LITHIUM STORAGE BEHAVIOR FOR VARIOUS KINDS OF CARBON
AS NEGATIVE ELECTRODE OF LITHIUM ION BATTERIES

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INTRODUCTION

Lithium secondary battery using carbon electrode inserted with Li ion has been developed to replace Li metal as a negative electrode [1]. Further development to increase battery capacity can be made by modifying the structure of carbon materials [2,3]. For example, a special type of carbon, such as those derived from poly-p-phenylene [4.5] and polyacene [6], has been found to give rise to an extremely high capacity (>1000 mAh/g). However, the mechanism of Li in these carbon materials with different crystallographic properties has not been understood. Furthermore, it is not clear how the battery performance correlate the structural parameters of the carbon materials used.

In the present paper various kinds of carbon materials, including PAN-, pitch-based and vapor-grown carbon fibers and poly-p-phenylen (PPP) based carbon which have different crystallographic and macroscopic structure, have been used as negative electrodes to study their electrochemical propaties. The battery performances of the negative electrodes are evaluated and characterized as a function of the carbon.

EXPERIMENT

Vapor-grown carbon fibers obtained by floating ultra-fine metal catalyst (VGCFs,

denoted as NV), mesophase pitch- and PAN-based carbon fibers, and PPP based carbon heat treated at 700 °C under Ar atmosphere, have been used to assemble the negative electrodes. The structural parameters of these carbon materials are summarized in Table 1. The electrolyte was composed of 1mol $LiClO_4$ in propylene carbonate (PC) . In the case of highly ordered graphite, 1mol $LiClO_4$ dissolved in a equal mixture of ethylene carbonate (EC) and diethyle carbonate (DEC) were used in order to avoid decomposition of electrolyte [7] and formation of by-product on the graphite surface [8]. The carbon sample of 1mg was mixed with polyethylene powder (in 10 wt%) as a binder. The potential of the carbon anode was monitored against the Li reference electrode via a luggin capillary using a three-electrode cell[9].

RESULTS AND DISCUSSION

Electrochemical behavior of the carbon fiber negative electrodes during insertion and desorption of Li ions has been investigated by voltammetry. Voltammetry measurement was carried out under scanning rate of 0.3 mV/min. in the range of 0.3 - 0 V. The Li insertion mechanism for the reduction of carbon electrode can be discussed in terms of staging phenomenon for GIC compounds. In the following, We classify carbon negative electrodes into four groups according to the shape of their voltammograms as shown in Fig. 1 and 2. Because of the irreversible behavior

Table 1 Heat treatment temperature and crystallite parameters of the samples.

sample		Heat treatment temperature (°C)	Average diameter (μ m)	Interlayer spacing d_{002} (Å)	Crystallite thickness Lc_{002} (Å)
Vapor grown carbon fiber	NV10	1000	~ 0.1	3.517	33
	NV20	2000		3.440	83
	NV26	2600		3.381	270
Mesophase pitch-based carbon fiber	P25	—	10	3.463	26
	P55			3.437	82
	P100			3.398	230
	P120			3.376	300
	HM50	—	10	3.424	140
	HM60			3.406	150
PAN-based graphite fiber	M46J	—	10	3.434	100
Polymer based carbon	PPP07	700	2 (powder)	3.77	13

Fig. 1 and 2. Because of the irreversible behavior of the electrochemical at the first cycle, the galvanostatic discharge and charge among 2.8 - 0 V cut-off potential. At the 2nd cycle, voltammogram for low crystalline carbon fiber (P25) shows a reduction and a oxidation peaks near 0 V. No other peaks are observed in the range of 0.3 ˜ 0 V vs. Li reference electrode. We suggest that the reaction of these low crystalline carbon fiber with Li is a simple doping-undoping process. The voltammogram of the high crystalline carbon (P100) present two reduction peaks and three oxidation peaks (Fig.1). The peaks labeled A and B correspond to the formation of 2nd and 1st stage Li-GIC, respectively [10]. Whereas peaks C, D and E correspond to the decomposition of 1st, 2nd and higher stage GIC respectively. The voltammogram of HM60 with intermediate crystallinity appear to have electrochemical behavior between P25 and P100. Only one reduction peak at 70 mV and two oxidation peaks at 100 and 160 mV have been observed. The reaction with Li for HM 60 is different from that of P25 and P100 fiber electrodes, because two separated peaks at about 70 mV and at 100 mV have not been observed in HM60. However a peak at 100 mV in oxide region has been detected both in P100 and HM60 . Fig.2 shows a voltammogram on PPP based carbon anode. The shape of the voltmmogram is similar to that of P25 anode. However the broad oxidation current near 0.8V was enhanced (indicated by arrow). It could be due to the fourth discharge-charge mechanism in such a highly disordered carbon [4].

CONCLUSIONS

Various kinds of carbon materials have been evaluated as negative electrodes of lithium secondary battery. We suggest that the performances of Li secondary battery depend strongly on microscopic structure of carbon materials used for negative electrode. The mechanism of Li-insertion into carbon negative electrode has been classified into four groups. We have found that the Li intercalation takes place in well-ordered graphite fibers, whereas the doping of Li ions occurs in the low crystallinity carbon fibers. Carbon fibers with intermediate crystallinity present a voltammogram between well- and dis-ordered carbon fibers. And Li doping process into extremely disordered carbon, PPP07, is largely different from that in carbons with low crystallinity anode. It has been shown that the crystallinity of the carbon is a important factor for the performances of Li secondary battery. A better control of microscopic and macroscopic structure of carbon materials is important to produce superior Li ion battery.

REFERENCES

1. T.Nagaura and T.Tozawa, Progress in Batteries & Solar Cells, 9 (1990) 209.
2. M.Endo, J.Nakamura, Y.Sasabe, T.Takahashi, and M.Inagaki, T.IEEE Japan, Vol.115-A, No.4 (1995) 349.
3. M.Endo, J.Nakamura, Y.Sasabe, T.Takahashi, and M.Inagaki, TANSO, No.165 (1994) 282
4. M.Noguchi, K.Miyasita and M.Endo, TANSO, No.155 (1992) 315. (in Japanese)
5. K.Sato, M.Noguchi, A.Demachi, N.Oki and M.Endo, SCIENCE, Vol.264, 22 (1994) 556.
6. S.Yata, H.Kinoshita, M.Komori, N.Ando, T.Kashiwamura, T.Harada, K.Tanaka and T.Yamabe, Synth. Met., 62 (1994) 153.
7. A.N.Dey and B.P.Sullivan, J.Electrochem. Soc., 117, No.2 (1970) 222.
8. R.Fong, U.von Sacken and J.R.Dahn, J.Electrochem.Soc., Vol.137, No.7 (1990) 2009.
9. M.Arakawa and J.Yamaki, J.Electroanal, Chem, 219 (1987) 222.
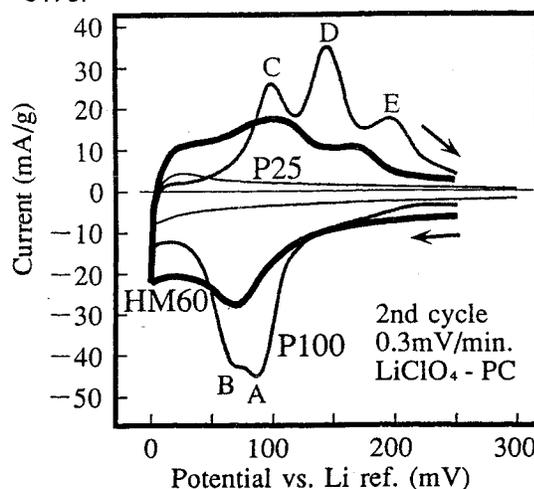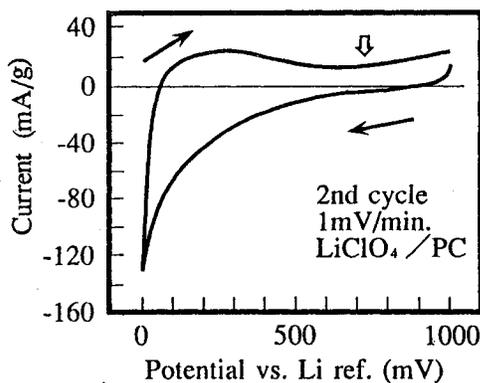10. J.R.Dahn, Phys. Rev. B, vol.44, No.17 (1991) 9170.

Fig.1 Voltammograms of several kinds of carbon fiber anodes.

Fig.2 Voltammogram of PPP07 anode.