

Preparation of Silicon Nanoparticles by Pyrolysis of Organosilicon Compounds inside the Porous Carbon

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How to cite this paper: Ota, M., Arai, K., Kuribara, A., Deguchi, Y. and Onozuka, K. (2020) Preparation of Silicon Nanoparticles inside the Porous Carbon. *Journal of Materials Science and Chemical Engineering*, 8, 1-6.

<https://doi.org/10.4236/msce.2020.82001>

Received: December 8, 2019

Accepted: January 13, 2020

Published: January 16, 2020

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Abstract

To increase the capacity of the negative electrode for lithium-ion secondary batteries, we prepared Si-containing carbon microspheres. The target compound was obtained by thermal decomposition of hexaphenyldisilane embedded in porous carbon particles that contained Si-nanoparticles characterized by various methods. When charging/discharging characteristics were evaluated using a cell having the obtained material as a negative electrode, a remarkable improvement in charging characteristics was observed.

Keywords

Lithium-Ion Secondary-Battery, Silicon Nanoparticles, Si-Containing Porous Carbon

1. Introduction

Negative electrodes with high energy densities are required for developing next generation energy-storage materials. Lithiation of silicon, aluminum, and stannum gives rise to large specific capacities: for instance, $\text{Li}_{22}\text{Si}_5$: 4200 mAh/g, AlLi : 993 mAh/g and $\text{Li}_{22}\text{Sn}_5$: 994 mAh/g [1]-[10]. Although these compounds have large specific capacities, they also have shortages. For example, negative electrodes made of silicon exhibited large volume changes when lithium ions were adsorbed. Volume expansion of more than 200% - 400% of the pristine silicon resulted in pulverization because of accumulated mechanical strain inside the crystal after repeated expansion and contraction [4] [5] [8] [9] [11]. Besides, silicon has been known for semiconducting nature. These properties caused the decrease in the rate and cycle characteristics. Previously, we have reported that

silicon nanoparticle-containing porous carbon microspheres improved the cycle characteristics and specific discharged capacity [12]. However, average particle diameter of silicon nanoparticles was around 50 nm and as a result the effective rate of silicon to lithium exchange was not improved. Therefore, the aim of the present research is to prepare silicon nanoparticles with more or less 20 nm in diameter using pyrolysis of organosilicon compounds inside the porous carbon. Electrochemical properties such as charge-discharge behavior, cyclic characteristics will be described in this report.

2. Experimental

2.1. Preparation of Porous Carbon

Phenolic resin (1.5 g) spheres were swollen in a mixture of sulfuric acid and nitric acid for 12 h at 80°C. Then, the mixed acid solution was added to 300 mL of water cooled in an ice bath, and the solution was stirred until sulfuric acid was homogeneously dissolved. After the exothermic heat dissipated, the aqueous solution was centrifuged (3000 rpm, 10 min), and the precipitates were collected. Porous carbon was prepared through a rapid pyrolysis of the precipitates at 1000°C.

2.2. Preparation of Si-Containing Porous Carbon

Hexaphenyldisilane was dissolved in 30 mL of THF, followed by the addition of 200 mg of porous carbon and stirring for 12 h. Then, THF was removed by heating under a reduced pressure. Thermal decomposition of the mixture was performed under N₂ at 500°C.

2.3. Characterization of Si-Containing Porous Carbon

The composition and structural analyses of silicon in the porous carbon particles were performed using a transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and X-ray diffractometry (XRD). Si-containing porous carbon was mixed with carbon black as a conductive additive, styrene-butadiene rubber as a binder, and carboxymethyl cellulose as a thickener in a mixing ratio of sample:conductive additive:(binder + thickener) = 8:1:1, dispersed on a copper foil. Using this electrode a coin cell was constructed with 1 mol/l LiBF₄/ED + DEC (1/1, v/v) as the electrolyte and Li foil as the counter electrode, and charge/discharge measurement was performed. Measurements were done at a current density of 100 mA/g and a potential range of 0.01 - 2 V (vs. Li/Li⁺).

3. Results and Discussion

3.1. TEM Images of Si-Containing Porous Carbon

Figure 1 shows the TEM images of Si-containing porous carbon: (a) Si-containing porous carbon, (b) magnified image of (a), (c) a single nanoparticle.

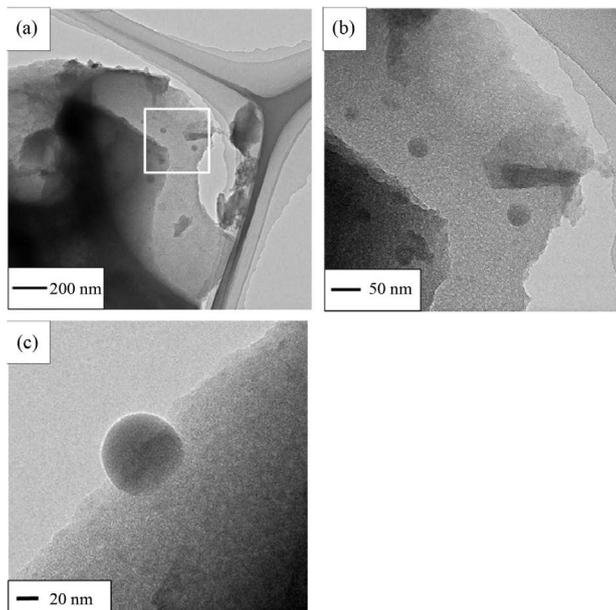


Figure 1. TEM images of Si-containing porous carbon: (a) Si-containing porous carbon, (b) magnified image of a rectangular area in the image (a), (c) nanoparticle.

TEM images of Si-containing porous carbon particle in **Figure 1** show the formation of Si nanoparticles with less than 30 nm in diameter inside the porous carbon microparticle.

3.2. EDX Measurement of Nanoparticle inside Porous Carbon

Figure 2 shows EDX patterns and contents of a nanoparticle.

The EDX pattern of the nanoparticle showed that the elemental composition of Si/C = 0.06, O/Si = 0.36, and O/C = 0.02. The result suggests that Si nanoparticle was possibly formed.

3.3. XRD Measurement

Figure 3 shows XRD patterns of (a) porous carbon and (b) Si-containing porous carbon.

Porous carbon (a) showed a broad diffraction band reminiscent of non-graphitizable carbon.

Si-containing porous carbon (b) showed a pattern similar to that of porous carbon.

No peaks assignable to Si or SiC were observed.

It is likely that this particle is made of amorphous carbon because of absence of crystalline peaks.

3.4. Characterization of Charge/Discharge Behavior of Coin-Type Secondary Battery Assembled with Si-Containing Porous Carbon Particle

Discharge and charge curves and cyclic behavior of Si-containing porous carbon

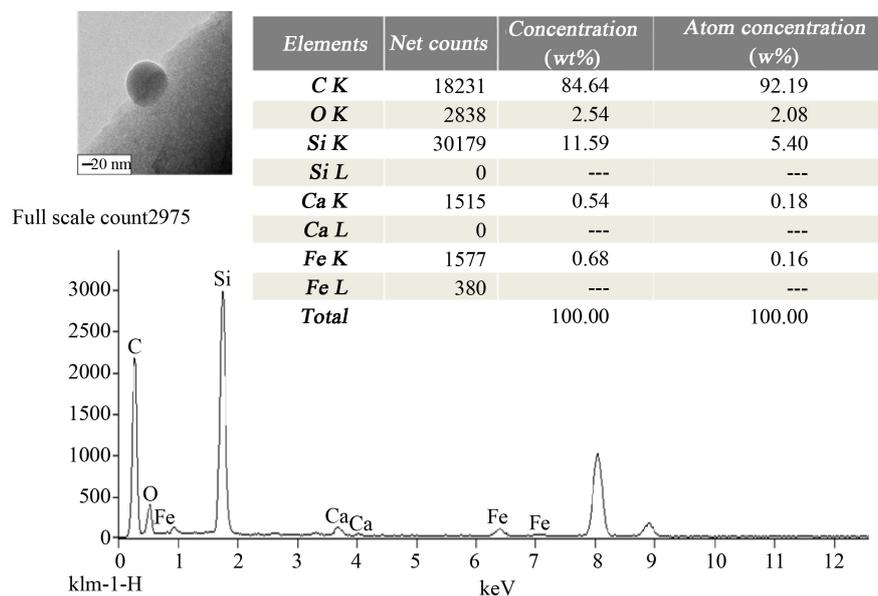


Figure 2. Elemental analysis of a nanoparticle in **Figure 1(c)** using EDX.

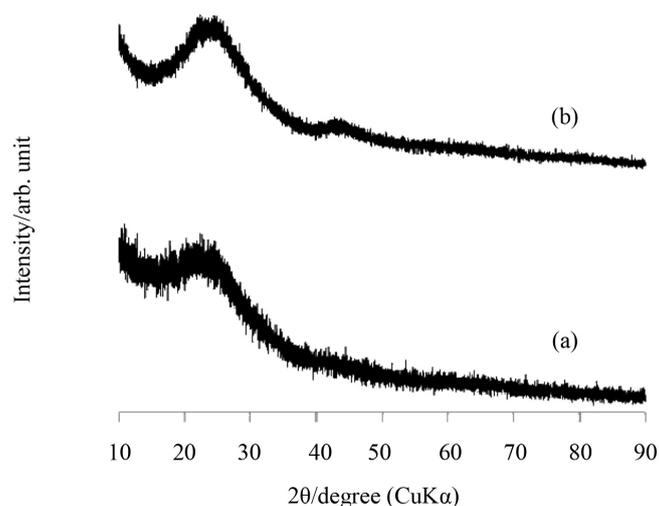


Figure 3. XRD patterns of (a) porous carbon and (b) Si-containing porous carbon.

cell were given in **Figure 4** and **Figure 5**, respectively.

Figure 4 shows the irreversible capacity was observed with initial charge/discharge curve of Si-containing porous carbon cell.

Figure 5 shows the cycle characteristics of discharge capacity. The discharge capacity in the first cycle was high, but, in the second cycle, the discharge capacity largely de-creased.

Table 1 shows the effect of Si on the discharge capacities. Discharge capacity of the porous carbon cell was 22.5 mAh/g, whereas, that of Si-containing porous carbon was 845 mAh/g. The discharge capacity of the porous carbon cell after second cycle, subsequently, decreased up to 6.4 mAh/g and the decay was about 28%. On the other hand, that of Si-containing porous carbon decreased up to

226 mAh/g with the decay of 27%. Thus, this decrease in capacity can be attributed, not clear at the pre-sent time, to the generation of solid electrolyte interface (SEI), but the content of Si relatively would raise the discharge capacity, compared with that of porous carbon cell.

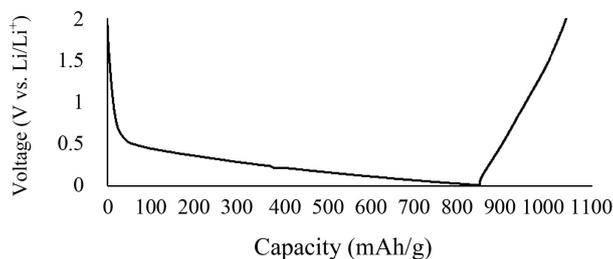


Figure 4. Discharge-charge curves of Si-containing porous carbon cell.

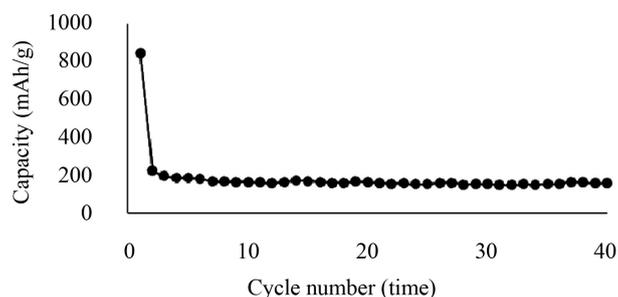


Figure 5. Cyclic behavior of Si-containing porous carbon cell.

Table 1. Discharge capacities after cycle performances.

Sample	1 st cycle	2 nd cycle	10 th cycle	40 th cycle
Porous carbon	22.5	6.4	6.1	9.2
Si-containing porous carbon	845	226	167	161

4. Conclusion

Silicon nanoparticles were formed by pyrolysis of hexaphenyldisilane adsorbed in pores of carbon. Formation of silicon nanoparticles was observed for hexenyldisilane but not for tetraphenylsilane. Discharge capacity showed 845 mAh/g in the first cycle but decreased greatly, later.

Acknowledgements

We are grateful to Dr. N. Yoshizawa and Dr. M. Kodama of AIST, Japan for the use of laboratory facilities and for many useful discussions, and Professor S. Hashimoto of National Institute of Technology, Gunma College for helpful discussions.

This research was supported by JSPS KAKENHI, Grant Number 16K06734.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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