

LITHIUM ION CAPACITIES OF CARBON GEL MICROSPHERES INCLUDING SILICON

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Introduction

Further improvement of Li-ion batteries is required due to the rapid development of portable electronic devices. The capacity of a lithium ion battery, which consists of a carbon material as the anode and a lithium transition metal oxide as the cathode, strongly depends on the lithium ion storage capacities of its electrodes. Therefore, in order to improve the capacity of lithium ion batteries, the development of materials having larger lithium ion capacities are desired.

Silicon is known to have an ability to store up to 4.4 lithium ions per atom, and therefore is a potential candidate for the anode material of batteries of the next generation. However, elemental silicon is not suitable for usage in batteries, as the reversibility of its lithium ion store-release process is poor. This problem can be overcome by dispersing it in a carbon host material. Such materials have been produced by thermal CVD using organic silicon compounds [1,2], and the co-carbonization of carbon precursors with polymers containing silicon [3-6]. However, the feasibility of such production methods is thought to be quite limited, as they require expensive equipment and/or expensive silicon sources.

In this work, carbon cryogel microspheres including silicon powder were prepared by simply adding silicon powder to the water phase during the inverse emulsion polymerization of resorcinol and formaldehyde, followed by drying and carbonization. The lithium ion reversible and irreversible capacities of the resulting microspheres were evaluated, and their stabilities during charge-discharge cycles were also tested.

Experimental

Resorcinol (R) and formaldehyde (F) and sodium carbonate (catalyst, C) were mixed in distilled water (W), and to this solution, ball-milled silicon was added (R/F = 0.5 mol/mol, R/C = 100 mol/mol, R/W = 0.5 mol/cm³, R/Si = 1.0 mol/mol). By keeping this mixture at 298 K, polycondensation of resorcinol with formaldehyde proceeded within it. Just before gelation, the viscous mixture was dispersed into a mixture of cyclohexane and a nonionic surfactant (Span 80), and gelation was completed. After thorough aging, the solvents in the obtained microspheres were exchanged with *t*-butanol, and freeze-drying was conducted. The dried materials were heated in an argon atmosphere, to a maximum temperature set in the range of 1273 K to 1573 K at a constant heating rate of 10 K/min, and kept at the maximum temperature for 1h. Finally, carbon gel microspheres including silicon were obtained.

The obtained materials were directly observed using a scanning electron microscope (Jeol Ltd., JSM-6340FS), and were characterized using X-ray diffraction analysis (Rigaku Co. Ltd., RINT/S).

Carbon electrodes were prepared by coating slurries of carbon materials and 10 wt% polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidone on copper foil. These electrodes were dried under vacuum at 393 K for 9 h, and then they were pressed at 9 ton/cm² for 10 min. A two-electrode cell was employed in our work. Li foil was used as the counter electrode and the electrolyte was a solution of 1 M LiClO₄ dissolved in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Cells were assembled in an argon-filled glove box. The galvanostatic Li charging and discharging experiments were conducted at a constant current density of 25 mA/g.

Results and Discussion

Figure 1 shows an SEM image of the obtained carbon cryogel microspheres including silicon. That of typical carbon cryogel microspheres, which do not include silicon, is also shown for comparison. Although the shapes of microspheres including silicon seem to be slightly distorted, a spherical shape is maintained, and even traces of silicon particles cannot be noticed. These results indicate that the silicon particles were completely wrapped with carbon.

Figure 2 shows the reversible and irreversible capacities of microspheres including

silicon carbonized at 1273 K. Those of carbon cryogels which include the same amount

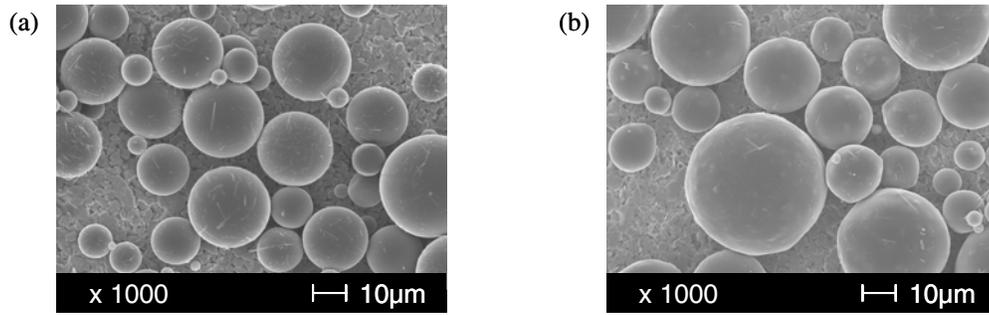


Fig. 1 SEM images of (a) typical carbon cryogel microspheres and (b) carbon cryogel microspheres containing silicon powder

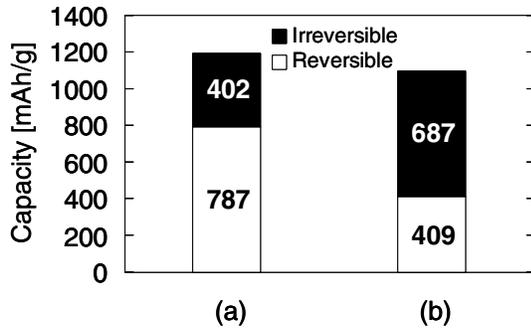


Fig. 2 Capacities of (a) carbon cryogel microspheres containing silicon powder and (b) milled carbon cryogel containing silicon powder

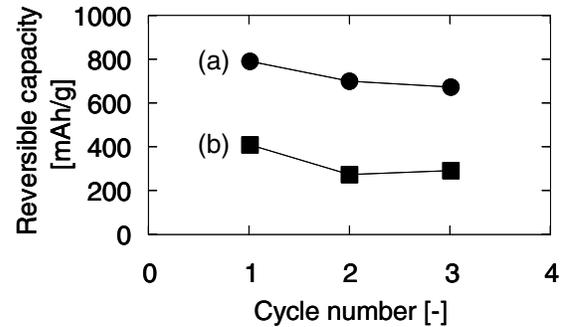


Fig. 3 Cyclic stabilities of (a) carbon cryogel microspheres containing silicon powder and (b) milled carbon cryogel containing silicon powder

of silicon, but synthesized as a lump and milled afterwards are also shown for comparison. Although the first charge capacities of both materials are quite similar, the reversible capacity of the microspheres is extremely higher than that of the milled material. Figure 3 shows the stability of the materials during consecutive charge-discharge cycles. Although slight capacity fading occurs, the microspheres manage to maintain a fairly high reversible capacity. Similarly, only slight capacity fading occurs in the milled material, but as the reversible capacity is low, it is assumed that only carbon is contributing to lithium ion storage.

Conclusions

It was found that carbon cryogel microspheres including silicon particles could be prepared by simply adding silicon particles to the water phase during the inverse emulsion polymerization of resorcinol and formaldehyde, followed by drying and carbonization. SEM images suggested that the included silicon particles were

completely wrapped with carbon. The obtained microspheres possess a high lithium ion reversible capacity. It was also found that the cyclic stabilities of silicon particles could be significantly improved by wrapping them with carbon.

Acknowledgements

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