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CREATION OF NANO- AND MICRO- SPACES IN CARBONS AND LORDING DISSIMILAR MATERIALS BY ELECTROSPINNING

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Introduction

This study aims to create functional carbon materials with controlled micro space by electrospinning, and to develop the electrode development for high-performance electric storage devices.

With the popularization of mobile devices, household appliances, hybrid vehicles, electric vehicles, and the like, the use of power storage devices is expanding, and further performance improvements are required. Its performance is dependent on the capacity of the electrode. Particulate graphite has been used for the anode materials of currently widely used lithium-ion rechargeable batteries (LIBs), but the battery characteristics close to the theoretical capacity (372 mAh/g) have been realized previously, and the capacity enhancement of LIBs has come to the forefront. Therefore, the study of new anode materials is essential to achieve further high performance of storage devices. There is silicon (Si) with a theoretical capacity of 4200 mAh/g as an anode material to replace graphite, but there are many challenges for practical applications, such as the destruction of Si structures due to the large volume expansion rate (300-400%) upon the intercalation of Li ions[1]. Therefore, in this study, a novel electrode material was developed, and charge/discharge characteristics were investigated by compositing Si with carbon nanofibers derived from polyacrylonitrile (PAN).

It has the advantage of obtaining a single nonwoven fabric with a large surface area because thin nanofibers in complex entanglement with each other by electrospinning[2]. The bulk density of nonwoven fabrics composed of nanofibers is small, and about more than 90 vol.% of them are occupied by space[3,4]. Mixing and electrospinning PAN with Si particles and the like to fabricate functional porous carbon materials with micro pore and meso pore connected multidimensional structure leads to the development of next generation energy devices. The development of the adsorption material of the new environmental pollutant which contributes to the environmental conservation can be expected, if the fine space can be finely controlled.

Materials and Methods

The addition of citric acid to Si micro particles milled to a particle size of about 100 nm in alcohol on a planetary ball milling, followed by carbonization treatment at about 1000°C, affords a material with carbon coating on the Si surface[5]. Coating with carbon is to prevent performance degradation due to oxidation of Si micro particles with increased specific surface area. Carbon-

coated silicon particles were fabricated in which this material was fine-grained with agate mortar. Scanning-electron microscopy (SEM) images of Si particles are shown in **Figure 1**.

Solutions of solvents N,N-dimethylformamide (DMF, $(CH_3)_2NCHO$) mixed with PAN, and Si particles were used for electrospinning. The ratio of PAN to Si particles is 2: 1 by weight. Electrospinning was used in anticipation of the preparation of porous materials by mixing different materials and the nanoscale effect. That is, nanospaces are created by the binding of heteromorphic molecules in which different substances are combined at the molecular size level. Voltage from 20 to 30 kV was applied between the nozzle and the collector for electrospinning. Ultrasonic vibration was also applied to the needle tip, which is the nozzle of electrospinning, to forcibly mix the materials during spinning as shown **Figure 2**. The texture and structure of the nanofibers were observed and analysed by SEM and transmission electron microscopy (TEM) combined with image processing[6].

In order to stabilize the nanofibers produced by electrospinning, they were heat-treated at 280°C in the air. Carbon nanofibers (CNF's) were made from them by heat-treatment at 700 to 1000°C in the nitrogen atmosphere. The prepared sample and polyimide (PI) and N-methyl-2-pyrrolidone (NMP) were kneaded, coated on a copper foil, and fired to prepare an electrode material[7].

The anode was formed of this material and was stored in a coin cell with lithium foil as a counter electrode Then charge and discharge experiments of anode of LIB were carried out.

Results and Discussion

SEM image of Si loaded CNFs prepared by electro spinning with ultrasonication is shown in **Figure 3**. Si particles larger than the nanofiber

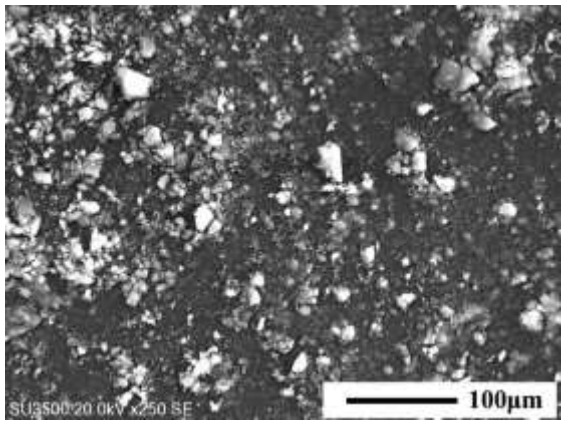

Figure 1. SEM image of carbon coated Si particles

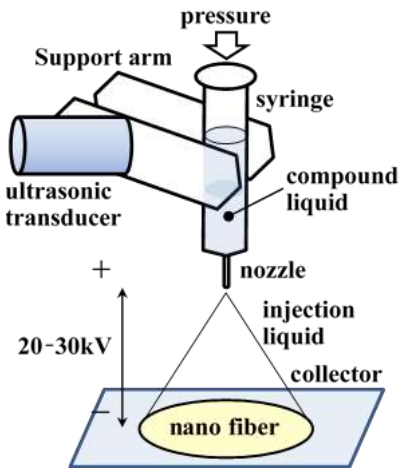

Figure 2. Electrospinning with ultrasonic vibration

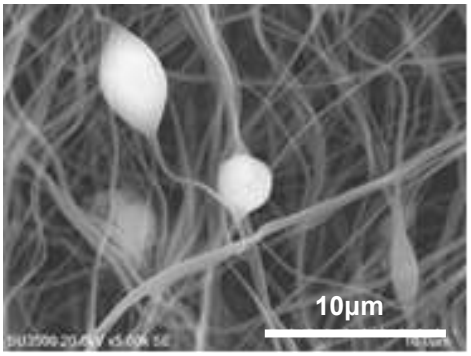

Figure 3. SEM image of CNFs prepared by electro spinning using the ultrasonic transducer

diameter can be efficiently incorporated into the nanofibers by electro spinning using the ultrasonic transducer. TEM image of the CNF containing Si particles is shown in **Figure 4**. Silicon crystals less than 5 nm are observed in the CNF.

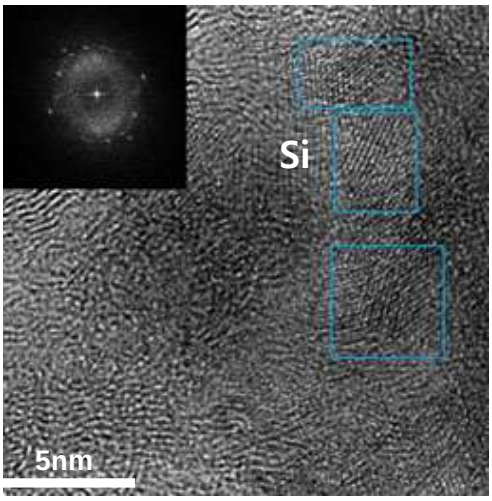

Figure 4. TEM image of the CNF containing Si crystals

Figure 5 shows the charge/discharge results of composite material of PAN and Si particles for the LIB anode. In the second cycle, a discharge capacity at 500 mAh / g was obtained, which was 1.3 times the theoretical capacity using graphite. Although the decrease in capacity from the second cycle to the fifth cycle was small, the capacity decreased to the same level as the theoretical capacity of graphite near 15 cycles. It is considered that electrode breakage occurs, such as Si particles on the CNF surface exfoliate from the fiber due to the volume change. The capacity at the first cycle charge reached 900 mAh/g, resulting in large irreversible capacity. It may be because the energy was used to form organic film (called solid electrolyte interface (SEI)) on the electrode surface.

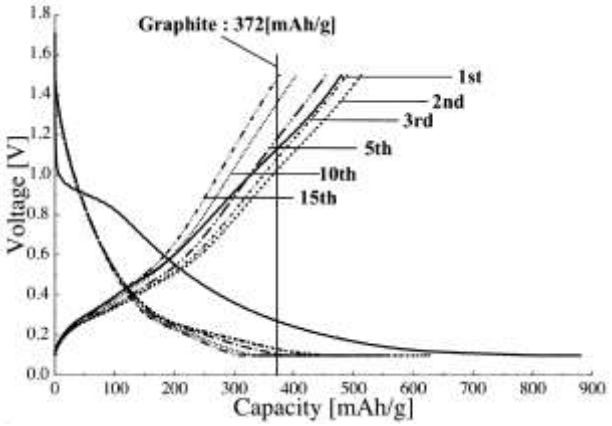

Figure 5. Charge-discharge characteristics of LIB negative electrode material

Conclusions

Nano spaces were created in the CNFs and Si particles were able to be contained in the CNFs. Not only large Si particles but also small Si particles were found to contain CNT. In the future, we would like to increase the proportion of Si particles and enhance their effects. In order to put the LIB using the present anode material into practical use, it is necessary to suppress the irreversible capacity at the first cycle.

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