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^7Li -nuclear magnetic resonance observations of lithium insertion into coke carbon modified with mesophase-pitch

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Abstract

Lithium intercalation into coke carbon modified with mesophase-pitch and heat-treated at 800, 1000, and 3000°C was observed using solid-state ^7Li -nuclear magnetic resonance (^7Li -NMR) spectroscopy. It was found that the fully lithiated state charged to 0 V in the modified coke heat-treated at 3000°C showed a peak at about 45 ppm; on the other hand, two peaks appeared at about 45 and 16–17 ppm in the modified coke heat-treated below 1000°C. The peak appearing at 45 ppm indicated that Li-GIC is present in the first stage, and the peak at about 16–17 ppm indicated that the lithium stored in the modified part has an ionic character greater than in the coke part and is not a lithium cluster. The lithiated states charged to 0.1 and 0.2 V and discharged to 0.1, 0.2 and 1.5 V from the charged state (0 V) are also described. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

To increase the charge–discharge capacity of carbon electrodes for use in lithium ion secondary batteries, much effort has gone into the search. Some researchers have tried to increase the charge–discharge capacity by surface modifications such as coverage with metals [1], milling graphite, coke or carbon fibers [2], mild air oxidation [3], heating natural graphite to 3000°C in an inert atmosphere, followed by fluorination or ozonization [4], and chemical oxidation [5]. In the previous paper [6], we attempted to improve the capacity of coke carbon, which is relatively cheap, but has a capacity of only 170–250 mAh/g, by covering the coke carbon with mesophase-pitch carbon and obtained a relatively large value over 300 mAh/g. In this paper, coke carbon was modified with mesophase-pitch carbon by heat treatment at 800, 1000, and 3000°C. Using these carbons, we investigated lithium insertion into the modified carbon at various charged and discharged states by solid-state ^7Li -nuclear magnetic resonance (^7Li -NMR) spectroscopy.

2. Experimental

Mesophase-pitch carbon powder was prepared by heating β -resin at 400°C in a nitrogen atmosphere, where the β -resin was extracted from coal-originated pitch and then ground. Graphitized coke carbon powder, which was obtained by heating cokes at 3000°C in a reductive atmosphere, and mesophase-pitch carbon powder were mixed in a 4:1 ratio by weight and mechanochemically heat-treated at 2.0 kg/cm² in air, i.e. when the mixture was ground using a grinding machine at the above pressure, the higher-softening-point powder (coke) was covered with the lower-softening-point mesophase-pitch powder. This mixture was then heated at 800, 1000 and 3000°C in nitrogen to obtain coke carbon modified with mesophase-pitch carbon, which is called modified carbon hereafter. SEM photographs and the characteristics of these carbons are shown in Fig. 1 and Table 1. The composite anode for the ^7Li -NMR measurement for various charged or discharged states of the modified carbon was fabricated by coating a mixture of 90 wt.% carbon and 10 wt.% PVDF (KF1000) on a copper foil. The coated electrode was pressed at 1.5 t/cm² and dried in a vacuum at 150°C to form a tablet of a 12 mm diameter. A glass filter, which served as the separator, and the reference electrode

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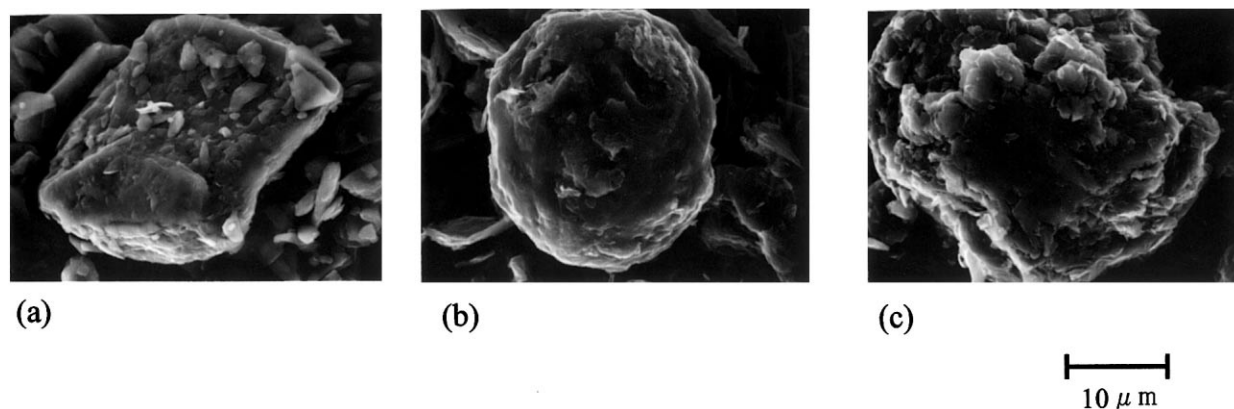


Fig. 1. SEM photographs of modified carbon heated at various temperatures: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C.

Table 1
Carbon characteristics

Sample	Crystallite size (Å)		BET surface area (m ² /g)	Average particle diameter (μm)
	<i>d</i> (0 0 2)	<i>L</i> _c (0 0 2)		
Modified carbon: HTT3000°C	3.36	>1000	1.03	14.7
Modified carbon: HTT1000°C	3.36	853	2.74	8.93
Modified carbon: HTT 800°C	3.37	655	2.99	11.8

were sandwiched between the carbon and counter electrodes. The charge–discharge tests were conducted at a constant current of 10 mA/g between 0 and 1.5 V versus Li/Li⁺ at 30 ± 1°C in a solution containing 1 M LiClO₄ in a 50 vol.% ethylene carbonate (EC) and 50 vol.% diethylcarbonate (DEC) solvent (Mitsubishi Chemical Co.) using a PC-controlled battery tester (Toyo System, TY-30TUOO). The reference and counter electrodes were both lithium foil. Test cells were assembled in a glove box filled with argon. The fully lithiated and various charged or discharged state modified carbons were examined using ⁷Li-NMR spectroscopy. The carbon electrodes in the various charged and discharged states were washed in DEC, dried and placed in NMR sample tubes in the argon glove box to measure the ⁷Li-NMR spectra using a JEOL EX270 spectrometer. The ⁷Li chemical shifts were indirectly calibrated in ppm relative to solid LiCl as the external standard.

3. Results and discussion

The second cycle charge–discharge curves for the modified carbon obtained at various heat treatment temperatures (HTT) are shown in Fig. 2. The modified carbon of HTT 3000°C produced the largest capacity in the region below 0.25 V, while that of HTT 1000°C produced the largest total capacity. The good cycleability of these carbons is shown in Fig. 3. The ⁷Li-NMR spectra of the modified carbon in various charged states were measured by the MAS method. Fig. 4 shows that the ⁷Li-NMR of the modified carbon

charged to 0.2 V versus Li/Li⁺ had chemical shifts of 7.8, 7.2 and 10.6 ppm corresponding to the modified carbons of HTT 3000, 1000 and 800°C, respectively. The sharp peak observed at –1 ppm for the 3000°C HTT modified carbon (a) seems to be due to the SEI (solid electrolyte interface) film [7]. By comparing these three spectra, it was found that the spinning side bands appeared (ssb) only in graphite such as the 3000°C HTT modified carbon (a) and not in the graphitizable carbon such as the mesophase-pitch corresponding to the HTT 1000 (b) and 800°C (c). These results

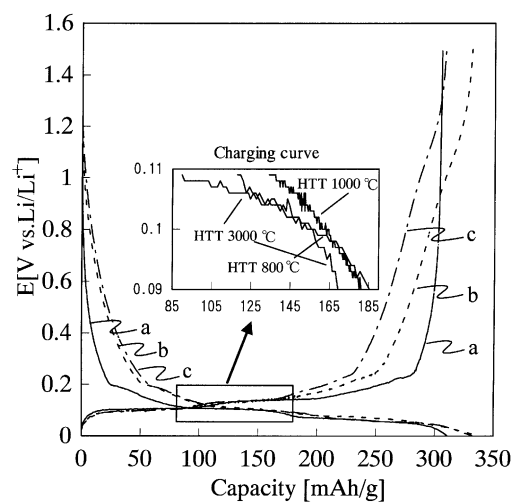


Fig. 2. Charge–discharge curve of modified carbon heated at various temperatures in 1 M LiClO₄/EC + DEC at 15 mA/g between 0–1.5 V: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C.

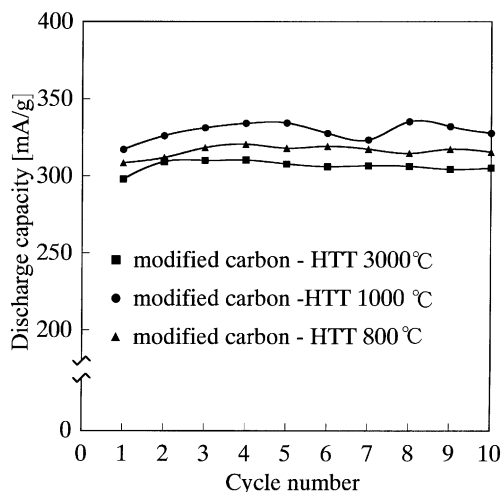


Fig. 3. Cycleability of modified carbon heated at various temperatures in 1 M LiClO₄/EC + DEC at 15 mA/g between 0 and 1.5 V.

indicate that the lithium inserted into the modified carbon stays in the modified layer and does not penetrate into the inner coke carbon when the modified carbon electrode is charged to 0.2 V. When the electrodes were charged to 0.1 V, the ⁷Li-NMR spectra changed as seen in Fig. 5. The peaks observed at 13.2, 12.5, and 13.4 ppm for the HTT 3000 (a), HTT 1000 (b), and HTT 800°C modified carbon (c), respectively, are mainly due to the lithium inserted into the graphite coke part of the modified carbon, because the ssb appeared in each case. By measuring the ⁷Li-NMR spectra for these

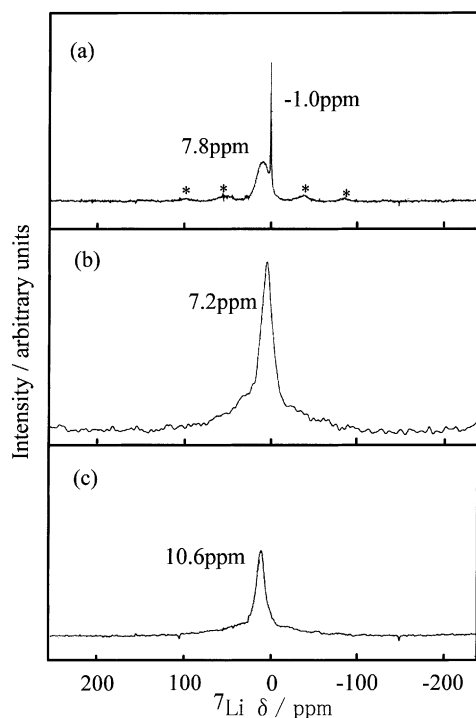


Fig. 4. ⁷Li-NMR spectra of modified carbon charged to 0.2 V in the second cycle: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C. Reference is LiCl ($\delta = 0.0$), (*): ssb (spinning side bands).

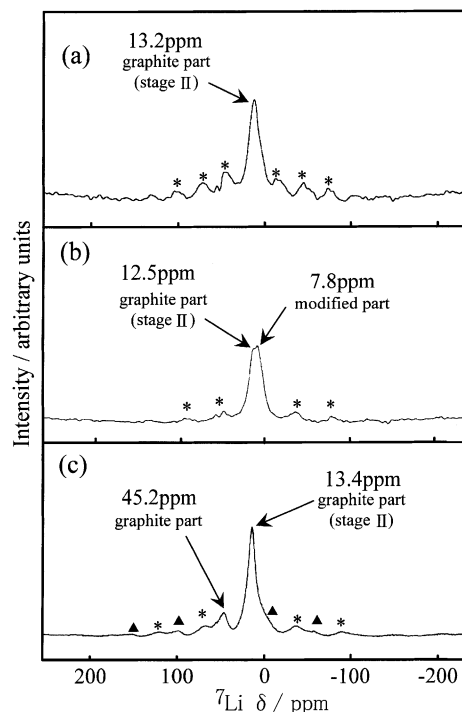


Fig. 5. ⁷Li-NMR spectra of modified carbon charged to 0.1 V in the second cycle: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C. Reference is LiCl ($\delta = 0.0$), (*): ssb (spinning side bands due to graphite part at 12.5 or 13.4 ppm); (\blacktriangle): ssb (spinning side bands due to graphite part at 45.2 ppm).

carbons using the static NMR method, a clear band at about 11 ppm centered between a couple of satellites appeared (not shown here). From the width between a couple of satellites, the calculated quadrupole coupling constant (e^2qQ/h) [8] was 37–38 kHz, suggesting that the band at about 11 ppm seems to be associated with the second-stage Li-GIC, i.e. the LiC₁₈ [9]. In the 1000°C HTT modified carbon (b) in Fig. 5, a peak at 7.8 ppm in addition to a peak at 12.5 ppm was observed, which may be due to the lithium being inserted into the modified layer because the ssb was not observed like those of (b) in Fig. 4. On the other hand, the peak due to the lithium inserted into the modified layer of the 800°C HTT modified carbon was not observed at about 7–8 ppm in (c) of Fig. 5, but it might be buried under the peak at 13.4 ppm. The peak at 45.2 ppm ((c) in Fig. 5) may be due to some lithium entering into the inner coke carbon charged to 0.1 V, because it shows spinning side bands. Fig. 6 shows the ⁷Li-NMR spectra of the modified carbon charged to 0 V in the second cycle. The main peaks with spinning side bands were clearly observed at 43.9, 44.4, and 43.6 ppm for HTT 3000 (a), HTT 1000 (a), and HTT 800°C (c), respectively, and the values of e^2qQ/h for these peaks were 45–46 kHz. Other peaks were observed at ca. 17.8 and 15.9 ppm as shown in (b) and (c) of Fig. 6, respectively. The peak at about 44 ppm indicated that the first-stage Li-GIC(LiC₆) is present [9], and the peak at about 17 ppm indicated that the lithium was stored in the modified mesophase-pitch part

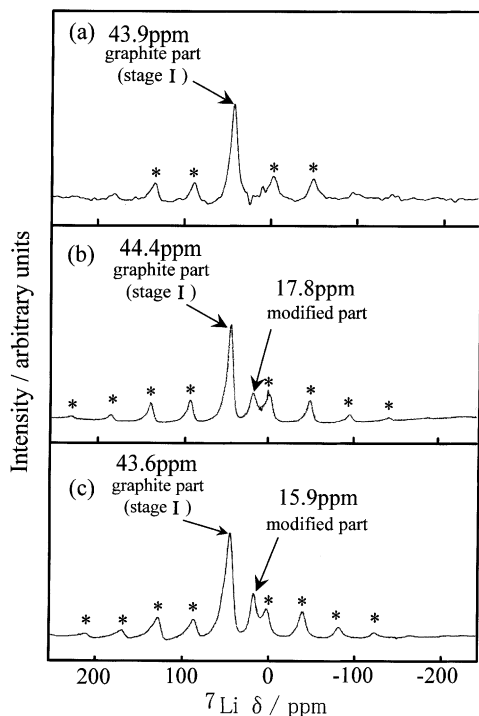


Fig. 6. ^7Li -NMR spectra of modified carbon charged to 0 V in the second cycle: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C. Reference is LiCl ($\delta = 0.0$), (*): ssb (spinning side bands due to graphite part).

because these peaks are not accompanied by the spinning side bands. This stored lithium in the modified part seems to be more ionic than that stored in the graphite coke part because the chemical shift for the former is smaller than that for the latter and is not a Li cluster. If so, the chemical shift should be a larger value such as 110 ppm [10].

The dynamic behavior of the intercalated Li nucleus was evaluated based on the spin-lattice relaxation time (T_1). The ^7Li NMR spectra of HTT 3000 and 1000°C charged to 0 V in the second cycle are shown in (a) and (b) in Fig. 7, respectively.

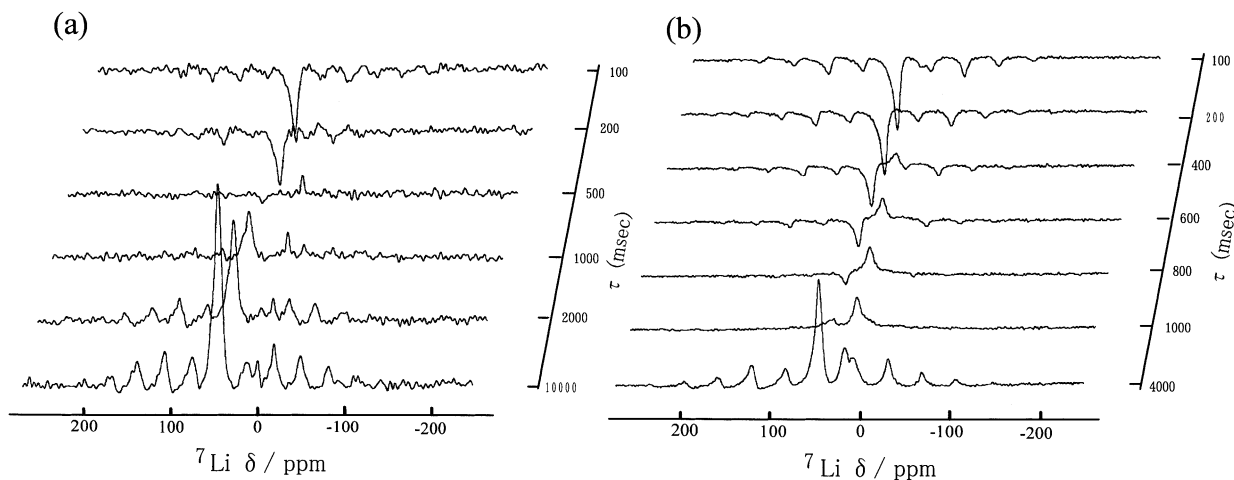


Fig. 7. ^7Li -NMR spectra of modified carbon charged to 0 V in the second cycle using the inversion recovery method as a function of τ . After the first 180° pulse, the relaxation of the NMR signals was recorded by applying the second 90° pulse at 5 s intervals: (a) HTT 3000°C; (b) HTT 1000°C.

Table 2
Relaxation time of modified coke

Sample	T_1 (s)	
	Graphite part	Modified part
Modified coke: HTT 3000°C charged to 0 V	1.8 ^a	1.8 ^a
Modified coke: HTT 1000°C charged to 0.2 V	– ^b	0.48
Modified coke: HTT 1000°C charged to 0.1 V	0.87	– ^c
Modified coke: HTT 1000°C charged to 0 V	1.8	0.38
Modified coke: HTT 800°C charged to 0 V	1.8	0.63

^a Only one peak appeared, and Li in the graphite the modified part could not be distinguished.

^b Li is not present in the graphite part at this potential.

^c Signal is too small to analyze the data although Li is present.

By continuously changing the recovery time, the peak at about 40 ppm symmetrically recovered for the HTT 3000°C sample. Therefore, it was determined that the lithium stored in coke carbon and the modified layer is only one component. For the HTT 1000°C sample, however, the behavior of the peaks at 40 and 15 ppm is different ((b) in Fig. 7), and two different species are found to be present in the coke carbon and in the modified layer. The T_1 values for the modified carbon heat-treated at the three different temperatures are tabulated in Table 2. For the 1000°C heat-treated carbon in the graphite part charged to 0.1 V, the T_1 value was 0.87 s. On the other hand, the T_1 values of the modified carbon heat-treated at 800, 1000, and 3000°C showed identical values of 1.8 s in the graphite part when they are charged to 0 V, which suggests that Li-GIC changed from the second stage (LiC_{18}) to the first stage (LiC_6) and that the dynamic behavior of the Li nucleus was restricted as the Li density in this first stage increased. However, the T_1 values of the modified part of the heat-treated carbon at 800 and 1000°C are significantly smaller compared with that of the graphite part (1.8 s); they are 0.38 and 0.63 s, respectively. This means that the Li nucleus stored in the modified

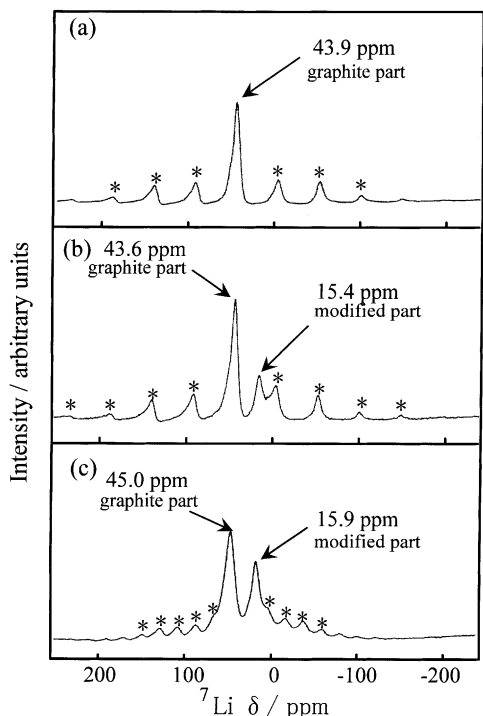


Fig. 8. ^7Li -NMR spectra of modified carbon discharged to 0.1 V in the second cycle: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C. Reference is LiCl ($\delta = 0.0$), (*): ssb (spinning side bands).

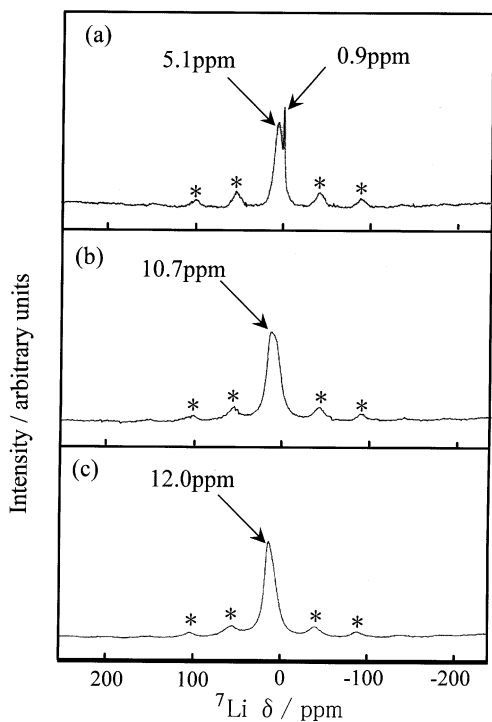


Fig. 9. ^7Li -NMR spectra of modified carbon discharged to 0.2 V in the second cycle: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C. Reference is LiCl ($\delta = 0.0$), (*): ssb (spinning side bands).

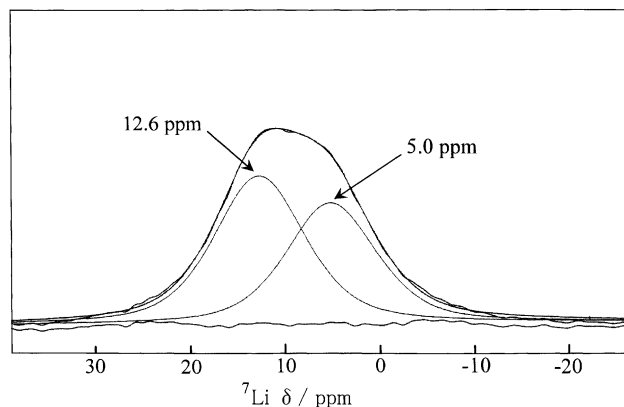


Fig. 10. Lineshape simulation for ^7Li -NMR spectrum of HTT 1000°C modified carbon discharged to 0.2 V in the second cycle.

layer can move more freely compared with that in the graphite part. Furthermore, the T_1 values in the modified part and bulk mesophase-pitch carbon itself (not shown here) heated at 800 and 1000°C did not change very much when charged from 0.2 or 0.1 V to 0 V. This may suggest that the lithium stored in the modified layer does not form a restricted structure like a stage structure.

When the fully charged electrodes were discharged to 0.1, they showed NMR spectra nearly to that of a charged state electrode (Fig. 6) as seen in Fig. 8. From these spectra, it is found that lithium essentially remains in the modified layer and the core coke part when each electrode is discharged to 0.1 V, though this is easily expected from the

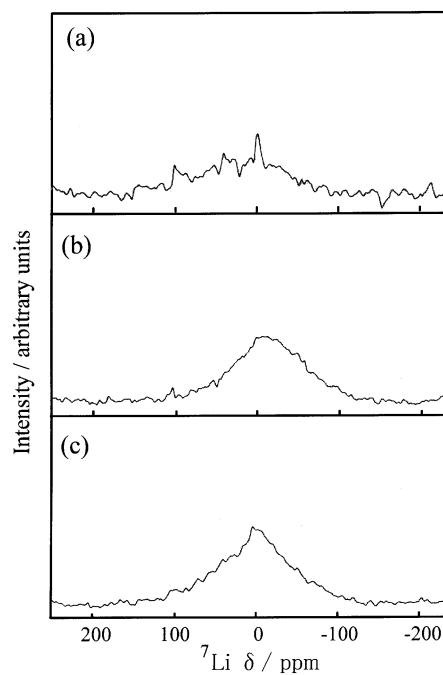


Fig. 11. ^7Li -NMR spectra of modified carbon discharged to 1.5 V in the second cycle: (a) HTT 3000°C; (b) HTT 1000°C; (c) HTT 800°C. Reference is LiCl ($\delta = 0.0$).

discharge curves in Fig. 2, where it is found that discharge progressed slightly at 0.1 V. Fig. 9 is the Li-NMR spectra of modified carbon discharged to 0.2 V in the second cycle. In the case of the HTT 3000°C modified carbon, the shape of the spectrum is similar to that of (a) in Fig. 4, i.e. the spectrum of HTT 3000°C modified carbon charged to 0.2 V, though its peak shifted slightly to a lower level. For the HTT 1000 (b) and 800°C (c) modified carbons, the main peaks at 10.7 and 12.0 ppm were found to consist of two components as shown in Fig. 10, where only the case of HTT 1000°C modified carbon was shown. The ssb of (b) in Fig. 9 belongs to the 12.6 ppm peak in Fig. 10 suggesting that Li still remains in the coke carbon when the HTT 1000 modified carbon was discharged to 0.2 V. The situation is the same for the HTT 800°C modified carbon. The peak at 5.0 ppm in Fig. 10 is caused by the lithium remaining in the modified part. Even when the modified carbon was discharged to 1.5 V, it was found that the lithium still remained because one broad and weak peak was observed in each carbon as shown in Fig. 11.

4. Conclusions

Using solid-state ^7Li -nuclear magnetic resonance (^7Li -NMR) spectroscopy for coke carbon modified with mesophase-pitch, lithium insertion phenomenon at various charged and discharged states was studied. It was found

that the fully lithiated state charged to 0 V in the modified coke heat-treated at 3000°C showed a peak at about 45 ppm, on the other hand, two peaks appeared at about 45 and 16–17 ppm in the modified coke heat-treated below 1000°C. The peak appeared at 45 ppm indicated that Li-GIC is present in the first stage and the peak at about 16–17 ppm indicated that the lithium stored in the modified part has an ionic character more than in the coke part and is not a lithium cluster.

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