

# Low temperature $^7\text{Li}$ -NMR investigations on lithium inserted into carbon anodes for rechargeable lithium-ion cells

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## Abstract

Lithium fully inserted into both graphitizable and non-graphitizable carbons has been investigated by  $^7\text{Li}$ -NMR spectroscopy at low temperatures. It was found that lithium only in the non-graphitizable carbons heat-treated at ca. 1000°C showed peak separation phenomena at temperatures below  $-30^\circ\text{C}$ . This peak separation is explained as exchange of lithium nuclei between different kinds of lithium species in the carbons. In addition, an equilibrium relationship between the lithium species in the non-graphitizable carbons was found in the temperature range from  $-30$  to  $-150^\circ\text{C}$ . © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Lithium-ion batteries; Carbon anode; Non-graphitizable carbon;  $^7\text{Li}$ -NMR

## 1. Introduction

Several non-graphitizable carbons heat-treated at ca. 1000°C give the capacity higher than  $\text{LiC}_6$  with a significant capacity in the potential range from 0 to 0.1 V (vs.  $\text{Li}/\text{Li}^+$ ) [1–6]; the capacity below 0.1 V looks as a plateau in charge and discharge curves of the non-graphitizable carbons. As the plateau capacity in the potential range below 0.1 V is very attractive for anodes of high energy-density batteries, several important efforts have been done in order to clarify the structural characteristics and the anode reaction mechanism of non-graphitizable carbons [1–6]. It is, however, difficult to understand structural change of carbons heat-treated at such a low temperature during lithium insertion and extraction processes only by X-ray diffraction analysis, because those carbon materials have only weakly periodic structures [1–3].

$^7\text{Li}$ -nuclear magnetic resonance ( $^7\text{Li}$ -NMR) spectroscopy gives direct information on lithium states in carbon anode materials [4–10]. In the previous papers, we have reported that the plateau capacity of non-graphitizable carbon fibers near 0 V corresponded to the formation of new lithium species which give the  $^7\text{Li}$ -NMR peaks

between 50 and 111 ppm (vs.  $\text{LiCl}$ );  $^7\text{Li}$ -NMR shift of lithium between the graphite layers is in the range from 0 to 50 ppm [9,10]. Furthermore, it has been found that  $^7\text{Li}$ -NMR spectra of a lithiated non-graphitizable carbon fiber measured at low temperatures below  $-70^\circ\text{C}$  display three different peaks, and NMR shift of one of the peaks is larger than that of lithium metal below  $-110^\circ\text{C}$  [6]. In this paper, lithium fully inserted into non-graphitizable carbon anodes has been investigated by  $^7\text{Li}$ -NMR spectroscopy at low temperatures, and it is indicated that lithium species are not only in interlayer spaces between graphite layers but also in microcavities neighboring to the edges of crystallites. In addition, we report the data which suggest that lithium species with metallic character and that in the interlayer spaces have an equilibrium relationship.

## 2. Experimental

Carbon fiber prepared from an isotropic petroleum pitch (nominal diameter of 10  $\mu\text{m}$ , FIP, Petoca), which was used as a precursor of non-graphitizable carbons, was heat-treated at 700, 1000, 1200°C. Natural graphite (NG-7, The Kansai Coke and Chemicals) and mesophase pitch-based carbon fiber (nominal diameter of 10  $\mu\text{m}$ , MCF, Petoca) heat-treated at 1200°C were used as graphitizable

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carbons. The carbons were mixed with 10 wt.% of poly-(vinylidene fluoride) binder (KF-1000, Kureha Chemical Industry) to form carbon electrodes. Electrochemical lithium insertion were performed in a three-electrode cell with  $1 \text{ mol dm}^{-3}$  solution of  $\text{LiClO}_4$  in a 50:50 (by volume) mixture of ethylene carbonate and diethylcarbonate (DEC) (battery grade, Tomiyama Pure Chemical Industry) at  $27^\circ\text{C}$ . The reference and counter electrodes were lithium metal. The fully lithiated carbons were prepared by short circuiting the cells for 12 h after galvanostatic reduction ( $25 \text{ mA g}^{-1}$ ) to 0 V. The carbon electrodes were washed in DEC (battery grade) and evaporated to dryness under vacuum for 15 min at room temperature. After drying, the electrodes were put in NMR sample tubes in a dry box and set into a wideline probe of a  $^7\text{Li}$ -NMR spectrometer ( $B_0 = 4.70 \text{ T}$ ;  $\nu_0(^7\text{Li}) = 77.8 \text{ MHz}$ ; CMX-200H, Chemagnetics). Line shift was measured with aqueous LiCl solution as an external standard.

### 3. Results and discussion

Fig. 1 shows  $^7\text{Li}$ -NMR spectra of the fully lithiated non-graphitizable carbon fibers recorded at 25,  $-30$ ,  $-70$  and  $-150^\circ\text{C}$ . While the spectra of all of the fully lithiated non-graphitizable carbons gave one peak at  $25^\circ\text{C}$ , the line shift of the peaks displayed a large variation, i.e., 13, 90, and 111 ppm (vs. LiCl) for the carbons heat-treated at 700,

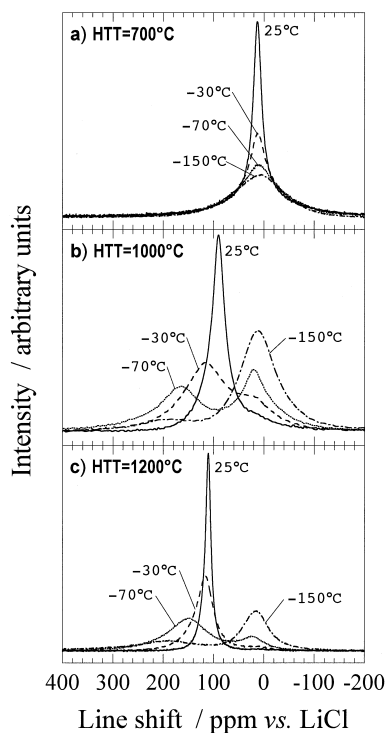


Fig. 1. Variation of  $^7\text{Li}$ -NMR spectra for the fully lithiated carbon fibers heat-treated at (a) 700, (b) 1000 and (c) 1200°C during cooling the samples; spectra recorded at 25 (solid line),  $-30$  (dashed line),  $-70$  (dotted line) and  $-150^\circ\text{C}$  (dashed and dotted line).

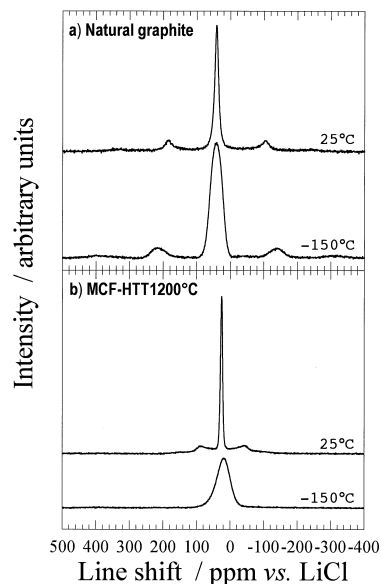


Fig. 2.  $^7\text{Li}$ -NMR spectra for the fully lithiated natural graphite and graphitizable carbon (MCF) heat-treated at  $1200^\circ\text{C}$ ; spectra recorded at 25 and  $-150^\circ\text{C}$ .

1000 and  $1200^\circ\text{C}$ , respectively. Since the  $^7\text{Li}$ -NMR shift of lithium electrochemically inserted into graphitizable carbons is in the range from 0 to 50 ppm [9,10], it is indicated that a noble lithium species, which is quite different from that in graphitizable carbons, forms in the carbon fibers heat-treated at 1000 and  $1200^\circ\text{C}$ . Moreover, the evidence for the new lithium species in the carbon fibers heat-treated at 1000 and  $1200^\circ\text{C}$  was more obvious in the NMR spectra taken at low temperatures below  $-30^\circ\text{C}$ . Lithium fully inserted into the carbon fibers heat-treated at 1000 and  $1200^\circ\text{C}$  showed a separation of NMR peaks below  $-30^\circ\text{C}$ ; one signal above 100 ppm (the high field) and the other signal at ca. 20 ppm (the low field). As reported in our previous paper [6], the spectra showed no spectral hysteresis between cooling and heating. Moreover, all the signals were deconvoluted to Lorentzian line shapes. Since NMR peaks fitting to Lorentzian lines are observed for liquid or gas phase species, the present results suggest that lithium atoms in the carbon fiber are diffusive. These results, thus, indicate that the variation observed in the spectra is likely ascribed to exchange of lithium nuclei among lithium atoms at different sites, and that the rate of exchange is slowed down on the time scale of NMR observation at low temperature, in agreement with the observed line broadening. On the other hand, lithium fully inserted into the carbon fiber heat-treated at  $700^\circ\text{C}$  gave one peak even at  $-150^\circ\text{C}$  and NMR shift of the peak was almost independent of temperature.

In order to assign the  $^7\text{Li}$ -NMR peaks at low temperatures below  $-30^\circ\text{C}$  to lithium species,  $^7\text{Li}$ -NMR spectra of the graphitizable carbons fully lithiated were also measured at 25 and  $-150^\circ\text{C}$ . Fig. 2 shows  $^7\text{Li}$ -NMR spectra of the natural graphite and the graphitizable carbon fiber

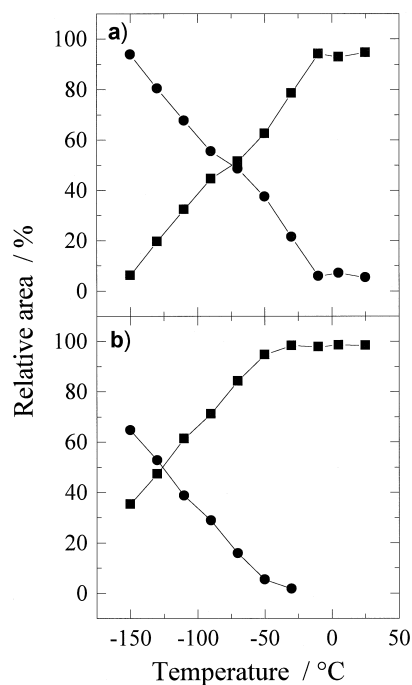


Fig. 3. Change of relative area of the <sup>7</sup>Li-NMR peaks in the low field (●) and the high field (■) as a function of temperature. (a) FIP-HTT 1000°C; (b) 1200°C.

(HTT = 1200°C) at a fully lithiated state. Although the <sup>7</sup>Li-NMR spectra of both the lithiated carbons at 25°C showed quadrupolar coupling satellites, both the carbons gave one peak in the <sup>7</sup>Li-NMR spectra even at -150°C. Moreover, shift of the <sup>7</sup>Li-NMR peaks of both the lithiated carbons was almost independent of temperature between 25 and -150°C. In fact, Conard et al. reported that the <sup>7</sup>Li-NMR shift of the first stage lithium-graphite intercalation compound (LiC<sub>6</sub>) prepared by a chemical method is independent of temperature [7]. Since the active site of both the carbons for lithium insertion is between ordered graphite layers [9–13], <sup>7</sup>Li-NMR shift of lithium species should be almost independent of measuring temperature. Therefore, the <sup>7</sup>Li-NMR peak at ca. 20 ppm of the non-graphitizable carbon fiber at temperatures below -30°C is likely ascribed to the lithium species in crystalline graphite layers in the carbon fiber which may exist even in non-graphitizable carbons to some extent.

On the other hand, high shifts of the signals might be explained as a Knight shift and correspond to lithium species with metallic character. Non-graphitizable carbons are considered to have microcavities among the grains having layered structures [2,3,14]. Therefore, lithium species corresponding to the peaks in the high field are inferred to be ascribed to lithium species formed in the microcavities of the non-graphitizable carbon fiber; lithium cluster formation has been proposed by some researchers [1,4]. As reported in our previous paper [5], the carbon fiber heat-treated at 700°C does not give clear plateau capacity in the chronopotentiogram of the charge-dis-

charge curve, though the carbon fibers heat-treated at 1000 and 1200°C give significant plateau capacity below 0.1 V. Thus, lithium species corresponding to the NMR peak in the high field at temperatures below -30°C are inferred to give the plateau capacity of the non-graphitizable carbon fibers heat-treated at 1000 to 1200°C below 0.1 V. The existence of the lithium species with metallic character is consistent with the result that the carbon fiber showed a significant capacity near 0 V.

As mentioned above, NMR peak separation phenomena of lithium in the non-graphitizable carbon fibers with lowering temperature should be explained as exchange of lithium nuclei among lithium atoms at different sites. However, lithium nuclei exchange in the carbon fibers is not simple, because intensity of both of the high field and the low field peaks was dependent on temperature, as shown in Fig. 3. Intensity of the high field peak markedly decreased with lowering temperature, whereas that of the low field peak increased.

In general, quantitative analysis in solid state NMR with the pulse Fourier transform method must be performed under appropriate conditions, particularly on dead-time of a detector after a pulse irradiation of radio wave for activation of nuclei. Because relaxation time,  $T_1$  and  $T_2$ , of the nuclei in a solid is relatively short, a long dead-time of a detector loses intensity of the NMR signals. Thus, quantitative validity for the NMR measurements was examined by using an internal standard. Table 1 shows the total area of the NMR peaks for the lithium fully inserted into the non-graphitizable carbon fibers heat-treated at 1000 and 1200°C determined by using the first stage lithium-graphite intercalation compound (Li-GIC; LiC<sub>6</sub>) as an internal standard. As the peaks for the first stage Li-GIC were observed in all the NMR spectra for the data in Table 1, it is sure that lithium in the Li-GIC as an internal standard did not affect the fully lithiated carbon fibers. Therefore, all the data in Table 1 indicates that the NMR measurement shown here has enough quantitative validity. Hence, it is concluded that composition of lithium species for the high field and the low field peaks is dependent on temperature.

Fig. 4 shows Van't Hoff plots for the ratio the lithium species for the NMR peak in the high field to that for the

Table 1  
Total area of the <sup>7</sup>Li-NMR peaks of the fully lithiated non-graphitizable carbons (FIP-HTT1000 and 1200°C) as a function of temperature

Temperature (°C)	Total area of <sup>7</sup> Li-NMR peaks <sup>a</sup>	
	FIP-HTT1000°C	FIP-HTT1200°C
25	1.00	1.00
-70	1.00	1.02
-130	0.95	0.99

<sup>a</sup>The area was measured with using the first stage Li-graphite intercalation compound (LiC<sub>6</sub>) as an internal standard and normalized by the values at 25°C.

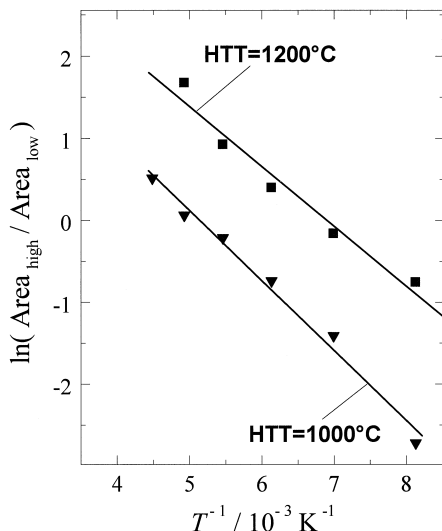


Fig. 4. Van't Hoff plot between the lithium species for the low field  $^7\text{Li}$ -NMR peak and the high field peak of the fully lithiated non-graphitizable carbon fibers heat-treated at 1000 ( $\blacktriangledown$ ) and 1200°C ( $\blacksquare$ ).

low field peak in the temperature range below  $-70^\circ\text{C}$ , and both the plots for the non-graphitizable carbon fibers heat-treated at 1000 and 1200°C gave linear correlation. This result suggests that the lithium species for the NMR peak in the high and the low field have an equilibrium relationship. Although the structures of both the lithium species with metallic character and the site for such lithium species in the non-graphitizable carbons are not identified only by  $^7\text{Li}$ -NMR analysis, the data shown here mean that the lithium species with metallic character is neighboring to the lithium species in the interlayer spaces between graphite layers.

#### 4. Conclusion

Lithium in non-graphitizable carbon fibers heat-treated at 1000 and 1200°C was classified at least into two species which gave the  $^7\text{Li}$ -NMR peak at ca. 20 ppm (vs. LiCl; the

low field) and above 100 ppm (the high field), respectively, in the spectra taken below  $-30^\circ\text{C}$ . The former lithium species is thought to be in the interlayer space between graphite layers, and the latter is inferred to be lithium clusters with metallic character. An equilibrium relationship between the both lithium species was found in the temperature range below  $-70^\circ\text{C}$ . Thus, the lithium species with metallic character is likely neighboring to the lithium species in the interlayer spaces between graphite layers.

#### Acknowledgements

The authors are grateful to Drs. Toshifumi Kawamura and Tomiji Hosotubo, Petoca, for preparing the carbon fibers and their discussion.

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