DEVELOPMENT AND DEGRADATION OF GRAPHITIC MICROTEXTURE IN CARBON NANOSPHERES UNDER A MORPHOLOGICALLY-RESTRAINED CONDITION

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Introduction

Carbon nanoparticles in spherical form are often produced in the similar process as that of carbon blacks. This type carbon nanoparticles attracts many attentions recently as the promising materials to achieve the superior high-rate charge-discharge performance in Li ion batteries, as well as their possibility to be used in a wide range of electrolyte. These advantages in the spherical carbon nanoparticles can be discussed based upon the characteristics of carbon structure in relation to the path of Li ions during the electrochemical process.

We have previously reported the graphitization process of carbon nanospheres in 200 nm diameter [1,2]. In the following study for using carbon nanospheres with diameter under 1000 nm to improve energy density and first coulomb efficiency of a Li-ion battery, we found that graphitic microtexture of some type of carbon nanospheres could be deteriorated by the heat-treatment at higher temperature. This phenomenon has been reported by a few authors [3] as a result of crystallites growth with excess strain, followed by an additional supply of thermal energy in a particle. Except this early and general scheme, little attention has been given to the mechanism of it so far.

This paper is intended as an investigation of the development and degradation mechanism of graphitic microtexture in carbon nanospheres by using carbon nanospheres with diameter between 500 nm and 1000 nm. We attempted to discuss the morphological and crystallographic change of heat-treated samples from the viewpoint of distribution of structure defects modified under a spatially-restrained condition.

Experimental

Carbon nanospheres (CNSs) commercially provided by Tokai Carbon Co. Ltd., with equivalent stokes diameter of 500 nm, 700 nm, and 1000 nm, were used in this study. Preparation process of the samples is basically explained as a pyrolysis of hydrocarbon gas in a silica furnace between 1000 and 1300 ^{o}C. Pristine samples were heat-treated at temperatures up to 2900 ^{o}C in Ar atmosphere. Hereinafter, these samples were referred to as CNS*s-t*, where *s* and *t* correspond to 1/10th of stokes diameter and 1/1000th of the heat-treatment temperature (p: pristine), respectively.

XRD measurements were carried out with CuKα (40 kV-20 mA) to evaluate structural parameters by the Gakushin method. Raman spectrum was obtained with Ar laser (laser energy: 2.41 eV, wavelength: 514.5 nm). SEM observation was also done to study the surface morphology of all the samples. TEM observation was carried out at an accelerating voltage of 120 kV. We examined carbon 002 lattice images, bright- and dark-field images, and electron diffraction patterns of each sample.

Results and Discussion

Structural parameters derived from XRD patterns of samples (Table 1) showed that, as the increase in heat-treatment temperature, d_{002} and Lc varied to show a development of graphitic stacking structure. These parameters also represented that the stacking structure was more developed in larger CNSs than in smaller ones in the graphitization process. Change in La by the heat-treatment was more complex. It was increased up to 2900 ^{o}C for CNS50-*t* and CNS70-*t* series. But for CNS100-*t* series, there was an increase up to 2600 ^{o}C (77.5 nm) followed by an obvious drop at 2900 ^{o}C (47.0 nm).

SEM observation for CNS50-*t* and CNS70-*t* series demonstrated that a feature of polyhedronization clearly appeared by the heat-treatment at 2000 ^{o}C and over. After the heat-treatment at 2600 ^{o}C and 2900 ^{o}C, these polyhedron faces with sharp ridgelines became concave to the center of the particles. CNS100-*t* series represented the progress of polyhedronization similar to other two series of CNSs up to 2600 ^{o}C. But CNS100-29 showed the rough surface in which step-like exfoliation of carbon texture was observed with a central focus on vertexes. This type of exfoliation frequently extended far away from the ridgelines in the polyhedral faces.

Figure 1 shows representative TEM results of carbon 002 lattice images for CNS70-*t* and CNS100-*t* series. In the microtexture of CNS samples heat-treated at 2000 ^{o}C, size of aromatic layers was estimated at 20-30 nm from their carbon 002 lattice images. Stacking structure of these layers was developed along the polyhedron face regions. Ridgelines with gentle curve were formed with continuously bent layers, while some ridges with large tilt angle were often composed of small stacking units. These types of structural defects were also confirmed by an observation of carbon 002 dark-field images. TEM observation of CNS70-29 and CNS100-29 heat-treated at 2900 ^{o}C frequently showed local but distinct collapses of graphitic microtexture in the ridge regions of polyhedrons, while graphitic structure with high crystallinity was still maintained in the face regions. These collapses include an exfoliation of aromatic layers in which the torn layers have a hairpin-like microtexture at their ends, and a crack of layer stacks with adjacent layer stacks.

These morphological and microtextural collapses, observed for CNS70-29 and CNS100-29, can be explained by the thermal shrinkage and distribution of structural defects in

the polyhedron ridge regions. That is, SEM observation of CNS particles pointed out that the polyhedron faces became concave to the center of the particles after the heat-treatment at 2600 °C and 2900 °C. The morphological change like this is regarded as a sign of shrinkage in this graphitization process, and can cause thermal stress in a CNS particle. Considering the aggregation of crystallographic defects around ridges, the thermal stress is likely to be focused in this region to deteriorate microtexture.

More specifically, the collapses of graphitic microtexture in the ridge region were not found in CNS with smaller diameter such as CNS50-29. For a numeric evaluation, we examined the presence of each type of damage to relate it to a size of a particle. This was conducted by counting the number of damaged (exfoliated or cracked) and non-damaged ridges in an arbitrary particle with measured diameter. For CNS70-29 and CNS100-29, ratio of ridge with either type of damage, and with an exfoliation only also, to a total number of ridges is obviously higher in CNS particles with larger diameter. Ratio of damaged ridge was also estimated for CNS70-26 and CNS100-26, demonstrating that there was almost no such a type of damage in these samples. It is obvious that the probability of structural collapse at the ridges in graphitized CNSs depends upon the size of CNS particles. This result can be discussed with the distribution of structural defect, although it is not simple to evaluate the crystallographic structure at each polyhedron face and ridge in every CNS particle. Considering the TEM results, the development of graphitic microtexture mentioned above is attributed to that in the face regions of polyhedronized particle. Suppose that there are structural defects in the ridge regions of graphitized CNS particles in any size, regardless of their types and numbers, thermal stress can be focused more easily in the ridge regions than in the face regions for graphitized CNS particles with large diameter. That is probably one of the reasons for the correlation represented in Fig. 1.

Conclusion

Development and degradation of graphitic microtexture in carbon nanospheres were studied. The carbon nanospheres with 500-1000 nm average diameter heat-treated over 2000 °C represented polyhedronized shapes on their surface, as well as graphitic microtexture in the particles. These morphological and microtextural features indicating a progress of graphitization were more developed by the heat-treatment up to 2600 °C. The collapse at the polyhedronized ridges at 2900 °C was reasonably explained based upon the focused stress in this region caused by the thermal shrinkage combined with the aggregation of structural defect. High crystallinity in the polyhedronized face region was also considered for the probability of the collapses.

Table 1. Structure parameters derived from XRD.

sample	HTT/℃	d_{002}/nm	Lc(002)/nm	La(110)/nm
CNS501p	0	0.3507	3.2	2.8
CNS50-20	2000	0.3401	20.7	22.7
CNS50-26	2600	0.3391	23.1	37.5
CNS50-29	2900	0.3376	35.7	72.7
CNS70p	0	0.3490	3.1	2.6
CNS70-20	2000	0.3403	21.2	31.3
CNS70-26	2600	0.3394	23.7	34.2
CNS70-29	2900	0.3380	36.9	67.2
CNS100p	0	0.3494	3.4	2.9
CNS100-20	2000	0.3398	25.0	38.2
CNS100-26	2600	0.3376	44.9	77.5
CNS100-29	2900	0.3369	63.2	47.0

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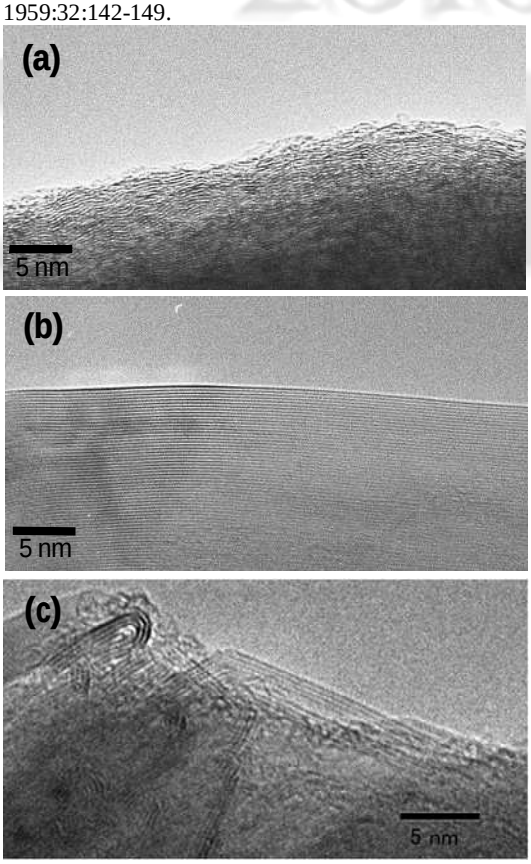

Fig. 1 TEM observation: Typical carbon 002 lattice images of (a) CNS70p, (b) CNS70-26, and (c) CNS100-29.