



# Silicon/soft-carbon nanohybrid material with low expansion for high capacity and long cycle life lithium-ion battery



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## HIGHLIGHTS

- We developed a new material exhibiting a long cycle life with a high anode capacity.
- Volume expansion of the electrode was 6.9% at an anode capacity level of 1100 mAh/g.
- The electrode material retained 80.9% of its capacity at 250 cycles in a full cell.

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## ABSTRACT

The present study aims at developing a silicon/soft-carbon nanohybrid material for high performance lithium-ion battery (LIB). It is composed of micronized silicon coated with so-called “soft-carbon” dispersed in soft-carbon matrix at nanometer level. This material is characterized with abundant nanosized voids with diameter of ca. 70 nm and hard bulk skeletal structure. It exhibited a long cycle life of 163 charging and discharging cycles with a large capacity of 850 mAh/g and retention rate up to 90% of the initial capacity in a half cell with Li-metal counter electrode. For this new material, the volume expansion ratio was 6.9% at a capacity level of 1100 mAh/g. This electrode capacity is approximately three times larger than that of graphite-based electrode currently used in LIB. Furthermore, this electrode retained 80.9% of its capacity at 250 cycles in a full cell with a LiCoO<sub>2</sub> counter electrode. Addition of 5 wt % fluoroethylene carbonate (FEC) to the electrolyte improved the retention up to 81.3% after 300 cycles. These results demonstrate the usefulness and high possibility of this material as the negative electrode of LIB.

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## 1. Introduction

Potential problems associated with natural resources including their depletion and increasing cost and challenges, such as global warming due to the increase in carbon dioxide generated by the combustion of natural resources, have become pronounced in recent years. This has accelerated the expansion of markets for environmentally friendly vehicles such as hybrid electric vehicles, plug-in hybrid electric vehicles, and fuel-cell vehicles. In particular, vehicles are highly anticipated owing to their environmental advantages stemming from their lack of carbon dioxide emissions; however, their actual ranges are still low compared to those of

gasoline-powered cars, and the advanced batteries with high energy densities as the power sources of such vehicles are strongly desired to increase their range. In this context, solid-state and metal-air batteries have become increasingly active research and development areas; however, their practical use has not yet been realized.

In this study, we focused on silicon-based electrode materials for lithium-ion battery (LIB); theoretical capacity is approximately 10 times greater than that of graphite electrode of LIB. Hitachi Maxell commercialized SiO negative electrode which is composed of major component of graphite and SiO additives. Panasonic preliminarily released large capacity battery (4.0 Ah) with Si-based negative electrode, but not yet commercialized. Thus, no practical application of LIB, taking advantage of large capacity of Si, has been performed. The greatest challenges that obstruct the practical use of silicon-based materials for LIB is their short cycle life that arises

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from the alloying of silicon and lithium during their charging and discharging processes and the change in their big volume through large expansion and contraction during the repeated desorption of lithium from the alloy. In previous studies, these effects have been well documented to adversely affect the cycle life of LIB. In addition, vehicles require batteries that span the vehicles' expected lifetime of as long as 15 years, which is similar to that of the automobiles based on gasoline internal-combustion engine.

Numerous studies to overcome this lifetime problem have already been conducted, including some reports that a longer battery lifetime can be achieved by lowering the absolute value of the volume change that occurs when silicon and lithium are alloyed; in these cases, longer lifetimes were achieved through the fabrication of thinned silicon electrodes [1–3] and micronization of the silicon [4,5]. However, the thin-film method has several shortcomings in terms of production costs that hinder its industrial development; specifically, the required manufacturing equipment is expensive, and its production speed is low compared to that of the method of applying an electrode paste, which is commonly practiced to produce LIB. Furthermore, micronized silicon forms SiO<sub>2</sub> via oxidation by oxygen when handled in ordinary atmosphere, which results in increased irreversible capacity during the initial charging of LIB prepared using this method. A large number of studies have been conducted on the conjugation of silicon and graphite [6–21]; however, uniform silicon–graphite composites are difficult to prepare, while the amount of added silicon is difficult to increase.

This study developed a new nanohybrid material, composed of carbon coated micronized silicon dispersed in soft-carbon matrix. It exhibited a long cycle life and suppressed the electrode expansion. These behaviors were discussed in connection with abundant nanovoids (diameter of ca. 70 nm) and hard bulk skeletal structure.

## 2. Experimental method

### 2.1. Synthesis of silicon/soft-carbon nanohybrid material

Slurry of silicon/ethanol containing 10 wt% silicon was prepared using commercially available single-crystalline silicon (manufactured by Kojundo Chemical Laboratory Co., Ltd., 75- $\mu$ m mesh, 99% purity) and ethanol. The mixture was milled with  $\Phi$ 0.2-mm zirconia balls in an SC10 wet bead mill (Nippon Coke and Engineering Co., Ltd.) for 5 h and then with  $\Phi$ 0.05-mm zirconia balls for 18 h [22]. The milled mixture was combined with citric acid and silicon in the ratio of 16.7:83.3–66.7:33.3 wt%. It was then transferred to an electric furnace for calcination under flowing argon (flow rate: 500 cm<sup>3</sup>/min) to obtain carbon-coated silicon granules. The carbonization/calcination procedure consisted of preserving and drying the sample at 60 °C for 1 h to remove ethanol, heating it at 500–900 °C for 4 h, and then left it to cool to room temperature.

The resulting carbon-coated silicon was mixed with poly-vinyl chloride (PVC, Sigma-Aldrich Corp., Cat. No. 189588), the soft-carbon precursor, in an agate mortar. It was set in an electric furnace for calcination under flowing argon (flow rate: 500 cm<sup>3</sup>/min). The calcination procedure consisted of heating the sample to a predetermined temperature at a heating rate of 5 °C/min, holding the sample at 600 °C for 1 h, and then allowing it to cool naturally. The sample was milled using an agate mortar or a planetary ball mill (P-7 type, Fritsch Co., Ltd.) after calcination.

### 2.2. Characterization of materials

The cross-sectional structure of the materials was observed using scanning transmission electron microscope (Hitachi High-Technologies Corp.) and HD-2700 field-emission scanning

transmission electron microscope (Hitachi High-Technologies Corp.). The carbonization yield of the carbon precursor was determined by TG-DTA analysis (Rigaku TG8120). The structure of the nanohybrid material was determined using Raman microscope (Renishaw) and X-ray diffractometer (Rigaku RINT 2200 V/PCSV). The particle size was determined using laser diffraction particle size analyzer (Horiba LA950). The surface area and the pore size distribution were determined by N<sub>2</sub>-adsorption/desorption analysis at 77 K (ASAP2020, Micrometrics Co.).

### 2.3. Electrochemical characterization

For the electrochemical measurements of the carbon-coated silicon and the carbon-coated silicon/soft-carbon nanohybrid material, they were settled on the copper foil according to the following procedures. The carbon-coated silicon, graphite (Hitachi Chemical, Co., MAG) and polyimide (varnish A, Ube Industries, Ltd.) were mixed in a ratio of 40:45:15 wt%, and the viscosity was controlled to a proper value using *N*-methylpyrrolidone. They were coated on a 35- $\mu$ m electro-deposited copper foil by the doctor blade method. The electrode was pressed using a roll press device and the loading level was adjusted to be 2.5–2.8 mg/cm<sup>2</sup>. The carbon-coated silicon/soft-carbon nanohybrid material was prepared by mixing the silicon/soft-carbon nanohybrid, carbon black, and polyimide (varnish A) in the ratio of 75:10:15 wt% and heating it according to the same manner as noted above.

For electrochemical test sample was cut into a  $\Phi$ 1.4-cm disc and drying it for 24 h in a vacuum at 100 °C. It was then transferred to an argon glove box to prepare a 2032-type coin battery by adding 0.1 cm<sup>3</sup> of 1 M LiPF<sub>6</sub> in an ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol %) mixture. The cell was assembled with a polyethylene microporous membrane separator and metal lithium foil or LiCoO<sub>2</sub> counter electrode. For the half-cell experiments, the constant current and constant voltage (CCCV) charging and discharging was performed within the range of 0.02 (0.10) to 1.5 V at rates of 0.05 C for the first and second cycles, 0.2 C for the third cycle, and 0.5 C for the fourth and subsequent cycles. For the full-cell experiments, the CCCV charging and discharging was conducted within the range of 4.0 to 3.0 V at rates of 0.05 C for the first/second cycles, 0.2 C for the third cycle, and 0.5 C for the fourth and subsequent cycles.

## 3. Results and discussion

### 3.1. Carbon-coated silicon fine particle

The carbon-coated silicon fine particle used in the present investigation was prepared using a wet mill. Silicon precursor with mean particle size of 25  $\mu$ m was milled to fine particles with the mean diameter of ca. 100 nm. The SEM image of silicon fine particle is shown in Fig. 1(a). The particles have rod-like shape. Several papers claimed that the cycle performance increased with flaky silicon because of the decrease of the absolute value of the electrode expansion [23–25]. Similar effect is expected for the present materials. In addition, the size of the silicon flakes of the present material is in the order of several tenth nm. This is smaller than usually reported value, order of micron [14,22]; it should be effective for the depression of the electrode expansion. The XRD parameters of pristine and milled silicon particles are shown in Table 1 with the data of BET surface area (Fig. S1). The full width at half maxima (FWHM) increased from 0.129° to 0.612° due to the milling. It means that crystallite size changed from 798.7 nm to 13.7 nm from the Debye-Scherrer equation. These data suggested a possibility of depressing the expansion in the alloying reaction. The SEM image and EDX of carbon-coated Si/soft carbon nanohybrid are

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