Effects of Pre-Lithiation on the Electrochemical Properties of Graphene-Like Graphite

Junichi INAMOTO,a,* Shunya MARUYAMA,a Yoshiaki MATSUO,a Satoshi UCHIDA,b Katsumi MAEDA,c and Masashi ISHIKAWAd

a Department of Applied Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Japan
b Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology, Ikeda, Japan
c IoT Device Laboratory, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki, Japan
d Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Japan

* Corresponding author: j.inamoto@eng.u-hyogo.ac.jp

ABSTRACT

Pre-lithiation of graphene-like graphite (GLG) was conducted and its effects on structural and electrochemical properties of GLG were investigated. When lithium naphthalenide was used for the pre-lithiation, a large amount of the solution was required for the intercalation of lithium ions into GLG. Moreover, binder in the composite electrode was degraded by the pre-lithiation and the discharge capacity considerably decreased. On the other hand, pre-lithiation of GLG with lithium metal resulted in the increase of interlayer distance to similar value to that of electrochemically full-charged GLG, even though the amount of the added lithium metal was equivalent to only 28% or 38% of SOC of the GLG. In addition, the decreases in the charge capacity were more than those expected from the amounts of lithium metal. The full and immediate interlayer expansion by the pre-lithiation of GLG suppressed the repeated exfoliation and re-formation of SEI unlike electrochemically charged GLG. Since the discharge capacities were almost identical to that of the pristine GLG, the coulombic efficiency was greatly improved. The issue of low coulombic efficiency of GLG at the initial cycle can be conquered by this method, and it would increase the probability of the practical application of GLG.

Key words: Lithium-ion Battery, Pre-lithiation, Graphene-like Graphite, Anode

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable devices for over two decades. Recently, LIBs are also applied to large-scale devices such as electric vehicles and energy storage system. However, conventional LIBs do not meet the requirements for the large-scale devices in terms of their capacity and rate capability. This is mainly because graphite, negative active material, shows limited theoretical capacity of 372 mAh g⁻¹ and poor rate performance. Therefore, innovation of anode materials with improved capacity and rate capability is essential for the LIBs for the large-scale devices. To overcome these intrinsic problems of graphite, several carbon-based materials such as carbon nanotubes, graphene, and other nanocarbons have been expected as new anode materials for LIBs because they have larger capacity and better rate capability compared to graphite. However, since they have intrinsically high specific surface area, they suffer from poor coulombic efficiency. In addition, since the most of these materials have rather high mean-discharge-potential, the accessible capacity decreases when used in practical LIBs. Although it is desirable for the new anode materials to have not only high capacity and good rate capability but also good coulombic efficiency and low working potential, there has been no material which meets all the above-mentioned requirements.

In this regard, we have recently introduced graphene-like graphite (GLG) as a new candidate for an anode material of LIBs, which can overcome these intrinsic difficulties of the carbon-based materials. The capacity of GLG reaches 608 mAh g⁻¹ with a cut-off voltage of 2 V, and it shows good cycle performance. In addition, the rate capability of GLG is superior to that of graphite; the capacity of GLG at 6 C remains 79% of the capacity at 0.1 C. GLG is synthesized via thermal reduction of graphite oxide (GO) under vacuum with quite small increasing-rate of temperature to avoid exfoliation of graphene sheets. Employing this unique process, interlayer spacing of graphene sheets was reduced to ca. 0.34 nm, and the specific surface area was around 30 m² g⁻¹, which were similar values to ordinal graphitic carbons. These properties of GLG contribute to less side reactions at the electrode/electrolyte interface, leading to improved coulombic efficiency compared to nanocarbons such as graphene. However, despite the improvement, the coulombic efficiency at the initial charge and discharge was no more than 56%, and this is not adequate for the practical use. As is well-known, solid electrolyte interphase (SEI) is formed on the carbon-based anode materials at the initial charging, and this process decreases the amount of active lithium-ion, leading to loss of accessible capacity. Similar to others, formation of SEI is considered to be a major cause of the irreversible capacity of GLG. In addition, it has been suggested that irreversible trapping of lithium ion by oxygen-containing groups in GLG is also the cause of the irreversible capacity. However, the coulombic efficiency of GLG was only slightly improved when it was treated with hydrogen gas atmosphere and the oxygen content of it was reduced. To decrease the irreversible capacity furthermore, we considered to intercalate lithium ion into GLG in advance of the initial charge, which is so-called pre-lithiation. So far, the pre-lithiation has been applied to many kinds of anode materials, and it was proved to be effective in reducing the irreversible capacity. There are several ways to conduct pre-lithiation such as electrochemical lithiation.
direct contact with lithium metal.\textsuperscript{16,17} treatment with lithium charge-transfer complexes.\textsuperscript{18–20} We have chosen the direct contact with lithium metal and the treatment with lithium charge-transfer complex as the pre-lithiation methods because they are simple and need no re-construction of cells for the following electrochemical measurement. In this study, the pre-lithiation of GLG was carried out via the direct contact with lithium metal or treatment with lithium naphthalenide complex, and the electrochemical and structural properties of pre-lithiated GLG was evaluated.

2. Experimental

Graphite oxide (GO) was synthesized from natural graphite (Z-SF, Ito graphite Co., Ltd.) based on the Brodie’s method.\textsuperscript{21,22} The GO was thermally reduced at 800°C under vacuum to synthesize graphene-like graphite (GLG). The detailed condition of the synthesis of GLG was described in our previous report.\textsuperscript{7} As a result of X-ray diffraction measurement, it was proved that the obtained sample had similar structural properties to the sample shown in our previous reports,\textsuperscript{7} indicating that GLG was successfully synthesized. The detailed condition of XRD measurement will be described later in this section.

The GLG was mixed with acetylene black (AB) and polyvinylidene difluoride (PVDF) with a weight ratio of 8:1:1 in N-methylpyrrolidone (NMP), coated on copper mesh, and dried to obtain a composite electrode. Loading density of the composite was ca. 17 mg cm\textsuperscript{-2}. Before composing a cell, pre-lithiation of the composite electrode with (1) lithium naphthalenide or (2) lithium metal was carried out. The treatment with (1) lithium naphthalenide was as follows. 5 mmol lithium metal and 2.5 mmol naphthalene was dissolved in 2-methyl tetrahydrofuran (2-MeTHF), obtaining lithium naphthalenide complex solution. The solution was dropped on the electrode and laid for 4 or 24 hours. In order to obtain GLG electrodes with different state-of-charge (SOC), volume of the dropped solution was varied from 0.23 to 1.15 mL, whose content of lithium were equivalent to 39–193% of SOC of the initial charge capacity of the GLG electrode (1000 mAh g\textsuperscript{-1}). The treatment with (2) lithium metal was as follows. 0.2 mm-thick lithium foil, which equivalent to 15–38% SOC of the GLG electrode, was pressed on the composite electrode. The electrode was immersed in 1 mol dm\textsuperscript{-3} LiClO\textsubscript{4}/ethylene carbonate + dimethyl carbonate (EC + DMC, 1:1) for 24 hours, obtaining the pre-lithiated GLG electrode. Using the pre-lithiated GLG electrode as a working electrode, a three-electrode cell was composed with lithium metal as a counter and a reference electrode and 1 mol dm\textsuperscript{-3} LiClO\textsubscript{4}/EC + DMC (1:1) as an electrolyte solution. Charge-discharge measurement was carried out with a battery charge-discharge system (HJ1001SD8, Hokuto Denko Corporation). The current density was 40 mA g\textsuperscript{-1} and cut-off voltage was 0–2 V. Note that reduction of GLG was denoted as charge, namely lithium-ion intercalation process. To evaluate the amount of pre-lithiation, the constant current and constant voltage (CCCV) discharge was also conducted. The pre-lithiated electrode was discharged up to 2.0 V with 40 mA g\textsuperscript{-1} of current density, then the potential was held at 2.0 V for 5 hours. All the pre-lithiation and cell composition were conducted in an Ar-filled glove box.

To clarify the effect of pre-lithiation on the structure of GLG, XRD measurement of pristine, pre-lithiated GLG was conducted using D2 Phaser (Bruker Corporation). The pre-lithiated and cycled electrode was moved to an air-tight sample holder in the Ar-filled glove box, and XRD was measured in Ar atmosphere.

3. Results and Discussion

Figure 1 shows the XRD patterns of pristine GLG and GLG treated with various amounts of lithium naphthalenide solution for 24 hours. The pristine GLG showed a sharp peak around 20 = 26°. After the treatment with the solution containing lithium equivalent to 39\% and 58\% of SOC, the peak slightly shifted to higher degree. It indicated that the oxygen-containing groups in the bulk of GLG was reduced and their interlayer distances decreased. However, the intercalation of lithium ion was not observed. After the treatment with the solution containing lithium equivalent to 97\% and 145\% of SOC, the shoulder peaks at lower angles were emerged, indicating intercalation of a small amount of lithium ions and slight expansion of interlayer distance of GLG. After the treatment with the solution containing lithium equivalent to 193\% of SOC, the peak around 26° was almost diminished, and a new peak at 29 = 19.25° was emerged. The interlayer distance was estimated at 0.46 nm, which was attributed to GLG electrochemically charged to ca. 0.2–0.3 V (ca. 80\% of SOC) estimated from our previous report.\textsuperscript{23} From these results, it was clarified that excessive amount of lithium naphthalenide solution was required to accomplish the pre-lithiation of GLG. However, after the pre-lithiation with excessive amount of the solution (145\% and 193\%), exfoliation of the composite electrode proceeded. This was probably because PVDF in the electrode was reduced and decomposed by lithium naphthalenide. Therefore, the following electrochemical measurements were conducted only for GLG treated with the solution containing lithium equivalent to 39\%, 58\%, and 97\% of SOC.

Figure 2(a) shows the initial charge and discharge curves of GLG with or without pre-lithiation by lithium naphthalenide. The amount of lithium equivalent to the SOC of GLG. Soaking time, open-circuit-potential (OCP) and coulombic efficiency of each electrode were shown in the figure. In order to compare the changes of the charge curves visually, end point of the curves was shifted to that of non-lithiated electrode in Fig. 2(b). At first, the soaking time was fixed to 24 hours, and the effects of the amount of the lithium naphthalenide solution on electrochemical properties were evaluated. Increasing the amount of the solution, the OCP lowered and charge capacity at 0.7 V decreased. From the results, we expected the pre-lithiated GLG would show much better coulombic efficiency than non-lithiated GLG. However, the pre-lithiation also made the discharge curves steeper and the discharge capacity decreased, leading to only limited effects in the initial coulombic efficiency. As described above, the treatment with the excess amount of the solution exfoliated the composite from current collector. Although no visible change was observed after the treatment with less amount of the solution, some parts of the composite was probably peeled off, resulting in decreased discharge capacity. In Fig. 2(b), the electrode treated with the solution containing lithium equivalent to 97\% of SOC obviously showed the steeper charge curve, while the electrode
treated with 39% and 58%-SOC solution showed similar profiles to the non-treated electrode. It clearly indicated that the treatment with the 97%-SOC solution largely degraded the electrode. To avoid the degradation of the electrode, the soaking time was decreased to 4 hours. The charge and discharge curves were also shown in the figures. The OCP of the electrode decreased to 0.85 V after 4-hour soaking, which was a similar value to the sample soaked for 24 hours. It suggested that the pre-lithiation thoroughly proceeded even after 4 hours. Since the electrode treated for 4 hours showed similar discharge and charge curves to those of non-treated electrode in Fig. 2(a) and (b), it was suggested that the electrode retained its composition during the 4-hour treatment. As a result, the initial coulombic efficiency reached 66.6%, which was 16% larger than that of non-treated electrode. However, the decrease in the discharge capacity was inevitable because of the partial degradation of the electrode by the solution. Therefore, we tried to dope lithium ion by direct contacting with lithium metal in the following section. In this method, certain amount of lithium metal was pressed on the electrode, and they were soaked into electrolyte solution. Since potential of the electrode was lowered to 0 V vs. Li+/Li by lithium metal on it, the lithium ion in the solution rapidly intercalated into GLG and pre-lithiation proceeded.

Figure 3 shows XRD patterns of pristine GLG, electrochemically fully charged GLG, and GLG treated with lithium metal. The pre-lithiated GLG showed peaks at 2θ = 19.17° (interlayer distance: $d = 0.46 \text{ nm}$) for the electrode treated with lithium equivalent to 15% of SOC and 18.30° ($d = 0.48 \text{ nm}$) for that treated with lithium equivalent to 20% of SOC, respectively. These values were similar to 2θ = 18.45° ($d = 0.48 \text{ nm}$) of the fully charged GLG. From the result, even though the amount of lithium metal was considerably small, the interlayer distance could be expanded to a similar extent to the fully charged GLG. In addition, although the interlayer distance of GLG was largely extended by the treatment with lithium metal, exfoliation of the electrode was not observed. This result was in marked contrast to the electrode treated with excess amount of lithium naphthenalene solution. This is probably because lithium naphthalenide itself was a strong reductant. Therefore, it reduced all the components of the composite electrode including PVdF. On the other hand, contacting the electrode with lithium metal only lowered potential of electron-conducting components in the composite. It follows that PVdF, an insulator, was not reduced, while GLG was reduced and intercalation of lithium ion proceeded. For this reason, the degradation of the composite electrode hardly occurred after the treatment with lithium metal.

Figure 3 shows XRD patterns of pristine GLG (a), electrochemically full-charged GLG (b), GLG treated with lithium metal equivalent to 15% (c) and 20% (d) of SOC.
intercalated into GLG and little consumed for SEI formation. The result also indicated that almost all the lithium metal was used for pre-lithiation especially with lithium metal. For the non-doped GLG, SEI is formed on its surface from the early stage of charge. However, since the gradual expansion of GLG proceeds during charging, the once formed SEI cannot stand up to the expansion, leading to repeated exfoliation and re-formation of SEI. As a result, the reductive decomposition of electrolyte solution continuously occurs, resulting in large irreversible capacity at the initial cycle. On the other hand, during the pre-lithiation of GLG with lithium metal, lithium ions are quite rapidly intercalated into it and the interlayer spacing of it increases. Since the reductive decomposition of electrolyte solution does not immediately occur, the most part of SEI is formed after the complete expansion of GLG. Therefore, in contrast to non-lithiated GLG, exfoliation and re-formation of SEI does not occur at the initial charge, resulting in less irreversible capacity. For this reason, the coulombic efficiency at the initial cycle was sufficiently improved by treating with lithium metal. Figure 7 shows the variations of OCP of GLG pre-lithiated with lithium metal, together with that of GLG during the 1st charge reported in our previous paper. The OCP of GLG decreased monotonically during electrochemical lithiation. When GLG was pre-lithiated with a small amount of lithium metal, the OCP values were only slightly lower than those observed during electrochemical lithiation of GLG. However, the potential apparently became lower when GLG was pre-lithiated with lithium metal equivalent to more than 30\% of SOC. As reported in our previous paper, the intercalation of lithium ions into GLG was slow at the beginning of charging probably because of the strong interaction of lithium ions with electronegative oxygen atoms introduced in GLG. After that, the diffusion of lithium ions in the interlayer space of GLG became much faster. This could be the reason why the surplus charge capacity was much larger for the GLG treated with the lithium metal equivalent to 38\% of SOC as observed in Fig. 4(b). From these results, we have succeeded in improving the initial coulombic efficiency of GLG by pre-lithiation especially with lithium metal. The amount of lithium metal needed for pre-lithiation of GLG was much smaller than that expected from the irreversible capacity of it.

4. Conclusion

This study clearly showed that the pre-lithiation could be a powerful means of decreasing the initial irreversible capacity of GLG. The pre-lithiation was conducted with lithium naphthalenide.
solution and lithium metal, and it was proved that using lithium metal was much more efficient. Even though the amount of lithium metal was equivalent to 28% or 38% of SOC of GLG, XRD patterns indicated that interlayer spacing expanded to the same extent as that of electrochemically fully charged (i.e. 100% of SOC) GLG. Surprisingly, charge and discharge measurement of the pre-lithiated GLG indicated that the decreased charge capacity was much larger than the capacity of lithium metal used for pre-lithiation. In addition, it was confirmed that the amount of doped lithium was less than or equal to the lithium metal used, indicating experimental error of weighting lithium metal was not the case. Therefore, we proposed the following plausible mechanism. For non-lithiated GLG, since once formed SEI could not stand up to the expansion and peeled off from the surface, leading to continuous reduction of the electrolyte and considerable irreversible capacity. On the other hand, the pre-lithiation with lithium metal rapidly and fully expanded the interlayer spacing. It follows that SEI was not immediately formed, and the most part of SEI formation proceeded after the full expansion of the interlayer space of GLG. Therefore, the irreversible capacity at the initial cycle was sufficiently decreased. Since the biggest issue of GLG was almost solved using pre-lithiation with lithium metal, the practical utilization of GLG gets more possibility.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00027.

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