

Anode characteristics of non-graphitizable carbon fibers for rechargeable lithium-ion batteries

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Abstract

Non-graphitizable carbon fibers heat-treated between 1000 and 1200 °C gave capacity higher than the capacity of LiC₆ (372 mAh g⁻¹) with a significant capacity below 0.1 V during oxidation. ⁷Li nuclear magnetic resonance (⁷Li-NMR) observation on lithium insertion into the carbon fibers suggested that lithium in the carbons are classified into two species. One of the lithium species was the same as that in graphitizable carbons. However, the other lithium species was quite different from that in graphitizable carbons, because the line shifts in the ⁷Li-NMR spectra of the carbon fibers fully lithiated to 0 V were between 80–110 ppm (versus LiCl); these shifts are larger than the maximum shift of lithium in graphitizable carbons (~45 ppm). In particular, a significant capacity below 0.1 V corresponded to the formation of a new lithium species. © 1997 Elsevier Science S.A.

Keywords: Lithium-ion batteries; Carbon anodes; Non-graphitizable carbon; Carbon fibers

1. Introduction

Several papers have reported that carbon anode materials heat-treated below 1400 °C give higher capacity than the capacity of LiC₆ (372 mAh g⁻¹) [1–9]. Graphitizable and non-graphitizable carbons heat-treated below 700 °C show a large capacity in the potential 0.5–1 V range [1–5]. On the other hand, several non-graphitizable carbons heat-treated at ~1200 °C also give capacity higher than that of LiC₆ with a significant capacity in the potential range below 0.1 V [6–9]. The capacity below 0.1 V is very attractive for anodes of high energy density batteries. Therefore, it is very important to investigate the mechanism for the high capacity below 0.1 V in non-graphitizable carbons. It is, however, difficult to understand the structural change of carbons heat-treated at such a low temperature during lithium insertion and removal processes only by X-ray diffraction (XRD) analysis, because those carbon materials have only weakly periodic structures. ⁷Li nuclear magnetic resonance (⁷Li-NMR) spectroscopy gives direct information on the lithium states in carbon anode materials [5,6,10]. In this paper, anode characteristics of

non-graphitizable carbon fibers heat-treated between 700 and 1400 °C were examined, and it has been found that non-graphitizable carbon fibers heat-treated between 1000 and 1200 °C also give capacity higher than that of LiC₆ with a significant capacity below 0.1 V. Lithium insertion into the non-graphitizable carbon fibers has been observed by ⁷Li-NMR spectroscopy in order to investigate the capacity below 0.1 V.

2. Experimental

Carbon fiber prepared from an isotropic petroleum pitch (FNPM, nominal diameter of 10 μm, Petoca), which was used as a precursor of non-graphitizable carbons, was heat-treated at 700, 1000, 1200, and 1400 °C. XRD patterns of the virgin carbon fibers were recorded with an X-ray diffractometer with Cu Kα radiation equipped with a graphite monochromator. The carbon fibers were mixed with 10 wt.% poly(vinylidene fluoride) binder in *N*-methyl-2-pyrrolidone solvent and the mixtures were spread onto a copper foil. Galvanostatic discharge/charge examinations were performed in a three-electrode cell with 1 M LiClO₄ in a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (battery grade, Tomiyama Pure Chemical Industries) at ambient temperature (27 °C). The reference

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and counter electrodes were lithium metal (battery grade, Honjou Metal). Because the carbon electrodes were the cathode in the cell, discharge (insertion) and charge (removal) were the reverse processes from those usually thought of in a battery. Discharge/charge curves were recorded between 0 and 2.5 V cut-off voltages at a current density of 25 mA g^{-1} . The lithiated carbon fibers were examined by ^7Li -NMR spectroscopy. 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 wide-line probe of a ^7Li -NMR spectrometer ($B_0 = 4.70 \text{ T}$; $\nu_0(^7\text{Li}) = 77.8 \text{ MHz}$; CMX-200 H, Chemagnetics Corporation). Line shift was measured with aqueous LiCl solution as an external standard.

3. Results and discussion

Fig. 1 shows XRD patterns of the virgin carbon fibers. The stacking order of graphite planes of the carbon fibers was at random (the turbostratic disorder structure), because the XRD patterns of the carbon fibers showed only (100) and (110) diffraction peaks at about 42° and 78° , respectively. Although intensity of diffraction peaks at about 20° , 42° and 78° increased a little with increasing heat-treatment temperature (HTT), the crystallinity of the carbon fibers was low and did not change significantly in the HTT range between 700 and 1400°C .

The discharge/charge curves were, however, significantly affected by HTT. In Fig. 2, the discharge/charge curves of the carbon fibers during the first cycle are shown. The anode characteristics of the carbon fiber heat-treated at 700°C were similar to those of graphitizable carbons heat-treated below 1000°C [2–5], i.e., the discharge/charge curves showed significant hysteresis in both the capacity and the potential. As HTT increased, the carbon fibers showed a maximum value of reversible capacity between 1000 and 1200°C : the reversible capacity x in Li_xC_6 of the carbon fiber heat-treated at 1000°C was ~ 1.2 (420 mAh g^{-1}). Furthermore, the

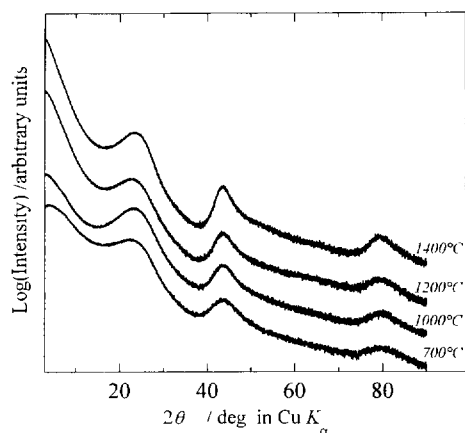


Fig. 1. X-ray diffraction patterns of the virgin carbon fibers

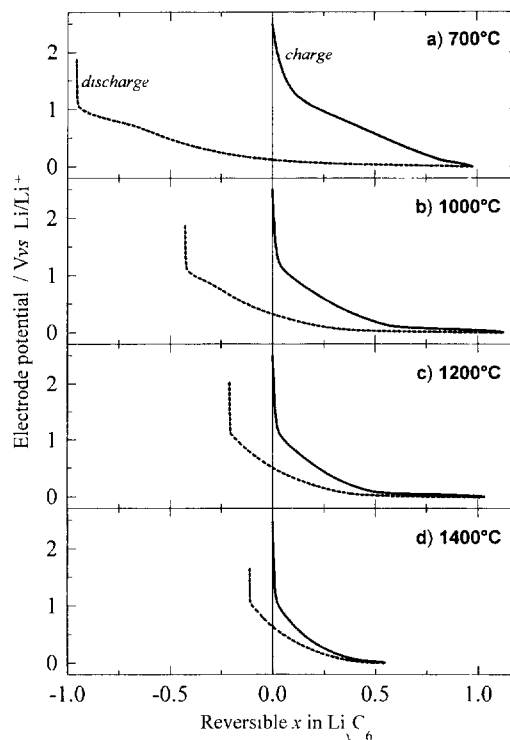


Fig. 2. (---) Galvanostatic discharge and (—) charge curves of the carbon fibers in 1 M $\text{LiClO}_4/\text{EC} + \text{DEC}$ (1.1 by volume) during the first cycle at a rate of 25 mA g^{-1} .

oxidation curves of the carbon fibers heat-treated at 1000 and 1200°C displayed a plateau in the potential below 0.1 V, as reported by Ishikawa et al. [6] and Zheng et al. [7–9]. This significant capacity below 0.1 V is very attractive for anodes of high energy density batteries. It has been reported that carbons heat-treated below 700°C also give reversible capacity x in Li_xC_6 higher than unity. Reversible capacity of carbons heat-treated below 700°C apparently increases with increasing the H/C atomic ratio; the carbons of which H/C is over 0.1 display x higher than unity [1,3]. On the other hand, the H/C ratio of the carbon fibers heat-treated above 1000°C was less than 0.07 and decreased with increasing HTT. This fact means that the excess capacity of the carbon fibers is not due to the hydrogen content. In addition, these anode characteristics of non-graphitizable carbons are quite different from graphitizable carbons heat-treated below 2000°C [3–5]. Graphitizable carbons heat-treated below 2000°C give very small capacity in the potential range below 0.1 V during oxidation [3–5]. Although it has been reported that graphitizable carbons give a significant capacity below 0.25 V, this capacity below 0.25 V is the lithium intercalation into the graphitic structure which consists of graphite layers having the stacking order described as the AB or ABC sequence [5,11,12]. The carbon fibers heat-treated at 1000 and 1200°C did not have the three-dimensional structure of graphite planes as mentioned above. These results indicate that the capacity of the carbon fibers below 0.1 V are due to a new lithium-insertion reaction as reported in previous reports [6–9].

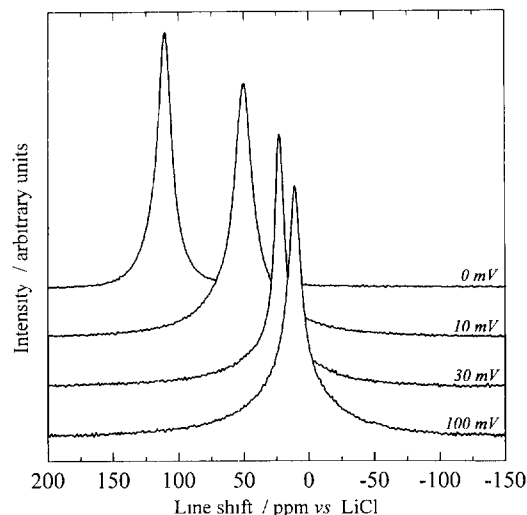


Fig. 3. Variation of ^7Li -NMR spectra of the carbon fibers heat-treated at 1200°C during the first discharge at a rate of 25 mA g^{-1} .

In order to examine lithium insertion into the carbon fibers, ^7Li -NMR spectra of the carbon electrodes at several points during the discharge/charge tests were recorded. In Fig. 3, changes in ^7Li -NMR spectra of the carbon fiber heat-treated at 1200°C during the first reduction are shown. The line shift of the carbon fiber at 0.1 V was 11 ppm . This value is equal to that of graphitizable carbons heat-treated at $\sim 1000^\circ\text{C}$ [5]. Thus, it is speculated that lithium insertion into non-graphitizable carbons above 0.1 V is similar to that into graphitizable carbons with low crystallinity. However, the line shift of the carbon fiber significantly increased, as the potential decreased below 0.03 V . In particular, the line shift of the carbon fiber fully reduced to 0 V was 110 ppm . Although this value is almost the same as the reported value for other non-graphitizable carbons [6], the value has not been observed in graphitizable carbons [5,10]. The maximum shift of ^7Li inserted into graphitizable carbons is $\sim 45\text{ ppm}$ for the second-stage Li-graphite intercalation compound (Li-GIC: LiC_{12}) [5,10]. Although the first-stage Li-GIC with extremely high lithium content (LiC_2) gives a shift of $\sim 260\text{ ppm}$ in the ^7Li -NMR spectrum, LiC_2 is obtained under an extremely high pressure [13]. Therefore, these results clearly indicate that a new lithium species forms in non-graphitizable carbons heat-treated at $\sim 1200^\circ\text{C}$. Because it has been proposed that the line shift of ^7Li (δ) in graphite are proportional to both the reciprocal of distance of Li–Li ($d_{\text{Li-Li}}$) in a lithium layer and the number of neighbor lithium atoms (N) at the nearest distance, i.e., $\delta \propto N/d_{\text{Li-Li}}$ [14], the density of the lithium species showing shifts above 45 ppm is thought to be higher than those in graphitizable carbons.

In Fig. 4, the electrochemical reactivity of the carbon fibers and line shift of ^7Li are plotted as a function of the electrode potential. The differential chronopotentiograms during oxidation clearly showed that the electrochemical reactivity of the carbon fibers heat-treated at 1000 , 1200 and 1400°C is significant in the potential range 0 to 0.13 , to 0.11 and to 0.07 V , respectively. The peaks in the differential chronopotentiograms

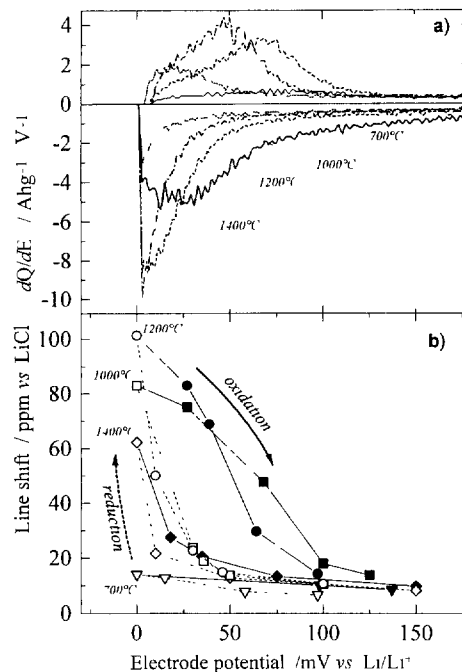


Fig. 4. Electrochemical reactivity and change in the line shift of ^7Li -NMR spectra of the carbon fibers in $1\text{ M LiClO}_4/\text{EC} + \text{DEC}$ (1:1 by volume): (a) the differential chronopotentiograms of the first discharge/charge curves of the carbon fibers heat-treated at 700 , 1000 , 1200 , and 1400°C at a rate of 25 mA g^{-1} , (b) line shift of the ^7Li -NMR spectra of the carbon fibers heat-treated at 700 , 1000 , 1200 , and 1400°C as a function of electrode potential during reduction (open symbol and dashed line) and oxidation (solid symbol and solid line) processes

during oxidation correspond to the plateau near 0 V in charge curves (the plateau region during oxidation). The line shift of ^7Li significantly increased, as the reactivity increased in the potential range below 0.05 V during reduction. In reverse, the line shift of ^7Li significantly decreased, as the reactivity decreased at the plateau region during oxidation. These results mean that a significant capacity of the carbon fibers in the plateau region is due to the new species of lithium [6–9]. Moreover, it seems that the new lithium species additionally appeared in the plateau region of the discharge/charge curves, because the line shift of ^7Li above 0.1 V is comparable with that of graphitizable carbons heat-treated at $\sim 1000^\circ\text{C}$. In fact, Hashimoto et al. [15] found that the lithium in a non-graphitizable carbon, which showed a shift of 90 ppm at room temperature, consist of two species of lithium by ^7Li -NMR measurements at low temperatures.

In Fig. 5, the reversible capacity of the carbon fibers is plotted as a function of HTT; reversible capacities, i.e. capacities during oxidation, are divided into two parts (the plateau region and the region above the plateau) according to the threshold voltages of 0.13 , 0.11 and 0.07 V for the carbon fibers heat-treated at 1000 , 1200 and 1400°C , respectively. The reversible capacity above the plateau region decreased with increasing HTT. This feature of the capacity against HTT is very similar to graphitizable carbons. However, the reversible capacity in the plateau region significantly appeared in the HTT range between 1000 and 1200°C . These

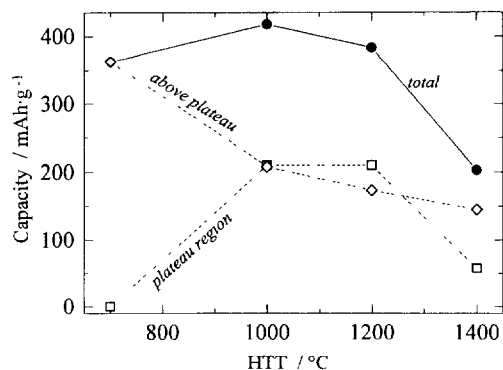


Fig. 5. Reversible capacity of the carbon fibers as a function of HTT: (●) capacity in the potential range 0 to 2.5 V; (□) in the plateau near 0 V during oxidation, and (◇) above the plateau.

results also indicate that high capacity of the carbon fibers heat-treated between 1000 and 1200 °C is due to the formation of the new lithium species, and that the formation of the new lithium species occur in addition to the lithium insertion similar to that in graphitizable carbons.

4. Conclusions

Non-graphitizable carbon fibers gave higher capacity than the capacity of LiC_6 (372 mAh g^{-1}) with a significant capacity below 0.1 V (the plateaus region). Although the capacity of the plateau region of the carbon fibers increased between 700 and 1200 °C, the capacity significantly decreased between 1200 and 1400 °C. In the plateau region, the ^7Li -NMR line shift of the carbon fibers heat-treated at 1000 and 1200 °C significantly increased during reduction and

decreased during oxidation. Therefore, it is indicated that the significant capacity in the plateau region near 0 V corresponds to the formation of a new species of lithium.

References

- [1] S. Yata, H. Kinoshita, M. Komori, N. Ando, T. Kashiwamura, T. Harada, K. Tanaka and T. Yamabe, *Synth. Met.*, 62 (1994) 153.
- [2] M. Hara, A. Satoh, N. Takami and T. Ohsaki, *J. Phys. Chem.*, 99 (1995) 16338.
- [3] A. Mabuchi, K. Tokumitsu, H. Fujimoto and T. Kasuh, *J. Electrochem Soc.*, 142 (1995) 1041.
- [4] T. Zheng, Y. Liu, E.W. Fuller, S. Tseng, U. von Sacken and J.R. Dahn, *J. Electrochem. Soc.*, 142 (1995) 2581.
- [5] K. Tatsumi, T. Akai, T. Imamura, K. Zaghbi, N. Iwashita, S. Higuchi and Y. Sawada, *J. Electrochem. Soc.*, 143 (1996) 1923.
- [6] M. Ishikawa, N. Sonobe, H. Chuman and T. Iwasaki, *Ext. Abstr., 35th Battery Symp. Japan, Nagoya, Japan, Nov. 1994*, Paper No. 2B09, p. 47.
- [7] T. Zheng, Q. Zhong and J.R. Dahn, *J. Electrochem. Soc.*, 142 (1995) L211.
- [8] J.S. Xue and J.R. Dahn, *J. Electrochem. Soc.*, 142 (1995) 3668.
- [9] Y. Liu, J.S. Xue, T. Zheng and J.R. Dahn, *Carbon*, 34 (1996) 193.
- [10] K. Tatsumi, K. Zaghbi, Y. Sawada, H. Abe and T. Ohsaki, in S. Megahed, B.M. Barnett and L. Xie (eds.), *Rechargeable Lithium and Lithium-Ion Batteries*, Proc. Vol. 94-28, The Electrochemical Society Proceedings Series, 1994, p. 97.
- [11] K. Tatsumi, N. Iwashita, H. Sakaebe, H. Shioyama, S. Higuchi, A. Mabuchi and H. Fujimoto, *J. Electrochem. Soc.*, 142 (1995) 716.
- [12] T. Zheng and J.R. Dahn, *Synth. Met.*, 73 (1995) 1.
- [13] J. Conard, V.A. Nalimova and D. Guerard, *Mol. Cryst. Liq. Cryst.*, 245 (1994) 25.
- [14] J. Conard, *Proc. First Scientific Workshop Electrochemical Materials, (Jan. 1996, Osaka, Japan)*, Paper No. 1-1, p. 17.
- [15] T. Hashimoto, T. Iriyama, S. Yamazaki, Y. Mori and H. Siroki, *Ext. Abstr., 36th Battery Symp. Japan, Sept. 1995, Kyoto, Japan*, Paper No. 1B06, p. 109.