Structural Investigation of Lithium-Intercalated Graphite

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Graphite carbon (C) is widely used as anode material in almost all Lithium (Li)-ion batteries. Li ions are relatively easily absorbed into layer structure of C, forming LiC_x intercalation compounds between LiC_6 and C. However, in spite of the fact that they are simple binary compounds, the structures have been left unclear for a long time, especially for compounds between LiC_{12} and C. This is probably because the Li concentrations are too low to determine the detailed structures. They should be, however, all layer stacking structures, which strongly suggests that they are very likely to form modulated structures.

LiC_x specimens for X-ray and neutron structural investigations were prepared by mechanical alloying method. X-ray diffraction measurements were carried out by the Debye-Scherrer method using Rigaku SmartLab X-ray diffractometer equipped with 0.7107 Å ($MoK\overline{\alpha}$) multilayer mirror monochromated source and D/tex Ultra one-dimensional silicon strip detector [1]. Neutron powder diffraction data were obtained using a time-of-flight powder diffractometer (BL09 beamline, SPICA) at the Japan Proton Accelerator Research Complex (J-PARC) [2].

Our structural investigation revealed that, as Li ions are extracted from LiC_6, structure of LiC_{12} emerges in addition to that of LiC_6 and both structures keep coexisting between LiC_6 and LiC_{12} phase. These two structures belong to the space group *P*6/*mmm*. However, as Li concentration gets smaller than LiC_{12}, the atomic arrangement of LiC_x begins to continuously change depending on x and these LiC_x (x>12) compounds crystallize into respective single modulated structures. $LiC_{\underline{x}}$ structures from LiC_{12} to C should be viewed as commensurately or incommensurately modulated four-dimensional structures characterized by modulation vectors $\boldsymbol{q} = \gamma \cdot \boldsymbol{c}^*$ [3], where γ allows any real number from 3/2 to 7/4 in response to the Li concentration. These modulated structures are assumed to belong to the space group $P\overline{6}m2(00g)$. In the ***a*-*b*** plane of LiC_x, Li atoms are not located at all the holes of the graphene honeycomb lattices in the structures of LiC_6 and LiC_{12}; they occupy specific lattice sites, forming a $\sqrt{3} \times \sqrt{3}$ ordered atomic arrangement [4]. However, as soon as Li concentration becomes smaller than LiC_{12}, Li atoms randomly occupy at every honeycomb lattice hole at an occupation rate of 33.3% (at x=12).

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