ANODIC PERFORMANCES OF CARBONS PREPARED FROM ISOTROPIC QUINOLINE PITCH

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Introduction

Electrochemical performances of carbon materials as an anode of lithium ion secondary battery have been extensively studied[1-3]. Recently, carbon materials which contain heteroatoms, for example, N, S, B, etc. in the hexagonal plane have attracted attention since they are expected to improve electrochemical properties or to interact with lithium. N-containing carbon materials can be prepared by CVD method using nitrogen containing materials like pyridine[4] or by the carbonization of pitch like substances with large nitrogen contents.

In this study, nitrogen containing carbons were prepared from isotropic quinoline pitch which was catalytically prepared with HF/BF_3 from quinoline. Their electrochemical performances were measured to confirm the effects of nitrogen, analyze the nitrogen chemistry and find correlation between the performances and structure.

Experimental

The carbon materials used in this study were prepared from isotropic quinoline pitch by heattreating at the range of 600-1200°C. Their structure was investigated, using element analysis, XRD, raman spectroscopy, and XPS. Their electrochemical performances were measured in terms of charge/discharge capacity, discharge potential and undischargeable capacity using a three electrode half cell. The electrolyte was 1M $LiPF_6$/EC+DMC(vol. ratio 1:1), and all operations were carried out in a dry box filled with Ar gas.

In this experiment, two methods of charging(lithium insertion into carbon electrode) were examined. One was constant current method(current density 0.2mA/cm^2) at potential range of 0 - 2 V. The other was limited potential method which was constant current charging to 0V(current density 0.2mA/cm^2) followed by constant potential charging(40h at 0V vs. Li/Li$^+$) to obtain the maximum capacity.

Results

Table 1 lists the compositions of carbons prepared from quinoline pitch at several HTT and holding times. Hydrogen contents decreased within the range of 600-700°C. However, nitrogen left in a considerable amount upto 1000°C, and then decreased rapidly within the range of 1000 - 1200°C.

Figure 1 shows the XPS spectra of N_{1s} obtained from ESCA. Nitrogens existed mainly in the form of pyridinic type identified to the peak of 398eV by HTT at 600°C, although they changed slightly to quaternary type identified to the peak of 401eV with longer carbonization time while total amount of nitrogens stayed unchanged. The peak of quaternary type became principal with the carbonization temperature exceeded 700°C. Nitrogen contents decreased with higher temperature gradually upto 1000°C and sharply by 1200°C.

Table 2 represents the capacities of carbons measured by two charging methods, respectively. When carbonization time was 1h, QP700-1 showed the maximum discharge capacity. However, QP600-20 and QP600-40 did more capacity than QP700-1. Such a result came from the decrease of impedance of electrode by longer holding time at 600°C. Two charging methods gave similar trend of capacity change of the carbons, although the method I allowed much smaller capacity.

Figure 2 compares discharge characteristics of NP-based and QP-based carbons by charging through two methods. The capacity of QP-based carbons at 600°C, 1h and 40h was much smaller than that of NP-based one regardless of HTT and time reducing the length of plateau at 1V. In contrast, QP1000-1 showed higher capacity than that of NP1000-1, reflecting the larger capacity in the range of 0.5 - 1.0 V.

Figure 3 shows the correlation between irreversible capacities and heattreatment temperature of carbons from NP and QP. Irreversible capacities of QP-based carbons at first cycle were larger than that of NP-based one[4]. However, irreversible capacities obtained from the difference in the capacities by constant potential charging and increased capacities by the constant potential charging suggests better cycleability of the QP-based carbons than that of NP-based carbons.

Discussion

Carbons prepared from quinoline pitch at lower temperature showed typical characteristics of soft carbon heattreated at lower temperature. Comparing with

NP-based carbons, within 600 - 800°C , the capacities were smaller than these of QP-based carbons. However, the capacitis of QP1000-1 were much higher than that of NP1000-1.

Irreversible capacities of QP-based carbons obtained from the difference of capacity between charging during constant potential and increased capacity by the constant potential charging were smaller than that of NP-based carbon when both carbons heattreated at the same temperature compared, although irreversible capacities at first cycle was relatively high.

References

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Table 1. Element analyses of carbons derived from isotropic quinoline pitch

Sample ID	C	H	N	H/C	N/C
QP600-1	83.35	3.09	9.86	0.44	0.10
QP600-20	84.17	2.25	10.00	0.32	0.10
QP600-40	83.87	2.20	10.01	0.31	0.10
QP700-1	88.11	0.87	9.42	0.12	0.09
QP800-1	89.40	0.54	8.78	0.07	0.08
QP1000-1	91.71	0.29	7.05	0.03	0.07
QP1200-1	96.00	0.14	3.47	0.02	0.03

Table 2. Charge/discharge capacities of carbons charged by different methods (Unit : mAh/g)

Sample ID	Method I(1)		Method II(2)	
	Charge	Discharge	Charge(3)	Discharge
QP600-1	773	255	326	278
QP600-20	969	500	284	651
QP600-40	952	490	268	608
QP700-1	752	424	181	602
QP800-1	657	359	177	524
QP1000-1	553	338	120	438
QP1200-1	425	254	87	300

(1) constant current charging(0.2 mA/cm^2 , 0 - 2 V)
(2) constant current charging(0.2 mA/cm^2, - 0 V)
+ constant potential charging(40 h at 0 V)
(3) capacities charged by constant potential method

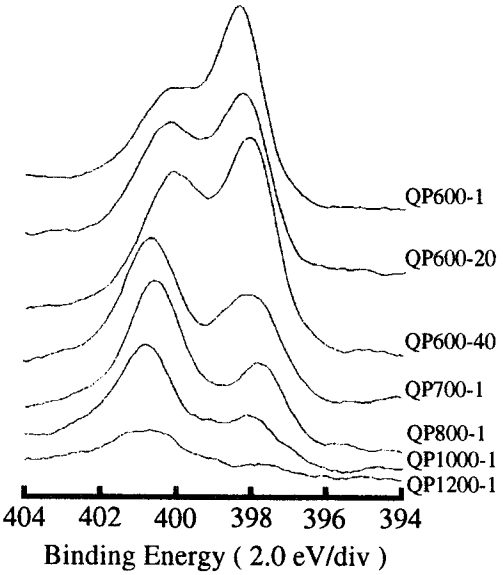

Figure 1. XPS spectra of N_{1s} for carbons derived from isotropic quinoline pitch

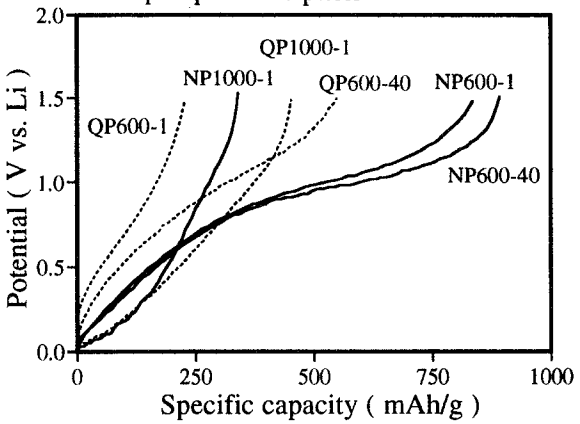

Figure 2. Discharge characteristics of carbons derived from different pitches(charged by limited potential method)

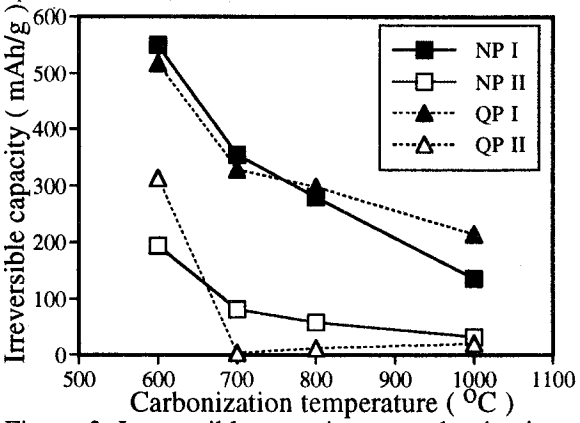

Figure 3. Irreversible capacity vs. carbonization temp. plots for each carbons

* Irreversible capacity
I : first cycle, constant current charging
II : charge capacity during constant potential method
- increased capacity by constant potential method