PREPARATION OF SILICON/CARBON COMPOSITES ANODE MATERIALS FOR HIGH CAPACITY OF LITHIUM ION BATTERY

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Introduction

Having good cycle performance, carbonaceous materials are currently used as anode for most commercial lithium-ion batteries. However, the capacity of such materials is relatively low. On the other hand, in $Li_{4.4}Si$ alloy, silicon has high theoretical capacity of 4200 mAh/g, far greater than that of carbon. However, the alloying process is associated with 300 vol% expansion, pulverizing the brittle electrode and resulting poor cycle ability. The free volume of the carbon materials with low crystallinity can act as a buffer to the volume swelling of silicon in the silicon impregnated vitreous pitch-carbon. In this study, silicon/carbon composites were prepared as anode materials of high capacity Li-ion secondary battery and their electrochemical properties were investigated.

Experimental

Petroleum pitch (softening point: 250°C) and silicone particles (Johnson and Matthey Co., 50~100 nm diameter) were mixed by 3:1 weight ratio in THF (tetrahydrofuran, 99.0%) and then heat treated in a furnace at 800-1300°C. The prepared composite was mixed with graphite (45.5, 55.5 and 65.5 wt%) as active anode materials. The electrode slurry was prepared by mixing and stirring the active anode materials, AB (acetylene black), and PVDF (polyvinylidene fluoride) in the weigh ratios of 85.5 : 7.5 : 7 in NMP. The resultant slurries were spread on copper foil substrates and after coating, the electrodes were dried in vacuum at 100°C for 24 h. 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1 : 1 : 1 by volume ratio) was used as electrolyte. Electrochemical measurements were carried our in a three–electrode system in which lithium metal was used as both the counter and reference electrodes. The cells were assembled in an argon-filled glove-box. The cell performance was estimated under a constant current of 0.2 C, and a voltage from 0 to 1.2 V at 30°C. FIB (Focused Ion Beam) analysis was conducted to confirm the impregnation of silicon into the pitch carbon.

Results and Discussion

Fig. 1 shows the cycle performance of silicon/carbon composite with different heat treatment temperatures. After heat treatment at 800□, the initial discharge capacity of the sample was 650 mAh/g, but the capacity decreased significantly with the increase of cycles. With the increase of heat treatment temperature, the crystallization degree of the pitch carbon increased and enhanced the cycle stability. The stability of pitch carbon/silicon composites heat treated at 800□ turned out to be poor with the increased content from 20 to 40 wt%, although the high initial discharge capacity was obtained. It was considered that the some of anode active materials were separated form the current collector because of the particle damage due to silicone volume expansion. However, the sample heat treated at 1100□ showed good stability with increasing pitch/silicon composites from 20 to 40 wt%. Fig. 2 shows that silicone can be impregnated into pitch carbon at 800 and 1000□ and the pitch carbon has free volume. Table 1 shows that the sample heat treated at 800□ with 30 wt% pitch carbon/silicon composite had an initial capacity of 538 mAh/g and 391 mAh/g after 20 cycles. In the case of samples heat treated at 1000□, the initial capacity was 605 mAh/g, being the highest value in current conditions. The initial discharge capacity of the sample containing 40 wt% of pitch/silicon composite heat treated at 1100°C was 346 $mAhg^{-1}$ and remain the same value even after 20 cycles.

Conclusions

Silicon/carbon composites were prepared and heat treated at different temperatures. The composite was mixed with different contents of graphite as anode materials for lithium-ion battery. The initial discharge capacity was the higher under lower heat treatment temperatures but the capacity decreased with the increase of cycles. Through the heat treatment, silicon was impregnated into the pitch carbon and the free volume of the pitch carbon could lower the particle damage caused by the volume swelling of silicon. As the heat treatment temperature increased, the initial discharge capacity decreased but the cycling stability improved.

References

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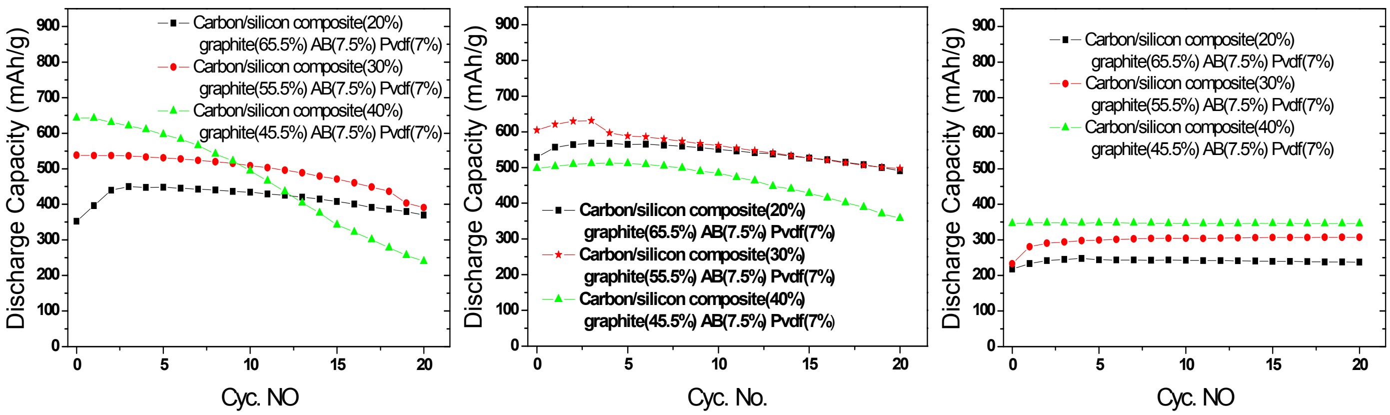
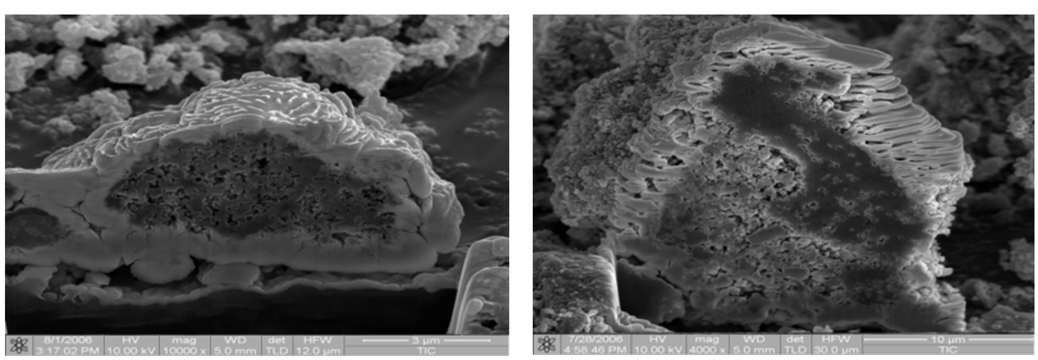


(a) (b) (c)

Fig. 1. Cycle performance of pitch carbon/silicon composites heat treated at (a) 800°C, (b) 1000°C, (c) 1100°C.

Table1. Discharge capacity and initial efficiency of pitch carbon/silicon composites

Temperature	Graphite (wt.%)	Pitch/silicon composite (wt.%)	Initial efficiency (%)	1st discharge capacity (mAh/g)	20st discharge capacity (mAh/g)
800°C	55.5	30	98	538	391
1000°C	55.5	30	78	605	500
1100°C	55.5	30	77	233	307
1100°C	45.5	40	97	346	346



(a) (b)

Fig. 2. FIB image of pitch/silicon composite at (a) 800°C and (b) 1000°C.