Relaxation Stage Analysis of Li inserted Graphite

Takashi Kitamura, Seungwon Park, Shigeomi Takai
and Takeshi Yao

Graduate School of Energy Science, Kyoto University
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Introduction

Recently, we have conducted the relaxation analysis for various electrode materials such as γ-Fe_2O_3[1-3], $LiMn_2O_4$[4], $LiFePO_4$[5], $LiCoO_2$[6], and $LiNiO_2$[7] after termination of electrochemical Li insertion/extracttion. Relaxation analysis makes transition of electrode material from kinetic state to equilibrium state clear.

Graphite is widely used as a negative electrode material for lithium ion rechargeable batteries. When lithium ion is inserted into graphite, various lithium-graphite intecalation compounds (Li-GICs) are formed dependent on insertion amount of lithium. Previously Yao et al.[8] synthesized Li-GICs by intercalating lithium into graphite electrochemically and analyzed the layered structures crystallographically by the one-dimensional Rietveld method. The one-dimensional Rietveld method was very powerful for the analysis of layered structures, and precise discussions for the change in the spacing between graphene layers for stage 1, stage 2, stage 2L, stage 3, and stage 4, were given.

In this study, we inserted lithium into graphite electro chemically and investigated the relaxation process by means of the X-ray Diffraction (XRD) .

Experiment

Natural graphite powder (LB-CG, Nippon Kokuen Japan) and poly(-vinylidene fluoride) was mixed with a ratio of 93 : 7 (weight ratio). N-methyl- 2-pyrrolidone was used as solvent. We spread the slurry on the copper foil. After drying, we punched out the copper foil with the graphite and used it as the working electrode. Lithium foil was used as the counter electrode. We inserted lithium electrochemically at a rate of 0.1C for 11 h using two electrode test cell (HS Cell, Hosen Co., Ltd.,). Ethylene carbonate (EC)/ dimethyl carbonate (DMC) (2:1 volume ratio) with 1 mol·dm^{-3} $LiPF_6$ was used as the electrolyte. After the termination of Li insertion, we immediately removed the working electrode from the cell and rinsed it in a glove box.

XRD patterns from 23 ° to 27° in 2θ were measured by using CuKα radiaton (UltimIV, Rigaku corp., Japan) for various relaxation time.

Results and discussion

In the XRD profile, peaks of stage1 001 and stage2 002 were observed. We fixed the each peak by Lorentzian function and obtained the integrated peak intensity precisely. From the integrated intensity of stage1 001 (I_1)and that of stage2 002(I_2) ,we calculated relative peak intensity (rI_1,rI_2) using the following equations.

$$rI_1 = \frac{I_1}{I_1 + I_2} \; , rI_2 = \frac{I_2}{I_1 + I_2}$$

Fig. 1 shows the change of relative peak intensities for each stage (rI_1, rI_2) with relaxation time. Fig. 1 shows that rI_1 decreased with the relaxation time and that rI_2 increased. It is considered that defective stage1 was formed at the lithium insertion process, and at the relaxation time, the defective stage1 separated to stage1 with no defect and stage2 .
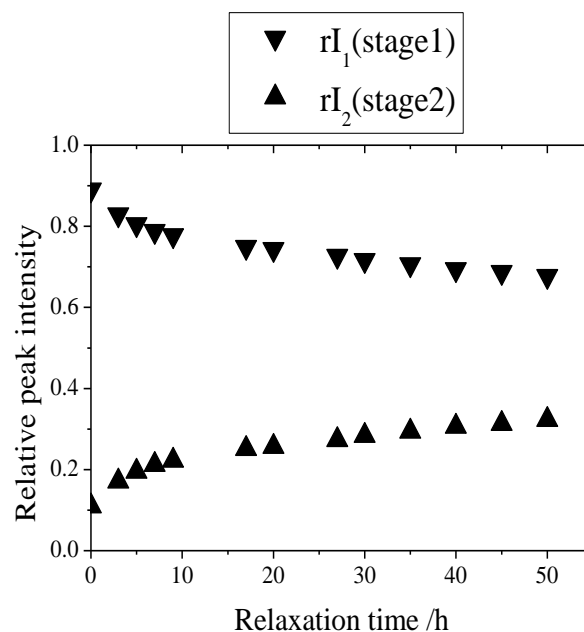

Fig.1 Change of relative peak intensity for stage1 (rI_1) and stage2 (rI_2)with relaxation time.

References

[1] M. Oda, M. Hibino, T. Yao, Meet. Abstr. - Electrochem. Soc. of Japan, p.8, 1A23 (2009).
[2] S. Park, M. Oda, and T. Yao, Solid State Ionics, 203, 29-32 (2011).
[3] S. Park, S. Ito, K. Takasu and T. Yao, Electrochemistry, 80 (10) 804-807 (2012).
[4] I. S. Seo, S. Park, and T. Yao, ECS Electrochem. Lett., 2 (1) A6-A9 (2013).
[5] S. Park, K. Kameyama, and T. Yao, Electrochemical and Solid-State Letters, 15 (4) A49-A52 (2012).
[6] I. Seo, S. Nagashima, S. Takai and T. Yao, ECS Electrochem. Lett., 2 (7) A72-A74 (2013).
[7] S. Nagashima, S. Park, I. S. Seo, and T. Yao, Meet. Abstr. – Electrochem. Soc. of Japan, p.5, 1A06 (2013).
[8] T.Yao, N.Ozawa, T.Aikawa, and S.Yoshinaga, Solid State Ionics, 175,199-202 (2004)