Relaxation Analysis of Graphite Anode Materials after Charge-Discharge Cycles

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ABSTRACT

Relaxation analysis has been carried out on fresh and charge-discharge cycled graphites to evaluate the effect of cycle process on the relaxation behavior after lithium insertion. While the formed stage I at charging partly transforms into stage II during relaxation, the cycled samples exhibit similar behavior as stage II. The charge-discharge cycles also restrict the relaxation variation in c-axis of stage II, even though lithium occupation ordering similarly occurs between the fresh and cycled samples. Variation in c-lattice of stage II would be the results of stage transformation from I into II, and charge-discharge process enables to follow the equilibrium stages rapidly at charging.

Keywords : Graphite, Stage Structure, Relaxation Analysis, Li-GIC

1. Introduction

Graphite has been employed as the practical anode material for lithium ion batteries due to its sufficiently low voltage, high specific capacity and low cost.1-3 The electrochemical behavior of graphite is based upon the lithium ion intercalation into graphene interlayers showing stage structures, where lithium ions typically occupy every n graphene interlayers at stage n.4-9 On charging, the stage number of Li-GIC (lithium graphite intercalation compound) decreases toward stage I with the ideal composition of LiC6.10-12 We have recently reported the structural relaxation behavior after the electrochemical lithium insertion into as well as extraction from graphite.9 Just after the lithium insertion, the formed stage I with some lithium occupation defects partly changes into stage II within 50 hours of relaxation time, i.e. defective stage I changes into the ideal stage I and II as shown in Fig. 1(a). Moreover, stage II with the stacking of higher and lower lithium concentration interlayers orders into the ideal stage II as Fig. 1(b) during the relaxation. Essentially the similar relaxation phenomena have been observed even after the lithium extraction. Namely, lithium ions migrate in Li-GIC in rather random manner during the charging or discharging process, while they would occupy the graphene interlayers in ordered manner thorough the structural relaxation.

The widely accepted model for lithium migration in Li-GICs to form the stage structure has been proposed by Daumas and Hérold (D-H model),10 in which in-plane lithium diffusion in the graphene interlayer enables the formation of stage structured domains. In terms of this model, the rate of stage change is associated with the in-plane lithium migration, which might be attributed by the charge-discharge cycles prior to the experiments due to the formation of preferred path. On the other hand, concerning that the stage change is accompanied by the shifts of graphene layers, the charge-discharge process before the last charging might facilitate the stage change by providing flexibility of graphene layer or some defects in Li-GIC. However, most of studies on this effect of preceding charge-discharge cycles to the electrode properties addressed to the surface condition including SEI formation, and no structural relaxation of bulk Li-GIC seems not to be investigated, although few studies focusing on the defect formation of graphite have been reported.13 In the present study, relaxation analysis has been carried out on the fresh and cycled graphite anode materials to clarify the contribution of charge-discharge process before the experiment to the relaxation phenomena.

2. Experimental

Active material of natural graphite powder (LB-GC, Nippon Graphite) was mixed with PVDF in the weight ratio of 93:7 to form the working electrode by spreading on the copper foil current collector, followed by drying in vacuum. The lithium metal counter-electrode and 1 M LiPF6 in EC/DMC solution (2:1 v/v, Kishida Chem.) were employed to fabricate the test cell (Hosen). The electrode has been charged with the current density of 0.1 C for 10 hours (nominal capacity) using a galvanostat (HJ-SM8, Hokuto Denko), which is referred as “1st charge” or “fresh sample” in this paper. Additional Li-GICs after charge-discharge cycles have been also prepared. Lithium ions were inserted and extracted up to the nominal capacity with the rate of 0.1 C for 1 time and 5 times with 1 minute of rest after every step, and finally lithium ions were inserted into the cycled electrode with 0.1 C rate for 10 hours like “1st charge”. These samples are presently referred as “2nd charge” and “6th charge” according to the number of charge process.

Relaxation analysis study has been carried out as the previous reports.12-17 After the termination of lithium insertion, the charged electrode with a copper current collector was immediately separated from the cells to prevent unfavorable local cell reaction,18 and washed with EC and EC/DMC solvents followed by drying in an Ar gas filled glove box. The electrode was then mounted on a sealed holder to set on an X-ray diffractometer (Ultima IV, Rigaku) using CuKα radiation. The diffracted X-ray was counted in the 2θ range between 11° to 53° at a rate of 10°/min19 with 0.01° step. The measurements were carried out after various relaxation times.

The Rietveld refinements were carried out using RIEVEC code19,20 with one-dimensional calculation along c-axis assuming...
co-existence of stages I and II. The structure factors used in the analysis were described in elsewhere. The mole fraction of each stage was deduced from the refined scale factor and unit cell volume. Two types of graphene interlayer distances in stage II, and as depicted in Fig. 1(c), were calculated from the refined structure factor.

3. Results and Discussion

Figure 2 shows X-ray diffraction patterns of Li-GICs of the (a) 1st, (b) 2nd and (c) 6th lithium insertions with various relaxation periods. In all the samples, diffraction peak of stage II is observed in addition to those of stage I even for the nominal charging capacity for LiC$_6$, which is presumably due to SEI formation. The peak of stage II seems to develop with the relaxation time in comparison with that of stage I. Figure 3 exemplifies the Rietveld refinement of XRD pattern for 6th lithium insertion collected after 53 hours of relaxation assuming stages I and II coexistence. Fairly good agreement has been attained between the measured and calculated patterns. The obtained molar ratios of stage I, $n_I$, thorough the Rietveld analysis are plotted against relaxation time in Fig. 4, in which the remains from unity should be for stage II. For all the samples, mole fraction of stage I gradually decreases with the relaxation time up to 50 hours, indicating that the formed stage I partly transformed into stage II during the relaxation period. Such trends are consistent with the previous study using pristine samples, although the stage variation is rather steeper in the present study for the higher current density (0.1 C for present study against 0.01 C for the previous). It is obvious that stage change at relaxation becomes gentle with the cycle process, as the initial value of $n_I$ for the 6th insertion is smaller than the others. Accordingly, charge-discharge cycles would facilitate the Li-GIC to follow the equilibrium stage structure during charging, allowing the smaller variation at the relaxation time. The refined c-length of the stages I and II are plotted versus relaxation time in Fig. 5. For the stage I, $c_1$ remains almost constant value during the relaxation for both first charge and charge-discharge cycled samples. A lot of in-situ or ex-situ studies have reported that $c_1$ was not largely altered by the lithium content or charging state, and in addition, our previous relaxation analysis using fresh graphite also exhibited almost invariant $c_1$ value. Then, charge-discharge process does not apparently attribute to the c-length of stage I, even though lithium concentration or distribution might be varied. On the other hand, $c_{III}$ gradually decreases with the relaxation time for all the samples.
with the charging current density as the previous report.9

while we obtained these distances by re-

is not largely attributed by the preceding charge-discharge process

Daumas-Hérold (D-H) model,10 in-plan lithium migration in stage II

time,

dc

changes in dc

Figure 5. Relaxation time variation of c-length for (a) stage I and

(b) stage II. Triangles: 1st, rectangle: 2nd and circles: 6th lithium

insertion.

as Fig. 5(b), which is also consistent with the previous work.9

However, the difference between the initial and relaxed (up to ~50 hours) c-lengths diminishes with the charge-discharge cycles.

As the c-length in stage II crystallographically consists of wider and narrower graphene interlayer distances, dw and dn in Fig. 1(c), we obtained these distances by refining the structure factors, which are plotted in Fig. 6. While dw increases with the relaxation time, dn decreases, showing no significant differences between the fresh and cycled samples within the experimental accuracy. It should be noted that the variation range of interlayer distance is wider than that of c-length in stage II, e.g. 0.06 Å for Δdw or Δdn against 0.01 Å for ΔcII even for the 1st charge. Although the change in c-length leads the variation of overall crystallite size, symmetrical changes in dw and dn do not, requiring only a shift of every other graphene layer. Since mainly acting interaction between the graphene layers is van der Waars force, only a shift of half number of graphene layers would be favorable rather than enhancement of lattice parameter. Assuming that graphene interlayer distance depends on the lithium occupation, lithium ion should move from the narrower graphene interlayer into the wider one to undergo the lithium occupancy ordering as shown in Fig. 1(b). In terms of the Daumas-Hérold (D-H) model,10 in-plan lithium migration in stage II is not largely attributed by the preceding charge-discharge process for the relaxation behavior of dw and dn although it is associated with the charging current density as the previous report.9

Considering that the fresh sample showing apparent stage change exhibited larger variation in c-length of stage II, decrease in cII would be mainly due to the newly created stage II which should possess wider interlayer distance, since twice of cI (~7.14 Å) is larger than cII (~7.04 Å).

In the present study, it is found that charge-discharge process would facilitate the transformation from stage I into stage II accompanied by the change in c-length, while it provides less contribution to the lithium occupation ordering in stage II without obvious change in c-length. Although most of charge-discharge studies on graphite have focused on the variation of surface condition in terms of electrode reaction,9 present study indicated that bulk properties of relaxation also altered by the charge-discharge cycles before the last lithium insertion. Further inves-
tigation should be made using NMR11 or Raman12 experiments to reveal the detailed relaxation mechanism of Li-GICs in terms of lithium diffusion or graphite layer properties.

4. Conclusion

We have performed X-ray relaxation analysis on fresh and charge-discharge cycled Li-GICs. It has been found that stage I is formed at charging followed by partial transformation into stage II at relaxation, while the charge-discharge cycles restrict the excess formation of stage I on charging. In addition, the variation of c-length at the relaxation can be ascribed by the stage change from I into II, which diminishes with the charge-discharge cycles. On the other hand, the lithium occupation ordering in stage II or in-plane diffusion of lithium ion seems not to be apparently influenced by the charge-discharge cycles.

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