PREPARATION OF FUNCTIONAL SI-CNF COMPOSITES FOR THE ANODIC MATERIALS OF LI-SECONDARY BATTERY

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Abstract

To achieve the complete cycle ability of Si or Si containing powders as anodic materials of Li-ion battery is still a challenging task. The enormous volumetric expansion of active particles in charge process should be a major reason for the destruction and inferior cycle performance of anode in Li-ion battery system. The present authors propose a novel concept for relieving such an expansion derived destruction of anode by providing the relaxation steric space between the active materials. Well balanced carbon nanofiber (CNF) and Si composites can establish the relaxation spaces for relieving the expansion tension in charge process. In the prepared Si/CNF composites, small CNFs which cover the Si particle surface like ivy can afford the electric conductive path of Si powder, and large CNFs can do the conductive network with particle each other. 20~150wt% of well balanced CNFs growth on the Si particle showed large discharge capacity of 800~1700 mAh/g with much improved cycle performance. Optimization of CNF growth on Si particles and structural analyses are now in progress.

Introduction

Carbon materials have accomplished major role in the commercialization of Li-ion batteries during last 20 years. Development of mobile devices strongly demands much larger capacity in the Li-ion battery. The capacity improvement by the optimization of battery systems has already reached its limitation and the only way to improve it remains in the enlargement of absolute capacity of active materials. Though intensive studies have been focused on the development of substitutes instead of carbon anodes so far, it is still a challenging task to develop the desirable one.

The present authors, herein, propose a novel solution concept for relieving the expansion of anode by providing the relaxation space between the active materials. We studied the steric relaxation effect CNFs which were grown on the surface of metallic Si particles for improving the cycle performance in Li-ion battery system. Optimization of CNF growing method and structural analyses were in progress.

Methods

0.4 ㎛ silicon powder (Tokuyama Chemicals, Japan) was used as an active Si material without further treatment. Nickel catalyst (Ni 1 wt% per Si) was prepared through the impregnation method with nickel nitrate solution as described in the previous paper [Russel 1954]. CNF was grown on Si particles through the catalytic pyrolysis of C_2H_4-H_2 mixed gas on Ni supported Si at 500℃ for 10min. The grown amounts of CNF were carefully controlled to around 100 wt% to the weight of Si particles. Prepared CNF/Si composite was pulverized under 45 ㎛ and used as an active material for performance test. For the performance comparison, CNF mixed Si (H-CNFs 100wt% per Si) and Ketjen EC mixed Si (KB-EC 100wt% per Si) were prepared.

The surface morphology was characterized with scanning electron microscope (JSM-6700F, JEOL, Japan) and X-ray photoelectron spectroscope (XPS, JUSCO, Japan).

For the preparation of electrode, the prescribed amounts of three materials (CNF/Si composites, H-CNF mixed Si, KB mixed Si) were bound onto a copper foil with styrene–butadiene copolymer binder (SBR, trade name BM-400B, ZEON, Japan). Sodium carboxymethyl cellulose (CMC) was added as a thickening agent. [Yoshio 2006]. The coated electrode was dried at 105℃ for 12hrs in vacuum oven. The electrode carefully controlled for containing 85 wt% active material, 5 wt% CMC and 10 wt% SBR. Disc-typed electrodes were punched for the fabrication of coin type cell (CR2032) with the cathode of Li metal and the electrolyte of 1M $LiPF_6$/ (EC: DEC [vol% 1:1]) (UBE Chemicals, Japan).

Electrochemical measurement was performed using a constant current and constant voltage method (CC-CV) with the current density of 150mA/g (ch. cut-off 15mA/g) in the potential range of 0~1.5 V versus Li/Li^+ (Toscat-3100, Toyo-system, Japan).

Results and Discussion

Figure 1 showed the SEM image of CNF/Si composites, H-CNF mixed Si, and KB mixed Si. In the CNF/Si composite, some amounts of CNFs with small and large diameters were homogeneously grown on the Si particles. H-CNF mixed Si, and KB mixed Si showed well dispersed CNF and KB in the Si particles.

Figure 2 showed XPS analysis of Si element of as-received Si particle, of CNF/Si composites, H-CNF mixed Si, and KB mixed Si. As-received Si showed high intensity of about 99eV. In CNF/Si composite, the peak intensity of 99eV was illustrated in low intensity, which meant that CNFs covered the surface of Si.

Figure 3 showed charge-discharge profiles until 3 cycles. CNF/Si composite showed the largest discharge capacity of 1663mAh/g and the best cycle performance, even if cycle performance was not still complete. H-CNF mixed Si and KB mixed Si showed inferior capacities and cycle performances to CNF/Si composite. From such results, the synthesized CNFs on Si particles were effective to improve the cycle performance by the relief of volumetric expansion of Si active materials in the charge process. The electrode of CNF/Si composite showed very low expansion ratio less than 30% by SEM before and after charge process, illustrating the steric relaxation effect CNF in the electrode expansion. The optimization of the amounts and ratios of CNFs to Si is now in progress.

Table 1 summarized the discharge capacity and the 1st cycle columbic efficiency of CNF/Si composites, H-CNF mixed Si, and KB mixed Si. CNF/Si composite and H-CNF mixed Si have batter capacities (1663, 1630mAh/g) and columbic efficiency (72.5, 74.4%), respectively, compared to those of K/B mixed Si.

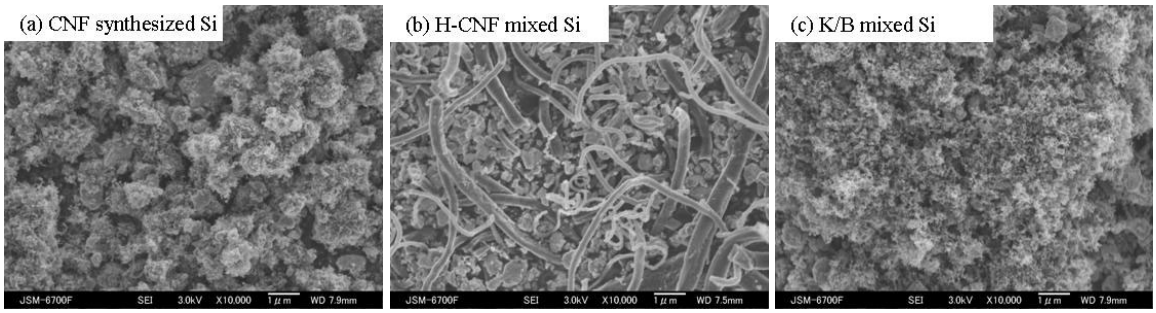


Figure 1. SEM images of a) CNF/Si composite, b) H-CNF mixed Si; c) K/B mixed Si, respectively.

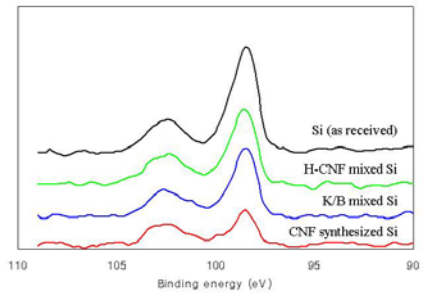
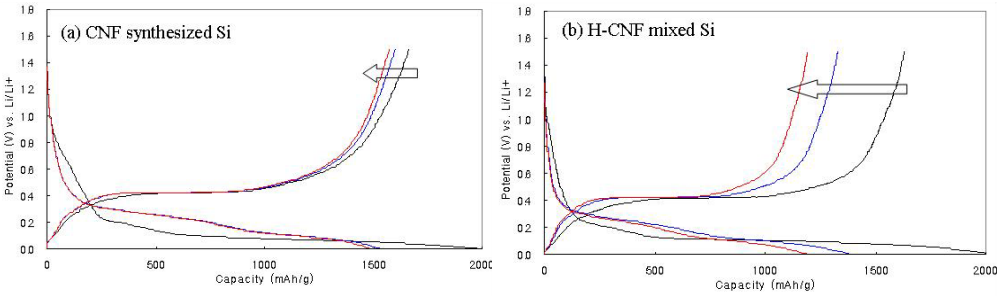


Figure 2. XPS analysis of Si element. a) Si(as received) b) CNF synthesized Si, c) H-CNF mixed Si, d) K/B mixed Si.



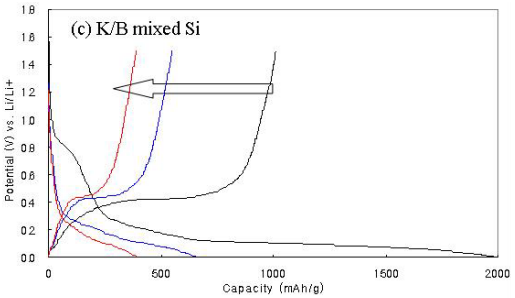


Figure 3. Charge-discharge profiles until 3 cycles. a) CNF synthesized Si, b) H-CNF mixed Si, c) K/B mixed Si.

Table 1. Electrochemical properties of 3 samples at the initial ch/dis. Cycle

Sample	Preparation conditions	Capacity (mAh/g)		Columbic efficiency (%)
		Charge	Discharge	
CNF synthesized Si	Synthesis at 500℃ for 10min. with C_2H_4/H_2. CNF synthesis 108% per Si weight.	2293	1663	72.5
H-CNF mixed Si	H-CNF mixture 100% per Si weight.	2190	1630	74.4
K/B mixed Si	K/B mixture 100% per Si weight.	2186	1013	46.4

Conclusions

Well balanced Si or Si containing powders and carbon nanofiber (CNF) composites can establish the relaxation spaces for relieving the expansion tension in charge process. In the prepared Si/CNF composites, small CNFs which cover the Si particle surface like ivy can afford the electric conductive path of Si powder, and large CNFs can do the conductive network with particle each other. 20~150wt% of well balanced CNFs growth on the Si particle showed large discharge capacity of 800~1700 mAh/g with much improved cycle performance. Optimization of CNF growth and structural analyses are now in progress.

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