Structure Analysis of Lithium-Graphite Intercalation Compounds by One Dimensional Rietveld Method

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Introduction:

Graphite is widely used as a negative electrode material for lithium ion rechargeable batteries. When lithium ions are inserted into graphite, lithium-graphite intercalation compounds (Li-GICs) are formed. It is considered that with the increase of lithium amount, a lithium layer is inserted into every four, three, two and one interlayer spaces between graphene layers and the stage 4, the stage 3, the stage 2 and the stage 1 compounds are formed, respectively. However, the layered structures of the stage compounds have not been clarified in detail from the point of X-ray crystallography. In this study, we have synthesized Li-GICs by intercalating and extracting lithium electrochemically. Then we have measured X-ray diffraction patterns. Because Li-GICs have a strong c-plane orientation, only *00ℓ* peaks are observed. By using one-dimensional Rietveld analysis, we have analyzed the change of the layer structures of the Li-GICs.

Experimental:

Li-GICs were prepared by electrochemically intercalating lithium into graphite and extracting lithium from graphite using a two-electrode cell at constant current density for various periods. Natural graphite powder (LB-CG, Nippon Kokuen Co., Ltd, Japan), poly(vinylidene fluoride) (PVDF) and n-methyl-2-pyrrolidone (NMP) was mixed and spread on a copper plate and used as the working electrode. Lithium metal foil was used as the counter electrode. 1 mol·dm^{-3} $LiPF_6$ solved in ethylene carbonate (EC) / dimethyl carbonate (DMC) (2:1 volume ratio) was used as the electrolyte. X-ray diffraction patterns of the obtained Li-GIC samples were taken with MoKα radiation. The tube voltage was adjusted to 33kV so that the second order reflection with half wavelength of MoKα should not arise. During the XRD measurement, the sample was placed in an argon-filled container with beryllium windows to avoid the influence from the environment. One-dimensional Rietveld structure analysis along c-axis was performed for the Li-GICs by using one-dimensional version of RIEVEC [1-3] and the layer structures were precisely determined.

Results and discussions:

The stage 1, the stage 2, the stage 2L, the stage 3, and the stage 4 compounds were obtained. Rietveld analysis was carried out for the each stage compound. For each sample, the calculated XRD pattern closely agreed with the observed pattern. Figure 1 shows Rietveld results for the stage 2 and the stage 3 obtained in lithium extraction process. In each pattern, *00ℓ* diffraction peaks with smaller 2θ than that of the main peak were clearly observed. The spacings between graphene layers for the stage 2 and the stage 3 obtained in lithium extraction process were similar to those for the stage 2 and the stage 3 obtained in lithium insertion process. The spacing between graphene layers with a lithium layer intercalated was maximal for the stage 2 and the spacing between graphene layers with no lithium layer intercalated was minimal for also the stage 2. No compound corresponding to the stage 2L, which was obtained in lithium insertion process, was observed in lithium extraction process.

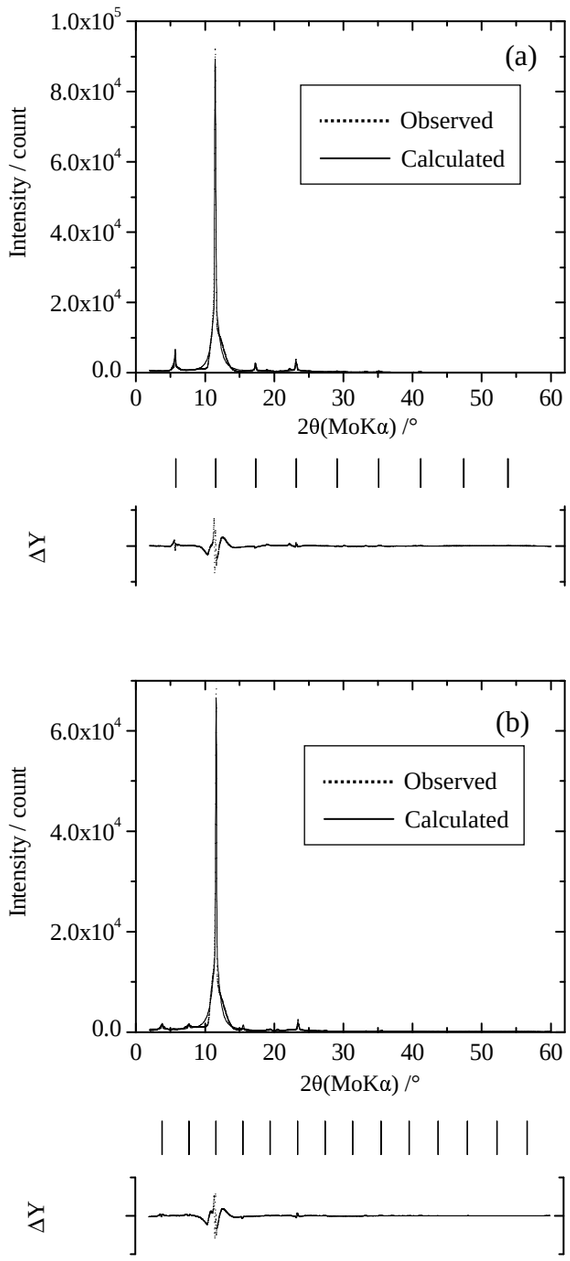

Fig.1 Rietveld results of (a) the stage 2 and (b) the stage 3 compounds obtained in lithium extraction process. The calculated and observed patterns are shown in the top by the solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflection. The trace in the bottom is a plot of the difference: observed minus calculated.

Reference:

[1] T. Yao, Y. Oka and N. Yamamoto, *Mater. Res. Bull.*, **27**[6] 669-675 (1992).
[2] T. Yao, Y. Oka and N. Yamamoto, *J. Mater. Chem*, **2**[3] 331-336 (1992).
[3] T. Yao, Y. Oka and N. Yamamoto, *J. Mater. Chem*, **2**[3] 337-340 (1992).