

# ADDITION OF SPECIALLY DESIGNED SiO-CNF AND Si-CNF COMPOSITES TO IMPROVE CAPACITY AND RATE PERFORMANCES OF ANODIC GRAPHITE FOR LI-ION BATTERIES

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## Introduction

Silicon is attractive material because of the higher capacity (4200 mAh/g) than graphite (372 mAh/g) as an anodic material of Li-ion battery (LIB). Nevertheless, silicon anode has not yet been commercialized because of the large volume expansion by 400% upon insertion and extraction of lithium ions, leading to internal cracks in the structure of its particle. The internal cracks cause poor contacts between the Si particles and current collector, and thus, Si anode shows poor cycle performances [1,2]. Recently, hybridizations of Si or SiO with other materials have been studied in order to improve electrochemical properties [3,4]. However some problems have still remained until now such as complicated manufacturing process of active material, difficulty of mass production, high cost, and so on.

We, herein, propose a novel solution to moderate volume expansion of anode by growth of carbon nanofiber (CNF) on the surface of Si or SiO active materials to reduce the expansion by rapping as to provide space among them for absorbing the expansion [5]. Si particles of 20 nm / 50 nm and SiO particles of 8  $\mu\text{m}$  sizes were first coated by pyrolytic carbon (PyC), and then CNFs were directly synthesized on them by CVD method. We studied the effect of the mixtures between PyC/CNF composite and graphite.

## Experimental

Nanometer-sized silicon particles (20 nm or 50 nm, Nanostructured & Amorphous Materials, Inc., USA) and a silicon monoxide particle (8  $\mu\text{m}$  SiO, Matsushita Denchi Kogyo, Japan) were used as a starting material in this study. To improve an attachment force of CNF with Si or SiO surface, the Si and SiO particles were first coated by pyrolytic carbon (PyC). In detail, PyC growth was carried out in a horizontal furnace; heated to 900°C at a heating rate of 10°C min<sup>-1</sup> under He gas flow, switched to mixed gas of CH<sub>4</sub> and H<sub>2</sub> (4 : 1), maintained for 1 h at 900°C, and then cooled down to room temperature in He gas flow. The amount of coated PyC was 20.9 wt% on 20 nm-Si, 15.6 wt% on 50 nm-Si and 1.8 wt% on SiO particles, respectively. Hereafter, the PyC-coated Si or SiO particles are referred to as Si/PyC or SiO/PyC,

respectively. Then, Si/PyC or SiO/PyC was immersed in ethanol solution of iron nitrate enneahydrate (Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, Wako chemical company, Japan), and then the slurry was stirred for 3 h at room temperature. The amount of the catalyst was carefully controlled to support 2 wt % Fe on the weight basis of metal catalyst. After evaporating the ethanol solvent at 60°C, the mixtures were dried at 105°C for 6 h under vacuum. CNFs were grown on Si/PyC or SiO/PyC using a fixed-bed reactor. Si/PyC or SiO/PyC with Fe (2 wt %) was placed in the center of horizontal tube furnace and heated to 600°C at heating rate of 10°C min<sup>-1</sup> in He gas flow. Then, the mixed gases of CO and H<sub>2</sub> were introduced for 30 min. The reactor was cooled down to room temperature in an He gas flow after the CNF growing step. The amount of the CNF growth was 71 wt % on 20 nm-Si/PyC, 47 wt% on 50 nm-Si/PyC and 53 wt% on SiO/PyC, respectively. The specimens with the grown CNF are designated as having “/CNF” as a suffix, e.g. Si/PyC/CNF.

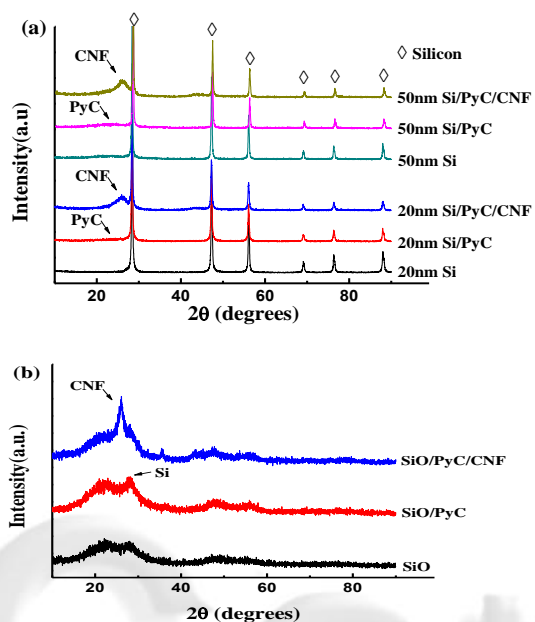
The surface morphology was observed by using transmission electron microscope (TEM, JEM-2100F, JEOL, Japan). Crystallographic properties were measured by X-ray powder diffractometer (CuK $\alpha$ , Ultima-III, Rigaku, Japan). The galvanostatic charge-discharge tests were carried out using coin-type cell of CR2032 with two electrodes, where Li metal foil was used as a counter electrode. To prepare the anode electrode, the mixed slurry of the prepared composites (10-30 wt%) mixed with synthetic graphite (MAG, Hitachi Chemical, Japan) as an active material, styrene-butadiene rubber (SBR, trade name BM-400B, ZEON, Japan) as a binder, and carboxymethyl cellulose (CMC) as a thickening agent, was coated onto copper foil (18  $\mu\text{m}$  thick), dried at 120°C under vacuum for 12 h, and then pressed by using a roll-type mill under 100 MPa of pressure. The pressed electrode was cut into discs ( $\phi$ 12 mm and about 60  $\mu\text{m}$  thick) and weighed by ultra-fine balance to calculate the amount of active material. Coin-type cells were assembled in a glove-box using polyethylene film (16  $\mu\text{m}$  thick) as a separator and 1M LiPF<sub>6</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol % , Ube Kosan, Japan) as an electrolyte. The electrochemical measurements were performed through charging and discharging by constant current (CC) with the current density of 30 or 100 mA g<sup>-1</sup> in the potential range of 0~1.5V versus Li/Li<sup>+</sup> (Toscat-3100, Toyo-system, Japan) at room temperature.

## Results and Discussions

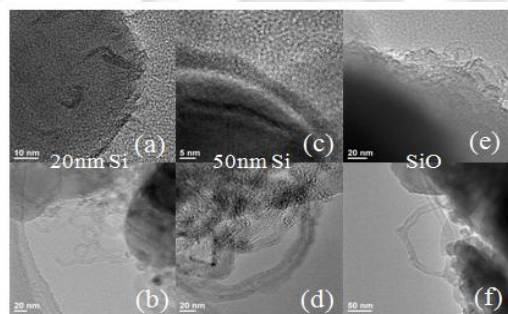
XRD profiles of (a) 20 nm-Si, 20 nm-Si/PyC, 20 nm-Si/PyC/CNF, 50 nm-Si, 50 nm-Si/PyC, 50 nm-Si/PyC/CNF and (b) SiO, SiO/PyC, and SiO/PyC/CNF are shown in Figure 1. After pyrolytic carbon coating, amorphous carbon peaks were shown very weak, although intensive peaks originated from the grown CNFs were clearly observed (Fig. 1a). Broad Si and SiO<sub>2</sub> peaks were observed in the intact SiO, indicating partial disproportionation for SiO to Si and SiO<sub>2</sub> (Fig. 1b). After pyrolytic carbon coating at 900°C, the pure Si peak was became remarkable, suggesting partial reduction of the SiO

particles. The CNF growth again gave strong CNF peak to be observed for the SiO system.

Figure 2 shows the TEM images of PyC and CNF composites on Si or SiO particles. Formation of thin pyrolytic carbon layers on the Si or SiO particles (Figs. 2a,c,e) and grown CNFs from surface of the particles (Figs. 2b,d,f) can be observed.



**Fig. 1** XRD patterns of (a) Si composites and (b) SiO composites.

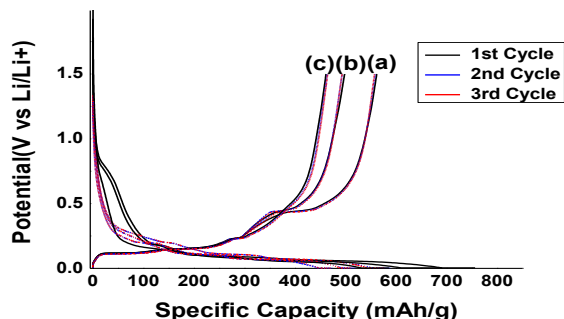


**Fig. 2** TEM micrographs of (a) 20 nm-Si/PyC, (b) 20 nm-Si/PyC/CNF, (c) 50 nm-Si/PyC, (d) 50 nm-Si/PyC/CNF, (e) SiO/PyC, and (f) SiO/PyC/CNF.

Figure 3 shows charge-discharge profiles of the mixtures of 20 wt% composites with MAG until 3 cycles. The 20 nm-Si/PyC/CNF composite showed the largest discharge capacity of 561 mAh/g. Moreover, all mixtures showed the good cycle performance up to 3 cycles. The intact Si or SiO particles showed inferior capacities and cycle performances to the composites (data not shown). Thus, it can be concluded that the composites with CNFs are effective materials to increase the LIB capacity.

Table 1 summarizes the discharge capacity and the 1<sup>st</sup> cycle columbic efficiency of the composites. For any

composite, the more the mixing amount of the composites, the higher the capacity. In case of initial efficiency, the SiO/PyC/CNF composites showed the highest values. Because of high surface area of composites, the increasing composite mixing amount would give rise to a decrease in the irreversible capacity loss of the anode.



**Fig. 3** Charge-discharge profiles of the composite 20 wt% mixtures with MAG until 3 cycles: (a) 20 nm-Si/PyC/CNF; (b) 50 nm-Si/PyC/CNF; c) SiO/PyC/CNF.

**Table 1. Electrochemical properties of mixtures at the 1<sup>st</sup> charge and discharge Cycle.**

Content (composite)	20nm Si		50nm Si		SiO	
	D.C. <sup>a</sup>	I.E. <sup>b</sup>	D.C.	I.E.	D.C.	I.E.
10%	449	80.3	423	77.7	402	81.8
20%	561	74.2	498	72.1	461	78.7
30%	665	67.4	536	67.5	526	74.4

a. D.C.: Discharge Capacity of 1<sup>st</sup> Cycle (mAh/g)

b. I.E. : Initial Efficiency of 1<sup>st</sup> Cycle (%)

## Conclusions

The addition Si or SiO composites with PyC and/or CNF to graphite showed higher capacity than graphite itself and good cycle performance. Further improvements of the LIB performance would be achieved through the optimization of the PyC coating and CNF growth processes.

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## References

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