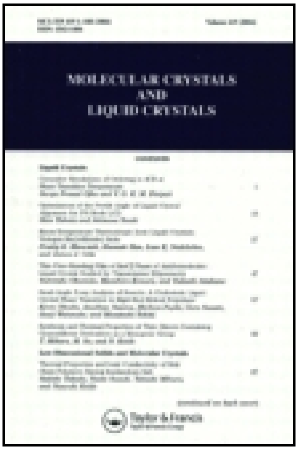

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LITHIUM SECONDARY BATTERY BASED ON INTERCALATION IN CARBON FIBERS AS NEGATIVE ELECTRODE

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Abstract Lithium secondary batteries using carbon as negative electrode with intercalated Li have been developed. Various kinds of carbon fibers with different crystallographic and macroscopic structure are applied as a negative electrode for the lithium secondary batteries with 1 mol $LiClO_4$/propylene carbonate electrolyte. The battery performances of the fibrous electrode are evaluated as a function of the structure of the carbon fibers. Not only the crystallographic structures but also the morphology of the fibers affect the battery performances. It was shown that Li is stored to form electrochemically the 1st stage compounds in well-ordered and even in disordered carbon fiber electrodes.

INTRODUCTION

High-performance secondary batteries which can afford as a power supply for portable electronic equipments have been extensively demanded. Especially, lithium secondary batteries have been actively studied and developed as one of the ideal battery. Recently, the lithium battery so called as *Li-ion battery* using intercalated Li to graphite, instead of Li metal electrode as a negative electrode, has been developed.[1] In the *Li-ion battery,*[1] the dendritic re-crystallization of Li on the metallic electrode can be prevented, so the batteries with high performances as well as high reliability are achieved. Further development of these batteries has been strongly expected by the suitable structural design of carbon electrode.[2,3] The theoretical Faradic capacity of the Li-GIC electrode is somewhat poor : 372 mAh/g, which corresponds to LiC_6 compound.

This is about one order smaller capacity than that of pure Li metal (3860 mAh/g). The Li storage mechanism in the battery based on the electrochemical introduction of Li to the different crystallographic grade of carbon electrodes is not yet fully understood. Also the correlation between the battery performances and the structural parameters of carbon electrode has not yet become clear.

In the present paper various kinds of carbon fibers, PAN-, pitch-based and vapor grown one, are applied to the negative electrode of a lithium secondary battery. These fibers have a characteristic micro- and macro-scopic structure. The battery performances of the fibrous anode are estimated and discussed in relation with the structures of the fibers, in which electrochemically introduced Li is stored to form the 1st stage compounds.

EXPERIMENTAL

Vapor-grown carbon fibers obtained by floating ultra-fine metal catalyst (VGCFs, denoted as NV),[4] mesophase pitch- and PAN-based carbon fibers have been used as a negative electrode for Li secondary battery with 1mol $LiClO_4$/propylene carbonate (PC) as an electrolyte.[2] The structural parameters of the fibers used are summarized in Table I. The potential of the fiber electrodes was monitored against the Li reference electrode via a luggin capillary using the experimental three-electrode glass cell.[2] The charge-discharge characteristics of the batteries were measured by galvanostatic cycles at a constant current of 150mA/g

TABLE I Structural parameters of the samples.

Samples		Heat treatment temperature (°C)	Diameter (μm)	Interlayer spacing (Å)	Crystallite thickness (Å)
Mesophase	(P25)	-	12	3.463	26
pitch-based	(P55)	-	12	3.442	96
carbon fiber	(P75)	-	10	3.411	131
(continuous	(P100)	-	10	3.398	230
yarn)	(P120)	-	10	3.376	300
Discontinuous					
pitch-based	(MF10)	1000*	10	3.510	24
carbon	(MF20)	2000*	10	3.433	156
fiber	(MF31)	3100*	10	3.374	230
PAN-based carbon					
fiber	(M46J)	-	10	3.434	100
VGCF	(NV11)	1100*	~0.1	3.517	33
(by floating	(NV20)	2000*	~0.1	3.440	83
catalyst)	(NV23)	2300*	~0.1	3.383	150
	(NV26)	2600*	~0.1	3.381	270
PPP(9)		700*	2 (powder)	3.767	13

(* ; heat treated in Ar for 10 min.)

(corresponding to current density of about 0.02 mA/cm^2 which is estimated from the specific surface area of each fiber sample). The charging time was 15~150 minutes, and the cut-off potentials of charge-discharge examinations were 0 ~ 2.8 V (vs. Li/Li$^+$).

RESULTS AND DISCUSSION

Figure 1 shows the typical charge-discharge characteristics after the first 5 cycles for various kinds of carbon fiber electrodes. The NV11 are a typical fiber with low crystallinity, and have annual ring type cross-sectional structure[4] which can relax the stress by cracking along the fiber axis[5] after several initial cycles of electrochemical Li introduction. As seen in Figure 1(a) the inclination of the discharge potential against time is relatively large, but its discharge time is rather longer than other samples. As shown in Figure 1(b), the discharge potential of NV26 (heat-treated VGCFs at 2600°C) having high degree of crystallinity is flat. But the charging curve has a plateau at about 0.5V (indicated by arrow), which is caused by decomposition of PC on the surface of the fibers.[6,7] The discharge time is shorter than that of NV11. Figure 1(c) shows the charge-discharge curve of P100 fibers. The crystallinity of the P100 is characterized being similar to that of NV26. In the discharge curve, two plateaus are observed (indicated by arrows). The first plateau might be due to the dissolution of lithium electrodeposited on the surface of the fibers during the charging, while no NV fibers exhibit this phenomenon. This phenomenon is different from that caused by staging, because no clear

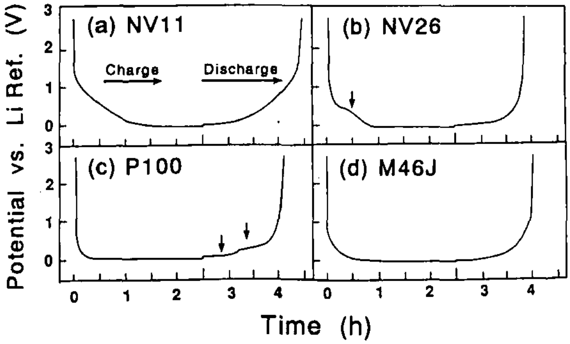

FIGURE 1 Charge-discharge characteristics of the carbon fiber negative electrodes (5th cycle).

staging phases during charging have been observed for the present electrodes in the charge-discharge characteristics.[8] And the potential, about 10mV, is considerably lower than that by staging of 110mV, reported previously.[8] These different types of potential profiles might be caused by the reaction sites of the fiber surface, depending on the fiber diameter. The extremely thin fibers (NV series) less than 0.1μm have larger surface area than P100 fibers and have many reaction sites where Li ions can penetrate quickly into the fibers. On the other hand, the charge-discharge characteristics of M46J (PAN-based high modulus fibers) electrode behaves like being between NV11 and NV26 (Figure 1(d)), due to the crystallinity of the M46J being intermediate between NV11 and NV26 fibers.

Figure 2 shows the discharged capacities (after the first 5 cycles) as a function of crystallite thickness (L_c) and interlayer spacing (d_{002}) of the fibers. These capacities are estimated after charging of the battery by 372 mAh/g, which is equivalent Faradic capacity to form the 1st stage compound of LiC_6. As seen in the figures, for more than about 250Å in crystallite thickness and smaller than 3.38Å in d_{002}, the discharged capacity drops sharply. This drop is caused by decomposition of PC[6,7] in such kind of well-ordered fibers, as an example indicated in Figure 1(b). Also the discharged capacity in the present PC battery system tends to increase in relatively disordered fibers. It suggests that the introduced Li ions into the rather defective fibers can be more reversibly discharged than in well-ordered ones. NV11 anode, which has a specific capacity of 282 mAh/g, exhibits a larger discharged

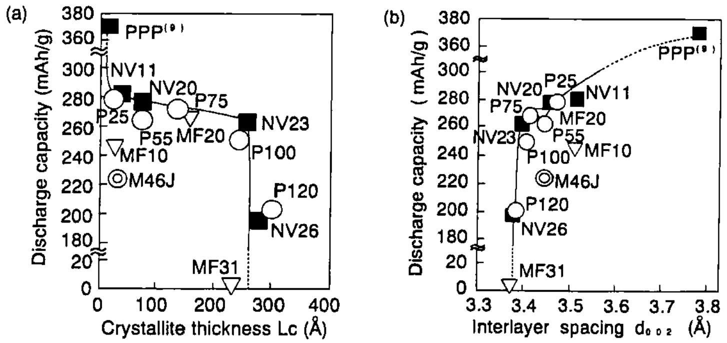

FIGURE 2 Discharge capacities (after the first 5 cycles) of the various kinds of carbon fiber electrodes against the crystallite thickness L_c (a) and d_{002} (b).

capacity than any other samples. This is consistent with the results that the extremely disordered carbons obtained from poly-para-phenylene (PPP) heat-treated as low as 700 °C showed discharged capacity as high as 370mAh/g.[9] Any direct evidences have not been obtained on the reversible capacities of about 280mAh/g of the low crystalline samples against the charging capacity of 372 mAh/g. But it could be envisaged that the low discharging capacities at 5th cycle of the present battery system are caused by energy loss by deformation of the graphite layers after Li intercalation as shown later in Fig.4, or by expansion of fiber diameters.

Figure 3 indicates X-ray diffraction patterns of Li doped fibers which were formed electrochemically in the battery by charging of 372 mAh/g for host fibers (P100 and P55). After charging, the color of the fibers yarn changed to gold (P100) or bronze brown (P55). Fibers were kept in the sealed sample holder during X-ray experiments in the ordinary atmosphere. From the patterns, Li intercalated layer spacing is estimated as 3.617 Å and 3.636 Å for P100 and P55, respectively. These correspond to about 6% increase of the interlayer spacing in pristine fibers. Same results were obtained by image analysis of TEM observation[10] on the pristine fibers and after charging as depicted in Figure 4 (NV26). The interlayer spacings are slightly increased (about 6%), and more defective fringes are observed after Li charging. It could be suggested that the Li^+ ions are stored between the carbon layers to form the 1st stage compounds by the charging process in well-ordered and even in disordered fibers, which have an influence upon the discharge properties.

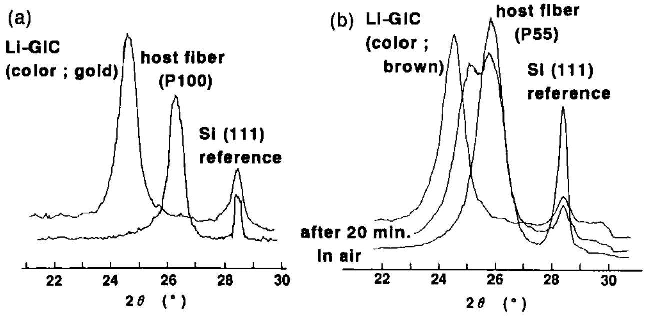

FIGURE 3 X-ray diffraction patterns (CuKα) of the host fiber P100 (a) and P55 (b) and of Li-GIC formed by charging in the battery and measured in ordinary atmosphere.

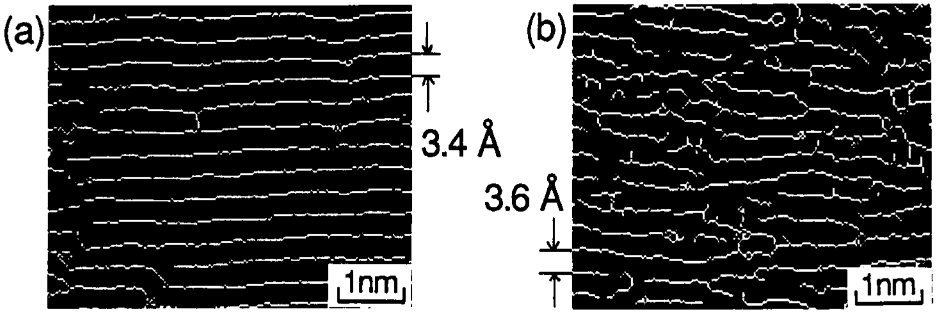

FIGURE 4 Image analyzed lattice fringes of pristine (a) and charged fibers (b) for NV26.

CONCLUSIONS

Carbon fibers have been evaluated as a negative electrode of Li secondary battery. It is suggested that the performances of present Li secondary battery with 1mol $LiClO_4$/PC electrolyte, such as discharge curve and capacity, depend strongly on the macro- as well as micro-scopic structure of the carbon fibers. Carbon fibers could be one of the most useful standard electrode material for understanding the battery mechanism, in which it still required to improve the performances by selection of electrolyte, solvent and well-controlled carbon in macro- and micro-scopic structures.

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REFERENCES

1. T.Nagaura and T.Tozawa, Progress in Batteries & Solar Cells, 9, 209 (1990).
2. M.Endo, J.Nakamura and Y.Okada, T.IEE Japan, 109-B, No.11, 499 (1989). (in Japanese)
3. M.Endo, Y.Okada and H.Nakamura, Synthetic Metals, 34, 739 (1989).
4. M.Endo, CHEMTECH, American Chemical Society, 18, 568 (1988).
5. M.Endo, H.Nakamura, A.Emori, S.Ishida and M.Inagaki, TANSO, No.150, 319 (1991). (in Japanese)
6. A.N.Dey and B.P.Sullivan, J. Electrochem. Soc., 117, No.2, 222 (1970).
7. M.Arakawa and J.Yamaki, J.Electroanal. chem., 219, 273 (1987).
8. J.R.Dahn, R.Fong and M.J.Spoon, Phys. Rev., 42, 10, 6424 (1990).
9. M.Noguchi, K.Miyasita and M.Endo, TANSO, No.155, 315 (1992). (in Japanese)
10. K.Oshida, M.Endo, T.Nakajima, S.L.di Vittorio, M.S.Dresselhaus and G.Dresselhaus, J. Mater. Res., 8, No.3, 512 (1993).