

TEM OBSERVATION OF CARBON NANOSPHERES AFTER ELECTROCHEMICAL LITHIUM INSERTION

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Introduction

Carbon nanospheres (CNSs) are known 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 including PC-based ones [Wang, 2005]. We have already reported the development of inhomogeneous microtexture in graphitized CNS particles by the characterization with XRD (X-ray diffraction) and TEM (transmission electron microscope) with the electron tomography attachment [Yoshizawa, 2006], which can be related to the path of Li ions during the electrochemical process.

On the other hand, numerous attempts have been made to analyze solid electrolyte interphase (SEI) formed on the surface of electrodes. SEI is known to be originated due to the decomposition of electrolyte on the electrode [Peled, 1998], and therefore examining SEI structure and composition can provide information on the behavior of ions at the interface during the charge-discharge cycles. Visualization of SEI with microanalysis by using TEM has given us a specific images of them much more than ever [Naji, 1999; Dollé, 2001], while the influence of charge-discharge conditions and surface structure of carbons was not been enough clarified.

In this study, we investigated the SEI structure formed on the CNS particles by TEM observation. Samples were kept under an airtight condition before they were set to TEM to prevent structural alternation.

Experimental

Samples

Carbon nanospheres (CNSs; Tokai Carbon Co. Ltd., 100 nm and 200 nm in diameter) and their heat-treated samples at 1500, 1800, 2000, 2200, 2500 and 2800 °C were used for negative electrodes. The pristine samples were prepared by a CVD method with hydrocarbon gas. Hereinafter, these samples were referred to as CNS s - t , where s corresponds is one-tenth of the average particle diameter before heat-treatment, t one-hundredth of the heat-treatment temperature (p: pristine). N₂ adsorption isotherm obtained at 77 K indicated that the heat-treated samples have few microspores in its texture with small specific surface area less than 20 m²/g. Raman spectrum of the samples indicated that graphitization proceeds according to the raise in heat-treatment temperature. Parameters I_D/I_G (intensity ratio of D-band to G-band) and FWHM(G) (full-width at half-maximum of G-band) of CNS20- t series of samples are summarized in Table 1.

Electrochemical process and TEM observation

The negative electrodes were composed of CNS samples (80% w/w), PVDF (10% w/w) and carbon black (10% w/w). They were mixed to make slurry, and then spread onto a Cu mesh. The charge-discharge process was done in the three-electrode cell with CNS as working electrode, Li metal as counter and reference electrodes, and LiBF₄/EC+DEC (1:1) as electrolyte. After the first cycle at a certain scanning speed, CNS particles in the negative electrode were collected in the glove box in Ar atmosphere, and transferred to TEM without exposure to air. TEM observation was carried out at an accelerating voltage of 100 kV.

Results and Discussion

Effects of scanning speed on SEI texture

TEM observation of CNSs collected from the negative electrode showed that the particles did not change the feature of their forms as well as microtexture during the electrochemical cycles. Exfoliation of aromatic layers was hardly found as far as we studied. Figure 1(a) indicates the typical surface image of CNS20-28 after the first charge-discharge cycle at 0.1 mV/s. The particle is totally covered with amorphous or less-crystalline SEI layer with 2-3 nm thickness. According to the electron diffraction patterns, the SEI included LiF in its texture, which was agreed to the result of XRD. Presence of LiF can be attributed to the reduction of LiBF₄ and is often related to the deterioration of the cell during cycling [Naji, 1999].

SEI was also found in the samples prepared at higher scanning speed, i.e., 0.2 and 0.5 mV in this study. But they seemed to be less stable because of the lacking in uniformity of density. Even so, the average thickness of SEI could be estimated at almost the same as that in the samples prepared at 0.1 mV/s.

SEI formed on CNS particles heat-treated at different temperature

Morphology of SEI showed the obvious dependence upon the effect of carbon structure controlled with heat-treatment temperature of CNS. As shown in Figure 1(b), texture of SEI on CNS20p typically observed had irregular surface, while SEI generated on CNS20-28 (Figure 1(a)) indicated the smooth surface. Concerning carbon structure related to the SEI formation, the SEI on hard carbon was reported to be thicker than that on soft carbon due to the difference in the number of edge planes [#]. In this study, thickness of SEI formed on CNS20p is admittedly larger than CNS20-28, but morphological difference was also obvious between these samples. Distribution of elements in these SEI layers is now under examination.

By the further observation, we found that SEI on CNS20-20 indicated almost the same morphology as that on CNS20-28, although degree of graphitization on the surface of these carbons is completely different. We would thus emphasize that density of edge planes, or number of structural defects, on the surface of carbon does not always conclude the morphology of SEI.

Table 1. Parameters estimated with Raman Spectrum.

Sample Description	Temperature/°C	I _D /I _G	FWHM/(G) cm ⁻¹
CNS20p	-	1.11	84.1
CNS20-15	1500	0.96	68.3
CNS20-18	1800	0.96	73.6
CNS20-20	2000	0.78	64.4
CNS20-22	2200	0.51	36.9
CNS20-25	2500	0.15	31.6
CNS20-28	2800	0.10	31.6

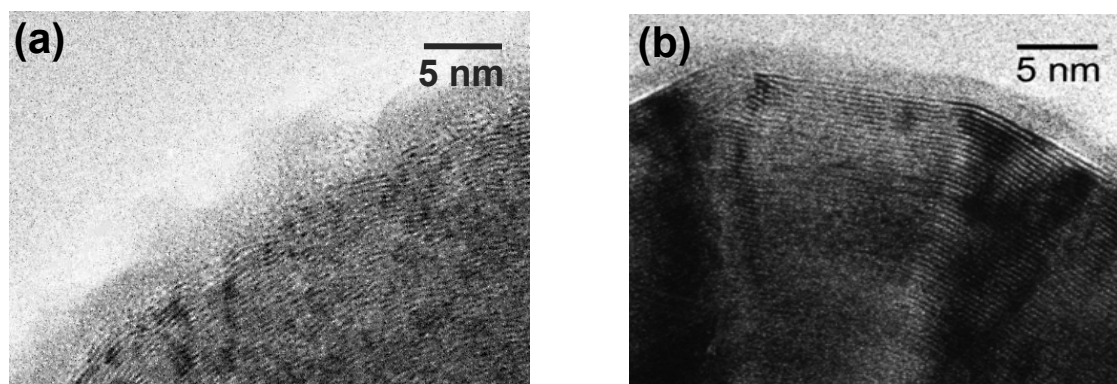


Figure 1. TEM observation of CNS particles in the negative electrodes after one cycle of charge-discharge at 0.1 mV/s. (a) CNS20p (b) CNS20-28

References

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