Solvated Lithium Ion Intercalation Behavior of Graphitized Carbon Nanospheres

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ABSTRACT

To prolong durability of lithium-ion batteries, stability of solid electrolyte interphase (SEI) formed at a graphite negative electrode should be improved, but the correlation of the SEI stability with the graphite structure is still unclear. This study focused on co-intercalation of dimethoxyethane (DME) into SEI-covered graphitized carbon nanosphere (GCNS) to investigate SEI degradation behavior. In situ Raman spectroscopy revealed that both ethylene carbonate (EC)-derived and propylene carbonate (PC)-derived SEIs partly passivated the DME co-intercalation, but the PC-derived SEI degraded more rapidly than the EC-derived one. Additionally, the SEI at GCNS heat-treated at 2900°C had less stability than that at GCNS heat-treated at 2600°C, which is attributable to the graphite layer stacking and surface morphology.

Keywords : Lithium-ion Battery, Graphite, Solid Electrolyte Interphase, Solvent Co-intercalation

1. Introduction

Recent application of lithium-ion batteries (LIBs) ranges from mobile devices to a power source of electric vehicles (EVs). For the application to the EVs, one of the most important issues involves an improvement in long-term durability. Hence the degradation of LIBs must be minimized during repeated charge and discharge cycles. In LIBs, passivation film called solid electrolyte interphase (SEI) kinetically protects the electrolyte from electrochemical decomposition at graphite negative electrodes.1,2 Degradation of SEI during charge and discharge cycles leads to an increase of internal resistance and capacity loss. Therefore, the stability of the SEI is directly responsible for the durability of LIBs and the factor that influences the SEI stability should be clarified. So far, there are a variety of studies to develop the electrolyte solutions and additives and various strategies for the fabrication of the superior SEI were proposed.3–17 Also, the SEI is dependent on the electrode structure. For example, the SEI achieved on the basal and edge planes of a graphite show different physical and electrochemical properties such as density, hardness, and conductivity.18–20 Hence, design of the graphite surface structure is important for the design of superior SEI. However, the effect of the graphite structure on SEI properties such as passivation ability and stability is not fully understood. Therefore, the relations among the graphite structure, the SEI formed on it, and the electrochemical behavior need to be investigated more in detail.

We investigated the electrochemical properties of a graphitized carbon nanosphere (GCNS) as a negative electrode material of LIBs to clarify the effect of the graphite structure on the reactivity with electrolyte solutions.21–23 The GCNS have a characteristic structure such as a small particle size less than 1 µm, a concentric orientation of graphite layers, and polyhedral shape covered with basal planes.24–26 In this study, we focused on the solvent co-intercalation behavior at GCNS. Since the solvent co-intercalation induces the subsequent changes such as electrolyte decomposition and graphite exfoliation,27–28 co-intercalation behavior should indicate the reactivity of the electrolyte solution with the graphite material. Additionally, solvent co-intercalation behavior at an SEI-covered graphite electrode indicates the stability of the SEI since the solvent co-intercalation at the graphite negative electrode is one of the reasons of the SEI degradation. The unique structure of GCNS is expected to be useful for correlating the reactivity of electrolyte solution and the properties of SEI with the graphite structure. Therefore, investigation of the solvent co-intercalation behavior at GCNS should be interesting from the view of SEI design. In situ Raman spectroscopy was used to observe the solvent co-intercalation behavior. On the basis of the investigation, the electrochemical behavior at graphite materials was correlated with the SEI-forming reagent and the graphite structure.

2. Experimental

GCNSs (Tokai Carbon) were used as a graphite material. They have an average diameter of 700 nm and heat treatment temperatures of 2600°C and 2900°C (GCNS-2600 and GCNS-2900, respectively). Composite electrodes were prepared on copper foil, containing the GCNSs and polyvinylidene difluoride (PVDF) by the weight ratio of 8:2. A part of the composite electrodes were pretreated to cover GCNS particles with SEI. For the pre-treatment, a three-electrode cell was used with the GCNS composite electrode as the working electrode, and lithium foil as the reference and counter electrodes. Hereafter, the electrode potentials are referred to vs. Li/Li+. The GCNS electrodes experienced three cycles between 3 and 0 V at a scan rate of 0.1 mV s⁻¹ in the ethylene carbonate (EC)- and propylene carbonate (PC)-based electrolyte solutions, where EC + diethyl carbonate (DEC) [1:1 by vol.] containing 1 mol dm⁻³
of LiClO₄ (Kishida Chemical) and PC containing 1 mol dm⁻³ of LiClO₄ (Kishida Chemical) were used as the solutions, respectively. After the pre-treatment, the electrodes were washed with dimethoxyethane (DME) and cyclic voltammetry was performed in DME-based electrolyte solution between 3 and 0 V at a scan rate of 0.1 mV s⁻¹ to investigate the DME co-intercalation behavior. The DME-based electrolyte solution was prepared by dissolving 1 mol dm⁻³ of LiCF₃SO₃ (Kishida Chemical) in DME (Kishida Chemical). GCNSs without the pre-treatment are also examined in the DME-based electrolyte solution.

For the in situ Raman spectroscopy, a specially designed cell was used with an optically polished TEMPAX™ glass plate as an observation window. The schematic diagram of the cell was shown previously. The GCNS composite electrode with or without the pre-treatments was used as the working electrode of the cell, and lithium foil was used as the reference and counter electrodes. DME containing 1 mol dm⁻³ of LiCF₃SO₃ was used as the electrolyte solution. Excitation line for Raman spectroscopy had a wavelength of 514.15 nm and a power of 50 mW. Spectra were acquired with T64000 spectrometer (Jobin Yvon) equipped with a charge-coupled device detector. All measurements were performed under an ambient temperature.

**3. Results**

**3.1 Electrochemical behavior of GCNSs in the DME-based electrolyte solution**

Figure 1 shows the cyclic voltammograms of GCNS-2600 in the EC- and PC-based electrolyte solutions. The sharp redox peaks observed below 0.3 V indicate the reversible lithium-ion intercalation and deintercalation for both EC- and PC-based electrolyte solutions. In contrast to many of other graphite materials, where lithium-ion intercalation does not take place in a PC-based electrolyte solution due to continuous electrolyte decomposition and graphite exfoliation, GCNS-2600 exhibited successful behavior in the PC solution. In the first scan, reduction current around 0.7 V was observed for both EC- and PC-based electrolyte solutions, which was attributed to the formation of EC- and PC-derived SEI, respectively. Because the current decreased in the following scans, the passivation at the GCNS surface by the SEI should be substantially completed in not only the EC solution but also the PC solution. Figure 2 shows the cyclic voltammograms for the GCNS-2600 and GCNS-2900 without any pre-treatments in 1 mol dm⁻³ LiCF₃SO₃/DME electrolyte solution at a scan rate of 0.1 mV s⁻¹.

Figure 1. Cyclic voltammograms for GCNS-2600 in (a) 1 mol dm⁻³ LiClO₄/EC+DEC and (b) 1 mol dm⁻³ LiClO₄/PC electrolyte solutions at a scan rate of 0.1 mV s⁻¹.

Figure 2. Cyclic voltammograms for (a) GCNS-2600 and (b) GCNS-2900 without any pre-treatments in 1 mol dm⁻³ LiCF₃SO₃/DME electrolyte solution at a scan rate of 0.1 mV s⁻¹.
during repeated cycles, the PC-treated one exhibited some decrease. The decrease in the GCNS-2900 was more significant than that for the GCNS-2600. The peak decrease behavior probably relates to the stability of SEI formed on the GCNSs.

3.2 In situ Raman investigation of GCNSs in the DME-based electrolyte solution

To investigate the structural changes of the GCNS, the Raman measurements were conducted in the DME-based electrolyte solution. Figure 4a shows the spectra for the GCNS-2600 without any pretreatments. The peak around 1580 cm\(^{-1}\), which is derived from graphite in-plane stretching mode and is called G-band, was observed above 1 V. From 0.8 to 0.6 V, a shoulder peak appeared and the main peak was shifted to the higher value, which is attributable to the formation of a Li-DME-graphite intercalation compound (GIC) due to the DME co-intercalation.\(^{30}\) The previous study reported the Li-DME-GIC formation behavior from natural graphite.\(^{29}\) During the DME co-intercalation into natural graphite, the Raman spectrum at 1 V exhibited the obvious peak split,\(^{29}\) indicating the formation of high-stage Li-DME-GIC. Contrastingly, GCNS exhibited almost identical spectra at 2 and 1 V, implying the suppression on the DME co-intercalation into GCNS at 1 V. In addition, the spectral changes of GCNS between 0.8 and 0.6 V involved only the peak shift and no significant peak splits were observed, which should indicate suppression on the formation of high-stage structure. In the EC-based electrolyte solution, similarly, GCNS exhibited the direct formation of the low-stage Li-GIC during the lithium-ion intercalation.\(^{25}\) Therefore, the staging behavior should be dependent on the structure of graphite rather than the kind of an intercalation substance. The spectral changes below 0.6 V implied DME decomposition within the graphite layers and graphite exfoliation.\(^{25,29}\)

Figure 4b shows the spectra for the GCNS-2600 pre-treated in the EC-based electrolyte solution. Significant peak changes indicating the formation of Li-DME-GIC were observed between 0.6 and 0.4 V. Since the co-intercalation onset potential of the EC-treated GCNS was lower than that of the untreated one, the DME co-intercalation was partly passivated at the GCNS covered with the EC-derived SEI, indicating that the SEI affect the DME co-intercalation behavior into GCNS. However, the Raman spectra indicated the co-intercalation at lower potentials even in the SEI-covered GCNS while the cyclic voltammograms exhibited no significant current attributable to the DME co-intercalation for the SEI-covered GCNS. The behavior, which may seem to be inconsistent, should be due to the characteristic structure of GCNS. Because the graphite layers in GCNS are developed in a concentric direction, the pathway connecting between outer and inner areas of a GCNS particle should be quite limited. Even if the outermost layers accept the DME co-intercalation, it should not directly affect the inner area. As a result, the DME did not proceed into the most part of a particle, as implied by the cyclic voltammograms. Figure 4c shows the spectra for the GCNS-2600 pre-treated in the PC-based electrolyte solution. The spectra were similar to those for the EC-treated GCNS (Fig. 4b), and thus the passivation ability of the DME co-intercalation is considered to be almost the same for the EC- and PC-derived SEI-covered GCNSs. Figure 4d shows the spectra for the GCNS-2900 pre-treated in the EC-based electrolyte solution. Compared to the case of the EC-treated GCNS-2600, the peak

Figure 3. Cyclic voltammograms for (a) EC-treated GCNS-2600, (b) PC-treated GCNS-2600, and (c) PC-treated GCNS-2900 in 1 mol dm\(^{-3}\) LiCF\(_3\)SO\(_3\)/DME electrolyte solution at a scan rate of 0.1 mV s\(^{-1}\).

Figure 4. Raman spectra for GCNSs in 1 mol dm\(^{-3}\) LiCF\(_3\)SO\(_3\)/DME electrolyte solution at various potentials during the potential scan from 2 to 0.1 V. (a) GCNS-2600 without pre-treatments, (b) EC-treated GCNS-2600, (c) PC-treated GCNS-2600, and (d) EC-treated GCNS-2900.
changes indicating DME co-intercalation was observed at a higher potential. In addition, GCNS-2900 exhibited the more obvious peak split than GCNS-2600, indicating the greater formation of high-stage Li-DME-GIC from GCNS-2900. Therefore, the SEI at GCNS-2900 probably suffered more intensive solvent co-intercalation than that at GCNS-2600.

4. Discussion

The onset potential of the DME co-intercalation into GCNS-2600 was lower than that of natural graphite. Additionally, the formation of the high-stage structure was suppressed in GCNS-2600 whereas the spectra for natural graphite exhibited obvious peak split. The Raman analysis clarified that the formation extent of the high-stage Li-GIC was dependent on the regularity of the particle surface stacking.22,23,26 In the graphite materials with highly ordered stacking, the formation of high-stage structure was more significant than that in the graphite with disordered stacking.31,32 The present results clarified that it was also applicable to the solvent co-intercalation. The disordered stacking structure of GCNS-2600 suppressed the formation of a high-stage Li-DME-GIC and lowered the solvent co-intercalation potential. The difference in the co-intercalation onset potential probably affected the reactivity of electrolyte solution at the electrode surface. Retardation of the co-intercalation should be favorable for the passivation of side reactions at the surface of GCNS-2600. In fact, GCNS-2600 exhibited the small side reactions not only in EC-based electrolyte solution but also in PC-based one, as shown in Fig. 1. In situ Raman spectroscopy of GCNS-2600 in the PC-based electrolyte solution clarified that no significant solvent co-intercalation occurred, resulting in the reversible lithium-ion intercalation and deintercalation without vigorous electrolyte decomposition and graphite exfoliation.

The SEI pre-formation improved the suppression of the solvent co-intercalation in both cases of the EC-derived and PC-derived SEIs, implying that the both SEIs have passivation ability against the electrolyte decomposition. The passivation ability of the SEI at GCNS-2600 was higher than that of the EC-derived SEI formed at natural graphite, which should relate to the surface structure of GCNS. TEM observation revealed that a GCNS-2600 particle is covered with almost perfect basal planes and few structural defects are found at the particle surface including the ridge regions.22,23,26 The smooth morphology with few reactive sites should be favorable for the passivation of side reactions at the surface of GCNS-2600. In addition, GCNS-2900 exhibited the more obvious peak split than GCNS-2600, indicating the greater formation of high-stage structure was suppressed in GCNS-2600 whereas the spectra for natural graphite exhibited obvious peak split.22 The Raman spectra indicated that the EC- and PC-derived SEIs have similar passivation ability of the solvent co-intercalation, the degradation of the PC-derived SEI was more significant, as implied by the decrease in the anodic peak of the cyclic voltammograms. This behavior may relate to the weak adhesion of the reduction product from PC on the electrode surface, as pointed in the literature.33,34 Compared with the EC-derived SEI, the PC-derived SEI should be sensitive to the degrading factors such as a volume change of graphite and an attack by solvents on the SEI, probably due to the weaker adhesion on the electrode. The SEI degradation causes an increase in side reactions and graphite destruction, resulting in the more significant peak fading in the cyclic voltammograms. The cycle stability of PC-derived SEI on GCNS-2900 was further poor. The TEM studies reported that local collapses of graphite structure such as cracks and exfoliations were found on GCNS-2900 particle surface due to the distortion concentrated to the ridge regions.22,23,26 Because of the relative complexity of the surface structure, the SEI on GCNS-2900 particle is considered to be less stable than that on GCNS-2600. Additionally, relatively high stacking order was confirmed in GCNS-2900.22 The ordered stacking should increase the solvent co-intercalation, resulting in more rapid SEI degradation. Therefore, the durability of the passivation ability should also depend on the graphite structure such as graphite layer stacking and surface morphology.

5. Conclusions

In this study, the solvent co-intercalation behavior and the SEI stability were correlated with the structure of the GCNS. Significant suppression on DME co-intercalation into GCNS was attributed to the disordered stacking. The stability of SEI formed on the GCNS differed by the surface morphology of the GCNS as well as the SEI reagents. The structural features such as disordered stacking and smooth surface morphology should be effective for the passivation of electrolyte decomposition and the improvement in the SEI stability, enhancing the durability of LIBs.

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