Electrochemical STM Study on Surface Morphology Change of HOPG Basal Plane in an Organic Electrolyte Solution

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To elucidate the mechanism of surface reactions on graphite anodes of lithium-ion secondary batteries, the morphology change of the basal plane of a highly oriented pyrolytic graphite (HOPG) anode in 1 M $LiClO_4$/ethylene carbonate-diethylcarbonate (1:1 by volume) was observed by electrochemical STM. When the sample potential was stepped to 1.1 V vs. Li/Li^+, hill-like structures of ca. 10 Å height appeared on the HOPG surface. The hill-like structure in the vicinity of a step was gradually spread out with time, and a part of it exfoliated. It was considered that the intercalation of solvent is responsible for the formation of the hill-like structure and that this process corresponds to the initial stage of solvent decomposition and subsequent film formation processes.

Carbon materials have been extensively studied for use in the anodes of secondary lithium-ion batteries. Many researchers have suggested that a protecting surface film is formed on carbon anodes during the first charge and suppresses further solvent decomposition.[1-4] Hence, the performance of a carbon anode strongly depends on the properties of the surface film. However, the mechanism of the film formation as well as its composition and morphology have not been fully clarified yet.

Electrochemical scanning tunneling microscopy (STM) is a powerful new technique for detailed structural and topographical characterization of electrode/electrolyte interfaces.[5] However, there have been few studies on electrochemical STM observation in organic electrolyte solutions. We succeeded in observing the morphology change of the surface of a highly oriented pyrolytic graphite (HOPG) in ethylene carbonate (EC)-diethylcarbonate (DEC) containing $LiClO_4$ by electrochemical STM. We report here preliminary results of the electrochemical STM observation.

HOPG (Le Carbone-Lorrain, PGGCL) was cleaved with an adhesive tape to obtain a flat basal plane. The HOPG electrode was mounted in the bottom of an electrochemical STM cell made of polytetrafluoroethylene. The geometric area of the electrode was fixed at 0.196 cm^2 using an O-ring and only the basal plane was in contact with electrolyte solution. The electrolyte solution was a 1:1 (by volume) mixture of EC-DEC containing 1 M $LiClO_4$. The counter and reference electrodes were platinum wire and lithium metal, respectively. Electrochemical STM images were obtained with an SPI3600 system (Seiko Instruments) using an apiezone wax-coated Pt/Ir tip in the constant current mode. The potential of the tip electrode was fixed at 3.0 V, and that of the working electrode was varied; hence, the bias voltage for tunneling was the potential difference between the two electrodes. The tunneling current was set at 0.5 nA. All measurements were carried out at room temperature in an argon-filled glove box.

The first and second cyclic voltammograms of the HOPG electrode in 1 M $LiClO_4$/EC-DEC were shown in Figure 1. Three peaks were observed at 733, 558 and 427 mV vs. Li/Li^+ in the first reduction. Corresponding re-oxidation peaks were not observed, indicating that these processes were irreversible. These processes were fully disappeared in the second sweep. It was reported that surface film formation on graphite electrodes occurs at around 0.8 V vs. Li/Li^+.[1] The processes that occur at 733, 558 and 427 mV are hence closely related to such solvent decomposition and surface film formation.

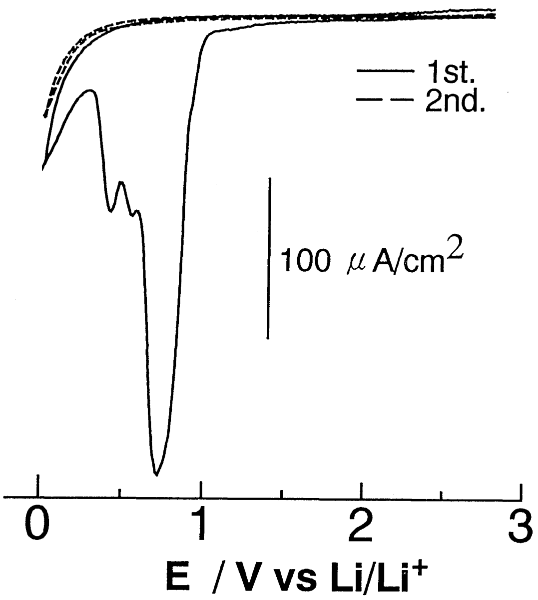

Figure 1. Cyclic voltammograms of freshly cleaved HOPG basal plane in 1 M $LiClO_4$/EC+DEC. $v = 20$ mV s^{-1}.

Cleaved basal plane of HOPG has an atomically flat surface; however, stepwise defects, so-called "steps" are often observed by STM. The step can be regarded as a kind of the active edge plane. We therefore carefully observed the surface in the vicinity of a step on the HOPG. When a freshly cleaved HOPG was immersed in the electrolyte solution, the open-circuit potential was about 3 V vs. Li/Li^+. Figure 2a shows an STM image of the basal surface of HOPG when the potential of HOPG was stepped to 2.8 V. A clear step of ca. 30 Å height was observed horizontally in Figure 2a. The image was unchanged with time at this potential.

The electrode potential was then stepped to 1.1 V, where the reduction corresponding to the first peak in Figure 1 began and current started to flow. Figures 2b and 2c show STM images at 4, 13 min after the potential was stepped to 1.1 V. In Figure 2b, two "hill-like" structures of ca. 10 Å height appeared in the upper part of the image and in the vicinity of the step edge. The top surface of each hill-like structure was atomically flat. While it is not clear how the former hill-like structure was formed, it is reasonable to consider that the latter hill-like structure was formed from the step edge and then spread out. In Figure 2c, the latter hill-like structure in the vicinity of the edge was spread out

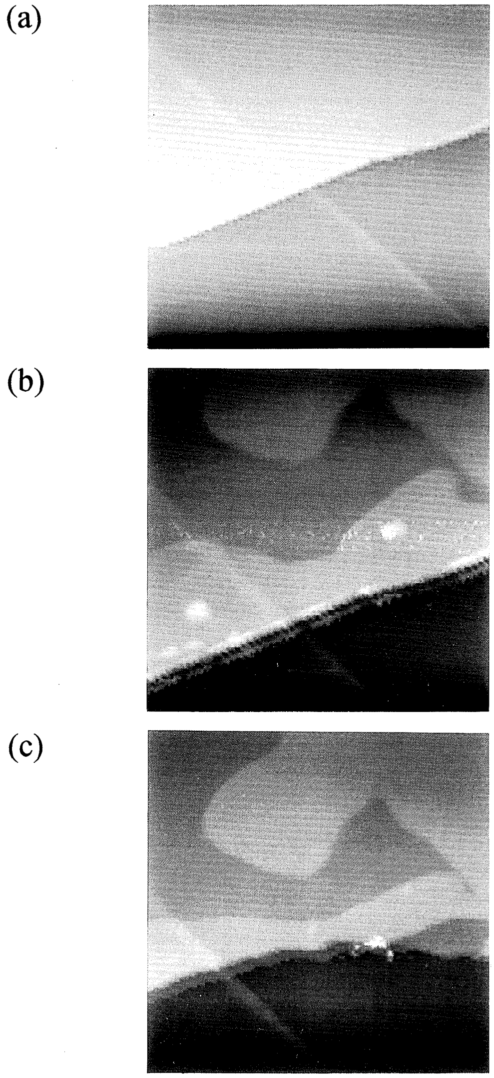

Figure 2. STM images of HOPG basal plane (a) observed at 2.8 V and observed at (b) 4 and (c) 13 min after the potential was stepped to 1.1V in 1 M $LiClO_4$/EC+DEC. The frame size of each image is 500 nm x 500 nm.

further, and a part of it exfoliated; the position of the step edge moved upward. Although the image slightly moved downward with time because of thermal drift of the sample, the morphology of other parts was kept almost unchanged from that in Figure 2b; hence, thermal drift cannot be responsible for this movement of the step.

We first suspected that the hill-like structure was formed by lithium intercalation into graphite. However, it is difficult to consider that lithium intercalation takes place at 1.1 V.[1,6-8] The interlayer spacings of pristine graphite and stage-1 lithium graphite intercalation compound (LiC_6) are 3.35 and 3.71 Å, respectively;[9] hence, the increase in interlayer spacing by lithium intercalation is 0.35 Å. The observed height of the hill-like structure was ca. 10 Å, which requires lithium intercalation into over 20 interlayers of an identical part. This is not unlikely to occur at this potential. Hence, it is reasonable to consider that some species with a much larger volume was intercalated into the interlayers. The observed height of the hill-like structure, ca. 10Å, is comparable to the interlayer spacings of stage-1 ternary graphite intercalation compounds of alkali metal with organic molecules, such as tetrahydrofuran and dimethoxyethane, prepared by a solution method.[10] Therefore, it is considered that the intercalation of solvent molecules is responsible for the formation of the hill-like structure. At the present stage, however, it is not clear as to which solvent, EC or DEC, was intercalated or whether the solvent was intercalated solely or with lithium. The reaction that takes place at this potential corresponds to the first reduction peak at 733 mV in Figure 1, and hence is closely related to solvent decomposition and subsequent film formation. Hence, the morphology changes of the STM image observed in the present study, i.e. the appearance and exfoliation of the hill-like structure, are considered to be an initial stage of surface film formation processes.

Unfortunately, we have not succeeded yet in observing STM images for further processes of surface film formation because clear images were not obtained at potentials more negative than 1.1 V under the present experimental conditions. Experiments are currently under way to observe the morphology change in more detail.

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