DSC curves, were proportional to the amount of charged electrode powder. These results suggest that SEI that is formed on graphite during charging would react with charged graphite at around 285 °C accompanied by exothermic heat.

TG-DTA/MS measurements were carried out to investigate the gas generated from charged electrode powder with an increase in temperature. Fig. 3 shows DTA curves of 4 mg of charged electrode powder placed in a hermetically sealed pan (Fig. 3a) and an open-type pan (Fig. 3b). The hermetically sealed powder gave an exothermic peak at about 278 °C, which is similar to that in the DSC curves shown in Fig. 2c. The exothermic peak in Fig. 3a was broader than that obtained by DSC; exothermic behaviors were observed at temperatures ranging from about 200 to 310 °C by DTA, while these were observed from around 240 to 300 °C by DSC. Since the same samples sealed in a hermetic pan were used in both measurements, these differences should be caused by the different measurement methods. Hence, the exothermic peaks observed in DTA (Fig. 3a) and DSC curves (Fig. 2c) should be equivalent. A DTA curve obtained using an open-type pan is shown in Fig. 3b. An exothermic peak was seen at around 260 °C. This behavior is similar to that obtained in a hermetic pan shown in Fig. 3a, while the peak temperature differed by 18 °C. The samples used in both measurements were the same. In addition, the samples would not react with the ambient gas because helium is inert, and hence these differences were caused by the different types of pans. Therefore, the exothermic reactions that occurred in the two types of pans were exactly the same. Mass signals of $m/z = 16$ and 44, which were obtained concurrently with the TG-DTA curves shown in Fig. 3b, were detected by MS, as shown in Fig. 3c. We previously reported that discharged graphite generated carbon dioxide at temperatures above 280 °C, which is quite different from the results obtained for charged graphite [20]. These results suggest that the mechanism of SEI decomposition should differ between charged and discharge graphite. In Fig. 3b, the mass signal of $m/z = 16$ appeared between 220 and 360 °C, together with a weak mass signal of $m/z = 15$. These results indicate that methane should be generated between 220 and 360 °C. This temperature range was similar to those seen for an exothermic peak in the DTA curve shown in Fig. 3b. Therefore, the exothermic reaction at around 260 °C was accompanied by methane evolution; i.e., SEI that is formed on graphite during charging should react with charged graphite to generate methane gas. The other mass signal of $m/z = 44$ was seen at temperatures ranging from 60 to 190 °C, together with a weak mass signal of $m/z = 29$. Therefore, these signals should be identified as not carbon dioxide but acetaldehyde or ethylene oxide. However, no exothermic or endothermic heat corresponding to the mass signals of $m/z = 44$ and 29 was seen in the DTA curve shown in Fig. 3b. The detailed mechanism for the generation of methane, acetaldehyde, and ethylene oxide has not been clear yet.

Figs. 4a–c shows DSC curves of 1 mg of electrode powder with 1 μl of an electrolyte, together with that of an electrolyte only (Fig. 4d). When charged electrode powder was sealed with an electrolyte in a hermetic pan, sharp exothermic peaks were observed at around 290 °C, following a broad peak at about 260 °C. On the other hand, only negligible small peaks were seen above 250 °C for a mixture of discharged electrode powder and an electrolyte, as shown in Fig. 4b. These results indicate that charged graphite should be involved in an exothermic reaction at around 290 °C, which is consistent with the above suggestion derived from Fig. 2. An exothermic peak was observed at about 278 °C when a mixture of uncharged electrode powder and an electrolyte was measured, as

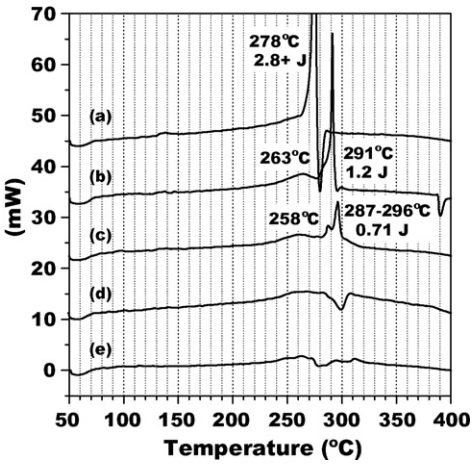

Fig. 5. DSC curves of a mixture of 1 μl of EC + DMC-based electrolyte solution and (a) 2.5 mg, (b) 1.25 mg, (c) 1.0 mg, (d) 0.68 mg, and (e) 0.30 mg charged graphite-electrode powder.

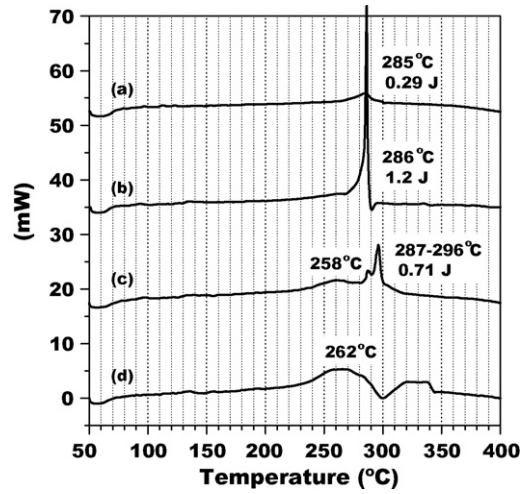

Fig. 6. (a) DSC curves of 1.0 mg charged graphite-electrode powder. DSC curves for a mixture of (b) 0.5 μl, (c) 1 μl, and (d) 2 μl of EC + DMC-based electrolyte solution and 1.0 mg charged graphite-electrode powder.

shown in Fig. 4c. This behavior was quite similar to that for an electrolyte only, as shown in Fig. 4d. In addition, Figs. 4c and d gave the same heat values of 0.54 J. Therefore, exothermic heats observed in Figs. 4c and d should be attributed to the decomposition of an electrolyte. The heat value for a mixture of charged electrode powder and an electrolyte was evaluated from Fig. 4a to be 0.71 J, which was larger than that obtained for a mixture of uncharged electrode powder and an electrolyte (0.54 J). These results indicate that electrolyte solution could generate a large amount of heat when it coexists with charged graphite, as compared to when an electrolyte is thermally decomposed by itself.

Fig. 5 shows DSC curves of 1 μl of electrolyte solution with a given amount of charged electrode powder (ranging from 0.30 to 2.5 mg). When a mixture of 1 μl of electrolyte solution and 2.5 mg of charged electrode powder was sealed in a hermetic pan, a very sharp exothermic peak was observed at around 278 °C. The exothermic reactions were so intense that the heat value exceeded the detection limit of the DSC instrument. Sharp exothermic peaks were observed at around 291 °C when the amount of coexisting charged electrode powder was 1.0 mg. However, the exothermic heat decreased with a decrease in the amount of the coexisting charged electrode powder; the heat values were evaluated to be 1.2 and 0.71 J when the amount of coexisting charged electrode powder was 1.25 and 1.0 mg, respectively. No noticeable peak was seen in DSC curves when the amount of coexisting charged electrode powder was less than 0.68 mg. These results clearly indicate that heat values should increase with the amount of charged electrode powder but not proportionally.

Fig. 6 shows DSC curves of 1 mg of charged electrode powder with a given amount of electrolyte solution (from 0 to 2 μl). When only charged electrode powder was measured, 0.29 J of heat was generated at around 285 °C, as shown in Fig. 6a. On the other hand, when 0.5 μl of electrolyte solution was also present, a very sharp exothermic peak appeared at about 286 °C (Fig. 6b). The heat value was evaluated to be 1.2 J, which was much larger than that for charged electrode powder itself, as shown in Fig. 6a. However, the exothermic heat decreased with an increase in the amount of coexisting electrolyte: 0.71 J was obtained when the amount of coexisting electrolyte was 1 μl (Fig. 6c) and only broad peaks were observed for 2 μl (Fig. 6d). Thus, a maximum value of the exothermic heat was obtained when the ratio of charged electrode powder to electrolyte solution was 1 mg/0.5 μl in the present work. These phenomena are discussed quantitatively below.

Based on reports in the literature, SEI formation on a graphite electrode proceeds preferentially by the reductive decomposition of cyclic carbonates such as EC, compared to linear carbonates such as DMC [10,11]. Aurbach et al. [21,22] investigated surface reactions that occurred at a graphite electrode in a variety of non-aqueous electrolytes by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and ac impedance spectroscopy. According to their work, the major constituent of the SEI formed in EC-based electrolyte is a reduction product of EC [$(CH_2OCO_2Li)_2$] [21]. Reaction schemes for the reduction processes of EC have also been proposed; there are two possible reaction paths for the formation of $(CH_2OCO_2Li)_2$; disproportionation of anion radical which is formed by a one-electron reduction of EC, and nucleophilic attack of CO_3^{2-}, which can be formed by two-electron reduction of EC, to another EC molecule. Based on the simplicity of the reaction paths, the former reaction path seems to be more likely. A graphite electrode gave an irreversible capacity of 45 mAh g^{-1} in the 1st cycle, as shown in Fig. 1. If this irreversible capacity was wasted for a one-electron reduction of EC to form SEI, then it follows that 1.2×10^{-5} mol of EC molecules was consumed per 1 g of graphite. These values are shown by solid bars in Figs. 7a and b, which were prepared based on the data shown in Figs. 5 and 6, respectively. SEI on a graphite electrode is known to grow up at a charged state at elevated temperatures accompanied by the reductive decomposition of an electrolyte and the self-discharge of the graphite electrode [6]. In this work, electrolyte solution coexisted with charged graphite-electrode powder in a hermetic pan. Hence, an electrolyte should be reductively decomposed accompanied by the consumption of mobile lithium-ions in charged graphite with an increase in temperature in DSC measurements, which results in SEI growth. The amount of the growth of SEI could be determined provided that the reductive decomposition of an electrolyte occurs by a one-electron reduction of EC; i.e. when a molar quantity of EC molecules in a coexisting electrolyte is larger than that of lithium-ions in charged graphite, all of the lithium-ions should be consumed to form SEI with an increase in temperature, and some amount of electrolyte solution remains. In the reverse case, there should be residual lithium-ions in charged graphite after all the electrolyte solution is depleted with an increase in temperature. The amount of EC molecules consumed during the increase in temperature is shown by a checked bar in Figs. 7a and b, which is accumulated on a solid bar that shows the amount of EC molecules consumed

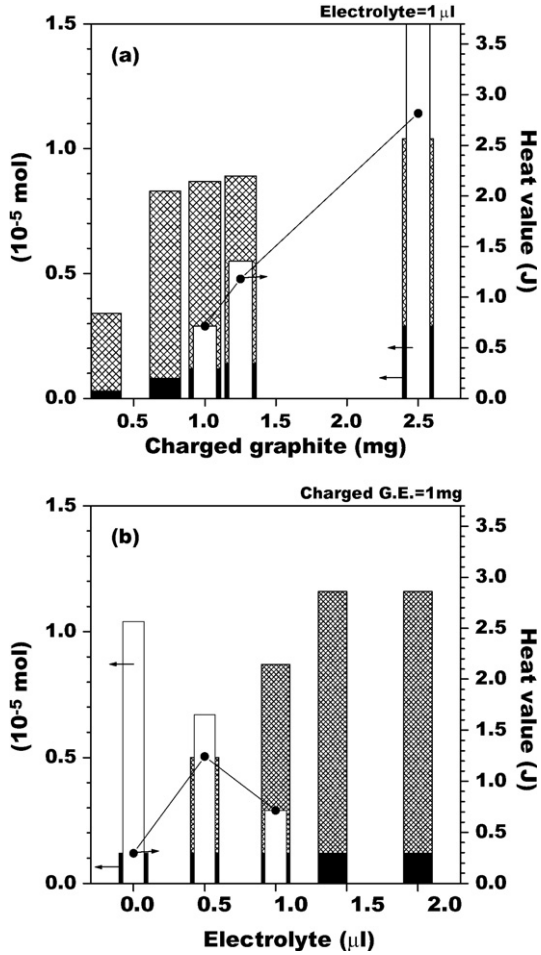

Fig. 7. Correlation between the heat values and the amounts of EC molecules and lithium-ions in graphite. The heat values, which were evaluated Fig. 1 and the heat values obtained from Figs. 5(a) and 6(b), are indicated by closed circles. The amount of EC molecules consumed during charging and during the increase in temperature is shown by solid and checked bars, respectively. The residual amount of lithium-ions in graphite after the increase in temperature is shown by an open bar.

during the initial charging. The residual amount of lithium-ions in graphite is shown by an open bar in Figs. 7a and b. The heat values, which were evaluated from exothermic peaks at about 285 °C in DSC curves shown in Figs. 5 and 6, are also shown by a solid circle in Figs. 7a and b. The heat values are consistent with the intersections of the residual amount of lithium-ions (open bar) and the total amount of EC molecules consumed (solid and checked bars accumulated). These results suggest that the heat values at around 285 °C should depend on the amount of SEI and lithium-ions in charged graphite. Thus, the exothermic reactions at around 285 °C should be attributed to the reductive decomposition of SEI by charged graphite. The heat value corresponds to 1.9 J per 1 μl of electrolyte solution, which is about 3.5 times larger than that of the thermal decomposition of electrolyte itself (0.54 J per 1 μl of electrolyte solution). This assumption can be examined by the Raman spectra of graphite-electrode powder after DSC measurements. The peak at around 1580 cm^{-1}, which is a well-known Raman active E_{2g} mode frequency of graphite, changes in association with the intercalation of lithium-ion into graphite [23]. Fig. 8 shows Raman spectra of graphite-electrode powder after DSC measurements for 4 mg of graphite-electrode powder without an electrolyte (Fig. 8a), and for a mixture of 1 mg of graphite-electrode powder and 2.0 μl of an electrolyte (Fig. 8b). A broad peak was observed in Fig. 8a, which

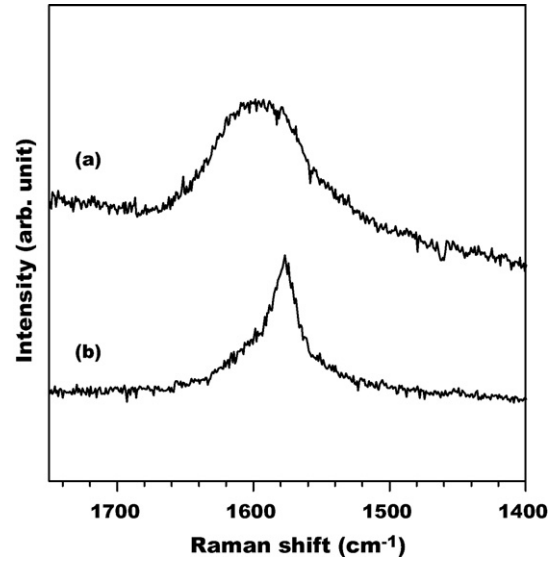

Fig. 8. Raman spectra of graphite-electrode powder after DSC measurements. The DSC measurements were carried out up to 400 °C for (a) 4 mg of graphite-electrode powder without an electrolyte, and (b) a mixture of 1 mg of graphite-electrode powder and 2.0 μl of an electrolyte.

is similar to that for natural graphite powder charged at around 0.1 V shown in Ref. [23]. These results suggest that there should be some amount of lithium-ions in graphite to form the stage structure of Li-GIC. On the other hand, a peak at around 1580 cm^{-1} was seen in Fig. 8b, which is assigned to E_{2g} mode frequency of pristine graphite powder. These results are consistent with the discussion shown in Fig. 7, and can support the above assumption. In this work, the temperature in DSC measurements increased at 5 °C min^{-1}, and then the exothermic reactions at around 285 °C could be attributed to the reductive decomposition of SEI by charged graphite. If the temperature increases more rapidly, reductive decomposition of electrolyte solution by charged graphite would be dominant kinetically.

4. Conclusions

The thermal stability of a graphite electrode was studied quantitatively by DSC. Exothermic peaks were observed at around 285 °C in DSC curves of charged electrode powder, while no peak appeared for discharged electrode powder. The heat values were proportional to the amount of charged electrode powder, and therefore SEI that is formed on graphite during charging should react with charged graphite at around 285 °C. TG-DTA/MS measurements of charged electrode powder gave mass signals attributed to methane at the corresponding temperatures. Hence, methane would be generated accompanied by exothermic reactions at around 285 °C.

Exothermic heats were negligible at temperatures above 250 °C when the discharged electrode powder was sealed with an electrolyte in a hermetic pan. On the other hand, exothermic peaks were seen in DSC curves for a mixture of charged electrode powders and an electrolyte. Their heat values varied depending on the ratio of electrolyte solution to charged electrode powder; a very large exothermic heat of 1.2 J was obtained when only 0.5 μl of electrolyte solution was present along with 1 mg of charged electrode powder. However, the heat value decreased with an increase in the amount of coexisting electrolyte. In this study, we examined these phenomena quantitatively.

The amount of electrolyte consumed for the formation of SEI was determined assuming that SEI is formed by a one-electron reduction of EC molecules, based on the literature. The amount of residual

lithium-ions in charged graphite was also estimated. As a result, it became clear that heat values at around 285 °C were closely related to the amount of lithium-ions in graphite and to the amount of EC molecules constituting SEI. Based on these results, the exothermic reactions at around 285 °C should be attributed to the reductive decomposition of SEI by charged graphite. The heat value due to the reductive decomposition of SEI by charged graphite at around 285 °C was about 3.5 times larger than that for the thermal decomposition of electrolyte itself. To enhance the safety of lithium-ion batteries, it would be necessary to develop new electrolytes with high thermal stability. The onset temperature of exothermic reactions needs to be raised and the heat values due to the direct decomposition of an electrolyte should be suppressed as much as possible. In addition, by considering the results in this work, future studies should also seek to reduce heat generation by the decomposition of SEI derived from an electrolyte.

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