Electrochemical intercalation behaviors of lithium ions into graphene-like graphite (GLG) were investigated at high cell voltages. The interlayer spacing of GLG started to increase at much higher cell voltages than that needed for graphite. It stepwise increased at a decrease in the cell voltages, indicating the staging phenomenon. The thermodynamic considerations suggested that the strong interaction between oxygen atoms introduced in GLG and lithium ions is responsible for the formation of intercalation compounds of desolvated lithium ions. The interlayer distance of GLG was more important than the content of oxygen in it for the decreased separation energy of carbon layers and, accordingly, for the onset voltage of the intercalation of lithium ions into it. The intercalation of desolvated lithium ions into GLG was achieved even in an electrolyte solution containing dimethoxyethane in which solvents are co-intercalated into graphite.

Graphite has been widely used as an anode for lithium ion batteries for portable devices such as laptop computers, cell phones, etc. However, its limited theoretical capacity of 372 mAh/g and relatively poor rate performance are not suitable for use in electric vehicles, etc. In this context, graphene-based carbon materials showing high capacity and rate performance have been introduced and widely studied. However, because of the intrinsically high surface area of graphene-based carbons, they suffer from low columbic efficiency. We have recently introduced graphene-like graphite (GLG) as a superior anode material for lithium ion batteries, showing a high capacity of 608 mAh/g with a cut off voltage of 2 V, high rate performance (the ratio of the capacity at 6 C and 0.1 C rates of 79%), and good cycling properties. This material is prepared from the thermal reduction of graphite oxide at 800 °C, carefully avoiding the exfoliation of the carbon layers. The regularity of the stacking of carbon layers of GLG is quite high and the surface area is low. Moreover, the morphology and interlayer spacing of it are similar to those of graphite, though it contains considerable amounts of oxygen and pores with the size of 1–5 nm within carbon layers mainly in the state of O=C. The lithium storage capacity of GLG is strongly related to the oxygen content and the large expansion of interlayer spacing during the intercalation of lithium ions was ascribed to the high capacity, reaching 673 mAh/g of discharge capacity. The coulombic efficiency of GLG was higher than those reported for graphene-based carbons, however, was still not enough high (50–56% with a cutoff voltage of 2 V). In the case of a graphite anode operated in an ethylene carbonate based electrolyte solution, solvated lithium ions are first intercalated into it and then the solvent molecules are reduced to form a lithium ion conducting passivation layer so called solid electrolyte interphase (SEI) at higher potential regions of around 0.8 V vs Li/Li⁺. This SEI layer effectively prevents the further decomposition of solvent molecules and the irreversible capacity is low. On the other hand, the origin of irreversible capacity of GLG has not been well known and it would caused by either the irreversibly trapped lithium ions to oxygen in it, the electricity needed to form SEI and reduction of solvent molecules at GLG surface which is not well covered with SEI. For the last issue, the structural changes of GLG during intercalation of lithium ions would be important. We have reported that lithium ions are intercalated into it at a higher cell voltage of 0.48 V and the interlayer spacing reached a very large value of 0.48 nm at 0 V. We have also found that all of the lithium species stored in fully charged GLG are in the ionic state, based on the 'Li NMR measurement. However, the intercalation behavior of lithium ions into GLG especially at the early stages of it has not yet been studied, which would be strongly related to the formation of SEI. Moreover, the mechanism of lithium storage in graphene-based carbons is not well understood because of their poor structural regularity, except for the results reported by Wang et al. They have indicated that lithium ions are intercalated between carbon layers, based on the TEM observation of lithium introduced nitrogen doped graphene operated in an all-solid-state cell.

In this study, the structural changes of various GLG samples during the first charging process especially at high cell voltage regions were investigated and the mechanism of the intercalation of lithium ions was discussed based on the thermodynamic considerations. We also think that the results in this study would give a new insight into the lithium storage not only in carbon materials with large interlayer spacings such as graphene-based carbons but also in soft carbons.

**Experimental**

Graphite oxide (GO) was prepared from natural graphite powder with an average diameter of 5 μm, based on the Brodie’s method. It was then heated at 700–900°C for 5 h and naturally cooled in the same manner as reported in our previous studies. They are denoted as GLGT (T; heat-treatment temperature). Air treated GLG800 obtained in our previous study was also used and was denoted as A-GLG800. The elemental analysis measurements of GLG700, GLG800, GLG900, and A-GLG800 showed that the oxygen contents of them were 4.1, 2.6, 1.5 and 5.9 at%, respectively. The interlayer spacings of them were determined by the X-ray diffraction measurement using Si powder as an internal standard and were 0.350, 0.339, 0.332, and 0.341 nm, respectively. They were mixed with acetylene black of conducting reagent and polyvinylidene fluoride as binder with a weight ratio of 8:1.1. The electrochemical measurement was performed in 1M LiClO₄-ethylene carbonate + dimethyl carbonate (EC+DMC, 1:1) by constant current (20 mA/g) or constant current voltage (5 h) methods. After charging to various cell voltages, the electrode was removed from the cell in a glove box filled with Ar and rinsed with DMC. It was then placed in a sample holder avoiding contact with air, and X-ray diffraction measurement was performed using Bruker D2 Phaser (CuKα radiation). The open circuit voltages of A-GLG800 at various states of charge were also monitored. In the case of voltages above 0.8 V, the open circuit voltages were recorded after 10 h. Otherwise the recording time was 5 h, because it took more time to reach almost constant values. The first discharge (de-intercalation of lithium ions) capacities and coulombic efficiencies of...
GLG700, GLG800, GLG900, and A-GLG800 were 575, 555, 486, and 608 mAh/g, and 51, 50, 50, and 56%, respectively.

The electrochemical intercalation of lithium ions into GLG samples was also performed in electrolyte solutions of 1 M LiCF<sub>3</sub>SO<sub>3</sub>-dimethylsulfoxide (DMSO) and 1 M LiCF<sub>3</sub>SO<sub>3</sub>-dimethoxyethane (DME).

Optimized structures for lithium-intercalated GLG with a composition of Li<sub>8</sub>C<sub>136</sub>O<sub>8</sub> and Li<sub>16</sub>C<sub>136</sub>O<sub>8</sub> were calculated by using the Quantum Espresso (ver. 5.0.2) program package as previously reported.<sup>5,7</sup>

**Results and Discussion**

**Intercalation of lithium ions into GLG.**—Figure 1 shows the X-ray diffraction patterns of A-GLG800 before and after charged to 1.0 and 0.9 V. The diffraction peak at 2θ = 26.2° (d = 0.341 nm) was observed for the pristine A-GLG800 and it was in almost the same position after charged to 1.0 V. At 0.9 V, a shoulder at 2θ = 25.7° (d = 0.347 nm) was observed, together with that of the pristine A-GLG800. At the same time, a broad peak at 2θ = 52.9° (d = 0.173 nm) also appeared, indicating the formation of intercalation compound of A-GLG800. Figure 2A shows the X-ray diffraction pattern of A-GLG800 after it was charged to 0.9 V and then it was kept at 0.9 V for 3 days by a constant current method shown in Fig. 1. The diffraction peak due to unreacted A-GLG800 disappeared and that at 2θ = 25.7° (d = 0.347 nm) was observed. This result indicates that the reaction occurring at higher cell voltages is slow, though, A-GLG800 electrode showed high rate performance.<sup>5</sup>

It has been known that the electrochemical reduction of graphite occurs above 1 V in lithium ion containing organic solutions such as carbonates or ethers, etc, forming intercalation compounds of lithium ions solvated by them. The reported repeat distance along c-axis (I<sub>c</sub>) values of stage 1 type intercalation compound containing Li ions solvated by carbonates or ethers are 1.09–1.24 nm.<sup>13,14</sup> The thicknesses of the intercalated species (d<sub>i</sub>) are calculated at between 0.71–0.91 nm by subtracting the thickness of graphite (0.335 nm) from these I<sub>c</sub> values. The (00n+2) line is most intensely observed for stage n type intercalation compound of solvated Li ions.<sup>13,15</sup> In such a case, the relationship between stage number “n” and the observed d value (d<sub>obsd</sub>) calculated from the most intense X-ray diffraction peak is expressed as d<sub>obsd</sub> × (n+2) = 0.341 × (n+2) + d<sub>i</sub>. Therefore, if the solvated Li ions are also inserted between the layers of A-GLG800, the stage numbers of n = 116–150 are expected using d<sub>obsd</sub> = 0.347 nm, which are not likely. This indicates that the inserted species are desolvated Li ions. It is difficult to determine the I<sub>c</sub> value of this sample using only two diffraction lines. However, two types of structures are expected based on the observed d spacing of 0.347 nm, assuming that the (00n) line is most intensely observed as in the case of lithium-intercalated graphite. One is the dilute stage 1 type material with I<sub>c</sub> = 0.347 nm and the other is stage 6 type one with I<sub>c</sub> = 2.08 nm. In the latter case, the thickness of the intercalated species of d<sub>i</sub> = 0.036 nm (0.371–0.335) which is observed for lithium-intercalated graphite.<sup>16,17</sup>
The interlayer spacing of the pristine C136O8 with an oxygen content of 5.5 mol% was 0.332 nm, which was slightly larger than that calculated for graphite (0.328 nm) in the same manner. The interlayer spacing of Li8C136O8 increased to 0.353 nm as the result of insertion of lithium ions. The increase in the interlayer spacing is therefore 0.021 nm and is similar to that observed for LiC6 (0.037 nm). In our previous paper, in the fully charged GLG, oxygen atoms migrated to the interlayer space of GLG, resulting in the large increase in the interlayer spacing of 0.14 nm.5 However, at this low level of lithium loading, the positions of oxygen atoms were almost identical to those in the pristine GLG and the lithium ions were still located at the positions with the same distance from both of the adjacent carbon layers. On the other hand, in the case of Li16C136O8 with a higher loading of lithium ions, the interlayer spacing further increased to 0.363 nm and some of the oxygen atoms slightly moved toward the interlayer space as was observed for GLG with higher lithium content observed in our previous study.5 This result also indicates that it is reasonable to think that high stage compounds were formed at the beginning of the electrochemical lithium storage in GLG.

Figure 4 shows the variation of d spacings of A-GLG800 after charged to various cell voltages as shown in Fig. 4. The d spacings calculated (d_{calc}) from various stage numbers of n based on the equation of $d_{calc} \times n = 0.341 \times n + d_i$ are also shown with broken lines in the figure. The stage numbers of lithium intercalated A-GLG800 changed from 6 to 4, 2 and then to 1, though the difference between observed and calculated d spacings became larger for the samples charged to lower cell voltages. We previously reported the large increase in the interlayer spacing of graphite oxides thermally reduced under H2 gas flow,18,19 when they were used as anodes of a lithium ion battery. However, the stage transformation phenomenon as shown above was not observed for these samples. This indicates that the present A-GLG800 with three-dimensional stacking regularity of carbon layers5 possesses graphite like nature though it contains a considerable amount of oxygen and the interlayer spacing of it is slightly larger than that of graphite.

Figure 5 shows the variation of d spacings of A-GLG800 after charged to various cell voltages as shown in Fig. 4. The d spacings calculated (d_{calc}) from various stage numbers of n based on the equation of $d_{calc} \times n = 0.341 \times n + d_i$ are also shown with broken lines in the figure. The stage numbers of lithium intercalated A-GLG800 changed from 6 to 4, 2 and then to 1, though the difference between observed and calculated d spacings became larger for the samples charged to lower cell voltages. We previously reported the large increase in the interlayer spacing of graphite oxides thermally reduced under H2 gas flow,18,19 when they were used as anodes of a lithium ion battery. However, the stage transformation phenomenon as shown above was not observed for these samples. This indicates that the present A-GLG800 with three-dimensional stacking regularity of carbon layers5 possesses graphite like nature though it contains a considerable amount of oxygen and the interlayer spacing of it is slightly larger than that of graphite.

Figure 6A shows the variation of open circuit voltage of A-GLG800 electrode during the intermittent charging as a function of time. The cell voltage steeply increased just after charging to various cell voltages and then gradually increased. Reflecting the slow kinetics of the intercalation of lithium ions into A-GLG800 at higher cell voltages, it took a long time to reach almost constant values. On the
The above results are very important in considering the origin of the unexpectedly low coulombic efficiency of GLG samples of around 50–56% independent of the oxygen content in them. Considering that the thickness of SEI layers formed on A-GLG800 was not so large based on the XPS measurement,\(^5\) the gradual increase in the interlayer spacing of GLG samples observed here is one of the main reasons for their low coulombic efficiency. The surface of GLG samples would not be fully covered with SEI during the increase in the interlayer spacing, resulting in the continuous decomposition of solvent molecules. Based on this idea, we are now trying to improve the coulombic efficiency, which will be reported in the near future.

**Thermodynamic considerations of the intercalation of lithium ions into GLG.**—It is also interesting that the intercalation of lithium ions occurred at much higher voltages than that observed for graphite (below 0.2 V vs Li/Li\(^+\)) despite that their interlayer spacings (0.332–0.350 nm) are almost similar to that of graphite (0.3354 nm). Figure 8 shows the Born-Haber cycles of the reductive intercalation of lithium ions or solvated lithium ions into graphite or GLG, based on the model used to discuss the oxidative intercalation of liquid or gaseous species into graphite.\(^{20}\) This ignores the entropic terms, however, well explained the degree of many intercalation compounds of fluorooanions with similar sizes.\(^{20}\) The formation of solvated lithium ions-intercalated materials could be related to three enthalpic terms as shown in Fig. 8A. They are the decrease in van der Waals interaction energy between graphene sheets that are separated by lithium ion (layer separation energy, hereafter E\(_s\)), the energy released during the addition of electron to graphene sheets (electron affinity, E\(_e\)) and the lattice stabilization energy of the intercalation compound produced (lattice energy, E\(_l\)). On the other hand, in case of the intercalation of lithium ions, the energy to remove solvents from solvated lithium ions (desolvation energy, E\(_{des}\)) is additionally needed as shown in Fig. 8B.

In the case of the electrochemical system, E\(_e\) depends on the applied potential and E\(_{des}\) is common regardless of the host materials. Therefore, the difference in the voltages where intercalation of desolvated lithium ions into GLG or graphite occur is ascribed to that in the sum of E\(_s\) and E\(_l\). For example, stage 2 type materials are formed around 0.85, 0.73, 0.72, 0.65, and 0.12 V vs Li/Li\(^+\) for GLG700, GLG800, A-GLG800, GLG900, and graphite, respectively, based on Figs. 5 and 7, and the literatures.\(^{16,21}\) This means that the sum of E\(_s\) and E\(_l\) is larger in the above order. The effect of oxygen atoms in graphite, E\(_e\), has not been quantitatively estimated, but the present result indicates that the interlayer distance between GLG layers, therefore, E\(_s\) is more important than the content of oxygen in GLG for the difference in the sum of E\(_s\) and E\(_l\). Consequently, the large difference of the stability of the intercalation compounds of GLG900 and graphite with similar interlayer spacings is ascribed to that in U\(_l\). As shown in Fig. 3, lithium ions preferably located near oxygen atoms. The

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**Figure 6.** (A): Variation of cell voltage during the intermittent charging as a function of time. (B): Variation of cell voltages for charging and the open circuit voltages observed after 5 or 10 h as a function of the charge capacity.

**Figure 7.** Variation of the interlayer spacing of GLG700, GLG800, and GLG900 after charged to various cell voltages as measured for A-GLG800. In this figure, the d\(_{calc}\) obtained using the equation of d\(_{calc}\) × n = d\(_{int}\) × n + d\(_c\), where d\(_{int}\) indicates the initial d values of GLG700, GLG900 before the intercalation of lithium ions are also shown with broken lines. Irrespective to the d\(_{int}\), the d spacing changed stepwisely, indicating that the stage transformation occurred during the intercalation of lithium ions. The d spacings which are not expected from the stage structure were observed especially at lower cell voltages. The migration of oxygen atoms to the interlayer space observed for GLG with a larger lithium content as shown in Fig. 3, after such sites are occupied by lithium ions and interlayer spacing greatly increased, additionally intercalated lithium ions are expected to move much faster.
stronger interaction between negatively charged oxygen and lithium ions than that between delocalized negative charge in graphite and lithium ions is responsible for the larger $U_L$ in GLG, and accordingly higher stability of the intercalation compound of it. Note also that lithium-intercalated GLG (Li-GLG) is more stable than the solvated lithium-intercalated GLG (Li-S-GLG). This means that the sum of $E_{des}$, $E_s$ (Li-GLG) and $U_L$ (Li-GLG) is smaller than that of $E_{des}$, $E_s$ (Li-S-GLG) and $U_L$ (Li-S-GLG). The $E_s$ (Li-GLG) is larger than $E_s$ (Li-S-GLG) because the size of solvated lithium ions is larger than that of lithium ions and the increase in the interlayer spacing is larger. Therefore, the much smaller $U_L$ for Li-GLG than Li-S-GLG is responsible for this phenomenon.

**Effect of electrolyte solutions on the intercalation behavior of lithium ions into GLG.**—Based on the above results, we expect that intercalation of desolvated lithium ions proceeds even in the electrolyte solutions containing organic solvents in which solvent co-intercalation into graphite occurs. Here, we chose DMSO and DME as solvents. It has been already reported that in the electrolyte solutions containing such solvents intercalation of solvated ions into graphite occurred.\(^\text{13}\)

Figure 9 shows the charge curves of GLG in the electrolyte solutions containing the above solvents, together with that in 1 M LiClO$_4$-EC+DMC.\(^\text{5}\) In a DMSO-based electrolyte solution, a plateau at 1.3 V was observed and the electrolyte solution colored black, indicating that intercalation of lithium ions solvated with DMSO molecules into GLG occurred as is the case of graphite, and GLG

![Figure 8](https://i.imgur.com/3G5.jpg)

**Figure 8.** Born-Harber cycles of the reductive intercalation of (A): solvated and (B): desolvated lithium ions into graphite and graphene like graphite.

![Figure 9](https://i.imgur.com/4G5.jpg)

**Figure 9.** First charge curves of GLG in (A): 1M LiCF$_3$SO$_3$-DMSO, (B): 1M LiCF$_3$SO$_3$-DME and (C): 1M LiPF$_6$-EC+DEC.
layers were finally exfoliated. On the other hand, in a DME-based solution, the charge curve was almost similar to that observed in the EC+DMC-based electrolyte.

Figure 10 shows the X-ray diffraction patterns of GLG after charged to 0 V in EC+DEC- and DME-based electrolyte solutions. The diffraction peak of GLG after charged in a DME-based solution was observed at $2\theta = 18.76^\circ$ ($d = 0.473$ nm), which was almost the same as that observed in EC+DEC ($2\theta = 18.45^\circ$ ($d = 0.481$ nm)). This strongly indicates that desolvated lithium ions were intercalated into GLG in the same manner as in an EC+DMC-based electrolyte solution. This finding is very important because GLG can be used in electrolyte solutions free from EC which melts at a high temperature and is not favorable for the use at lower temperatures.

Conclusions

In this study, we have investigated the electrochemical intercalation behaviors of lithium ions into various GLG samples, especially at high cell voltage regions. The interlayer spacings of GLG started to increase at much higher cell voltages than that observed for graphite. It stepwisely increased as the decrease in the cell voltages, indicating the staging phenomenon. To the authors’ best knowledge, this staging phenomenon has not been observed for carbon materials other than graphite. It seems that the diffusion of lithium ions was slow at higher cell voltage regions.

The thermodynamic considerations suggested that the strong interaction between oxygen atoms introduced in GLG and lithium ions is responsible for the formation of intercalation compounds of desolvated lithium ions at high cell voltages, which is not observed for graphite. The lithium ions started to be intercalated at higher cell voltages into GLG samples with larger interlayer spacings. This indicates that the interlayer distance of GLG was more important than the content of oxygen in it for the decreased separation energy of carbon layers and accordingly, for the higher onset voltages of the intercalation of lithium ions into it. Based on these behaviors, the intercalation of desolvated lithium ions into GLG was achieved even in an electrolyte solution containing dimethoxyethane in which solvents are co-intercalated into graphite.

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