

^7Li NMR and ESR analysis of lithium storage in a high-capacity perylene-based disordered carbon

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Accepted 24 September 1996

Abstract

The lithium storage mechanism of perylene-based disordered carbon (PBDC) heat-treated at 550 °C, which is a promising material for use as the anode in lithium-ion cells, was studied by solid-state ^7Li NMR and ESR analysis. PBDC is one of carbonaceous materials containing condensed aromatic rings, and showed a high reversible specific capacity of about 800 mAh/g with large hysteresis in the charge/discharge profile. ^7Li NMR spectra for the lithiated PBDCs exhibited two bands at the insertion of above 900 mAh/g. Band A at 7 ppm and band B at 0.3 ppm versus LiCl were assigned to lithium in reversible and irreversible storage sites, respectively. The results of ^7Li NMR analysis supported the presence of ionic lithium located on aromatic rings. ESR spectra for PBDC lithiated by over 300 mAh/g showed sharp and broad signals. The intensity of the broad signal varied significantly with lithium insertion. The variations of ^7Li NMR and ESR spectra with lithium insertion were interpreted by the presence of two kinds of insertion sites: the layer structure site (L-site) and the unorganized carbon site (U-site) located between the L-sites. © 1997 Elsevier Science S.A.

Keywords: Disordered carbons; Lithium insertion; Nuclear magnetic resonance; Electron spin resonance

1. Introduction

Soft-carbons and hard-carbons heat-treated from 550 to 1000 °C and hard-carbons heat-treated at ~1000 °C have specific capacities higher than that of lithium intercalated graphite (LiC_6 , 372 mAh/g) as the anodes for lithium-ion cells [1–6]. These carbon materials are disordered carbons containing condensed aromatics or micropores, or both [5,6]. The former carbon materials show capacities of 500–700 mAh/g with large voltage hysteresis, while the latter show capacities at ~600 mAh/g with little hysteresis. Hence, the lithium storage mechanism for carbon materials heat-treated from 550 to 1000 °C is different from that for hard-carbons heat-treated at ~1000 °C. The authors have investigated the lithium storage mechanism of PBDCs heat-treated between 550 and 1000 °C by IR analysis [5].

In this paper, the lithium storage mechanism of PBDC heat-treated at 550 °C was studied as a typical disordered carbon with high capacity and large hysteresis by solid-state ^7Li NMR and ESR measurements. The origin of the high lithium storage is discussed.

2. Experimental

The carbon material employed was PBDC prepared by heat-treatment of 3,4,9,10-perylenetetra-3,4,9,10-carboxylic dianhydride (PTCDA, Merk–Shuchardt) at 550 °C in an argon atmosphere. The PBDC contained aromatic rings, and the H/C atomic ratio was 0.26 [5]. Charge (insertion)/discharge (extraction) tests for the PBDC electrodes were carried out by charging to 0 V versus Li/Li⁺ for 40 h at a constant current density of 0.25 mA/cm² and discharging to 2 V at 0.25 mA/cm². The cell and electrode construction were the same as those described previously [5,7]. The electrolyte used was a solution of 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). The lithiated PBDC electrodes were washed with DEC solvent, and then dried under vacuum for 1 h to remove the DEC solvent before ^7Li NMR and ESR measurements. ^7Li NMR spectra were measured using a solid-state ^7Li NMR spectrometer (Nihon Denshi, resonance frequency for ^7Li was 155.4 MHz, JNM-LA400WB) with magic angle spinning (MAS) using LiCl as an external standard. All experiments were carried out at 20 °C in a dry argon atmosphere.

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3. Results and discussion

Fig. 1 shows typical charge/discharge curves of a PBDC electrode. PBDC had a reversible capacity of 804 mAh/g and showed large hysteresis in the charge/discharge profile. The authors have considered that the high capacity and the large hysteresis are attributed to lithium stored in 'unorganized carbon' site (U-site) on aromatic rings. We and others previously reported that the disordered carbons heat-treated below 1000 °C have two kinds of lithium storage sites [7–10]. One is the layer structure site (L-site) with a random graphite layer stacking and the other is the U-site. Disordered carbons heat-treated below 1000 °C have a 'turbostratic structure' with random graphite layer stacking and unorganized carbon [11,12]. The unorganized carbons consist of groups of tetrahedrally bonded carbon or highly buckled graphene

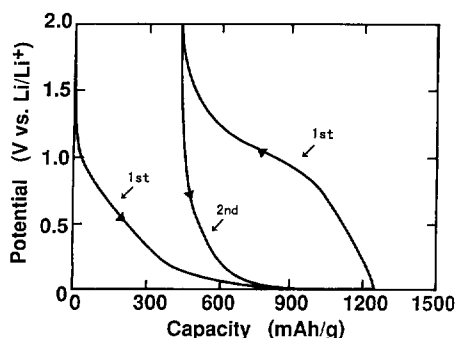


Fig. 1. Charge/discharge curves of PBDC electrode at the first and the second cycle

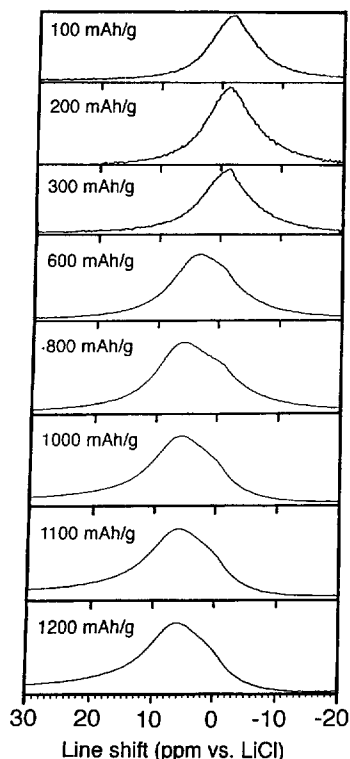


Fig. 2. Variation in ^7Li NMR spectra of PBDC with lithium insertion at the first cycle.

sheets placed between turbostratic structural regions. Some hetero-elements (e.g. H and O) in organic precursors would remain in the unorganized carbon, since the disordered carbons were prepared by heat-treatment of the precursors below 1000 °C. Recently, it was reported that the high capacity and the large hysteresis of disordered carbons are well correlated to the H/C atomic ratio [1,8]. Our previous IR analysis of lithiated PBDC indicated the presence of an ionic complex composed of lithium ions and condensed aromatic rings with negative charge in PBDC [5].

Fig. 2 shows the variation of ^7Li NMR spectra of PBDC during the first charge. The spectra were simulated with combinations of two Lorentzian functions as shown in Fig. 3. A sharp band peaking in the range of -1.57 to -1.38 ppm versus LiCl (band B) appeared when lithium was inserted at 100 mAh/g. At 300 mAh/g, another band peaking at 2.30 ppm appeared. Band A was shifted significantly from 2.30 to 7.11 ppm as lithium insertion proceeded from 300 to 900 mAh/g, while the shift of band B was slight (0.31 ppm at 900 mAh/g). Both bands were shifted linearly with lithium insertion up to 900 mAh/g as shown in Fig. 4. The shift of band A was more significant than that of band B. In contrast,

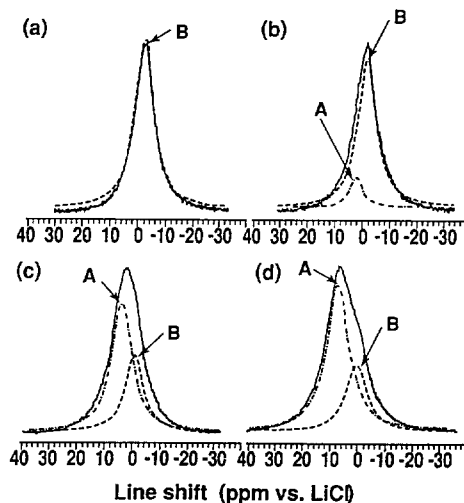


Fig. 3. ^7Li NMR spectra and its simulated curves of lithiated PBDC at various insertion capacities at the first cycle. (a) 100 mAh/g; (b) 300 mAh/g; (c) 600 mAh/g, and (d) 900 mAh/g. (—) experimental curve, (---) simulated curve for band A, and (· · ·) simulated curve for band B.

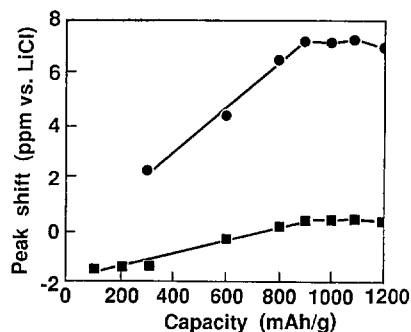


Fig. 4. Relationship between line shift of (●) bands A and (■) B and insertion capacity of the lithiated PBDC

the peak positions of both bands remained almost unchanged above 900 mAh/g. During extraction of lithium, band A disappeared after the extraction of above 500 mAh/g, whereas band B remained at -0.5 ppm until the end of extraction (800 mAh/g).

Sato et al. [13] have reported that the band B is due to the presence of covalent Li_2 molecules in polyphenylene-based carbon. However, the authors consider that band B is assigned to ionic lithium or a lithium compound which is formed by electrochemical or chemical reaction between the lithium ion and hetero-elements (H or O) in disordered carbons because band B appeared in the high potential range of 0.5–1 V versus Li/Li^+ and remained until the end of extraction of lithium. Such behavior of band B is very similar to that of the irreversible peak observed at 1540 cm^{-1} in IR spectra [5]. The ionic lithium assigned to band B hence is trapped in irreversible sites, which leads to a large irreversible capacity at the first cycle. On the other hand, from the results of IR measurements [5], band A is considered to be assigned to ionic lithium stored in reversible sites. The line shift (< 10 ppm) of the lithiated PBDC was much smaller than that reported for lithium intercalated graphite (~ 41 ppm) [14], which is due to the ionic character of lithium stored in the small layer structure and on the aromatic rings [14]. Fig. 5 shows the peak intensity $A/(A+B)$ ratio of band A to the sum of bands A and B. The $A/(A+B)$ ratio increased significantly with lithium insertion in the range of 300–600 mAh/g, but increased slightly above 600 mAh/g. Such a change in $A/(A+B)$ ratio indicates that the lithium insertion mechanism in the range of 300–600 mAh/g is different from that above 600 mAh/g. The authors consider that the reversible site for band A may be attributed to the L-site in the range of 300–600 mAh/g and to the U-site on the aromatic rings above 600 mAh/g.

Fig. 6 shows the variation of ESR spectra of the PBDC during the first charge. A broad signal in ESR spectra was clearly observed when lithium was inserted by over 300 mAh/g. A sharp signal was observed from the initial stage, and is closely related to band B in ^7Li NMR spectra. The peak intensity BP/SP ratio of the broad peak signal (BP) to the sharp peak signal (SP) changed significantly with lithium insertion as shown in Fig. 7. It is noted that the slope of the

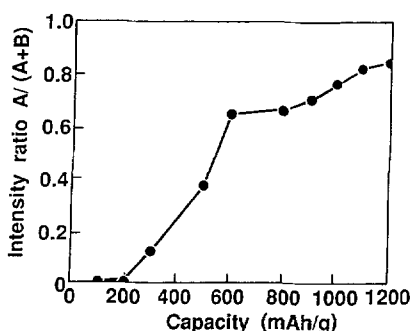


Fig. 5. Change in the intensity $A/(A+B)$ ratio for the PBDC with lithium insertion

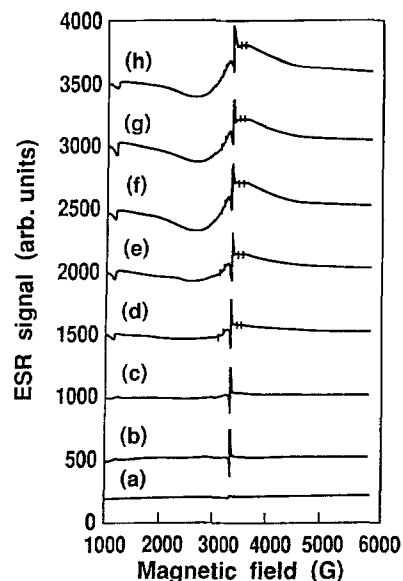


Fig. 6. ESR spectra of the lithiated PBDC at various insertion capacities at the first cycle: (a) 0 mAh/g; (b) 100 mAh/g; (c) 200 mAh/g; (d) 300 mAh/g; (e) 400 mAh/g; (f) 600 mAh/g; (g) 800 mAh/g, and (h) 900 mAh/g.

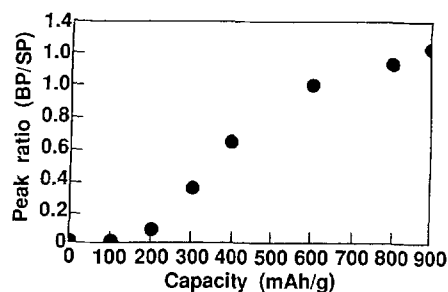


Fig. 7. Change in the peak intensity BP/SP ratio in ESR spectra with lithium insertion.

ratio changed at 600 mAh/g, which is very similar to that of the intensity ratio of $A/(A+B)$ shown in Fig. 5. The change of the broad peak signal with insertion is attributed to a change in density of electronic states at the Fermi level of the lithiated PBDC. The details of the variation of ESR spectra of lithiated carbons are currently under investigation.

4. Conclusions

^7Li NMR spectra of the lithiated PBDCs at insertion of above 900 mAh/g exhibited two bands attributable to the reversible site at 7 ppm and the irreversible site at 0.3 ppm versus LiCl . The shift in ^7Li NMR spectra during lithium insertion supported the concept that lithium stored in disordered carbons with condensed aromatic rings has an ionic character. The variations of ^7Li NMR and ESR spectra indicated that lithium insertion mechanism in the range of 300–600 mAh/g was different from that above 600 mAh/g. The lithium insertion mechanism of disordered carbons was interpreted by the presence of two kinds of insertion sites; the L-site and the U-site located between the L-sites. In addition,

the origin of the high lithium storage is attributed to the ionic lithium in the U-site on the aromatic rings.

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