 Electrochemical study of Highly Ordered Pyrolytic Graphite Surface Film Formation by in-situ Atomic Force Microscopy

Eunkyoung Kim and Juhyoun Kwak

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

In-situ electrochemical atomic force microscopy (ECAFM) was used to study the surface film that forms on highly ordered pyrolytic graphite (HOPG) electrode during cathodic polarization. Cyclic voltammetry experiments confirmed that distinct reduction reactions occur when the potential of a fresh HOPG electrode is swept from 2.4 to 0.01 V vs. Li/Li⁺. The reactions appear to be irreversible, since no evidence of corresponding oxidation reaction was observed. ECAFM results, when combined with cyclic voltammetry data, suggest that these contribute to form surface film. The surface film is differently formed dependent on electrolyte. It is observed by ECAFM that the morphology of surface film in 1 M LiClO₄–EC/DMC is more smooth and compact than that in 1 M LiPF₆–EC/DMC. When considered with the second cycle of CV experiment, the ECAFM results confirm that the further electrolyte decomposition has the correlation with the formation of surface film.

I. Introduction

The carbon materials have been extensively studied for use in the anodes of secondary lithium ion batteries [1,2,3]. A most attractive anode material for these batteries is graphite, which has two advantages, (i) high capacity, because Li can intercalate reversibly with this material eventually reaching a stoichiometry of LiC₆, and (ii) the potential profile of this process which is low and flat [4].

At the graphite electrode, lithium ions are intercalated into graphite upon charging and deintercalated upon discharging. During the initial charging of a battery, it is believed that an insoluble and adherent film forms on the electrode surface before Li⁺ itself is reduced [5,6]. This film is referred to as a “solid electrolyte interface” (SEI) [7], and it insulates the graphite electrode against direct reaction with the electrolyte. It is well known that the SEI is formed by the reduction of the lithium salts such as LiClO₄, LiPF₆, and the organic solvents such as EC, DMC and PC. Therefore, the electrochemical stability and reversibility of carbon electrodes vary greatly with the type of electrolyte used [8].

The emergence of atomic force microscopy (AFM) as a valuable technique for the surface studies opened the door for in-situ morphological studies of electrode surfaces during electrochemical processes under potential control [9-16]. It is redundant in the literature that there is a strong correlation between the morphology and cycle life of carbon anodes in lithium ion batteries. Inaba et al. [9,13] have used electrochemical scanning tunneling microscopy (STM) to image changes at a step formation on a highly ordered pyrolytic graphite (HOPG) surfaces. While in-situ electrochemical experiments are possible with STM, this instrument has a limitation in observing the SEI since only electrically conductive samples can be imaged and a high faradic current at low potentials often interferes with the imaging mechanism [12,14]. Hence, electrochemical atomic force microscopy (EC-AFM) is a powerful new technique to investigate the SEI film, which is nonconductive sample.

In the present study, the surface chemistry of the graphite electrode in nonaqueous organic solution has been investigated by using in-situ electrochemical AFM (EC-AFM) in combination with cyclic voltammetry.

II. Experiment

EC-AFM experiments were conducted with a Topometrix Discover TMX 2000 AFM system using BAS 100b potentiostat. The experiments were conducted in contact mode, using a V-shaped silicon nitride cantilever (200 µm wide, 0.032N/m spring constant). The scan rate was 4 Hz, with 300 lines per image. Working electrode was HOPG (SPI Supplies, SPI-2). HOPG was cleaved with an adhesive tape to obtain a flat basal plane.

All measurements were carried out at room temperature in an argon-filled glove box. It should be emphasized that the experiments related to each solution entailed AFM measurements on the same electrode area.

All Potentials reported in this section were recorded relative to a Li/Li⁺ reference. The working electrode potential was scanned from 2.4 to 0.01 V and back to 2.4 V at 0.4 mV/s. The AFM tip was withdrawn from the surface so as not to interfere with the electrochemical reactions, except when an image was desired. This lessened any surface effects caused by the tip itself. The images were taken at approximately 200 mV intervals.

The electrolyte used were 1 M LiClO₄ in EC/DMC (1:1) [electrolyte A], and 1 M LiPF₆ in EC / DMC (1:1) [electrolyte B]. EC/DMC is 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Their water contents were measured using Karl-Fischer titration and were below 50 ppm of water.

III. Results and discussion

(1) Cyclic Voltammetry

The Electrochemical behavior of HOPG was first examined by cyclic voltammetry to obtain information about surface reactions on HOPG. Fig. 1 and Fig. 2 present the first and second cyclic voltammograms of the HOPG electrode in 1 M LiClO₄–EC/DMC (Electrolyte A), and 1 M LiPF₆–EC/DMC (Electrolyte B) solutions. Both Fig.1 and Fig. 2 show a broad peak at around 1.3 V. This is due to trace water in nonaqueous electrolyte solutions [17]. Trace water is electrochemically reduced on graphite electrodes to form hydrogen and OH⁻ at potential < 2V vs. Li/Li⁺ [17]. Both gaseous hydrogen and the strongly nucleophilic OH⁻ anions are detrimental to the shelf
and cycle life of a battery. It should be noted that the solvent reduction commences at 1.0 V Li/Li$^+$ and proceeds intensively below 0.8 V Li/Li$^+$, irrespective of the kind of electrolyte salt.

Three peaks were observed at 0.72, 0.55 and 0.4 V in the first anodic sweep in Electrolyte A and two peaks were observed at 0.64 and 0.3 V in Electrolyte B. The Reoxidation peaks corresponding to these reduction peaks were not observed in the following anodic sweep. This indicates that these processes are irreversible. The cathodic reactions in the first cycle are contributed to the formation of surface film [6,18,19]. This surface film is called the solid electrolyte interface (SEI) by Peled for the first time [7]. The decomposition of EC solvent and the competitive reduction of salt build up the SEI. The SEI film is said to be composed mainly of (CH$_2$OCO$_2$Li)$_2$ and Li$_2$CO$_3$ in EC-containing electrolytes [17,21].

The reduction peaks fully disappeared in the second sweep in Electrolyte A, but the sharp peak at 0.3 V remains in Electrolyte B. It is known that PF$_6^-$ anion occurs several reduction reactions [8,17,18,20]. Especially, the trace HF, which is generated from the decomposition of electrolyte B salt, dissolves the formed film and makes the surface film porous. LiF salt contributes to the resistive and nonhomogeneous surface film formation, since LiF surface films are more resistant to lithium migration than carbonate films [21]. The compact and passivating surface films isolate the graphite electrode from the solution, which stabilize the electrode. In this case, these surface films act as a screen, which allows only Li ion transport through them, while keeping solvent molecules out [20-21]. These play an important role further electrochemical EC reduction and obtaining good cycle life [6]. Therefore, the surface films are unstable in Electrolyte B, hence result in the further reduction in the second cycle. In comparison with LiClO$_4^-$ the poor cycleability in LiPF$_6$ is attributed to these properties [5-8,17-19,27].

PF$_6^-$ (salt anion) is reduced simultaneously with the solvent in the applied potential range of 0.25 to 0.6 V Li/Li$^+$. Thus the interference of the salt reduction with the compact passivating formation of the surface film aggravates the passivity of the surface film in Electrolyte B. It is concluded that the surface film formed in LiClO$_4^-$ EC/DMC solution provides better passivity than those formed in LiPF$_6$ – EC/DMC.

(2) EC-AFM

In the previous sections, it is proved that the reduction of the electrolyte commences at 1.0 V and proceeds to lower potential during the first cathodic sweep and is irreversible. These peaks are not the result of lithium intercalation. Significant lithium intercalation was prevented by the limited exposed-edge surface area [13].

Intercalation can not occur through the basal surfaces of HOPG, which compromised the vast majority of surface exposed to electrolyte solution. Cleavage steps in the basal plane expose edge surfaces, which appear as cracks or lines in ECAFM images. The darker area is lower region and the lighter area is higher region in Fig. 3. The images taken from 2.4 V to 1.6 V were very similar. Fig. 3 (a) show the HOPG electrode at a potential of 1.6 V. Fig. 3 (b) begin to form deposits on the edge at a voltage of 1.0 V. By a potential of 0.7 V, deposits can be seen on both edge and basal planes of the HOPG electrode (Fig. 3 (c)). It is observed that the step appears indistinctly at 0.4 V (Fig. 3 (d)) because both step and basal plane are completely covered with the deposits. That is, it was observed that the deposits commence to form on active sites steps from 1.5 V to
ECAFM images of HOPG in electrolyte B are shown in Fig. 4. Fig. 4 (a) show the HOPG surface at 2.2 V. We observed that the deposits occur on both basal and edge surface at 1.1 V (Fig. 4 (b)). In view of the small difference between 2.2 V and 1.1 V, the thin surface films seem to be formed. Fig. 4 (c) show that the image of the surface at 0.7 V, where electrolyte reductions occur. Some deposits are seen to enlarge at the edge, for which two possibilities can be considered. One is that the formed deposits grow up. The other is that the new deposit species are formed. As suggested by Kanura et. al. [15], this is due to HF which is produced by the reaction of PF₆⁻ anion with water [17–18]. HF reacts with both Li₂CO₃ and ROCO₂Li to form LiF, and solubilizes the carbonates initially formed and replace them with salt reduction products [21,27].

In the previous sections, we explained that the initially formed deposits (Li₂CO₃ or ROCO₂Li) are dissolved and simultaneously new deposits (LiF) are formed. By the potential of 0.1 V (Fig. 4 (d)), the new deposits cover both edge and basal surface of HOPG. Evidently, the deposits of 0.7 V grow up and new deposits are formed on the basal plane. The surface is covered with the new deposits, which are larger than the previous ones. The aging process increases the interfacial resistance of lithium electrodes in these solutions considerably because the LiF surface films are more resistant to lithium migration than the carbonates. Because the SEI in LiPF₆ is porous and nonuniform, these films cannot prevent the further reduction reaction. These results agree with the CV of Fig. 2, which the reduction occurs in second cathodic sweep in LiPF₆.

IV. Conclusions

This work proves that ECAFM is an effective in-situ technique for studying surface film formation and morphology on HOPG in nonaqueous electrolyte. The surface film is formed by the reduction of solvent and electrolyte salt. It is demonstrated that the surface film in LiClO₄–EC/DMC is more stable, compact and homogeneous than that in LiPF₆–EC/DMC, since the decomposition of electrolyte salt, LiPF₆, interfered with the formation of surface film. It is confirmed that the initial surface film dissolves and then the new deposits are formed in LiPF₆–EC/DMC.

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