



# Consideration of carbon structure effect on thermal stability of carbon anode for Li ion rechargeable batteries

Chang-Keun Back\*, Jai Prakash

Department of Chemical and Environmental Engineering, Illinois Institute of Technology, Chicago, IL 60616, United States

## ARTICLE INFO

### Article history:

Received 16 January 2011

Received in revised form 24 March 2011

Accepted 26 March 2011

Available online 4 April 2011

### Keywords:

Thermal stability

Carbon anode

Li-ion batteries

Heat of reaction

## ABSTRACT

Thermal stability of carbon structure anode materials for Li-ion rechargeable batteries is studied with the consideration to carbon physical property and structure. Differential scanning calorimeter (DSC) thermal test shows that the thermal decomposition of fully delithiated carbon anode materials at an elevated temperature to about 230 °C generate weak exothermic heat and the heat amount is in the linear relation to their carbon specific surface area. Meanwhile, the fully lithiated carbon anode materials generates much stronger exothermic heat in the same temperature range and the heat amount is largely differed with their carbon structure. X-ray diffraction (XRD) and DSC tests reveal that intercalated lithium inside the carbon structure is involved in thermal reactions with aqueous liquid electrolyte and the evolved specific heat per lithium mol is largely differed with the carbon structure.

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## 1. Introduction

The safety issue of Li ion rechargeable batteries incorporating the non-aqueous electrolytes has become of great concern in their potential applications, especially as the application of this kind of batteries has expanded from small sized portable electronics to the large scale applications such as hybrid electric vehicles (HEV) and electric vehicles (EV). There have been great efforts to enhance the safety of Li ion batteries by approaching from the viewpoint of material development [1,2] to safety related cell designing [3,4]. It is known that the thermal stability of carbon anode is critical to the thermal runaway of Li ion batteries as its thermal decomposition arises at relatively low temperature around 100 °C [5,6] and those heats enables to induce much higher heat evolution from cathode decomposition and its reaction with organic electrolyte at higher temperature [7,8]. There had been a number of reports discussing carbon property related thermal stability of carbon anodes in various electrolyte systems [5,6,9–11]. Carbon structure is considered as the other important parameter that may influence the thermal stability of carbon anode. The understanding of carbon structure relevancy to the thermal stability of carbon anode is very important, especially in the times when non-graphite structure carbon has been newly attracted as anode material for HEV owing to its high power capability [12,13]. In this study, it was attempted to

clarify the effect of carbon structure on the thermal stability of carbon anode materials by using four different carbon materials. DSC and XRD analyses on the carbon anode materials at various state of charge were performed, and their thermal property was quantitatively measured and investigated with the correlation to their carbon structure.

## 2. Experimental

Carbon electrodes were prepared by the doctor blade method. Slurry containing 84 wt% carbon, 8 wt% acetylene carbon black (Alfa Aesar), and 8 wt% poly vinylidene difluoride (PVDF) binder was coated on a thin copper current collector. After coating, the laminate was dried at 80 °C in air overnight and at 80 °C in vacuum for 4 h. Coin cells (2032) were constructed from these carbon electrodes, polyethylene/polypropylene microporous membrane (Celgard 2300), and Li metal as the counter and reference electrode. The electrolyte solution was 1.2 M LiPF<sub>6</sub> in the mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (3:7 as weight). A typical carbon electrode contains about 4 mg of active carbon materials. Electrochemical cycling of the cells was performed with a BT-2043 Arbin cyler at C/10 h in the voltage cut-off of 0.0–1.2 V vs. Li/Li<sup>+</sup>. After five charge/discharge cycles, the electrodes were lifted from the cells and the carbon materials peeled off the copper current collector. The carbon electrode material was introduced into stainless DSC capsules (Perkin-Elmer) in argon filled globe box. The DSC measurements were carried out with a DSC7 apparatus (Perkin-Elmer) with the heating rate of 10 K/min in the temperature range of 50–400 °C. The powder X-ray diffraction measurements on the carbon samples were performed by using a Rigaku diffractome-

\* Corresponding author at: Precedence Development Group, Samsung SDI Co., LTD. 508, Sungsung-dong, Cheonan-si, Chungcheongnam-do, 330-300, Republic of Korea. Tel.: +82 070 7125 0231; fax: +82 41 560 3695.

E-mail address: [backchat@iit.edu](mailto:backchat@iit.edu) (C.-K. Back).

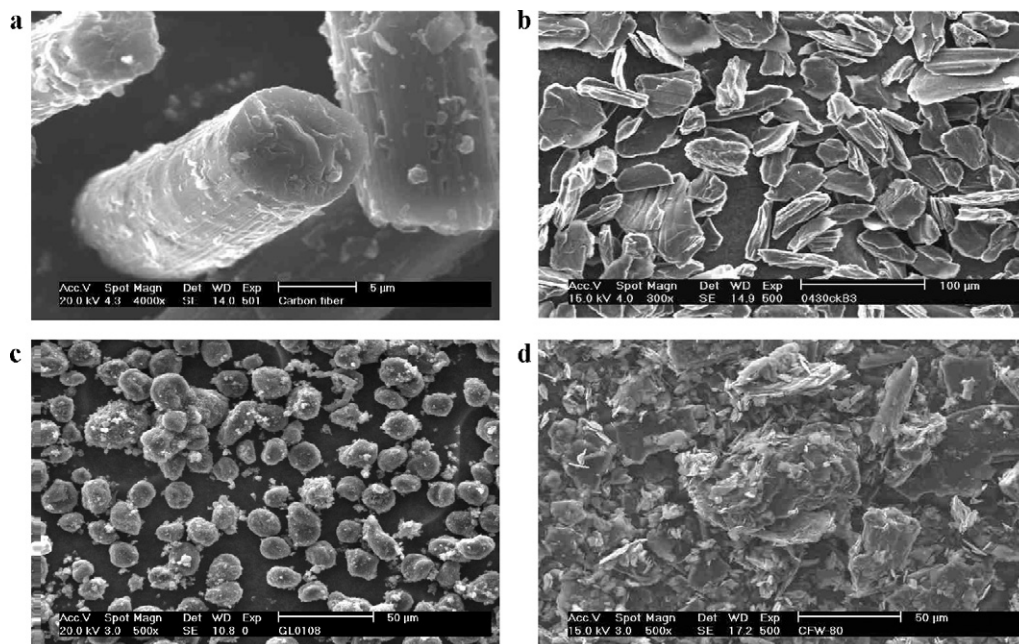


Fig. 1. FE-SEM images of the carbons studied in this work: (a) carbon fiber, (b) soft carbon, (c) MCMB, and (d) hard carbon.

ter equipped with a copper target X-ray tube and a diffracted beam monochromator.

### 3. Results and discussion

FE-SEM images of the carbon samples are presented in Fig. 1. Carbon fiber has a cylindrical shape formed by graphene layers stacked each other along its fiber axis with an average particle size of about 13  $\mu\text{m}$ , while MCMB has a spherical shape in size range of 20–30  $\mu\text{m}$ . Flaky shaped and coarsely agglomerated forms are observed in soft carbon and hard carbon, respectively. In Fig. 2, XRD structural analyses on the carbons show that carbon fiber and MCMB are of highly organized graphite structure as their  $d_{002}$  diffraction peaks at 26.7 two theta are very sharp and highly intense, while soft carbon and hard carbon have amorphous non-graphite structure when their  $d_{002}$  diffraction peaks are very broad and low intense. The physical properties of the carbon samples are listed in Table 1.

First five electrochemical cycles of the carbon cells assembled with the carbons were carried out in voltage cut-offs of 0.005–1.2 V vs.  $\text{Li}/\text{Li}^+$  at C/10 h, and the carbon cells were fully delithiated to

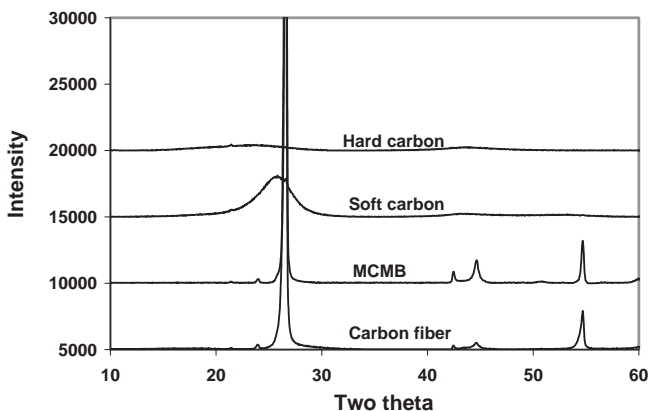


Fig. 2. Powder X-ray diffraction patterns of the carbons.

1.2 V vs.  $\text{Li}/\text{Li}^+$  or fully lithiated to 0.005 V vs.  $\text{Li}/\text{Li}^+$  for DSC thermal test. The first charge and discharge profiles of the carbon cells are presented in Fig. 3. The graphite structure carbon cells of carbon fiber and MCMB show the low and plateau potential profiles mostly in the voltage range below 0.2 V vs.  $\text{Li}/\text{Li}^+$  with stage change phenomena from stage 4 to stage 1. Meanwhile, the amorphous structure carbon cells of soft carbon and hard carbon show the sloping potential profiles because of their highly distorted structure and variously distributed active sites for Li ion intercalation [14,15]. The small current appeared at about 0.7 V vs.  $\text{Li}/\text{Li}^+$  during the first discharging process in the carbon cells is ascribed to the irreversible formation of solid electrolyte interface layer on the carbon surface from the electrolyte decomposition and reduction with Li ion. The first discharge capacity and the columbic efficiency of the first cycle are about 350 mAh/g and 92%, respectively, in the graphite structure carbon cells, while those of the amorphous structure carbon cells are rather lower to about 270 mAh/g and 85%, respectively. In Fig. 4(a), DSC profiles of the fully lithiated carbon electrode materials of carbon fiber and hard carbon are presented. Lithiated amounts of the carbon electrodes are about  $X=0.9$  and 0.67 in  $\text{Li}_x\text{C}_6$  for carbon fiber and hard carbon, respectively. Both the carbon electrode materials show the same onset temperature of about 78  $^\circ\text{C}$ . Four different thermal peaks, three exothermic peaks and one endothermic peak, are observed in the test temperature range of 50–400  $^\circ\text{C}$ . The first exothermic peak indexed to (a) around 100  $^\circ\text{C}$  is considered to come from the thermal decomposition of SEI layer [16], specifically thermal decomposition of thermally unstable organic components of lithium alkyl carbonate to inorganic component of lithium fluoride [17]. The second exothermic peak of (b) shown from about 140  $^\circ\text{C}$  and broadly continued to 230  $^\circ\text{C}$  is ascribed to the thermal

Table 1  
Physical properties of four different carbons.

Carbon	Particle size ( $\mu\text{m}$ )	BET surface area ( $\text{m}^2/\text{g}$ )	$d_{002}$ (nm)	$L_c$ ( $\text{\AA}$ )
MCMB	20–30	1.19	3.45	365
Carbon fiber	13	2.8	3.55	334
Soft carbon	40–50	1.8	7.06	24
Hard carbon	30–40	3.4	–	–

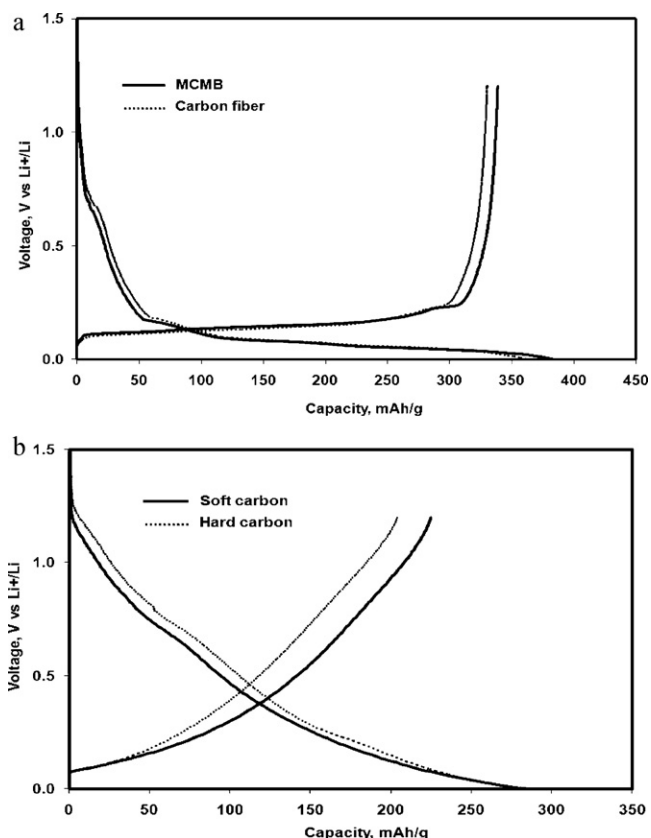


Fig. 3. First charge and discharge profiles of the carbon cells: (a) the graphite structure carbon cells of MCMB and carbon fiber; (b) the non-graphite structure carbon cells of soft carbon and hard carbon.

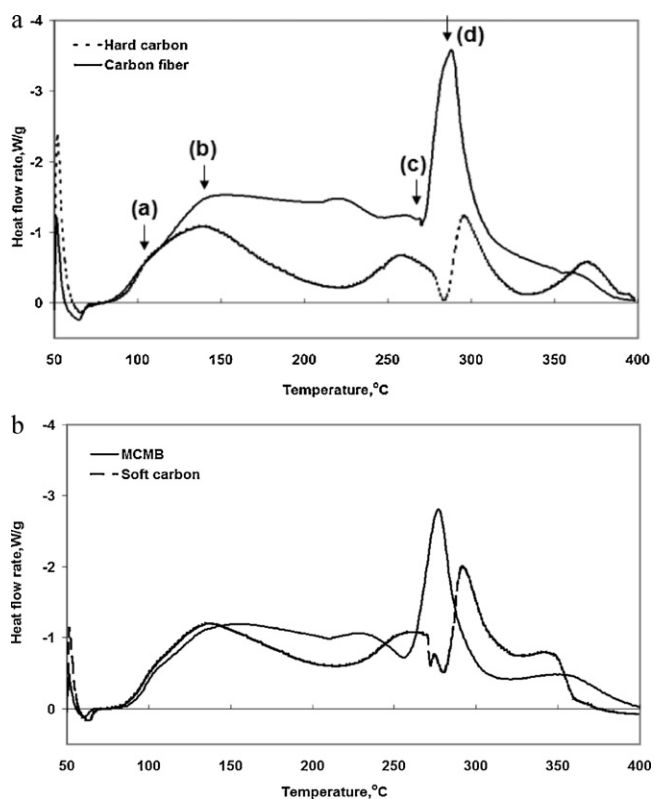
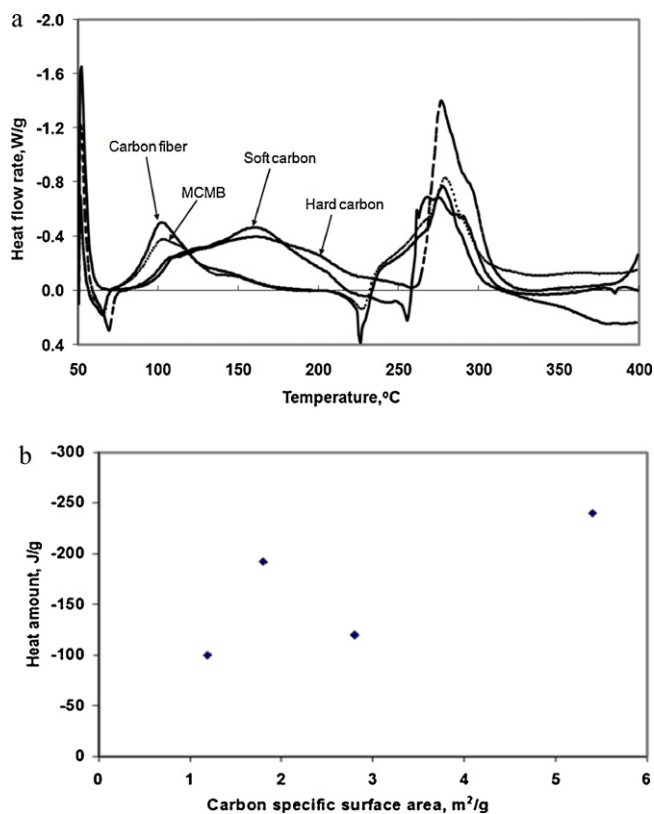


Fig. 4. DSC profiles of (a) the fully lithiated carbon fiber and hard carbon, and (b) the fully lithiated MCMB and soft carbon.

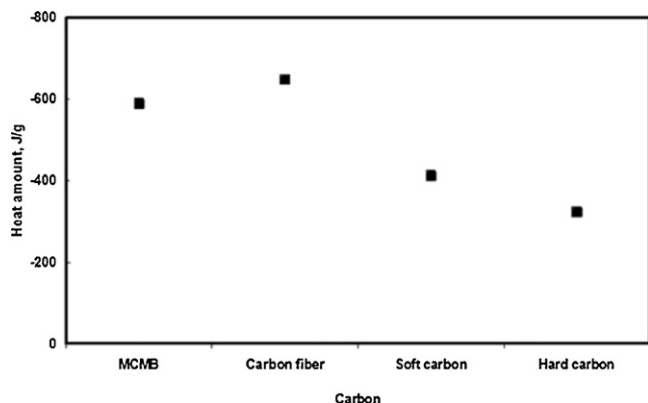
reactions of intercalated lithium inside the carbon structure with the organic electrolyte. The thermal reaction proceeds when SEI layer on the carbon surface breaks down at an elevated temperature and new carbon surface is exposed to organic electrolyte to react with the intercalated lithium [18]. The thermal reaction will be ceased only when all of intercalated lithium depletes by the thermal reactions with an organic electrolyte or decomposed SEI layer on the carbon surface becomes too thick for intercalated lithium inside the carbon structure to penetrate through. The endothermic peak of (c) around 275 °C is considered to result from the thermal decomposition of  $\text{LiPF}_6$  [16] and its reaction with EMC [19]. The final exothermic peak of (d) at about 285 °C is related to the carbon structural collapse and followed direct reactions of residual intercalated lithium with the organic electrolyte and also to the thermal reactions of  $\text{LiPF}_6$  with EC and PVDF [19]. As compared between the thermal stability of the carbon electrodes, the exothermic heat rate is much stronger in the carbon fiber electrode material than in the hard carbon electrode material in the overall test temperature range. Especially if the heat generated in temperature range to about 230 °C is only considered, the evolved heat amount is almost two times bigger in the carbon fiber electrode material than in the hard carbon electrode material. The heat generated in the temperature range is considered to be very critical in the safety issue of Li ion rechargeable batteries because it can induce much stronger exothermic heat by leading in the thermal decomposition of delithiated cathode material at higher temperature. From this consideration, this study had been mainly focused on characterizing the thermal stability of the carbon electrode materials at an elevated temperature to about 230 °C. It is well known that the thermal stability of lithiated carbon electrode is considerably different with the content of intercalated lithium. Yang et al. [6] reported that the exothermic heat generated from lithiated carbon electrode in temperature range to about 250 °C increases with the content of intercalated lithium. However, as the intercalated lithium amount is higher than about  $X=0.5$  in  $\text{Li}_x\text{C}_6$ , the exothermic heat amount becomes saturated and does not increase any more regardless of the content of intercalated lithium. They claimed that since decomposed SEI layer on the carbon surface becomes very thick, intercalated lithium inside the carbon structure cannot penetrate through to react with an organic electrolyte. Similar result had been reported by Dahn et al. [17]. The group showed that the amount of intercalated lithium lost by the thermal reactions with an organic electrolyte at an elevated temperature to about 200 °C is below  $X=0.5$  in  $\text{Li}_x\text{C}_6$ . Those reports suggest that the large difference of thermal stability between the lithiated carbon electrodes of carbon fiber and hard carbon is not originated in their different initial intercalated lithium amount because both the carbon electrodes are initially enough lithiated above  $X=0.5$  in  $\text{Li}_x\text{C}_6$ . The large different thermal stability between the lithiated carbon electrodes of carbon fiber and hard carbon is interested enough, especially if considering that the specific surface area of hard carbon is higher than that of carbon fiber. Similar results are observed in DSC tests of lithiated MCMB and lithiated soft carbon electrode materials, as presented in Fig. 4(b). It shows that the lithiated MCMB electrode material generates stronger exothermic heat than the lithiated soft carbon electrode material even though the latter has higher specific surface area than the former by about 50%. It is normally known that the carbon electrode composing of carbons having higher specific surface area generates stronger exothermic heat than the others because the heat evolved in the temperature range to about 230 °C mainly results from the thermal decomposition of SEI layer on the carbon surface and from the thermal reactions of intercalated lithium with an organic electrolyte. Obviously, when DSC thermal test was carried out on the fully delithiated carbon electrodes, the heat amount generated in the considered temperature range to about 230 °C is roughly in the linear relation to the carbon spe-



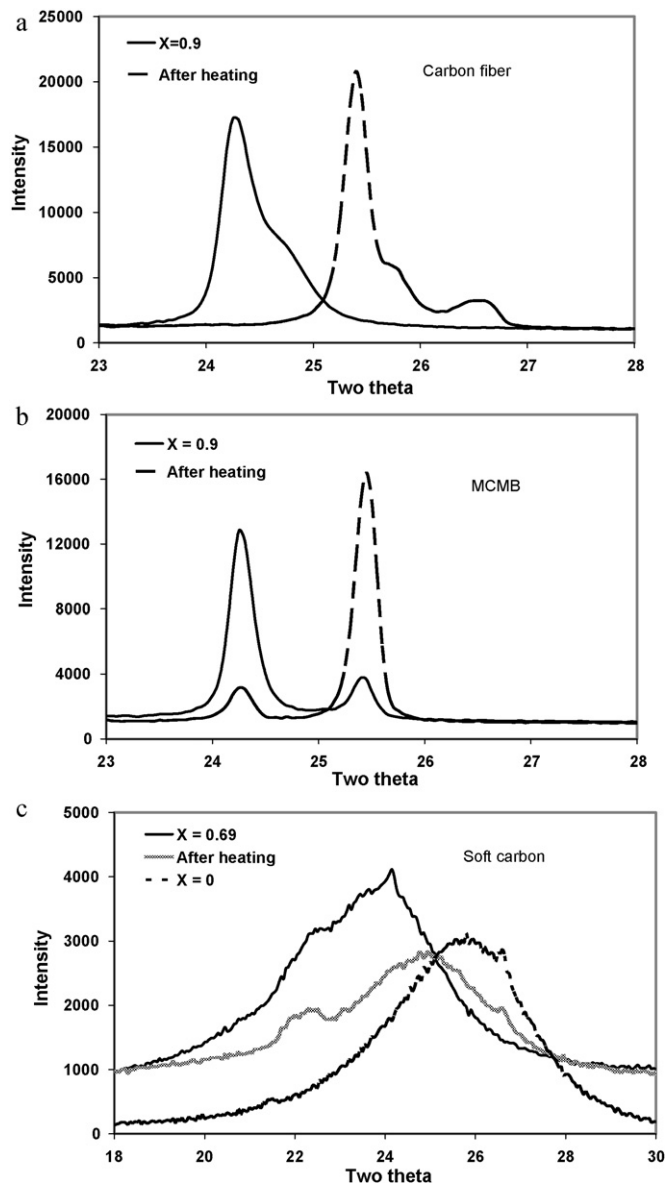
**Fig. 5.** Thermal stability of the fully delithiated carbon electrode materials: (a) DSC profile of the carbon electrodes; (b) the evolved heat amounts for the temperature range between 50 and 230 °C against the carbon specific surface area.

cific surface area, as presented in Fig. 5. This result suggests that the carbon specific surface area is a controlling factor for the thermal stability of the fully delithiated carbon electrode. In addition, there had been several other reports [20] to discuss the relationship between carbon electrode thermal stability and irreversible capacity since exothermic heat can be evolved from the thermal reactions between intercalated lithium that are trapped inside the carbon structure during electrochemical cycle and an organic electrolyte.

Unlike in the fully delithiated carbon electrode materials, the carbon specific surface area is not an important factor to control the thermal stability of the fully lithiated carbon electrode materials. Instead, carbon structure seems to be more involved in determining the thermal stability of the fully lithiated carbon electrode materials, as shown in Fig. 6. The figure shows that the heat amount

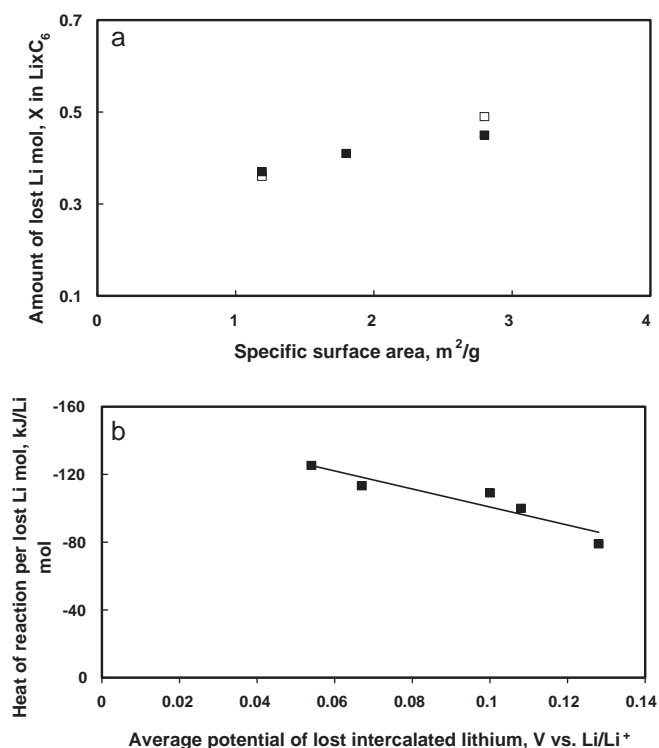


**Fig. 6.** The evolved heat amount of the fully lithiated carbon electrodes for the temperature range between 50 °C and 230 °C.



**Fig. 7.** Diffraction peak of  $d_{002}$  for the lithiated carbon electrode materials before and after heating to 230 °C: (a) carbon fiber; (b) MCMB; (c) soft carbon.

evolved in the temperature range to about 230 °C is relatively larger for the graphite structure carbon electrodes of carbon fiber and MCMB than for the amorphous structure carbon electrodes of soft carbon and hard carbon. For more schematic investigation into the thermal stability of the fully lithiated carbon electrodes and its relevancy to the carbon structure, the amount of intercalated lithium lost during the heating to about 230 °C was quantitatively measured by using XRD. Carbon fiber and MCMB were lithiated to  $X=0.9$  in  $\text{Li}_x\text{C}_6$ , while soft carbon was lithiated to  $X=0.67$  in  $\text{Li}_x\text{C}_6$  because of its limited capacity. Hard carbon was excluded from the test because of its severe amorphous structure. In Fig. 7, X-ray diffraction peaks of  $d_{002}$  before and after heating to 230 °C are presented for the carbon electrodes. After heating, the diffraction peak of  $d_{002}$  shifts to higher angle, as interlayer spacing distance between graphene layers of the carbon structures decreases due to the removing of intercalated lithium. Characteristic stage changing phenomena, the shift of  $d_{002}$  diffraction peak angle from stage 1 to stage 2 or pristine with the removing of intercalated lithium, is observed in the graphite structure carbon electrodes of carbon fiber and MCMB, whereas a non-linear shift of  $d_{002}$  diffraction



**Fig. 8.** (a) The amount of consumed intercalated lithium plotted against the carbon specific surface area where the black and blank squares mean the first and second test results, respectively, and (b) the specific heat of reaction per consumed Li mol as a function of the average potential of the consumed intercalated lithium.

peak angle without the stage changing phenomena is observed in the amorphous structure soft carbon. Based on the change of  $d_{002}$  diffraction peak angle and its intensity, the amount of lost intercalated lithium was estimated for each carbon electrode material. The amount of lost intercalated lithium is different each other, but none of them exceeds the amount of  $X=0.5$  in  $\text{Li}_x\text{C}_6$ , consisting with the results by others [6,17]. The amount of lost intercalated lithium is correlated to the carbon specific surface area, as presented in Fig. 8(a), and it shows that they are roughly in the linear relationship between them. This result indicates that more amount of intercalated lithium is lost from the carbon structure material upon the heating to about  $230^\circ\text{C}$  as the carbon specific surface area is higher. The other consideration was made with a specific heat of reaction per lost intercalated Li mol because, thermodynamically, if an electrochemical potential of intercalated lithium is higher, then thermal energy generated from the thermal reaction with an organic electrolyte would be higher [21]. In actual, there is a big difference of an average electrochemical potential of intercalated lithium between the graphite structure carbons and the amorphous structure carbons, as seen with their different voltage profiles in Fig. 3. The average discharge potentials of the graphite structure carbons of carbon fiber and MCMB are about 0.091 V and 0.087 V vs.  $\text{Li}/\text{Li}^+$ , respectively, while that of the amorphous structure soft carbon is about 0.28 V vs.  $\text{Li}/\text{Li}^+$ , which means that the average electrochemical potential of intercalated lithium is differed between the carbon structures by as much as about 18.235 kJ/Li mol. In Fig. 8(b), the specific heat of reaction per lost intercalated Li mol is plotted against the average potential of the lost intercalated lithium, which clearly shows that they are roughly in the reverse linear relationship. This result indicates that the thermal stability of the lithiated carbon electrode is considerably influenced by its carbon structure, and so although the graphite structure carbon electrode material lost relatively small amount of intercalated

lithium during the heating to about  $230^\circ\text{C}$  because of its small carbon specific surface area, it can generate stronger exothermic heat by its high specific heat of reaction per lost intercalated Li mol.

#### 4. Conclusions

The thermal stability of different carbon structure electrode materials at two different states of the fully delithiated and the fully lithiated were studied using DSC and XRD. DSC thermal tests on the fully delithiated carbon electrode materials show that the thermal stability of them at an elevated temperature to about  $230^\circ\text{C}$  is largely depended on its carbon specific surface area, as most of exothermic heat is resulted from the thermal decomposition of SEI layer on the carbon surface. Meanwhile, the thermal stability of the fully lithiated carbon electrode materials is largely differed with its carbon structure so that the graphite structure carbon electrode materials generate relatively higher exothermic heat than the amorphous structure carbon electrode materials. XRD structural analyses on the fully lithiated carbon electrode materials before and after heating to about  $230^\circ\text{C}$  show that the amount of lost intercalated lithium is roughly in the linear relation to their carbon specific surface area. However, the specific heat of reaction per lost intercalated Li mol is much higher in the graphite structure carbon electrodes than in the amorphous structure carbon electrode, explaining the reason why the former has stronger exothermic heat evolution property than the latter.

#### Acknowledgments

This work was supported by the Chemical Technology Division of the Argonne National Laboratory. The authors are grateful to Dr. Khalil Amine of the Chemical Technology Division, Argonne National Laboratory, for encouragement and support.

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