Investigation of the Surface Film Forming Process on Nongraphitizable Carbon Electrodes by In-situ Atomic Force Microscopy

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ABSTRACT

In-situ atomic force microscopy (AFM) was applied to the investigation of surface film formation processes on a nongraphitizable carbon electrode. A glassy carbon (GC) plate with heat-treatment at 500°C was used as a model electrode of the nongraphitizable carbon. The in-situ AFM was combined with a cyclic voltammetry measurement. Based on the results, the effect of different electrolyte solutions was investigated and the thickness of the surface film on GC was found to be thinner than that on highly oriented pyrolytic graphite.

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Keywords : In-situ Atomic Force Microscopy, Surface Film, Glassy Carbon

1. Introduction

Nongraphitizable carbon is preferred as a negative electrode in lithium-ion batteries (LIB) for use in electric vehicles (EVs). Compared with the graphitic carbon used in practical LIBs, nongraphitizable carbon shows a large capacity, high-rate performance, and smooth potential profile.^{1–8} Among these characteristics, a smooth potential profile is important because monitoring of the battery voltage is compulsory for controlling the state of charge. Although nongraphitizable carbon has already been used in some EVs, it has not been investigated as fundamentally as graphitic carbon. The drawback of nongraphitizable carbon is the formation of surface film. The reaction potential of nongraphitizable carbon is as low as that of graphitic carbon; therefore, a reductive decomposition reaction of an electrolyte solution must occur and a passivation surface film such as the solid electrolyte interphase (SEI) on the graphitic carbon should be formed. However, the surface film formation process on nongraphitizable carbon is not fully understood. Therefore, the composition of the surface film on sucrose-derived nongraphitizable carbon after a charge–discharge cycle was investigated by ex-situ X-ray photoelectron spectroscopy, and the surface film was reported to be thicker than that of a graphitizable carbon.⁹ Recently, the surface film formation process on resorcinol–formaldehyde-derived nongraphitizable carbon was investigated by in-situ small-angle neutron scattering.¹⁰ From the results, the thickness of the surface film was estimated to be 1 nm and a chemical change in the surface film during the lithium-ion insertion process was also suggested.¹⁰ Based on the literature to date, including these two papers, there is no unified explanation about the surface film on nongraphitizable carbon. Our group has been investigating the formation process of SEI on graphitic carbon (highly oriented pyrolytic graphite; HOPG) by in-situ atomic force microscopy (AFM).^{11–18} Using this technique, the formation process and the thickness of the surface film on nongraphitizable carbon can be clarified.

In this study, a mirror-polished glassy carbon plate was used as a binder-free model electrode of the nongraphitizable carbon and the surface film formation process on the glassy carbon plate was observed by in-situ AFM.

2. Experimental

In this study, GC20 (Tokai Carbon) heat-treated at 500°C in air for 1 h was used as the mirror-polished glassy carbon plate. In our

previous study,¹⁹ the lithium-ion transfer process between GC20 and the liquid electrolyte interface was strongly influenced by the heat treatment at 500°C. The pores of pristine GC20 were closed and the lithium-ion insertion process did not proceed properly, and the heat-treatment process was conducted to obtain the correct electrochemical properties of GC20.

In-situ AFM was conducted using a specialized three-electrode cell, as in our previous papers.^{11–14} A working electrode was GC20 with or without heat treatment at 500°C and the counter and reference electrodes were lithium foils. In order to investigate the differences caused by the solvent, the electrolyte solutions were either a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) or propylene carbonate (PC), both containing 1 mol dm^{−3} lithium perchlorate (LiClO₄) purchased from TOMIYAMA PURE CHEMICAL INDUSTRIES, LTD. and the water content of 20 ppm was guaranteed. The observation mode was a contact mode in an Ar-filled glove box (MIWA MDB-1B+MS-P60SN, dew point < −76°C). Hereafter, electrode potential refers to Li/Li⁺. The electrode potential was swept from the open circuit potential (ca. 3 V) to 0.1 V at 2 mV s^{−1} to observe the surface morphology of GC20.

3. Results and Discussion

As observed via Raman spectroscopy, the X-ray diffraction measurement, and Fourier transform infrared (FT-IR) spectroscopy, there is no obvious change between GC20 with and without heat treatment. Therefore, GC20 with heat treatment can be used as a model electrode for nongraphitizable carbon.

Figure 1 shows the cyclic voltammogram during the 1st cycle and in-situ AFM images (5 × 5 μm²) of GC20 in LiClO₄/EC+DEC (1:1) during potential sweep. In each AFM image (Figs. 1(b)–(g)), the scan direction (upper arrow or lower arrow) and potential range are described. The dark lines in the AFM images are polishing flaws. Because the position of the dark lines did not change during cyclic voltammetry, it is guaranteed that the same region was observed during the experiment. In the cyclic voltammogram (Fig. 1(a)), a clear redox peak below 1 V was observed and this peak is assigned to the lithium-ion insertion/extraction process. Compared with the cyclic voltammogram of HOPG, a clear reduction peak due to electrolyte decomposition was not observed. This behavior is in agreement with previous literature.^{19,20} This result indicates that the reductive decomposition of the electrolyte solution and the surface

Figure 1. (Color online) In-situ AFM images and cyclic voltammogram of GC20 in 1 mol dm⁻³ LiClO₄/EC+DEC (1:1, vol. ratio). Scan rate: 2 mV s⁻¹.

Figure 2. (Color online) In-situ AFM images and cyclic voltammogram of GC20 in 1 mol dm⁻³ LiClO₄/PC. Scan rate: 2 mV s⁻¹.

film formation on nongraphitizable carbon are lesser than those with the graphitic carbon. The formation potential of the surface film was not clear from the electrochemical result; therefore, the formation process of the surface film was investigated by in-situ AFM. In the AFM images (Figs. 1(b)–(f)), there was no morphological change until the potential reached 0.75 V (dot-line). Below 0.75 V (Fig. 1(f)), the number of small deposits (white objects in dot-line circled region) was clearly increased. These deposits would be decomposition products of the electrolyte solution. With the increase in the reduction current in the cyclic voltammogram, the number of deposits increased, and these deposits did not disappear during the anodic scan, as shown in Fig. 1(g). Therefore, the deposits were stable and could act as the surface film. Additionally, the formation of the hill or blister due to the co-intercalation reaction reported for

HOPG^{11–13} was not observed in this study. Therefore, it can be considered that the co-intercalation reaction did not proceed in the case of GC20 as opposed to HOPG. Based on the AFM images (Figs. 1(f) and (g)), the surface film formation on GC20 with heat treatment starts from 0.75 V and continues to 0.1 V. Although the surface film formation potential of 0.75 V was lower than the reduction potential of alkyl carbonates proposed by in situ FT-IR (1.5 to 1.0 V),²¹ the difference between the reduction potential of alkyl carbonates and formation potential of the surface film is not contradictory because the reductive decomposition products formed at higher potential might be unstable. Our result is in agreement with the result of the in-situ small-angle neutron scattering.¹⁰

Figure 2 shows the cyclic voltammogram during the 1st cycle and in-situ AFM images (5 × 5 μm²) of GC20 in LiClO₄/PC.

Figure 3. (Color online) Large area AFM images of GC20 after cyclic voltammetry for 1 cycle in (a) $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC}+\text{DEC}$ (1:1, vol. ratio) and (b) $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$.

Lithium-ion insertion/extraction can occur in PC-based electrolyte solutions in the case of nongraphitizable carbon. Therefore, the surface film formation process in PC-based electrolyte solution would be interesting. There is no clear difference between the cyclic voltammograms obtained in EC-based electrolyte solution and those obtained in PC-based electrolyte solution. This indicates that unlike the behavior of HOPG, the electrochemical behavior of GC20 in PC-based electrolyte solution might be the same as that in EC-based electrolyte solution. However, in the AFM images, although a small clear deposit was observed starting from 0.75 V, the height of deposits at lower potentials (Fig. 2(g)) was lower than that in Fig. 1(g). This result indicates that the decomposition products of PC-based electrolyte solution formed a thinner surface film than EC-based electrolyte solution. To confirm this hypothesis, the thickness of the surface film was estimated. The procedure of this experiment was reported elsewhere.^{11–13} Figure 3 shows expanded areas ($7 \mu\text{m} \times 7 \mu\text{m}$) of the typical AFM images observed in each solution. In each image, the $5 \mu\text{m} \times 5 \mu\text{m}$ area is seen as a rectangular hole where the deposits were scraped off during repeated scanning. The deposited layer remained outside. From the height profile in Fig. 3(a), the thickness of the surface film formed in an EC-based electrolyte solution during the 1st cycle was roughly estimated to be below 14 nm. From Fig. 3(b), the thickness of the surface film in PC-based electrolyte solution cannot be estimated, and this result would indicate that the thickness of the surface film formed in PC-based electrolyte solution was considerably thinner than that of the surface film formed in EC-based electrolyte solution. This difference is interesting; however, the reason is not clarified at the present stage. In addition, the thickness of the surface film formed in EC-based electrolyte solution was smaller than that observed for HOPG (40 nm) obtained by the same method.¹¹ The

co-intercalation reaction was not observed by in-situ AFM at GC; therefore, it is considered that the morphology of surface film was related with the co-intercalation reaction and surface film formation process without the co-intercalation reaction would give thinner surface film.

4. Conclusion

Surface film formation processes on GCs were investigated using in-situ AFM. During the surface film formation process, the co-intercalation reaction of solvated-lithium ion did not occur. The surface film on GC in PC-based electrolyte solution was found to be especially thin compared with surface film on GC in EC-based electrolyte solution. In addition the thickness of the surface film formed on GC was thinner than that of HOPG. This is probably because the surface film formation process on GC is not accompanied by the co-intercalation reaction of solvated-lithium ion.

Acknowledgments

This work was partially supported by CREST, JST.

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