

PREPARATION OF GRAPHITIZED P-CNFs FOR ANODE MATERIALS OF LI-ION BATTERY

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Abstract

Graphitized platelet carbon nanofibers (g-p-CNFs) were prepared through the thermal CVD of carbon monoxide over Fe catalyst at 600°C and followed to heat treat at 2800°C with various conditions. Graphitized p-CNF series showed d_{002} of 3.360~3.365 Å, similar with graphite single crystal (3.354 Å). Raman spectroscopy of them valued ID/IG of 0.21 ~ 1.23. Such CNFs of high graphitization degree showed high capacity of 307~330mAh/g under constant current test from 0 to 1.5V which are almost same with that of natural and synthetic graphites (312~322mAh/g). Checking the rate performance is now in progress.

Introductions

Carbonaceous materials, especially graphite, have accomplished an active role in the realization of Li-ion batteries during the last 20 years [Dahn et al, Mabuchi et al, and Iijima et al]. Although carbon nanomaterials such as carbon nanotube (CNT) and carbon nanofiber (CNF) have been expected as potential materials for Li-ion battery as special functional materials with high rate performance, actual proof was not still achieved. Relatively low discharge capacity in the available potential range (0 ~ 0.5 V vs. Li/Li+) is major reason for non-commercialization. Recently, CNF with high graphitic property was reported [Yoon et al.].

In this study, the present authors prepared special CNFs with very high graphitization degree and evaluated their performances as anodic materials for Li-ion battery. Optimal conditions for higher graphitization were examined in the graphitization step.

Experimental

The precursor platelet carbon nanofiber (p-CNF) was prepared through the thermal CVD of carbon monoxide at 600°C over Fe catalyst using a conventional horizontal tube furnace. The prepared p-CNF was further heat treated with various conditions. P-CNFs were further heat-treated at 2800 °C for 10 min, then followed to treat with nitric acid at room temperature for 3 days, and finally heat treated again at 2800 °C for 10 min. Commercial natural graphite (SP, Nippon Kokuen, Japan) and synthetic graphite (MAG, Hitachi Chem., Japan) were used as reference carbon materials.

The crystallographic properties were evaluated with X-ray diffraction method (Rint-2000, Rigaku, Japan) and Raman spectroscopy (NRS-2000B, Jasco, Japan). Surface area was measured by N₂-BET (Belsorp, Nippon-bell, Japan), and morphology was measured with HR-SEM (JSM-6700F, Jeol, Japan).

CNF slurry was coated on a copper foil with mixing state of CNF and certain amount of binder (SBR, trade name BM-400B, ZEON, Japan). The coated electrode was dried at 105°C for 12hs in vacuum. The final compositions of dried electrode were carefully controlled to contain 85 wt% CNF, 5 wt% CMC and 10 wt% SBR. Disc-typed electrodes were made up to coin cell (CR2032) using Li metal as a counter electrode. 1M LiPF₆ (EC: DEC [vol% 1:1]) supplied from UBE Chemicals was used as an electrolyte. Charge/discharge performance was tested with a constant current method (CC) of 30mA/g at 0~1.5 V using TOYOCAT 3000 (TOYO system, Japan).

Results

Table 1, Figures 1 and 2 show physical properties of prepared p-CNF, graphitized p-CNFs and reference graphites. G-p-CNF and G-g-p-CNF-N/A have showed high graphitization degree which was almost same with graphite single crystal but 10~15 times higher surface areas.

Table 1. Physical properties of p-CNF series and graphites.

No	Item	Details	Selective physical properties			
			Elemental analysis H/C (%)	Raman spectra ID/IG	XRD $d_{002}(\text{\AA})$	N ₂ -BET Surface area(m ² /g)
1	p-CNF	600°C synthesis	0.25	1.23	3.363	68
2	g-p-CNF	1→2800°C heat treatment	0.10	0.21	3.365	43
3	g-p-CNF-N/A	2→HNO ₃ treatment	0.14	0.60	3.360	54
4	g-g-p-CNF-N/A	3→2800°C heat treatment	0.11	0.24	3.362	47
5	SP	Natural graphite	-	-	3.355	< 4
6	MAG	Synthesized graphite	0.14	-	3.354	< 4

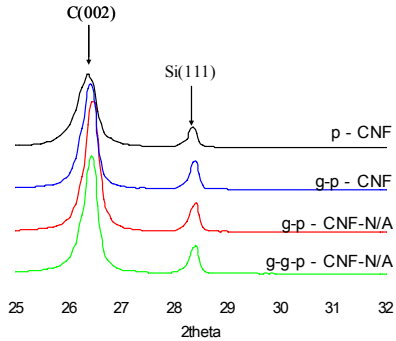


Figure 1. X-ray diffraction patterns of p-CNF series.

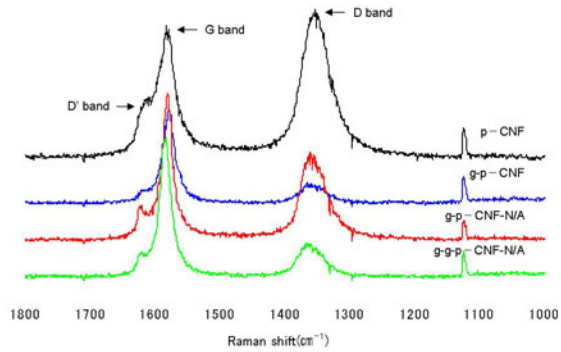
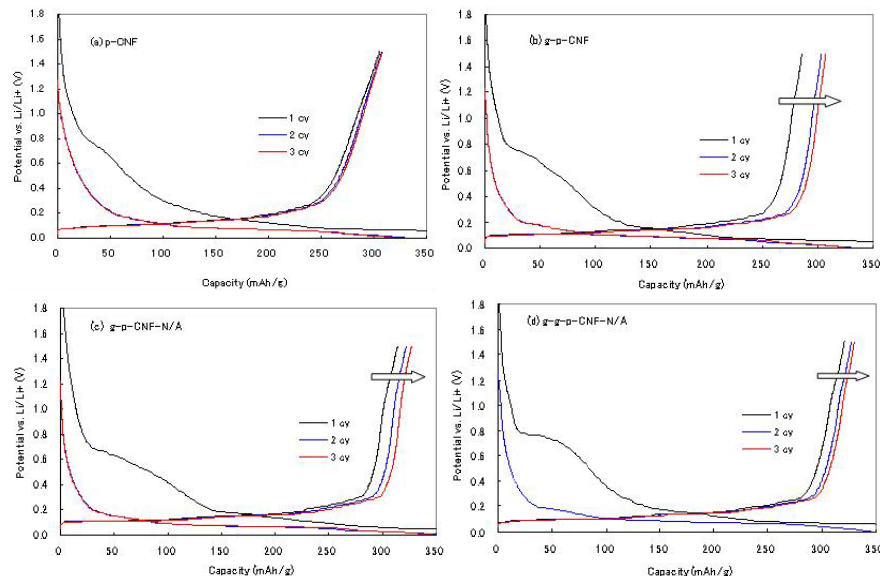


Figure 2. Raman spectra of p-CNF series.

Table 2 and Figure 3 show the charge-discharge properties of p-CNF series and reference graphites. P-CNFs showed the discharge capacities of 286~321 mAh/g and 1st cycle coulombic efficiencies of 52.5~60.4%.

Table 2. Electrochemical properties of p-CNF series and graphites at the initial ch/dis. cycle.

Item	Capacity (mAh/g)		Coulombic efficiency (%)
	Charge	Discharge	
p-CNF	506	306	60.4
g-p-CNF	491	286	58.2
g-p-CNF-N/A	598	314	52.5
g-g-p-CNF-N/A	539	321	59.5
SP	415	322	77.6
MAG	387	312	80.6



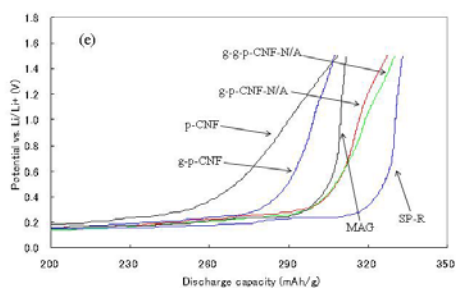


Figure 3. Galvanostatic charge–discharge profiles of p-CNF series.

a) p-CNF, b) p-CNF graphitized at 2800°C, c) graphitized p-CNF treated by HNO₃, d) re-graphitized p-CNF after HNO₃ treatment, e) discharge curve at 3rd cycle according to samples.

Figure 4 shows SEM images of p-CNF series. P-CNF appeared unchanged dimensions and shapes with nitric acid treatment and repeated graphitization.

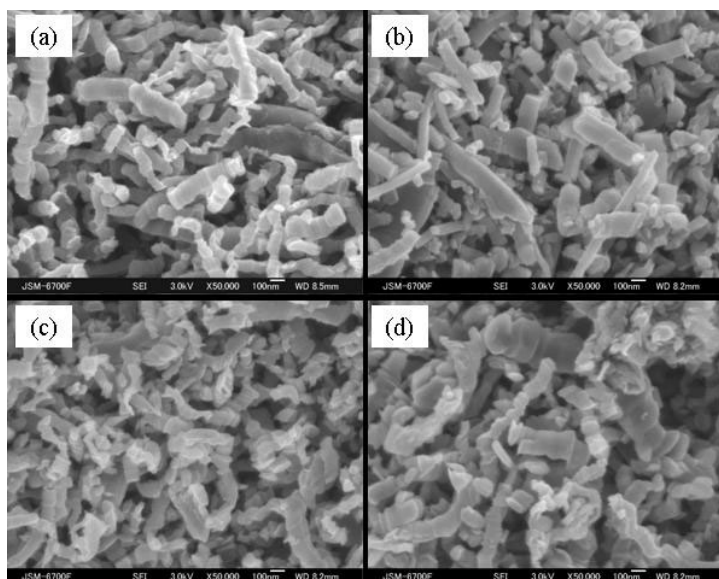


Figure 4. SEM morphology of p-CNF series.

a) p-CNF, b) p-CNF graphitized at 2800°C, c) graphitized p-CNF treated by HNO₃, d) Re-graphitized p-CNF after HNO₃ treatment.

Conclusions and discussions

The graphitization and nitric acid treatments can make physical properties of p-CNF reach to graphite single crystal. The discharge capacities of 286~321mAh/g was defined with p-CNF series which were very similar to those of graphites. The improvement of 1st cycle efficiency is necessary for realistic application as anodic material for Li-ion battery.

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