Pyrocarbon-coating on powdery hard-carbon using chemical vapor infiltration and its electrochemical characteristics

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Abstract

Using the pressure-pulsed chemical vapor infiltration technique, thin pyrocarbon films were coated on the surface of the hard-carbon particles. The crystallinity of pyrocarbon shell was higher than that of the core carbon. The BET surface area and the pores with the diameter of 1.5–5 nm were extremely decreased after coating with 7 wt.% pyrocarbon. These changes in the nano-scaled structure of carbon surface could lead to the reduction of irreversible capacity. The cycleability was improved by pyrocarbon-coating, which would be attributed to the increase of the surface roughness on sub-micron scale by coating with the pebble-like pyrocarbon film to increase the adhesion among the particles by the organic binders.
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1. Introduction

Pyrocarbon-coating by chemical vapor deposition was recently applied to graphite-based anodes of lithium-ion secondary battery to improve the anode performance especially in propylene carbonate (PC)-based solvent [1–3]. In this process, low crystalline pyrocarbon shell covered the surface of high crystalline graphite core, which successfully prevented the decomposition of PC solvent. In order to achieve high coulombic efficiency at first cycle without reducing the reversible capacity, thin pyrocarbon film with uniform thickness is desired because the capacity of pyrocarbon (soft carbon) is generally lower than that of the high crystalline graphite. In the case of the continuous gas-flowed CVD, thick films are easily formed on external surface of the porous substrates or the particle-packed beds. In order to achieve the uniform coating on the conventional CVD, it is necessary to repeat the CVD treatment and the removal of films by polishing the external surface or the soft grind of particles at several times.

Rotation of a reactor was recently attempted to obtain a uniformly coated carbon layer [4]. The pressure-pulsed chemical vapor infiltration (PCVI) method consists of repetition of the following steps; evacuation of the reaction vessel, instantaneous introduction of the source gas, and holding to allow deposition [5–7]. This process allows homogeneous infiltration of matrix through the thickness of the preforms under suitable conditions because of rapid penetration of the sources gas throughout the preform without pre-heating [8,9]. In addition, instantaneous introduction of the source gas and evacuation of the reacted gas are repeated at relatively short intervals in PCVI process, therefore, nucleation in gas phase is restrained, and crystal growth on the surface of substrate is promoted in evacuation step. These are effective in increasing the crystallinity of pyrocarbon film, resulting in high coulombic efficiency at first cycle [10,11].

In case low crystalline carbon such as non-graphitizing carbon (hard-carbon) is used for the core material, the pyrocarbon shell has higher crystallinity compared with the core carbon. This structure would lead to reduce the large irreversible capacity observed in the bare hard carbon. In this study, PCVI was adopted to coat with pyrocarbon on the surface of hard carbon particles, and the relation between structure and electrochemical behavior was investigated.

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2. Experimental

As-received hard carbon beads with average diameter of 3 μm (Mitsui Miring Co. Ltd.) were encapsulated using the porous holder made from the filter paper, then carbonized at 1000 °C in Ar for 4 h.

Coating with pyrocarbon was performed using the typical PCVI apparatus [10]. 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 °C.

Charge–discharge cycling was made at 25 °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 3 mV versus Li/Li^+ for 24 h (CCCV method) and constant current of 60 mA g^{-1} (CC method), respectively.

3. Results and discussion

From the wide range of the observation by scanning electron microscope (SEM), it appeared that thin pyrocarbon films were coated on most of the surfaces of the spherical carbon particles. Fig. 1 shows the typical SEM images of the original hard-carbon powder (a) and the sample coated with 7 wt.% pyrocarbon (b). It can be observed that the pyrocarbon film has the pebble-like projections sized below 0.1 μm. Therefore, the roughness of the particle-surface appears to increase on sub-micron scale by coating with the pebble-like pyrocarbon film. From X-ray photoelectron spectroscopy, it was found that the surface oxygen concentration of the coated sample was about half as much as that of the original carbon. It is supposed that the surface functional groups containing oxygen atom are decreased while pyrocarbon is coated in CH_4–H_2 reductive atmosphere at high temperature.

Table 1 shows the structural properties of the original and the pyrocarbon-coated hard-carbon powders. A d_{002} value calculated from X-ray diffraction (XRD) peak of the pyrocarbon-coated sample is 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
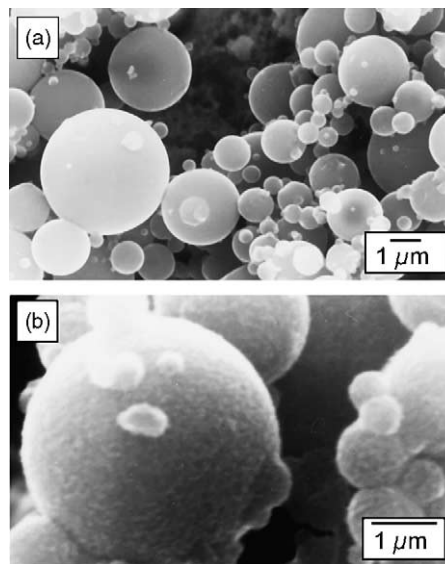

Fig. 1. SEM images of the original hard-carbon powder (a) and the sample coated with 7 wt.% pyrocarbon (b) after 500 pulses in PCVI.
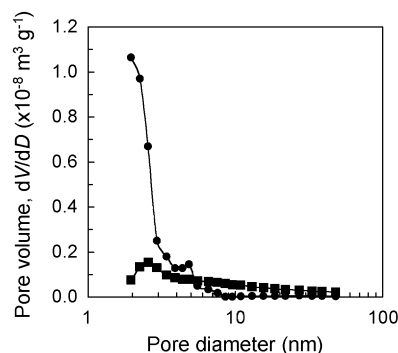

Fig. 2. Pore volume distributions of the original hard-carbon powder (●) and the sample coated with 7 wt.% pyrocarbon (■) after 500 pulses in PCVI.

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. The BET surface area is decreased from 25 m^2 g^{-1} of the original particles to 8.5 m^2 g^{-1} after coating with 7 wt.% pyrocarbon. From pore volume distribution analysis as shown in Fig. 2, it is found that the pores with the diameter of 1.5–5 nm are extremely decreased by pyrocarbon-coating, however, the volume of large pores above 10 nm is rather increased.

Fig. 3 shows the charge–discharge curves at first and 10th cycles of the original carbon powder (a), the samples coated with 7 wt.% pyrocarbon (b) and 47 wt.% pyrocarbon (c).

Table 1
Structural properties of original carbon beads and pyrocarbon-coated sample

Sample	d_{002} by XRD[a] (nm)	R (I_D/I_G) value by Raman spectroscopy[a]	Surface area by BET[b] (m^2 g^{-1})
Original carbon beads	0.373	1.42	25
Pyrocarbon-coated carbon beads	0.348	1.22	8.5

[a] Measured for the sample with 47 wt.% pyrocarbon after 5000 pulses in PCVI treatment.
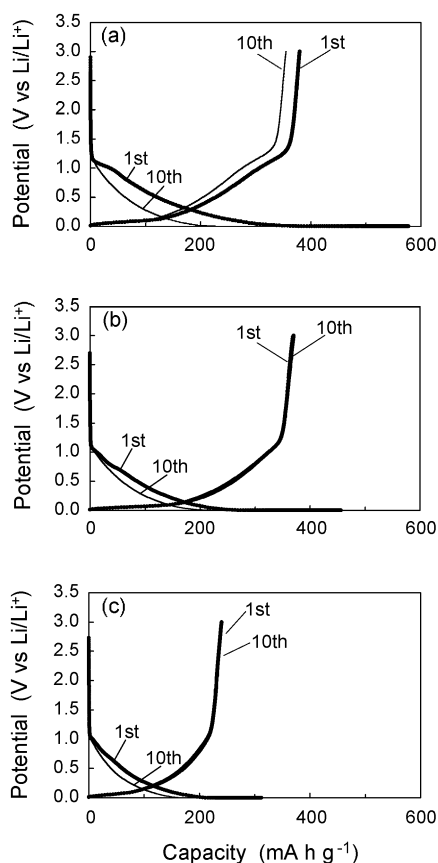[b] Measured for the sample with 7 wt.% pyrocarbon after 500 pulses in PCVI treatment.

Fig. 3. Charge–discharge curves at first and 10th cycles of the original carbon powder (a), the samples coated with 7 wt.% pyrocarbon (b), and 47 wt.% pyrocarbon (c). Number of pulses in PCVI: (b) 500 and (c) 5000.

The charge–discharge profiles of the original carbon powder (a) and the sample coated with 7 wt.% pyrocarbon (b) are similar to that observed in typical non-graphitizing carbon having the disordered structure. High irreversible capacity of $200\,\mathrm{mA\,h\,g^{-1}}$ is observed in the original carbon beads, reflecting the low crystalline disordered structure and high surface area. Irreversible capacity is reduced to around $100\,\mathrm{mA\,h\,g^{-1}}$ by coating with 7 wt.% pyrocarbon. As mentioned above, the coated pyrocarbon film has higher crystallinity and lower surface area than those of the core carbon. In addition, the surface functional groups containing oxygen atom would be decreased while pyrocarbon is coated in CH_4–H_2 reductive atmosphere at high temperature. These structural features of pyrocarbon would cause the decrease of irreversible reaction as decomposing the electrolytes and trapping lithium. As shown in Fig. 3(c), irreversible capacity can be decreased with increasing the mass fraction of pyrocarbon, however, the charge capacity (Li de-intercalation) is 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. For the original carbon beads as shown in Fig. 3(a), the decline in the charge capacity is observed after 10th charge–discharge cycling. The cycleability can be improved by coating with

pyrocarbon (Fig. 3(b) and (c)). It is revealed from the SEM images (Fig. 1) and the pore volume distribution analysis (Fig. 2) that the volume of large pores above 10 nm is rather increased by pyrocarbon-coating although the pores with the diameter of 1.5–5 nm are extremely decreased. These results indicate that the roughness of the particle surface was increased on sub-micron scale by coating with the pebble-like pyrocarbon film. These structures would be effective in increasing the adhesion among the carbon particles by the organic binders termed anchor effect, resulting in the increases of the resistance to the failure of electro-conduction among the carbon particles during the charge–discharge cycling.

Thus, pyrocarbon-coating successfully lead to the reduction of irreversible capacity and the improvement of cycleability. However, rate performance of the present sample would be deteriorated because of decreasing the effective reaction area due to the reduction of BET surface area by pyrocarbon-coating. On the other hands, "geometric surface area" on sub-micron scale is rather increasing as shown in SEM images (Fig. 1). This result may be preferable to improve the rate property. The detail of the relation between the structure and rate performance is now open to further investigation.

4. Conclusion

Thin pyrocarbon films having the relatively high crystallinity could be coated on the surface of the low crystalline hard-carbon particles using the PCVI technique. Irreversible capacity was reduced from $200\,\mathrm{mA\,h\,g^{-1}}$ to around $100\,\mathrm{mA\,h\,g^{-1}}$ by coating with 7 wt.% pyrocarbon, reflecting the high crystallinity and low surface area of pyrocarbon. Irreversible capacity was further decreased with increasing the mass fraction of pyrocarbon, however, the charge capacity (Li de-intercalation) was also decreased. Thin pyrocarbon film with uniform thickness was desired in order to achieve high coulombic efficiency at first cycle without reducing the reversible capacity. The cycleability was also improved by pyrocarbon-coating, which would be attributed to the increase of the surface roughness in sub-micron scale by coating with the pebble-like pyrocarbon film to increase the adhesion among the particles by the organic binders.

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