Thermal stability of graphite anode with electrolyte in lithium-ion cells

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Abstract

Thermal stability of electrochemically lithiated graphite with 1 M $LiPF_6$/EC + DMC and PVdF-binder has been investigated. DSC measurements using an airtight sample case reveal a mild heat generation started from 130 °C with a small peak at 140 °C. The mild heat generation continued until a sharp exothermic peak appeared at 280 °C. The heat evolved in the small peak at 140 °C decreased by storage of the lithiated graphite with PVdF and the electrolyte at 50 °C for 3 days before the DSC measurements. The lithiated graphite with the electrolyte without PVdF-binder did not show the small peak at 140 °C. The peak at 140 °C seems to be caused by the reaction (the Solid Electrolyte Interphase (SEI) formation) of the electrolyte and lithiated graphite, whose surface is covered by poly(vinylidene flouride) (PVdF)-binder without formation of SEI at a lower temperature. The mild heat generation from 140 to 280 °C is the reaction of the lithiated graphite and the electrolyte through SEI (SEI formation), because there was no such mild heat generation when non-lithiated graphite was used. The peak at 280 °C is probably a direct reaction of lithiated graphite and electrolyte by a breakdown of SEI. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion cell; Graphite anode; Electrolyte; Thermal stability; DSC; PVdF-binder

1. Introduction

Lithium-ion cells are widely used as power sources for portable electric devices. Recently, the study to utilize high-performance lithium ion battery for power sources of electric vehicles (EV) and other large-size equipment is proceeded by many corporations and laboratories. However, large-size lithium ion batteries are not used practically because there are some safety concerns associated with the scaleup of these batteries. Safety of lithium-ion cells is mainly related to thermal reactivity of the materials in the cell. Several exothermic reactions occur inside a cell as its temperature increases. It is generally considered that 'thermal runaway' occurs if heat output exceeds thermal diffusion. However, 'heat output' and 'thermal diffusion' valances at a high temperature if we consider safety-vent opening, which releases high temperature gas to the outside of a cell. Fire can be seen if a material is heated to a high temperature and as a result, the thermal radiation waves become visible [1]. For this reason, many researchers have carried out thermal stability studies on these batteries [2–17]. Among them, thermal studies [5,7,9–14,17] are related to the anode stability.

The thermal stability of carbon anodes in an electrolyte is controlled by a solid electrolyte interphase (SEI) formed on the lithiated carbon anode. Edstrom et al. [17] reported that thermal breakdown of the SEI, when using $LiBF_4$ electrolytes starts at 58 °C (Graphite,

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LiBF$_4$/EC + DMC) [13], while use of LiPF$_6$ shifts the breakdown temperature to 102 °C [5,10]. However, Zhang et al. [7] suggested that the exothermic reaction (MCMB, LiPF$_6$/EC + DMC) at around 130 °C is related to the surface passivation of the lithiated carbon materials. von Sacken et al. [5] also proposed a reaction model based on a simple heterogeneous reaction between the electrolyte solvent and the lithiated carbon, where the reaction produces a passivating film on the carbon surface. Richard and Dahn [10] reported that the initial form of self-heating rate profile at around 100 °C (MCMB, LiPF$_6$/EC + DEC) was a result of the conversion of metastable solid electrolyte interphase (SEI) components to stable SEI components. The question thus arises as to what the real reason for the exothermic reaction is at around 100 °C. In this work, a differential scanning calorimeter is used to perform a thermal stability study of a lithiated graphite anode in LiPF$_6$/ ethylene carbonate (EC) + dimethyl carbonate (DMC) electrolyte in detail.

2. Experimental

A coin cell with a graphite anode and a counter electrode of Li metal sheet was used in all experiments. Anode electrodes used in this study were prepared by mixing 95 wt.% of natural graphite (LF-18D from Chuestu Graphite) with 5 wt.% of poly(vinylidene fluoride) (PVdF)-binder (KF#9100 from Kureha Chemical) dissolved in 1-methyl-2-pyrrolidinone (NMP). The slurry was coated onto a 0.1-mm-thick copper current collector. The electrodes were then dried for 12 h at 70 °C in a vacuum oven. Graphite anodes without PVdF-binder were fabricated by compressing the graphite powder onto the copper current collector using an oil hydraulic press at about 3 tons.

The cells were assembled using a 15-mm diameter anode, a lithium foil as a counter electrode, polypropylene separator (Celgard 3501), and 1 M LiPF$_6$/EC + DMC (1:1 v/v) electrolyte from Tomiyama Chemical. All work was carried out in an argon filled glove box.

The cells were cycled between 0.01 and 1.5 V with a relaxation period of 60 min at the end of the charge, at a constant current of 0.2 mA/cm^2. After two cyclings in this condition, the cells were charged to

0 V with the time limit of 372 mA h/g to obtain a fully charged anode.

The thermal stability of those anodes with 1 M LiPF$_6$/EC + DMC (1:1 v/v) electrolyte was monitored by a TG-DSC apparatus (Rigaku Thermo plus TG8110, Rigaku, Japan). Each sample for TG-DSC measurement was packed in a stainless steel pan, which was then crimp-sealed in a glove box filled with argon. Leakage from the case did not occur, as was confirmed by the TG data, which was measured at the same time as the DSC measurements. All of the DSC experiments were carried out at a heating rate of 5 °C/min.

3. Results and discussion

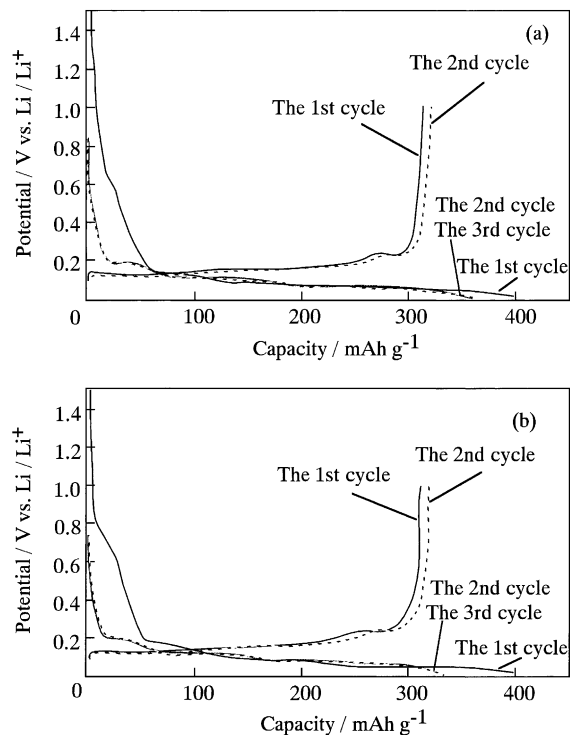Fig. 1 shows the cycling profile of a graphite anode with a lithium foil as a counter electrode. Fig. 1(a)

Fig. 1. The cycling profile of a graphite anode with a lithium foil as a counter electrode: (a) is the profile of a usual graphite anode containing PVdF-binder; (b) is the profile of a graphite anode without containing PVdF-binder made using an oil hydraulic press.

presents the profile of a usual graphite anode containing PVdF-binder. Fig. 1(b) shows the profile of a graphite anode without containing PVdF-binder made using an oil hydraulic press. The third discharge capacity of those samples are nearly 300 mA h/g. Thus, the lithiated PVdF-free anode is used for DSC measurement.

Fig. 2 shows DSC curves of (a) the fully lithiated graphite with the electrolyte and PVdF (the usual graphite anode), (b) the fully lithiated graphite with the electrolyte (the anode made using an oil hydraulic press), (c) the fully delithiated graphite with the electrolyte and PVdF (the usual graphite anode), (d) the fully lithiated graphite with PVdF (the usual graphite anode) with a washing/vacuum-drying pro-
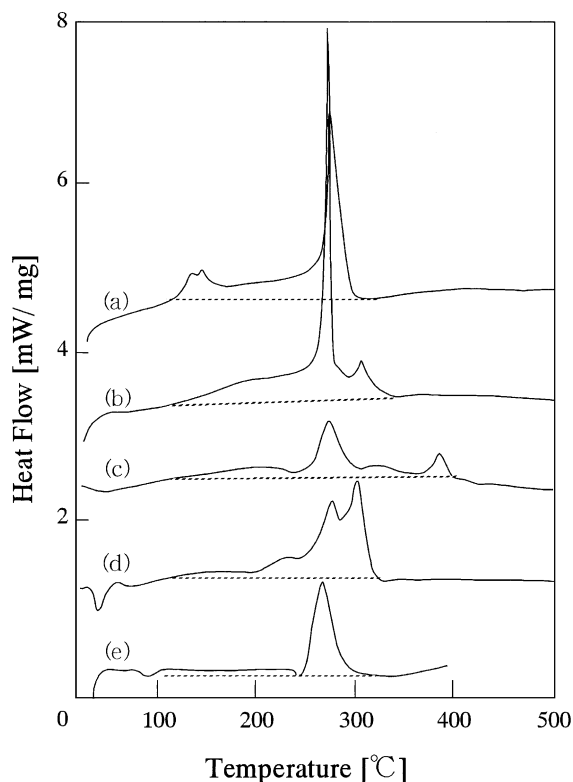

Fig. 2. DSC curves of (a) the fully lithiated graphite with the electrolyte and PVdF (the usual graphite anode), (b) the fully lithiated graphite with the electrolyte (the anode made using an oil hydraulic press), (c) the fully delithiated graphite with the electrolyte and PVdF (the usual graphite anode), (d) the fully lithiated graphite with PVdF (the usual graphite anode) with a washing/vacuum-drying procedure, and (e) the electrolyte (1 M LiPF$_6$/EC + DMC).

cedure, and (e) the electrolyte. The washing/vacuum-drying procedure for sample (d) is performed to remove the electrolyte. The precise process is the washing of the anode with EC + DMC (1:1 v/v) solvent several times followed by vacuum-drying at 60 °C for 3 h. The heat flow is based on the total weight of the sample. The sample (a) shows a mild heat generation started from 130 °C with a small peak at 140 °C. The mild heat generation continued until a sharp exothermic peak appeared at 280 °C. The lithiated graphite with the electrolyte without PVdF-binder (sample (b)) did not show the small peak at 140 °C. Also, samples (c) and (d) did not show the small peak at 140 °C. Therefore, three components of PVdF-binder, the lithiated graphite, and the electrolyte are necessary to show the small peak at 140 °C. Richard and Dahn [10] reported from their experiments using an accelerating rate calorimeter (ARC) that the peak of self-heating rate profile vs. temperature at around 100 °C (MCMB, LiPF$_6$/EC + DEC) was a result of the conversion of metastable SEI components to stable SEI components. Their experiments were carried out at adiabatic conditions. We believe that the peak of self-heating rate profile at around 100 °C corresponds to the small peak at 140 °C in our experiments. Therefore, sample (b) should show the small peak at 140 °C, if the consideration of Richard and Dahn [10] is correct. From our experiments, the small peak at 140 °C seems to be caused by the reaction (SEI formation) of the electrolyte and lithiated graphite, whose surface is covered by PVdF-binder without formation of SEI at a lower temperature. PVdF-binder covers some surface area of graphite when an anode is fabricated. After charging, graphite particles are lithiated and SEI is formed on the surface of the graphite particles. However, the PVdF-binder-covered area of the graphite particles do not form SEI because PVdF-binder protects the contact of the lithiated graphite particles and the electrolyte at room temperature. The protection effect of PVdF-binder changes to be not sufficient at an elevated temperature. Probably swelling of PVdF-binder by the electrolyte occurs at an elevated temperature. Okamoto et al. [14] reported that the small peak at 140 °C disappears after aging graphite anode (with PVdF) with LiPF$_6$/EC + DMC + diethyl carbonate (DEC) electrolyte. A similar experiment was undertaken using our materials. Fig. 3 shows the DSC curves
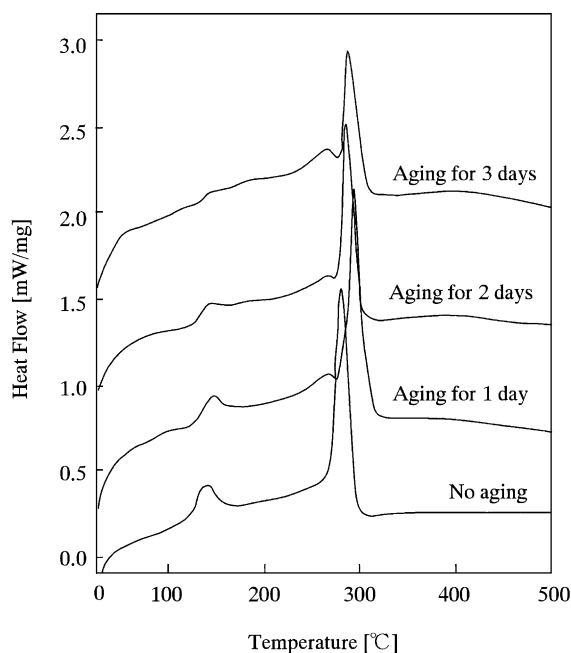
Fig. 3. DSC curves after aging at 50 °C for 0, 1, 2, and 3 days.

after aging at 50 °C for 0, 1, 2, and 3 days. The amount of exothermic heat at 140 °C decreased with increasing of the aging days. PVdF-binder is swelled by the electrolyte during the aging at 50 °C. Then SEI is formed at the covered area of the graphite particles by PVdF-binder during the aging.

DSC measurements were carried out for PVdF and PVdF with Li metal. PVdF begins to decompose at 400 °C. PVdF with Li metal shows exothermic reaction from 290 °C. Therefore, a peak at 390 °C in Fig. 2(c) shows the decomposition of PVdF. A peak at 300 °C in Fig. 2(d) shows the reaction of PVdF with the lithiated graphite.

A mild heat generation continued from 130 °C until a sharp exothermic peak appeared at 280 °C for samples (a) and (b) in Fig. 2. As considered by von Sacken et al. [5], this mild heat generation is caused by a simple heterogeneous reaction between the electrolyte solvent and the lithiated carbon, where the reaction produces a passivating film on the carbon surface. In other words, the mild heat generation comes from the reaction of lithiated carbon with the electrolyte to form new SEI. The lithiated graphite and electrolyte can react if the electrolyte permeates the SEI to reach the lithiated graphite surface. Therefore,

samples (c) (delithiated graphite) and (d) (without the electrolyte) in Fig. 2 show a very small heat generation in this region compared with the DSC curves of samples (a) and (b). The very small heat generation may be caused by reactions of components in SEI.

In order to make clear that the SEI growth at temperatures from 130 °C until a sharp exothermic peak appeared at 280 °C, DSC samples were preheated to a certain temperature and then they were cooled to room temperature. After this process, DSC measurements were carried out. Fig. 4 shows the results, where (a) is the sample without PVdF and no preheating (corresponding to sample (b) in Fig. 2), (b) is with PVdF and preheated up to 140 °C, (c) is with PVdF and preheated up to 150 °C, and (d) is with PVdF and preheated up to 160 °C. The heat generation from 135 °C decreased with increasing the preheating temperature because a thick SEI is formed by the preheating.
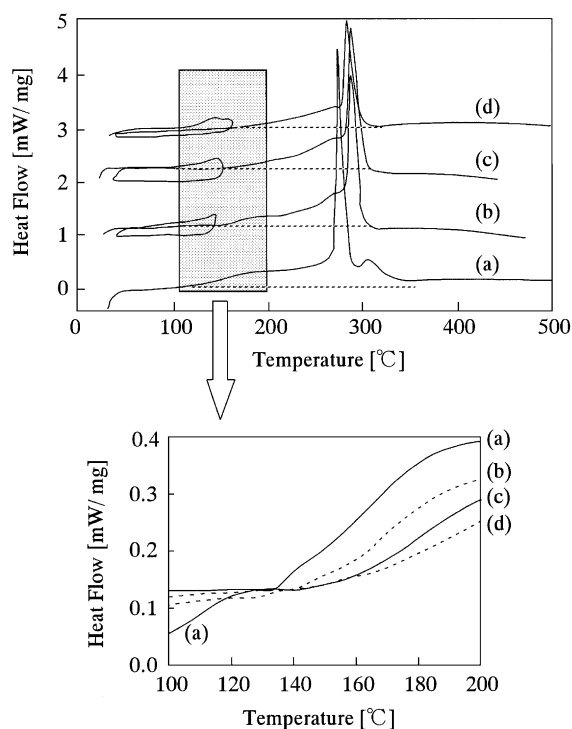

Fig. 4. DSC curves after preheating: (a) is the sample without PVdF and no preheating (corresponding with sample (b) in Fig. 2); (b) is with PVdF and preheated up to 140 °C; (c) is with PVdF and preheated up to 150 °C; (d) is with PVdF and preheated up to 160 °C.

A sharp exothermic peak at 280 °C is observed if both the lithiated graphite and electrolyte co-exist as shown in Fig. 2. Therefore, the exothermic reaction is a direct reaction of the lithiated graphite and electrolyte caused by a breakdown of SEI. The electrolyte also decomposes at around 280 °C. The electrolyte decomposition may cause the breakdown of SEI.

4. Conclusions

Based on the results of this study, we conclude that the small peak at 140 °C is caused by the reaction (SEI formation) of the electrolyte and lithiated graphite, whose surface is covered by PVdF-binder without formation of SEI at a lower temperature. A mild heat generation continued from 130 °C until a sharp exothermic peak appeared at 280 °C, which came from the reaction of lithiated carbon with the electrolyte to form a new SEI. A sharp exothermic peak at 280 °C is a direct reaction of the lithiated graphite and electrolyte caused by a breakdown of SEI. Although the results were obtained for natural graphite (LF-18D) and 1 M $LiPF_6$/EC + DMC electrolyte, we believe that similar results will be obtained for other combinations of carbon and electrolytes.

Acknowledgements

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