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Effect of mild oxidation of natural graphite (NG7) on anode-electrolyte thermal reactions

Received: 11 October 1999 / Accepted: 1 March 2000

Abstract The effect of mild oxidation of natural graphite (NG7) and some other parameters on the reaction between a fully lithiated graphite anode (Li_xC_6 , $x = 1.0\text{--}1.1$) and 1 M lithium hexafluoroarsenate in ethylene carbonate and diethyl carbonate electrolyte (1:2, v/v) were studied by differential scanning calorimetry (DSC). It was found that mild oxidation of the graphite suppressed the exothermic reaction of the fully lithiated anode with the electrolyte, most probably as a result of the formation of a more stable and chemically bonded solid electrolyte interphase. Separation and removal of the small graphite particles from the anode mixture suppressed this reaction further. It was also found that the copper current collector, the amount of electrolyte and binder as well as other parameters have a significant influence on the heat evolution as measured by DSC.

Key words Natural graphite · Thermal reactions · Lithiated anode · Differential scanning calorimetry

Introduction

We have recently shown that mild oxidation of two synthetic graphites and natural graphite (NG7) improves their performance in $\text{Li}/\text{Li}_x\text{C}_6$ cells [1–4]. The reversible capacity of the natural graphite (Q_R) increased (up to 405 mAh/g), the irreversible capacity (Q_{IR}) and the degradation rate decreased. In addition, mild oxidation increases the reproducibility of the performance characteristics and makes the graphite electrode less sensitive to electrolyte impurities. STM images of the burnt graphites show nanochannels with openings of a few nanometres.

It was suggested [1–4] that these nanochannels form at the zig-zag and armchair faces between two adjacent crystallites and in the vicinity of defects and impurities. XPS studies showed the formation of ketone and carboxyl groups on the surface of the graphite after the mild oxidation process. Performance improvement was attributed to better wetting of the electrode surface by the electrolyte, to accommodation of the extra lithium at the zig-zag, armchair and other edge sites and nanovoids, and to the formation of a chemically bonded solid electrolyte interphase (CB-SEI). This is bonded to the surface oxide and acid groups which were formed in the mild oxidation process. The thermal stability of the fully charged 550 mAh prismatic Li-ion cells (Sn-doped $\text{Li-CoO}_2/\text{LiPF}_6$ EC:DMC:DEC/graphitic carbon) and their components were investigated [5]. It was found that the cell self-heating exothermic reactions start at 123 °C, and thermal runaway occurs near 167 °C. The thermal runaway is close to the decomposition of the positive electrode material [5]. DSC measurements of lithiated graphite-electrolyte (186–340 mAh/g) samples show several exothermic peaks starting at 130 °C [6, 7]. The first peak was suppressed after passivation of the graphite surface, indicating a surface reaction between the lithiated graphite and the electrolyte [7].

We believe that an SEI which is chemically bonded to the graphite surface has a lower tendency to peel off from the anode during heating. Thus, it is expected that the CB-SEI improves the thermal stability of the Li-ion battery.

The goal of this work was to study, using the DSC technique, the effect of mild oxidation and other parameters on the thermal behavior of the lithiated graphite anode when in contact with the electrolyte.

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Experimental

The electrochemical characterization of the natural graphite (NG7, Kansai Coke) was carried out using $\text{Li}/\text{Li}_x\text{C}_6$ cells. These

3–5 cm² cells consisted of a porous graphite electrode, supported by a copper foil, a lithium foil (Foot Mineral) supported by a nickel Exmet screen, a Celgard 2400 separator and electrolyte containing 1 M lithium hexafluoroarsenate (LiAsF₆) and a 1:2 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The water content in the electrolytes, measured with the use of Karl Fisher model 652K coulombmeter, was lower than 40 ppm. Samples of NG7 powder were air-oxidized at 550 °C for 30 and 20 min, respectively, followed by a fast cooling to room temperature. The weight loss was 15% and 7.5%, respectively. Another 7% burn-off NG7 sample was oxidized at 500 °C for 3 h and cooled slowly. The air volume in the furnace was 175 L and the weight of the sample was about 5 g. It should be mentioned that when oxidizing 3–5 batches of the same graphite at nominally identical conditions the weight loss varied by 1–2% (for example from 6 to 8%). In previous publications [3] we studied the electrochemical properties of graphite powders which had been burnt to different extents. A change of 1–2% in the weight loss does not significantly influence the electrochemical properties. Separation and removal of the smallest graphite particles were performed using the decantation method, i.e. 20 mL of cyclopentanone was added to a portion of 500 mg graphite. After magnetic stirring and a few seconds rest, the cyclopentanone was decanted together with the small particle fraction (these electrodes were denoted as modified electrodes). The graphite lost due to this process was approximately 2% of its initial mass. The graphite electrodes were produced using the doctor-blade technique by applying the paste, which consists of 5% (w/w) PVDF and 95% (w/w) NG7 graphite powder in cyclopentanone, to the copper foil. The electrodes were 50 μm thick and some were rolled to a thickness of 30 μm. The graphite electrodes were dried for 1 h in air and 6 h in vacuum at about 150 °C. We used copper foil similar to that used in Li-ion batteries. The copper foil underwent the same procedure before each experiment, namely annealing at 400 °C in vacuum for 4 h and washing in AR isopropanol.

BET measurements were taken using a NOVA 2200 surface analyzer (Quantachrom). Cell-cycling tests were carried out on a 16-bit Maccor 2000 Battery Tester at 50 μA/cm² over the voltage range of 0.8–0.005 V. The samples for DSC measurements were prepared in a VAC glove box. Some of the electrodes were washed with dry DMC or a solvent mixture of EC:DEC 1:2 (v/v) and dried in the glove box. The electrodes were analyzed after the third full intercalation and a 24 h rest. Precise portions of the electrodes, together with a measured amount of the electrolyte (injected with the use of a 10 μL ILS microsyringe), were hermetically sealed in alodined (covered by high resistant and compact surface oxide film) aluminum DSC pans. Such pans are completely inert to our system. We ran a DSC test between metallic lithium and the alodined pan. No reaction took place until 180 °C, when a clear endotherm of Li melting was observed. The experimental value of the enthalpy of the lithium melting is equal to the theoretical one. DSC measurements were taken using TA Instruments module 910 and system controller 2100 at a ramp rate of 10 °C/min. The energy values were calculated from the peak area and straight baselines. The reaction rate is proportional to the height of the heat flow peak (HFP).

Results and discussion

The first step was to establish the effect of air-oxidation on the BET surface area of the graphite. BET measurements show that the surface area of the pristine sample is 6.2 m²/g (Table 1). After mild oxidation (7–15% weight loss) the surface area decreased to 5.6 m²/g. XRD measurements, performed previously in our laboratory, showed that there is no change of the position and width of the lines of the mildly oxidized NG-7 as compared with the pristine one.

Table 1 BET measurements of natural graphite (NG7) before and after mild oxidation

Type	Surface area (m ² /g)
Pristine	6.2
7–7.5% burn-off	5.6
15% burn-off	5.7
5.6–6.3% burn-off modified	4.8

To determine the effects of mild oxidation, small particles separation, electrode porosity and binder content on the reversible and the irreversible capacity, cycling tests were performed. Cycling tests show (Table 2) that after mild oxidation (15% burn-off sample) the reversible capacity increased by 10% to 409 mAh/g and the irreversible capacity decreased by about 10% when compared with the pristine sample. Modification (small particles separation and removal) of this burnt sample led to a further decrease of the irreversible capacity (to 76 mAh/g). However, the reversible capacity also decreased to 361 mAh/g. After rolling of the graphite electrode, the irreversible capacity of the pristine sample decreased, while the reversible capacity remained unchanged. Mild oxidation followed by slow cooling (7% burn-off sample) increased the irreversible capacity, while fast cooling (7.5% burn-off sample) decreased it. The reversible capacity was similar for all the burnt samples (x values of about 1.1). Similar high x values for oxidized graphite were recently published by Ein-Eli and Koch [8]. Modification of both the 7% and 7.5% burnt samples resulted in a decrease of the irreversible capacity (to about 65 mAh/g) and the reversible capacity (to about $x = 0.97$). The amount of binder in the modified 7.5% burnt samples did not have a significant effect on the reversible or the irreversible capacities.

The decrease of the irreversible capacity, after mild oxidation, is attributed in part to the smaller surface

Table 2 The effect of mild oxidation, rolling and modification of NG7 graphite on the performance characteristics of a Li-ion cell (each result is an average of 2–4 cells)

Type	OCV 24 h rest after the third intercalation (mV)	x in Li _{x} C ₆	Q_R (mAh/g)	Q_{IR} (mAh/g)
Pristine	66	1.00	372	112
15% burn-off	71	1.10	409	103
Modified 15% burn-off	63	0.97	361	76
Pristine ^a	70	1.00	372	85
7% burn-off ^a	65	1.10	409	116
Modified 7% burn-off ^a	70	0.98	365	68
7.5% burn-off ^a	70	1.07	398	75
Modified 7.5% burn-off ^a	75	0.94	350	65
Modified 7.5% burn-off ^{a,b}	80	0.97	361	65

^a Rolled electrodes

^b Electrodes contain 2.5% PVDF

area. In the 7% burnt sample, the irreversible capacity increased in spite of the smaller surface area. The reduction of the irreversible capacity after modification is associated with a further reduction in the surface area as a result of the separation of the small ash graphite particles. Rolling of the graphite electrodes decreased their porosity and hence their surface area as well, causing the irreversible capacity to decrease.

The OCV of the fully lithiated 7–15% oxidized graphite samples ($\text{Li}_{1.1}\text{C}_6$) measured after a 24 h rest is not lower than that of the pristine samples, showing that the extra lithium capacity is not associated with metallic lithium, or with clusters of lithium atoms in graphite pores.

As was shown by Okamoto et al. [7], DSC is a useful tool for the evaluation of the safety of the Li-ion batteries. It is necessary to assess the thermal stability of the cell components as well as those factors which affect the thermal behavior of the complete battery. In this study, we run several DSC tests of the LiAsF_6 electrolyte in contact with pristine and modified fully lithiated graphite samples, varying their volume ratio and with or without the presence of a copper current collector. The experimental data are presented in Figs. 1–8 and a number of more important parameters are shown in Tables 3–5.

Commonly the enthalpy value, proportional to the peak area on the thermogram, is used to characterize the heat of thermal transition or reaction at constant pressure. However, in our experiments, gas is evolved simultaneously with almost all reactions; therefore we prefer to use the term “internal energy change” (ΔU) instead of “enthalpy change” (ΔH).

Before studying the anode-electrolyte reactions we ran DSC tests on the solvents, electrolyte and electrolyte in contact with the current collector. DSC traces of the EC:DEC mixture (Fig. 1, plot a) show three clear

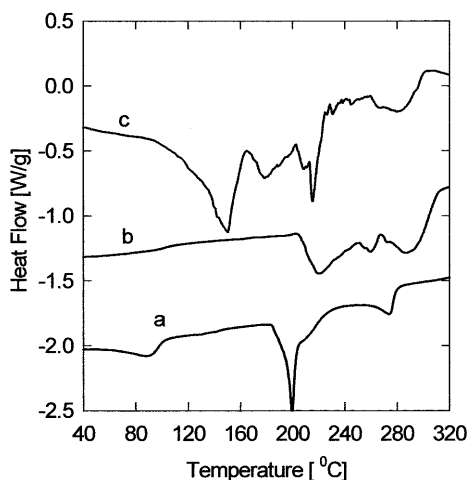


Fig. 1 DSC traces for 5 μL samples: *a* EC:DEC 1:2 (v/v) solvent mixture (shifted by -2 W/g); *b* 1 M LiAsF_6 EC:DEC 1:2 (v/v) electrolyte (shifted by -1.5 W/g); *c* the same as *b* with a copper current collector. The heat flow values are in units of W per g of electrolyte

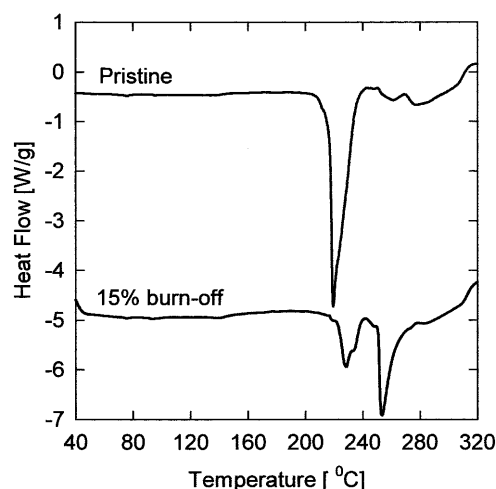


Fig. 2 DSC traces for 5 μL of electrolyte containing 2 mg NG7 graphite before (pristine) and after mild oxidation (15% burn-off, shifted by -4.5 W/g). The heat flow values are in units of W per g of electrolyte

endothermic peaks. Taking into account that (1) the onset temperatures of the endothermic peaks do not coincide with the boiling points of the solvents and (2) no visible dimension changes were noted after the runs, we may relate the endothermic peaks of the DSC run (Fig. 1, plot a) to the partial decomposition process of the solvents and interactions between their products. The pans can withstand an internal gas pressure of 3 atm. However, minor leaks of the gases resulting from solvent decomposition cannot be completely eliminated. So in the worst case only a portion of the gases formed in the solvent decomposition process may leak outside the pan. In addition, the returning of the baseline to its original level indicates that the pans did not lose much of the electrolyte, if any. From Fig. 1,

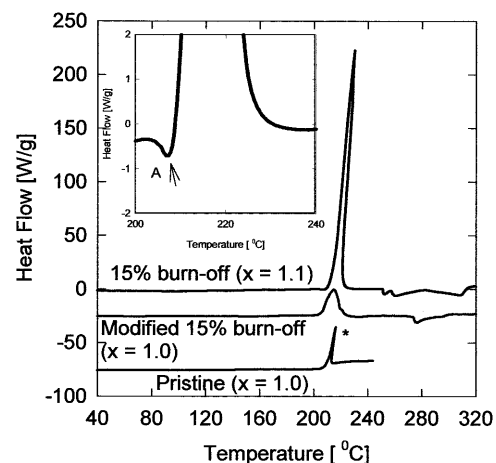


Fig. 3 DSC traces of washed, fully lithiated graphite-electrolyte samples (the modified and the pristine samples were shifted by -25 W/g and -75 W/g, respectively). The electrolyte/graphite ratio is 5 $\mu\text{L}/2$ mg. The heat flow values are in units of W per g of graphite. The * indicates where the sample exploded

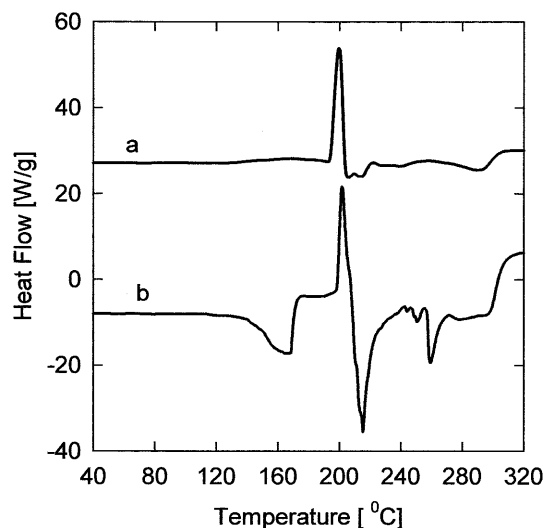


Fig. 4 DSC traces of electrolyte with rolled, unwashed, fully lithiated pristine graphite: *a* without a copper current collector (shifted by 30 W/g); *b* with a copper current collector. The electrolyte/graphite ratio is 5 $\mu\text{L}/0.2$ mg. The heat flow values are in units of W per g of graphite

plot b, it is clear that the decomposition was delayed and its rate was reduced by the addition of the LiAsF_6 salt. The copper current collector has a significant impact on the thermal stability of the electrolyte. When the 0.1 cm^2 copper current collector is in contact with the electrolyte, the endothermic peaks, appearing on thermogram, are broader and shifted about 70°C toward lower temperatures (Fig. 1, plot c). The total energy of the endotherms increased by about 10% as a result of the catalytic electrolyte decomposition by the copper. The fact that both the copper foil and the salt addition change the position and energy

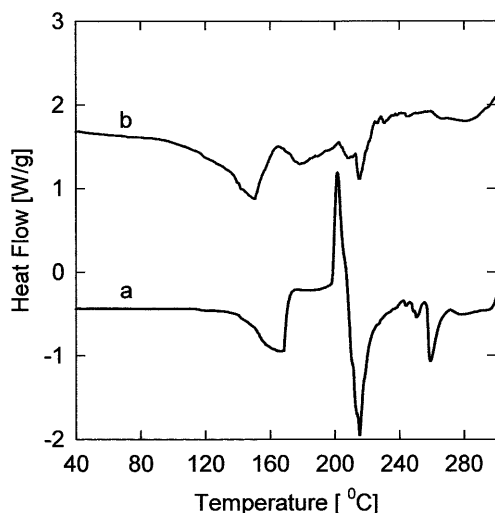


Fig. 5 DSC traces of electrolyte decomposition (5 μL): *a* with fully lithiated pristine graphite on a copper current collector; *b* with a copper current collector shifted by 2 W/g. The heat flow values are in units of W per g of electrolyte

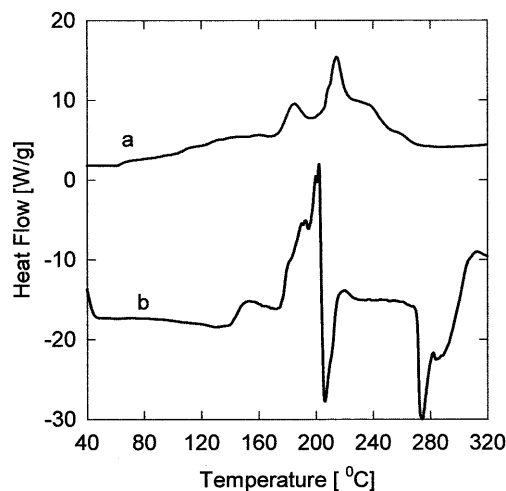


Fig. 6 DSC traces of rolled, unwashed, fully lithiated graphite after mild oxidation (7%) without a copper current collector: *a* without electrolyte addition; *b* with 5 μL electrolyte addition (shifted by -15 W/g). The electrolyte/graphite ratio is 5 $\mu\text{L}/0.2$ mg. The heat flow values are in units of W per g of graphite

of the peaks can serve as indirect evidence of our interpretation considering the assignment of endothermic DSC peaks.

Pristine and 15% burn-off un lithiated graphite further catalyzed electrolyte decomposition (Fig. 2). The overall energy value of the electrolyte thermal transitions (in contact with graphite samples) was five times as large as the DSC trace of pure electrolyte (Fig. 1, plot b). It should be mentioned that this decomposition starts at 200°C , while the same process with a copper current

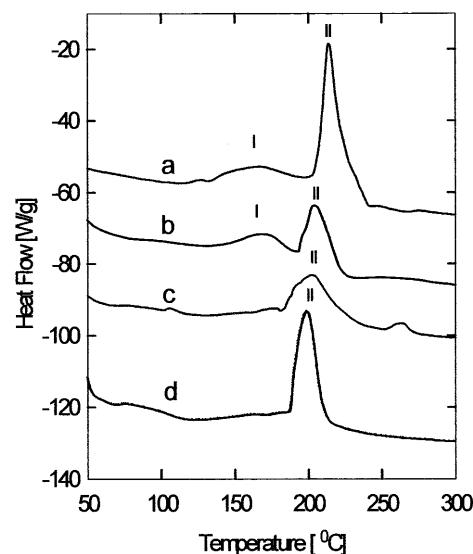


Fig. 7 DSC traces of rolled, unwashed, fully lithiated graphite on a copper current collector with the electrolyte: *a* pristine; *b* 7.5% burn-off (shifted by -10 W/g); *c* modified 7.5% burn-off (shifted by -50 W/g); *d* modified 7.5% burn-off (shifted by -75 W/g) containing 2.5% PVDF (instead of 5% PVDF). The heat flow values are in units of W per g of graphite. The electrolyte/graphite ratio is 1 $\mu\text{L}/0.2$ mg

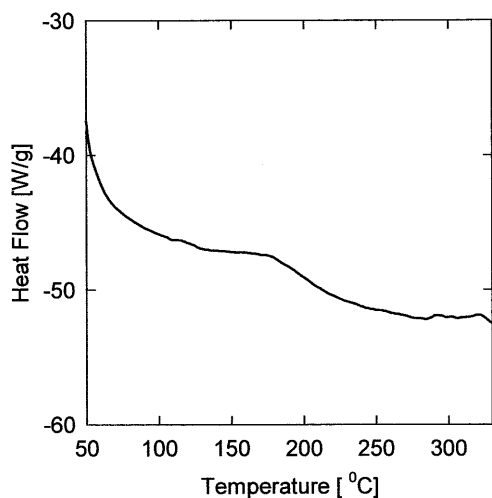


Fig. 8 DSC trace of fully lithiated, modified, 7.5% burnt graphite. The sample was washed in DMC and vacuum dried for 4 h

collector starts at about 90 °C. Mild oxidation caused strong depression of the first sharp decomposition peak. However, it did not influence the overall energy. The broadening of the endothermic peaks, which exhibit the decrease of the decomposition rate, is associated, presumably, with a smaller surface area of the burnt graphite, and with the difference of their surface groups [4].

Figure 3 shows the DSC traces for the washed and fully lithiated graphite/5 μ L electrolyte samples. It can be seen that only one exothermic peak exists at about 210 °C. In the DSC run of the pristine graphite sample, the exothermic reaction produces a great amount of heat and releases a lot of gas, causing an explosion of the DSC pan. In the case where the graphite was mildly oxidized (although it contains 10% more lithium), the explosion was prevented [9]. In addition, the exothermic peak of the mild oxidized graphite was depressed and shifted from 210 to 214 °C (Table 3). Modification of the burnt graphite resulted in a dramatic lowering of the peak height (from 225 W/g for the burnt sample to 25 W/g for the modified sample) and the energy of the exotherm and the reaction rate decreased from 3610 to 1460 J/g and from 10 to 2 W/g per °C, respectively.

The exothermic peak is preceded by a small endothermic peak (A in insert of Fig. 3). It is suggested that

Table 3 DSC data of washed, fully lithiated NG7 graphite with 1 M LiAsF₆ EC:DEC 1:2 (v/v) electrolyte^a

Type	T_p (°C)	T_{onset} (°C)	ΔU (J/g) ^b	Heat flow peak (W/g) ^b	Slope (W/g per °C) ^b
Pristine	—	210	—	—	—
15% burn-off	230	214	3610	225	10
Modified 15% burn-off	215	206	1460	25	2

^a Samples were washed in a solvent mixture of EC:DEC 1:2 (v/v). The electrolyte to graphite ratio is 5 μ L/2 mg

^b Graphite weight

Table 4 SEI materials in LiAsF₆ EC:DEC electrolyte

Compound [10, 11, 12]	Molar concentration (%) [4, 11]	T_m (°C) ^a
LiF	50	845
Li ₂ CO ₃	15	723
Li ₂ O	—	1700
As	1	615 (subl.)
As ₂ O ₃	1	193 (subl.)
As ₂ O ₅	1	315 (decomp.)
Polymers	10	?
Semicarbonates (ROCO ₂ Li)	20	200 (decomp.) [10]
	—	—

^a All T_m data were taken from [12], unless otherwise specified

this endothermic peak can be attributed to the decomposition of some SEI materials such as polymers, ROCO₂Li, (CH₂OCO₂Li)₂ and ROLi. Decomposition of such products at 200 °C was analyzed by temperature programmed desorption mass spectrometry (TPD-MS) measurements [10]. Table 4 shows the melting or decomposition temperature of the SEI products. It is obvious that compounds such as LiF, Li₂CO₃, Li₂O, As and As₂O₅ are thermally stable up to 600 °C. However, compounds such as As₂O₃, some polymers and especially semi-carbonates are thermally unstable and decompose at about 200 °C. In addition, polymers and semicarbonates are expected to dissolve in the electrolyte at high temperatures. These dissolution and decomposition processes can lead to the destruction of at least part of the SEI and would be followed by a vigorous reaction of the lithium, released from lithiated graphite electrode after partial SEI destruction, with the electrolyte. Another factor which must be considered in analyzing the effect of mild oxidation on the thermal behavior of the lithiated graphite is the effect of mild oxidation on the chemical composition of the SEI on the cross-section of the graphite particle. We found [11] that the chemical composition of the SEI had changed owing to the oxidation of the graphite. The change in the concentration ratio of the organic materials to the inorganic compounds in the SEI depends on the type of electrolyte. The formation of the chemically bonded SEI at the cross-section may help at least to partially avoid or slow the exfoliation of the graphite crystallites during the thermal reaction with the electrolyte and, by this means, to slow the reaction down.

Running DSC tests with unwashed fully lithiated graphite in contact with the electrolyte resulted in lower energy values for the exothermic reaction and for the peak height as compared with the washed samples. Figure 4 shows the DSC traces of the unwashed, fully lithiated pristine graphite sample with electrolyte. The exothermic reaction with the energy value of 880 J/g occurs at about 200 °C and is followed by several small endothermic peaks (Fig. 4, plot a). The addition of a copper current collector (plot b) resulted in the appearance of a new endothermic peak at about 165 °C ($\Delta U = 1350$ J/g), a decrease of the exothermic energy

Table 5 DSC data of unwashed, lithiated NG7 graphite on a copper current collector with 1 M LiAsF₆ EC:DEC 1:2 (v/v) electrolyte^a

Type	ΔU_I (J/g) ^b	ΔU_{II} (J/g) ^b	$\Delta U_{T(EX)}$ (J/g) ^b	$T_{P(I)}$ (°C)	$T_{P(II)}$ (°C)	Peak height (W/g) ^b	Slope (W/g per °C) ^b
Pristine	-450 ± 250	-3000 ± 450	-4500 ± 1500	160 ± 6	210 ± 4	25 ± 14	2.3 ± 1
7.5% burn-off	-390 ± 250	-1100 ± 300	-2200 ± 1000	158 ± 8	200 ± 8	14 ± 3	1.7 ± 1
Modified 7.5% burn-off	-	-1300 ± 800	-1300 ± 800	-	204 ± 7	12 ± 3	1.2 ± 1
Modified 7.5% burn-off ^c	-	-2500 ± 800	-2500 ± 800	-	205 ± 6	20 ± 8	1.9 ± 1

^a All values are average values of at least three samples. The electrolyte to graphite ratio is 1 μ L/0.2 mg

^b Graphite weight

^c Electrodes contains 2.5% PVDF (instead of 5%)

value to 700 J/g and a decrease of the peak height from 30 to 25 W/g. In addition, the overall energy of the endothermic transitions following the exothermic reaction increased from 1520 to 2900 J/g. It is suggested that the prewashing process damages the SEI by dissolving some of its constituents (such as polymers and semi-carbonates) and causing a fast vigorous reaction.

Figure 5 shows the thermograms of electrolyte decomposition by copper (plot a) and of a fully lithiated graphite electrode not separated from the copper current collector (plot b). In this case the heat flow values are calculated with respect to the weight of the electrolyte in the DSC pan. It is obvious that the low-temperature endothermic peak at about 165 °C of the graphite electrode coincides with that of the electrolyte. The high-temperature endothermic transitions of the two samples are also similar and fall into the same temperature range. Such thermal behavior indicates that the endothermic reactions during heating of the lithiated graphite electrode with the electrolyte are due to the catalytic decomposition of the electrolyte and of some of the reduction products accelerated by the copper current collector.

Figure 6 shows the effect of electrolyte content on the DSC scans for unwashed 7% burnt samples. The exothermic reaction of the sample without electrolyte addition starts at 60 °C with an overall energy value of 4300 J/g (plot a). Electrolyte addition resulted in an endothermic reaction starting at about 80 °C (plot b). The temperature of the exothermic reaction is shifted to 175 °C and the energy value is lowered to 1300 J/g. Furthermore, the reaction rate of the main 200 °C peak was increased from 0.5 W/g per °C to 0.75 W/g per °C. Thus, it can be concluded that the electrolyte addition resulted, on the one hand, in a cooling effect by increasing the rate of heat dissipation and by endothermic electrolyte decomposition. On the other hand, the kinetics of the exothermic reaction of lithiated graphite with the electrolyte increased as a result of higher electrolyte content in the DSC pan. The complex, interdependent effects of the copper current collector and electrolyte content on the thermal behavior of lithiated graphite electrodes are very important features that may

be used, when optimized, to improve the thermal stability of Li-ion batteries.

It seems (Fig. 6, plot b) that the 7% burnt graphite has a catalytic effect on electrolyte decomposition similar to that of the copper current collector. It caused a decrease in the exothermic peak height (from 27 to 18 W/g) and in the reaction rate (from 4.6 to 0.6 W/g per °C) for the pristine (Fig. 4, plot a) and for the 7% burnt samples (Fig. 6, plot b), respectively.

To analyze the thermal behavior of practical cells, the DSC test results of the unwashed samples with a copper current collector must be considered, owing to the resemblance to the real conditions in the Li-ion cell. With the same objective in mind, the electrolyte volume in our subsequent DSC tests was reduced from 5 μ L to 1 μ L for 0.2 mg graphite. The last value reflects more precisely the ratio of electrolyte volume to graphite amount in a practical cell. Table 5 summarizes the average values of the energy, the peak temperatures and heights, and the reaction rates for the major exothermic reaction.

In general, a large standard deviation for the DSC data was observed. We assume that this relates mainly to the variation in the amount of electrolyte in the DSC pan, caused by electrolyte traces left in the electrode pores. In spite of this, the shapes of thermograms were easily reproduced and a clear tendency was observed. Figure 7 (plot a) shows a typical DSC curve of the fully lithiated pristine sample with 1 μ L of electrolyte. An observed exothermic reaction starts at 120 °C as a small broad peak followed by a very sharp exotherm at about 210 °C and several very small endotherms. The reduced amount of the electrolyte results in a dramatic increase of the overall energy of the exothermic transitions (from 700 to 4500 J/g); however, the reaction rate was about three times slower.

A typical DSC trace of the fully lithiated 7.5% burnt graphite with 1 μ L electrolyte is presented in Fig. 7, plot b. This thermogram was similar to the DSC scan of the pristine graphite. It should be emphasized that the mild oxidation process reduced the overall exothermic energy value by about 50% (to 2200 J/g) and the reaction rate by 40% (Table 5), although it contains 10% more lithium.

Separation of the smallest particles (modification of graphite) resulted in the disappearance of the broad exothermic peak at about 160 °C (Fig. 7, plot c). The energy and exothermic reaction rate were also decreased by this modification.

Plot d in Fig. 7 shows the DSC trace of the fully lithiated graphite electrode with the reduced (2.5%) concentration of the PVDF binder. The thermogram has a similar shape to that of the electrode containing 5% PVDF. However, the energy value, exothermic reaction rate and peak height were 1.5–2 times larger (Table 5). It is suggested that the binder reinforces the structure of the graphite anode and may prevent the exfoliation of graphite. Thus, decreasing the amount of binder may cause the acceleration of the exothermic reactions owing to electrode disintegration.

Figure 8 shows a typical DSC curve of a fully lithiated ($x = 1.1$) “golden” 7.5% burnt graphite in the absence of electrolyte traces (it was washed by DMC and vacuum dried). Neither exothermic nor endothermic reactions were observed, showing a thermodynamic stability of SEI products towards the fully lithiated graphite. The only thermal transition observed was a baseline change starting at 175 °C, indicating a change in the heat capacity of the sample. This change is related to a phase transition in the lithiated graphite or in the SEI. The nature of this transition is far from understood yet, but it may damage the SEI and cause the exothermic reaction of the lithiated graphite with the electrolyte.

Summary

The effect of mild oxidation of natural graphite (NG7) and some other parameters on the thermal reactions of fully lithiated graphite and LiAsF₆ EC:DEC electrolyte was studied by DSC. It is suggested that the broad exothermic peak (at 50–109 °C) is related to the reaction of small lithiated graphite particles with the electrolyte. It was found that mild oxidation slowed the exothermic reaction of the lithiated graphite with the electrolyte, most likely as a result of the formation of a chemically different, more stable chemically bonded SEI. Two main reactions occur simultaneously upon heating of the anode of a Li-ion battery with electrolyte: the exothermic reaction of the lithiated graphite with the electrolyte and the endothermic reaction of electrolyte decomposition.

Separation of the smallest graphite particles and also increasing the PVDF binder content from 2.5 to 5% suppressed the exothermic reaction further. The copper current collector and the amount of electrolyte have a significant influence on the DSC traces, which are relevant to the thermal stability of the Li-ion battery. It appears that the unwashed lithiated graphite samples have a lesser exothermic reaction rate than that of the washed samples. It is suggested that the washing process damages the SEI by dissolving some of its constituents.

We used for cell thermal testing a LiAsF₆-based electrolyte, while most of the Li-ion batteries consist of a LiPF₆-based electrolyte. However, our findings and conclusions, considering small graphite particles separation, solvent decomposition and the effect of chemically bonded SEI, are considered to be general. We believe that our experiments indicate ways to improve the thermal stability of Li-ion cells.

Acknowledgements We would like to thank the Ministry of Science for financial support and the Kansai Coke Company for supplying NG7 powder.

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