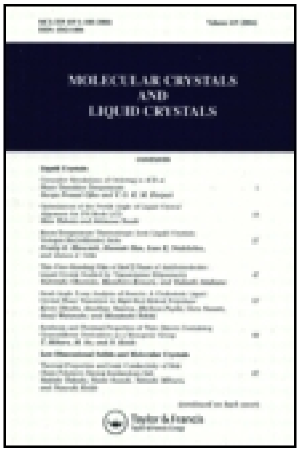

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^{7}Li NMR Study of Li Intercalated Carbons Prepared by Electrochemical Method

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^{7}Li solid-state nuclear magnetic resonance (NMR) is employed to investigate the mechanism of electrochemical lithium-intercalation in various carbon materials. Multiple resonance line shapes observed in fully lithiated carbons indicate that several intercalant sites exist under distinct spin-interaction environment, and they are substantially dependent upon physical nature of host structure. The temperature dependence of resonance spectra in disordered carbons prepared at relatively low carbonization temperature considerably differs from that observed in lithiated carbons with graphite structure.

Keywords: ^{7}Li NMR; lithium intercalation; carbon and graphite

INTRODUCTION

Intensive studies to understand the mechanism of lithium intercalation in carbon material have been recently focused since practical use of carbon as an excellent anode material for Li-ion secondary battery.[1] Electrochemical systems with a reversible lithium storage close to the theoretical capacity of graphite (372 mAh/g for LiC_6) have been successfully designed and demonstrated.[2] Numerous carbon materials prepared via various synthetic routes are currently under investigation to meet increasing demand for a high capacity anode.[1] A substantial progress was recently made by the introduction of disordered carbon prepared at relatively low carbonization temperature.[3-6] Models proposed to explain its high capacity, exceeding that of graphite, suggest that the mechanism of Li-intercalation depends considerably on the structure of carbon host.[3-6]

The nuclear magnetic resonance spectra provide valuable information on spin interactions in host-intercalant heterogeneous systems and dynamics under distinct host-surroundings. In the present work, ^{7}Li NMR line shapes of several fully lithiated carbons with different host structure are comparatively studied. We focus on the temperature dependence of multiple ^{7}Li NMR line shapes to investigate the mechanism of electrochemical storage of lithium in carbons.

EXPERIMENTAL

Graphite powders (BG-35) were supplied by Superior Graphite Co., and meso-carbon microbeads heat-treated at 1000°C (MCMB 6-10), 2800°C (MCMB 6-28S) and non-graphitizable Hard Carbon were supplied by Osaka Gas Co.. The structural information from X-ray diffraction patterns and the 1st cycle charge capacities are summarized in TABLE I. Slurries prepared by mixing carbons with 5 wt% PVDF in NMP are coated on copper foils and dried under vacuum at 120 °C. Resulting electrodes were exposed to galvanostatical Li intercalation as an anode in a sandwich cell, with a lithium counter electrode, mixed solvent of EC/DEC (1:1), and 1 M $LiPF_6$ as electrolyte. After washing the electrodes in fresh solvent and drying under vacuum, samples were peeled off the copper foils and packed into the NMR tube under argon atmosphere. 77.727 MHz ^{7}Li NMR experiments were carried out by using Bruker MSL200 spectrometer.

RESULTS & DISCUSSION

TABLE I XRD structure and charge capacity of carbon materials

Sample	d_{002} (Å)	L_c (Å)	Charge capacity (mAh/g)
BG-35	3.355	340	698
MCMB6-28S	3.380	231	455
MCMB6-10	3.514	12.9	508
Hard Carbon	3.744	3.6	772

FIGURE 1 shows the ^{7}Li NMR solid echo line shapes at T = 300 K for various fully lithiated carbon samples. Resonance frequency for the principal peak in each spectrum varies from +10 ppm to +80 ppm with respect to lithium chloride reference. Relatively small peaks at −20 ~ +20 ppm are commonly observed in most of the materials. All peaks are well fitted to Lorentzian type, and the full width at half maximum (FWHM) of the principal peak is less than 2 kHz at T = 300 K, indicating fast motion of lithium in carbon host structure.

Samples with graphite structure (BG-35 and MCMB 6-28S) show typical ^{7}Li NMR shifts corresponding to the Knight shift in the 1st stage Li-graphite and satellite features originating from quadrupolar interactions.[7,8]

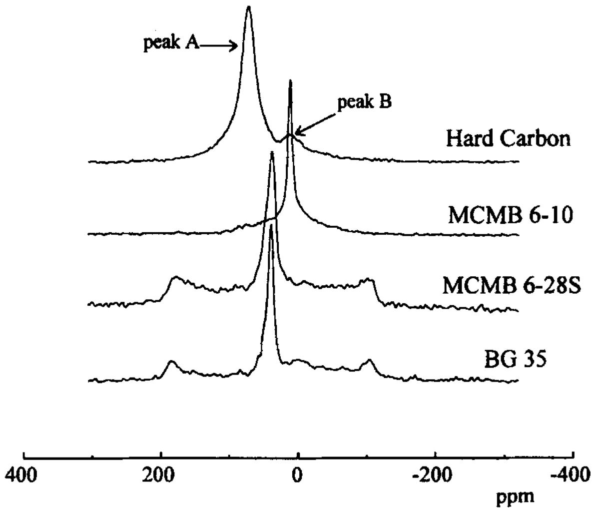

FIGURE 1 ^{7}Li NMR solid echo line shapes at T = 300 K.

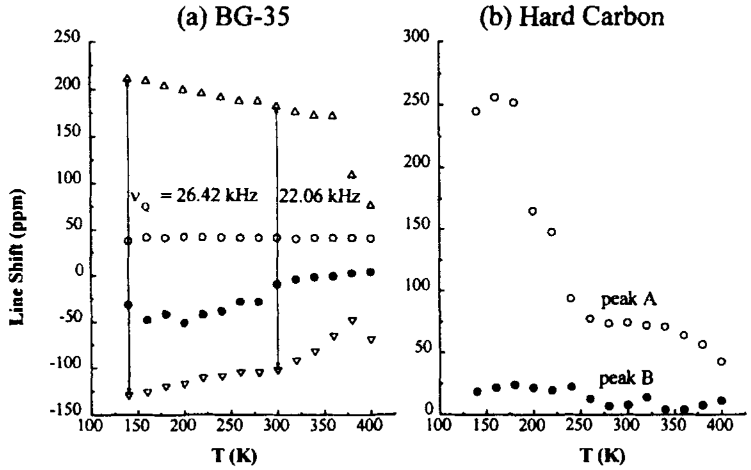

FIGURE 2 Temperature dependence of ^{7}Li NMR line shifts: (a) Knight shift (○), two NQR lines (△,▽) and the shift near 0 ppm (●); (b) peak A (○) and peak B (●). (See text.)

The line shifts of BG-35 in FIGURE 2(a) show that the Knight shift at +40.8 ppm is temperature independent, and nuclear quadrupole resonance (NQR) frequency changes linearly from $\nu_Q = 22.1$ kHz at T = 300 K to $\nu_Q = 26.4$ kHz at T = 140 K. The ^{7}Li resonance spectrum of MCMB 6-10 is similar to that of graphite in shape but shows a principal line shift at 12.9 ppm and suppressed NQR lines of $\nu_Q \sim 2$ kHz at T = 300 K. The up-field shift from +40.8 ppm for BG-35 to +12.9 ppm for MCMB 6-10 could arise from lithium intercalation into in-plane graphitic structure incompleted by low carbonization temperature, or from higher stage intercalation of lithium.[9]

The ^{7}Li NMR spectra of lithiated hard carbon show the superposition of two Lorentzian line shifts at 74.1 ppm (peak A) and 7.6 ppm (peak B) at T = 300 K. Such a multiple line shape with a resonance peak higher than +50 ppm can be observed only for samples charged above 400 mAh/g. The line shift of peak A drastically increases up to +250 ppm, a value close to the Knight shift of metallic lithium (+265 ppm), or that observed from highly dense Li-GIC

(+260 ppm)[10], when temperature is lowered down below 250 K, as shown in FIGURE 2(b). The intensity of peak A remarkably drops at low temperature, and peak B appears as a major resonance, as similar to earlier observation by K. Tatsumi *et. al.* in nongraphitizing carbon fibers.[11] The transition in ^{7}Li resonance spectra observed at T = 250 K suggests a possibility to form meta-stable partially ionic clusters at high level of lithium concentration, due to highly disordered physical nature of hard carbon. Similar down-field shifts of ^{7}Li NMR have also been observed in high composition lithium intercalation compound such as $Li_xMo_6S_8$ and $Li_xMo_6Se_8$.[12]

There are several ways to interpret ^{7}Li NMR line shifts observed in the range between −20 and +20 ppm. In most cases, up-field shifts originate from a diamagnetic shielding when Li atoms are more or less completely ionized. Such highly ionized atoms could be responsible for the irreversible Li storage, since thin layers of passivated lithium compounds are known to be formed on the surface during the electrochemical intercalation of lithium in carbon.[13] Materials of well defined morphology such as MCMB show less irreversible capacity and less contribution to ^{7}Li NMR shift near 0 ppm. On the other hand, the principal line shift at 12 ppm in MCMB 6-10 which corresponds to the peak B of hard carbon could be interpreted as lithium sites of in-plane graphite structure contributing to the reversible lithium storage capacity.

SUMMARY

^{7}Li NMR measurements of electrochemically lithiated carbons with various host structures show the multiple NMR line shifts corresponding to distinct intercalation sites of lithum. The major line shifts in the range between +10 and +40 ppm are common feature inherited from the Knight shift in lithium-graphite layered structure and substantially dependent upon the nature of disorder in host structure. The line shift at +74.1 ppm observed in hard carbon and its temperature dependence suggest a formation of meta-stable partially ionic clusters of lithium at highly lithiated states. We discussed the practical importance of tracing the lithium sites from NMR spectra with respect to the reversible storage of lithium in carbons.

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