

PREPARATION OF NANOSILICON/CARBON COMPOSITES VIA AN ELECTROCHEMICAL REDUCTION OF NANO-SIZED SILICA EMBEDDED IN CARBON MATRICES

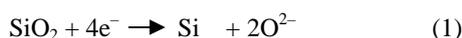
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Introduction

As a new class of an ultra-high capacity anode material for Li-ion batteries, nano-Si/carbon composites have a considerable potential [1, 2]. In such composites, nano-Si can store lithium faster than bulk Si, and the carbon matrix serves nano-Si with an electrical path to compensate the poor electrical conductivity of Si. Though Si has an extremely high theoretical capacitance up to 4200 mAh/g, its cyclability is quite poor due to the significant volume expansion upon the Li insertion into Si. To overcome this problem, the introduction of an appropriate buffer space around Si is very effective [1, 2]. For the preparation of nano-Si/carbon composites, various methods have been proposed so far, e.g., a mechanical mixing of nano-Si and carbonaceous matrices [3], a formation of carbon around nano-Si [4, 5], silane-CVD onto the carbon [6], and a template assisted synthesis [1].

Herein, we present a new synthesis pathway of nano-Si/carbon composites with the buffer nanospace around nano-Si via an electrochemical reduction of nano sized SiO₂ embedded in a carbon matrix, according to the synthesis scheme shown in Fig. 1. A nano-SiO₂/carbon composite (Fig. 1a) is used as a starting material. The composite was immersed into a molten CaCl₂ and then electrochemically reduced. During this step, SiO₂ is reduced into Si at a three-phase interface of SiO₂ (reactant), carbon (electron path), and molten CaCl₂ (solvent for a product, O²⁻), according to the following equation [8];



Upon the reduction of SiO₂ into Si, its volume is decreased to 40%, and a cavity is formed around Si as a result. The molten CaCl₂ can be impregnated into the cavity, and the reduction can continuously proceed (Fig. 1b). After finishing the reduction and a removal of CaCl₂, the nano-Si/carbon composite is obtained.

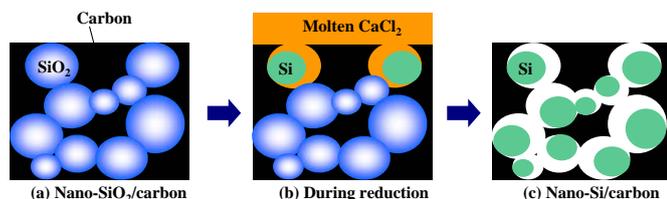


Fig. 1 Synthesis scheme of nanosilicon/carbon composite through an electrochemical reduction in molten CaCl₂.

Experimental

The nano-SiO₂/carbon composite (Fig. 1a) was synthesized based on a sol-gel method by using tetraethoxysilane and furfuryl alcohol as silica and carbon sources, respectively [7]. Carbonization temperature was 900 °C and the obtained nano-SiO₂/carbon composite contain ca. 53 wt% of SiO₂. Generally, sol-gel synthesized SiO₂ comprises a network of SiO₂-nanoparticles as is shown in Fig. 1a, and the size of SiO₂-nanoparticles can be precisely controlled by the synthesis conditions. In the present nano-SiO₂/carbon composite, the SiO₂ framework size was set to approximately 3.2 nm. The composite is a plate-shape of 20 x 10 x 1 mm. The composite plate was wound with a Mo wire and then immersed into a molten CaCl₂ (850 °C) together with a counter electrode (graphite) and a reference one (Ag/Ag⁺). All the electrochemical experiments were done inside a glove box filled with Ar gas. The reference electrode was calibrated by Ca²⁺/Ca potential before every electrochemical experiment. First, a cyclic voltammetry experiment was conducted in the potential range of 0.2 to 1.9 V (vs. Ca²⁺/Ca) to analyze the electrochemical response of the composite plate. Electrochemical reduction was done at a constant potential of 0.3 or 1.0 V (vs. Ca²⁺/Ca) for 1 h. After taking out the composite plate from the molten CaCl₂, it was washed with pure water and ethanol.

The samples were analyzed with X-ray diffraction (XRD) and a transmission electron microscope (TEM).

Results and Discussion

Fig. 2 shows a cyclic voltammogram of the nano-SiO₂/carbon composite plate. In the molten CaCl₂ at 850 °C, SiO₂ is reduced into Si according to the equation (1) below 1.1 V (vs. Ca²⁺/Ca), and a following reaction also occurs below 0.53 V [8];



In Fig. 2, the cathodic current slightly increased below 1.1 V, and further increased below 0.8 V. Since carbon is not electrochemically reduced in the potential range of the voltammogram, the cathodic current can be ascribed to the

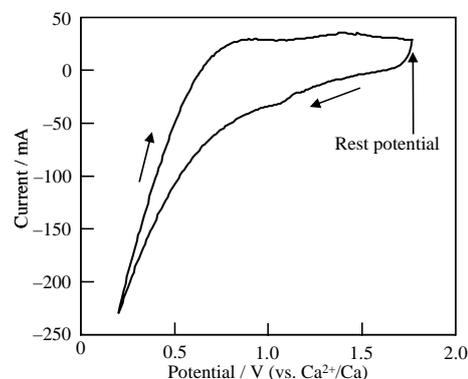


Fig. 2 Cyclic voltammogram of SiO₂/carbon nanocomposite measured at 850 °C in molten CaCl₂. Scan rate is 0.02 V/s.

reduction of the nano-SiO₂ in the composite.

We then carried out the constant reduction of the composite plate at 0.3 and 1.0 V. Assuming that all current was used for the equation (1), we calculated the reduction ratio of SiO₂ (reduced SiO₂ / SiO₂ in the original composite) to be 86% and 9% for the cases of 0.3 V and 1.0 V, respectively.

Fig. 3 shows XRD patterns of the nano-SiO₂/carbon composite before and after the electrochemical reduction. The pristine composite (Fig. 3a) shows two broad peaks at $2\theta = 23^\circ$ and 43° . The former corresponds to a synthetic peak of amorphous SiO₂ ($2\theta = 22^\circ$) and carbon (002) ($2\theta = 26^\circ$). The latter peak corresponds to carbon (10). The XRD pattern of the reduced composite at 1.0 V (Fig. 3b) is almost the same as that of the pristine sample, indicating that SiO₂ was rarely reduced. On the other hand, the sample reduced at 0.3 V (Fig. 3c) shows a much different XRD pattern. The peak at $2\theta = 23^\circ$ becomes very small. This is a direct evidence of the SiO₂ reduction. When a pure SiO₂ is reduced in the molten CaCl₂ at 0.3 V, CaSi₂ is formed by the reaction (2) [8], but in Fig. 3c,

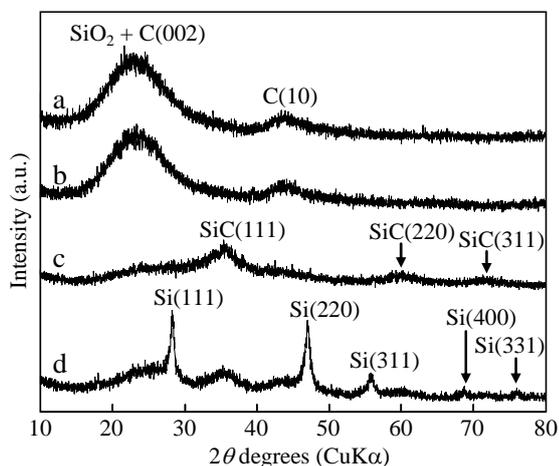


Fig. 3 XRD patterns of (a) nano-SiO₂/carbon composite before reduction, (b) the sample reduced at 1.0 V, (c) the sample reduced at 0.3 V, and (d) the sample reduced at 0.3 V and then washed with HF.

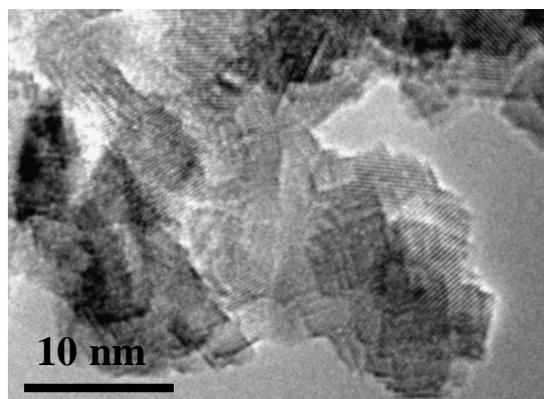


Fig. 4 A TEM image of the sample reduced at 0.3 V and then washed with HF.

the peaks of CaSi₂ cannot be observed. Instead, SiC peaks were observed. In the case of the reduction at 1.0 V (Fig. 3b), SiC was not formed. This result means that SiC cannot be formed simply by immersing the nano-SiO₂/carbon composite into the molten CaCl₂ at 850 °C, and therefore, it is clear that the SiC formation is due to the electrochemical reduction at 0.3 V. Interestingly, after a HF washing of the sample that was reduced at 0.3 V to remove unreacted SiO₂, intense Si peaks appeared (Fig. 3d). A TEM image of this sample was shown in Fig. 4. There are a lot of nano-crystals with the size of less than 10 nm, which can be ascribed to Si and SiC. We are now trying to understand the reason for the Si formation by the HF washing. And, the obtained Si/carbon composite is now undergoing the performance examination as an anode of the lithium ion-battery.

Conclusions

A nano-SiO₂/carbon composite which has bicontinuous nanostructure was prepared through a sol-gel method. Then, the silica embedded in the carbon matrix was electrochemically reduced in molten CaCl₂ at 850 °C. Though SiO₂ was not so much reduced at 1.0 V (vs. Ca²⁺/Ca), it was reduced at 0.3 V and formed SiC. And, after HF washing of the composite reduced at 0.3 V, very intense Si peaks were appeared in its XRD pattern. From TEM observation, the particle sizes of the formed Si were found to be less than 10 nm.

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