

Surface-modification of carbon for lithium-ion battery using chemical vapor infiltration

Yoshimi Ohzawa, Hideki Sakakibara, Tsuyoshi Nakajima

*Dept. of Applied Chemistry, Aichi Institute of Technology,
Yachigusa 1247, Yakusa-cho, Toyota 570-0392, Japan*

E-mail: ohzawa@aitech.ac.jp

URL: <http://aitech.ac.jp/~ohzawa/>

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Introduction

Low crystalline carbon such as non-graphitizing carbon has received the attention for its high reversible capacity, which exceeds the theoretical capacity of graphite for the anode of lithium ion battery. However, irreversible capacity is often high for these disordered carbons.

Pyrocarbon-coating by CVD was recently applied to graphite-based anodes of lithium-ion secondary battery to improve the anode performance, especially in propylene carbonate containing solvent [1]. The pressure-pulsed chemical vapor infiltration (PCVI) allows the homogeneous coating with relatively high crystalline pyrocarbon through the thickness of the porous substrate under suitable conditions [2-3], resulting in high first coulombic efficiency of pyrocarbon-based anode [3]. In present study, the relation between surface structure and electrochemical properties was investigated for the powdery hard carbon beads and the samples coating with pyrocarbon using PCVI methods.

Experimental

As-received hard carbon beads with average diameter of 3 μm (Mitsui Mining Co. Ltd) were encapsulated using the porous holder made from the filter paper, then carbonized at 1000 $^{\circ}\text{C}$ in Ar for 4 h.

Coating with pyrocarbon was performed using the typical PCVI apparatus [3]. The source gas mixture of CH_4 (50%) - H_2 was allowed to flow into a reservoir. It was instantaneously introduced (within 0.1 s) into the reaction vessel up to 0.1 MPa, and the pressure was held under the same condition to allow matrix deposition for 1.0 s (holding time). Then, the reacted gas was evacuated to below 0.7 kPa within 1.5 s. This cycle of the sequential steps was defined as one pulse, and repeated to the desired number of times. The temperature for PCVI treatment was kept at 1100 $^{\circ}\text{C}$.

Charge/discharge cycling was made at 25 $^{\circ}\text{C}$, using a three electrode cell with metallic lithium as counter and reference electrodes, in 1 mol L^{-1} LiClO_4 EC/DEC (1:1) solution. Discharging and Charging were performed under the condition of constant current of 60 mA g^{-1} followed at constant potential of 3mV vs. Li/Li^+ for 24 h (CCCV method) and constant current of 60 mA g^{-1} (CC method), respectively.

Results and discussion

Table 1 shows the structural properties of the original and the pyrocarbon-coating carbon powders. A d_{002} value calculated from X-ray diffraction (XRD) peak of the pyrocarbon-coated sample is around 0.348 nm, which is much lower than that of the original hard-carbon. R -value calculated from Raman spectra of original carbon is slightly decreased by coating with pyrocarbon. From these results by XRD and Raman spectroscopy, it is considered that the crystallinity of pyrocarbon shell is higher than that of the core carbon. BET surface area was decreased from 25 $\text{m}^2 \text{g}^{-1}$ of the original particles to 8.5 $\text{m}^2 \text{g}^{-1}$ after coating with 7 wt% pyrocarbon. From pore volume distribution analysis, it was found that the pores with the diameter of 1.5–5 nm were extremely decreased by pyrocarbon coating, however, the volume of larger pore above 10 nm was rather increased.

Table 2 shows the charge-discharge capacity data at first cycle of the original carbon powder (a), the samples coated with 7 mass% pyrocarbon (b) and 47 mass% pyrocarbon (c). High irreversible capacity of 200 mAhg^{-1} is observed in the original carbon beads, reflecting the low crystalline disordered structure and high surface area. Irreversible capacity is reduced to 100-135 mAhg^{-1} by coating with 5-8 wt% pyrocarbon. As mentioned above, coated pyrocarbon has higher crystallinity and lower surface area than those of the core carbon. These structural features of pyrocarbon would cause the decrease of irreversible reaction as decomposing the electrolytes and trapping lithium. Irreversible capacity could be decreased with increasing the mass fraction of pyrocarbon, however, reversible capacity was also decreased. Thin pyrocarbon film with uniform thickness is desired in order

to achieve high coulombic efficiency at first cycle without reducing the reversible capacity. The cyclability could be improved by coating with pyrocarbon. From the SEM images, it was observed that the roughness of the particle surface appeared to increase in sub-micron scale by coating with the pebble-like pyrocarbon film, which would effectively increase the adhesion among the particles by the organic binders.

Table 1: Structural properties of original and pyrocarbon-coating carbon beads.

Sample	d_{002} by XRD / nm	R value by Raman spectroscopy
Original carbon beads	0.373	1.42
pyrocarbon-coating carbon beads ^{a)}	0.348	1.22

a) Number of pulses, 5000; mass fraction of pyrocarbon, 47%.

Table 2: Data of capacity and coulombic efficiency at first cycle for original carbon beads and samples coating with pyrocarbon.

Sample	Mass fraction of pyrocarbon / %	Reversible capacity / mAhg ⁻¹	Irreversible capacity / mAhg ⁻¹	Coulombic efficiency / %
(a) original	0	380	197	65.9
(b)	7	360	96	78.9
(c)	47	248	62	80.0

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Biographical Sketch

Name : Yoshimi Ohzawa

Born : 1964

Nationality : Japanese

Affiliation : Dept. of Applied Chemistry, Aichi Institute of Technology,
Yachigusa 1247, Yakusa-cho, Toyota 570-0392, Japan

E-mail: ohzawa@aitech.ac.jp

URL: <http://aitech.ac.jp/~ohzawa/>

Title : Associate Professor

Academic Background : Graduate School of Engineering,
Nagoya University, 1989 Graduation.

Degree : D. Eng. (Nagoya University, 1998)

Professional Organizations : The Electrochemical Society(US), The Chemical Society of Japan, The Electrochemical Society of Japan, The Carbon Society of Japan (The Editorial Board of Tanso).

Field of Study : Electrochemistry, Inorganic Chemistry.

Key Words of Specialized Field : Chemical Vapor Deposition (CVD), Chemical Vapor Infiltration (CVI), Battery, Carbon

Outline of Research : Synthesis of inorganic materials such as carbon, Si, SiC and TiN from gas phase using CVD/CVI process and its application to ceramics composites for structural materials, porous materials for high-temperature filter and electrode materials for batteries.

