SYNTHESIS OF SI/C COMPOSITES WITH NANOCAVITIES AROUND SI NANOPARTICLES AND THEIR PERFORMANCE FOR LI INSERTION/EXTRACTION

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Introduction

Graphite has often been used as an anode material in commercial lithium ion batteries. Though graphite has the upper limit of the capacity, 372 mAh/g, further high capacity is required for recent mobile electrical devices, especially for electric vehicles. Silicon (Si) has attracted a great deal of interest as an alternative anode material from its very high theoretical capacity, 4200 mAh/g [1]. However, Si has several problems which should be solved as an anode material. First, Si has low electrical conductivity. Second, the lithium (Li) insertion rate into Si is not so high compared with the case of graphite. These problems significantly lower the rate performance of the battery. Third, the volume of Si expands up to 4 times when Li is inserted into Si. This drastic volume change can totally destroy the structure of the whole electrode, resulting in a quite poor cyclability. To overcome the first two problems, the size of Si should be reduced. So far, various kinds of nano-Si, such as a Si thin film [2], Si nanoparticles [3], and Si nanowires [4], have been prepared and exhibited better rate performances than bulk Si. And, for the third problem, it has recently been revealed that the introduction of buffer space around Si is effective to inhibit electrode destruction [3-5]. Until now, a morphological design of Si and its surrounding buffer space is still challenging.

Herein, we prepare silicon/carbon (Si/C) composites with a nanocavity around each Si nanoparticle according to a synthesis scheme shown in Fig. 1. Si/SiO_2 core-shell nanoparticles are embedded in a carbon matrix (Fig. 1a), which will play a role of conductive paths to Si nanoparticles. Then, SiO_2 shell is removed to obtain Si/C composite (Fig. 1b). The nanocavities allow the Si volume expansion during charging without the electrode destruction (Fig. 1c).
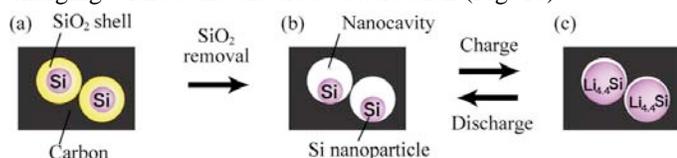
Fig. 1 A synthesis scheme of the Si/C composite and its structure change during charge-discharge cycling.

Experimental

The external surface of Si nanoparticles (Nanostructured & Amorphous Materials Inc., average diameter is ca. 50 nm) was oxidized by a calcination at 900 °C for 10, or 90 min in air flow to obtain Si/SiO_2 core-shell nanoparticles, which will be referred to as $Si/SiO_2(X)$ (X = oxidation time). It should be noted that the thickness of the surface SiO_2 shell can be continuously controlled simply by changing the oxidation time. The pristine nanoparticles, $Si/SiO_2(0)$, are also covered with a thin SiO_2 shell. The Si/SiO_2 nanoparticles were molded into a circular pellet (12 nm in diameter, 1mm in thickness) by pressing them at 700 MPa for 1 h. An excess amount of polyvinylchloride (PVC) was put on the pellet, and they were heat-treated in N_2 flow at 300 °C for 2 h. During this step, PVC turned to liquid pitch and it infiltrated into the interparticle cavities in the pellet. Then, a further heat-treatment was conducted at 900 °C for 1 h to carbonize the pitch. The resulting composite was washed with 0.5 wt% hydrofluoric acid for 90 min to remove the SiO_2 shells, and then an annealing was accomplished at 900 °C for 1 h in N_2 flow. The Si/C composites thus obtained will be referred to as $Si/C(X)$ (X corresponds to those in their parent $Si/SiO_2(X)$).

The structures of the samples were observed by a transmission electron microscope (TEM: JEOL, JEM−2010). The amounts of Si in $Si/SiO_2(X)$ and $Si/C(X)$ were estimated from the whole weight change of these samples during their calcination at 1400 °C for 2 h by using a thermogravimetry analyzer (Shimadzu, TGA-55H). Upon the calcination, all of the carbonaceous matter is burnt and all of Si can be oxidized into SiO_2.

The performance of the Si/C composites for Li insertion/extraction was examined with a three-electrode cell at 25 °C in 1 M $LiPF_6$ electrolyte solution (Tomiyama, EC:DEC=1:1 in weight ratio). A working electrode was prepared by mixing Si/C composite and polyvinylidene fluoride in the weight ratio of 8 : 2. As counter and reference electrodes, lithium foils were used. The working electrode was charged (Li insertion) and discharged (Li extraction) at a constant current of 200 mA/g between 0.01 and 1.5 V by using a galvanostat (Hokuto Denko Co., HJ1001SM8A).

Results and Discussion

Fig. 2 shows TEM images of the Si/SiO_2 core-shell nanoparticles and the corresponding Si/C composites. As is found from Fig. 2a, the pristine Si nanoparticles ($Si/SiO_2(0)$) already have thin (ca. 6 nm) SiO_2 shells on their surfaces. On the other hand, $Si/SiO_2(90)$ has a thicker but uniform shell (ca. 11 nm, in Fig. 2b), indicating that the simple air oxidation allows the uniform growth of the SiO_2 shell. Fig. 2c and d show TEM images of Si/C(0) and Si/C(90), which were synthesized from $Si/SiO_2(0)$ and $Si/SiO_2(90)$, respectively. The size of the nanocavities in each of the two Si/C composite well agrees with the size of the SiO_2 shells in the corresponding Si/SiO_2 core-shell nanoparticles. From the Si amount in the Si/SiO_2 core-shell nanoparticles, a volume ratio of $(Si + SiO_2)/Si$ can be calculated (Table 1), and this ratio can be regarded to be equal to a (Si + nanocavity)/Si volume ratio in the corresponding Si/C composite. If this value is 4, it means that the nanocavity around each Si particle is large enough for the Si volume expansion. It is clearly found that the $(Si + SiO_2)/Si$ volume ratio can be increased with

increasing the oxidation time of Si nanoparticles, and is over 4 in Si/C(90) (Table 1). The longer oxidation time, however, decreases the Si amount, resulting in the decrease of the theoretically maximum capacity which is estimated by assuming the capacities of Si and C to be 4200 and 372 mAh/g, respectively (Table 1). Though Si/C(90) contains only 23 wt% of Si, its theoretical capacity (1250 mAh/g) is still much higher than the graphite (372 mAh/g).
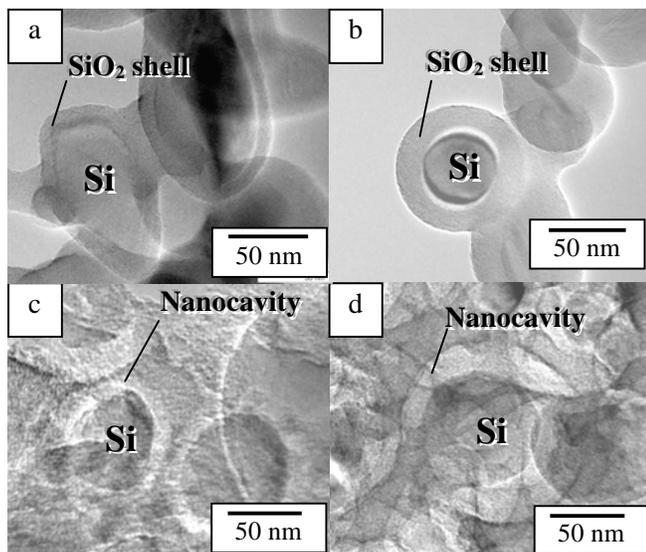
Fig. 2 TEM images of Si/SiO$_2$ core-shell nanoparticles (a, b) and Si/C composites (c, d); a) Si/SiO$_2$(0), b) Si/SiO$_2$(90), c) Si/C(0), d) Si/C(90).

Table 1. The volume ratio of (Si + SiO$_2$)/Si in Si/SiO$_2$(X), Si amounts in the Si/C composites, and theoretical capacities of the composites.

Sample	(Si + SiO$_2$)/Si volume ratio[a]	Si amount (wt %)	Theoretical capacity (mAh/g)
Si/C(0)	1.96	47	2170
Si/C(10)	2.20	37	1790
Si/C(90)	4.80	23	1250

[a] The value in the corresponding Si/SiO$_2$(X).

In order to evaluate the charge-discharge capacity derived only from Si, the capacity of C was experimentally determined by using the carbon sample prepared from PVC through the same heat-treatment process but without Si/SiO$_2$ nanoparticles and the capacity of Si was calculated by subtracting the contribution of C from the total capacity of the Si/C composite (an inset of Fig. 3). Fig. 3 shows the change of such capacities of Si in the Si/C composites with cycle numbers. In Si/C(0), the composite which has a small nanocavity size, the capacity rapidly decreases to 0 within 8 cycles. But in Si/C(10), which has a larger cavity size than Si/C(0), the cyclability is slightly improved. And, Si/C(90) shows significantly better cyclability than the others. Thus, Fig. 3 clearly indicates that enough large cavity size is crucial to achieve a better cyclability of Si. The 1st discharge capacity of Si in Si/C(90) is as high as 2520 mAh/g-Si, which is 60 % of the theoretical capacity of Si, and even at the 20th cycle, it still retains 1310 mAh/g-Si. However, the 1st discharge capacity of the whole Si/C(90) composite is not so outstanding (756 mAh/g, an inset of Fig. 3), due to its low Si content (Table 1). In order to increase the total capacity of the Si/C composite, it is necessary to further increase the Si content.
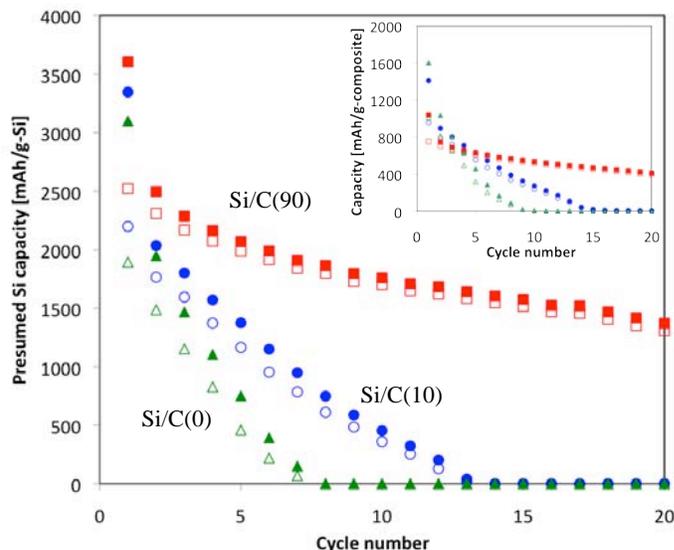
Fig. 3 The change of the charge-discharge capacities of Si with cycle numbers, together with the total capacity of the Si/C composite (inset). Solid and open symbols mean charge and discharge capacities, respectively.

Conclusions

Si/C composites with nanocavities around Si nanoparticles were synthesized. The nanocavity size can be tuned precisely by simply changing an oxidation time of the precursor Si nanoparticles. With increasing the nanocavity size, Si showed higher capacity and longer cycle life.

References
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