

# SEI FORMATION BEHAVIORS ON WELL-DEFINED CARBON SURFACES FOR LITHIUM ION BATTERY SYSTEM

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## Introduction

In lithium ion batteries, solid electrolyte interphase (SEI) is essential to determine the high rate capability, shelf life, cycle life and safety [1]. SEI is principally formed during first charging and responsible for an irreversible capacity loss. SEI layer acts as solid state diffusion path of lithium ions as well as a passivation layer against co-intercalation of solvent molecules [2]. Peled et al have found that the surface chemistry and morphology of the SEI vary with the basal and edge planes of highly ordered pyrolytic graphite (HOPG) and mild air-oxidation of graphite improves its performance in  $\text{Li/Li}_x\text{C}_6$  cells [3,4]. In our previous work, it was found that the well-defined edge and basal surfaces of carbon nanofibers (CNFs) can be controlled by high temperature heat treatment, and subsequent nitric acid treatment. In this study, the present authors attempted to track the SEI formation behaviors on well-defined edge and basal planes controlled by the high temperature heat treatment, and the nitric acid treatment.

## Experimental

The CNFs used in this study were prepared from catalytic decomposition of carbon monoxide and hydrogen gases on iron catalyst. Pulverized iron catalyst particles (500 mg) were uniformly dispersed onto a quartz reactor located in a furnace using acetone. The quartz reactor was heated up to  $640^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  under the  $\text{N}_2/\text{H}_2$  mixed gases ( $\text{N}_2/\text{H}_2 = 9/1$ , total 2 L/min). The reactant gases of  $\text{CO}/\text{H}_2$  (4/1, total 2 L/min) then flowed over iron catalyst at  $640^\circ\text{C}$  for 4 h, and finally cooled down to room temperature in  $\text{N}_2$  gas flow. Synthesized platelet-type CNFs were treated with 10 wt%  $\text{HCl}$  for 72 h to remove iron catalyst, filtered with distilled water and then dried at  $110^\circ\text{C}$  for 12 h in vacuum (PCNF). PCNF was heat-treated at  $2800^\circ\text{C}$  for 10 min for the further graphitization (GPCNF), and then treated with 10 wt%  $\text{HNO}_3$  at  $155^\circ\text{C}$  for 28 h (GPCNF-NA). Carbon, hydrogen and nitrogen contents were measured by elemental analysis. The crystallographic parameters ( $d_{002}$  and  $L_{c002}$ ) of the CNFs were measured by XRD (Ultima-III,  $\text{CuK}\alpha$ , Rigaku). Structure and surface morphology of the CNFs were examined by scanning electron microscope (SEM, JSM-6700F, JEOL) and transmission electron microscope (TEM, 200 kV, JEM-2100F, JEOL). The electrochemical properties of the CNFs were studied by the galvanostatic charge/discharge measurement using CR2032 two electrode button cell and cyclic voltammetry using three electrode system. Li metal foil

was used as a counter electrode and reference electrode. The working electrode was prepared by mixing 90 wt% active material and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidone (NMP). The mixed slurry was coated onto a copper foil for two electrode button cell, spread uniformly onto a copper disk (dia. 10 mm) for three electrode system, and then dried in a vacuum oven at  $120^\circ\text{C}$  for 3 h. The electrolyte solution was 1 M  $\text{LiClO}_4$  dissolved in ethylene carbonate (EC) / diethyl carbonate (DEC) (1:1 vol%, Kishida Chemical, Japan). The charge / discharge cycle test was performed at 1 C-rate between 0.003 and 3 V vs.  $\text{Li/Li}^+$  (Toscat-3100, Toyo system, Japan). Cyclic voltammetry was carried out at a scan rate of  $1\text{mV}/\text{sec}$  between 0.003 and 3V vs.  $\text{Li/Li}^+$  (Potentiostat, HZ-3000, Hokuto Denko, Japan). The specimens were scraped from the copper disk, washed in dimethyl carbonate (DMC, Kishida Chemical, Japan) and then dispersed on copper grids covered with carbon film to observe the SEI formation behaviors by TEM. Assembly of cells and measurements were carried out a room temperature in an argon-filled glove box with a dew point less than  $-70^\circ\text{C}$ .

## Results and Discussion

Elemental compositions and crystallographic parameters of PCNF, GPCNF and GPCNF-NA are summarized in Table 1. Heat treatment at  $2800^\circ\text{C}$  increased C contents and decreased O contents of PCNF. Nitric acid treatment increased N and O contents, suggesting an introduction of nitrogen- and/or oxygen-containing functional groups to edge surfaces of GPCNF-NA. PCNF showed a high degree of graphitization by itself, and its values of average interlayer spacing ( $d_{002}$ ) and average height of stacking ( $L_{c002}$ ) were  $3.365 \text{ \AA}$  and 57 nm, respectively. Figure 1 shows surface morphology of PCNF, GPCNF and GPCNF-NA observed by TEM. GPCNF (b) and GPCNF-NA (c) showed highly graphitized layers unlike PCNF (a). GPCNF (b) showed closed loop ends on the surface, thus its surface can be regarded as curved basal planes. Nitric acid treatment cut off the closed loop ends and consequently free edges were exposed.

Figure 2 showed the galvanostatic charge-discharge profiles and differential capacity-voltage plots of the first two cycles for PCNF, GPCNF and GPCNF-NA that were charged and discharged at 1 c-rate between 0.003 and 3.0V. The presence of irreversible capacity can be observed from the differential capacity-voltage plots. It is associated with the formation of SEI on CNFs surfaces by the decomposition of electrolyte. The cathodic reaction of PCNF, GPCNF and GPCNF-NA initially appeared at 0.84, 0.72 and 1.0 V, respectively. The cathodic peak of PCNF, GPCNF and GPCNF-NA was observed at about 0.6 V. Spahr et al. have reported that the pure ethylene carbonate was decomposed at a potential of about 0.55 V vs.  $\text{Li/Li}^+$  [5]. The irreversible reaction apparently occurs in the presence of ethylene carbonate as electrolyte component. Charge-discharge capacity, irreversible capacity and coulombic efficiency of the first two cycles were summarized in Table 2. The discharge capacity of CNFs was higher than the theoretical capacity of

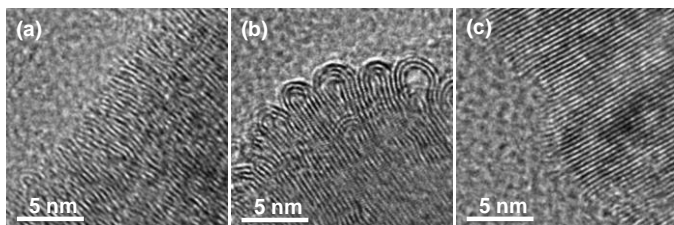
graphite (372 mAh/g). Irreversible capacity of PCNF, GPCNF and GPCNF-NA were 281, 219 and 234 mAh/g, respectively. The high irreversible capacity of PCNF is probably due to abundant active edge planes on the surfaces, whereas the low irreversible capacity of GPCNF is probably related to inactiveness of the curved basal planes composed of closed loop ends on the surfaces. Figure 3 shows the SEI formed on edge planes of PCNF and basal planes of GPCNF after cyclic voltammetry experiment at a scan rate of 1 mV/sec. The SEI formed on PCNF and GPCNF surfaces had an amorphous morphology similar to carbon film of copper grid. The SEI thickness observed by TEM was about 15~25 nm for edge planes of PCNF and about 3~5 nm for basal planes of GPCNF, respectively. Peled et al have found that the SEI thickness of edge planes is larger than that of basal planes on HOPG [3]. The SEI thickness of GPCNF-NA will be examined in the further study.

**Table 1. Physical Properties of PCNF, GPCNF and GPCNF-NA**

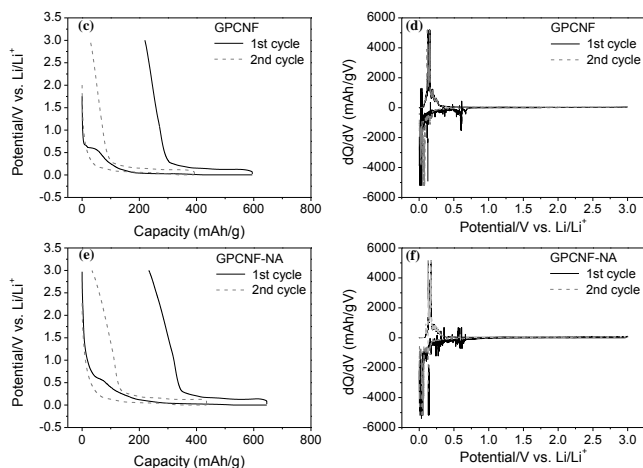
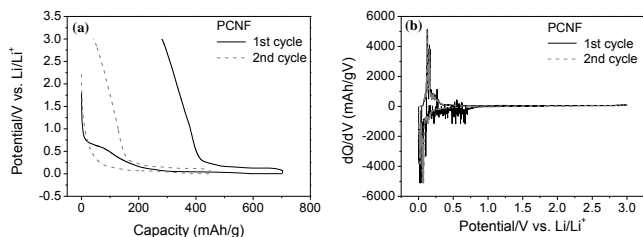
Type	Elemental Analysis (wt.%)					XRD Properties	
	H	C	N	O (diff. %)	H/C ratio (%)	$d_{002}$ (Å)	$L_{c002}$ (nm)
PCNF	0.21	99.16	0.00	0.63	0.21	3.365	57
GPCNF	0.10	99.87	0.00	0.03	0.10	3.366	62
GPCNF-NA	0.16	98.15	0.09	1.60	0.16	3.364	73

**Table 2 Electrochemical Properties of PCNF, GPCNF and GPCNF-NA**

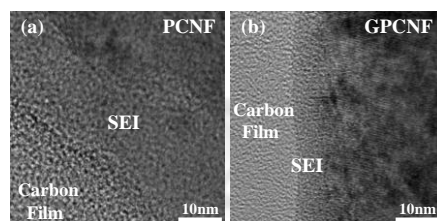
	Capacity of 1 <sup>st</sup> cycle (mAh/g)				Capacity of 2 <sup>nd</sup> cycle (mAh/g)			
	Charge	Discharge	Irreversible	Efficiency (%)	Charge	Discharge	Irreversible	Efficiency (%)
PCNF	703	422	281	60.0	450	409	41	90.9
GPCNF	595	376	219	63.2	393	365	28	92.9
GPCNF-NA	646	412	234	63.8	435	401	34	92.2



**Fig. 1** TEM Images of PCNF (a), GPCNF (b) and GPCNF-NA (c)



**Fig. 2** The galvanostatic charge-discharge profiles (a, c, e) and differential capacity-voltage plots (b, d, f) of the first two cycles for PCNF (a, b), GPCNF (c, d) and GPCNF-NA (e, f).



**Fig. 3** TEM images of SEI formed on PCNF (a), GPCNF (b).

## Conclusions

By the 2800 °C heat treatment, basal planes of PCNF were developed by the formation of closed loop ends on PCNF surfaces. The subsequent nitric acid treatment recovered active edge planes by the cut-off of closed loop ends on GPCNF surfaces. PCNF, GPCNF and GPCNF-NA showed the higher capacity than the theoretical capacity of graphite (372 mAh/g). GPCNF had the lower irreversible capacity than PCNF and GPCNF-NA. The thickness of the formed SEI was about 15~25 nm for edge planes of PCNF and about 3~5 nm for basal planes, respectively. These results suggest that the curved basal planes of GPCNF reduced the irreversible capacity loss for the SEI formation.

## References

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