AFM Study on Surface Film Formation on a Graphite Negative Electrode in a LiPF$_6$-based Non-Aqueous Solution

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AFM을 이용한 LiPF$_6$를 주성분으로 하는 비수용액중에서의 흑연 음극 표면에 형성되는 피막에 관한 연구

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Abstract The mechanism for the surface film formation was studied by *in situ* Atomic Force Microscopy (AFM) observation of a highly oriented pyrolytic graphite (HOPG) basal plane surface during cyclic voltammetry at a slow scan-rate of 0.5 mV s^{-1} in 1 mol dm^{-3} (M) LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Decomposition of the electrolyte solution began at a potential around 2.15 V *vs.* Li$^+$/Li on step edges. In the potential range 0.95-0.8 V *vs.* Li$^+$/Li, flat areas (hill-like structures) and large swelling appeared on the surface. It is considered that these two features were formed by the intercalation of solvated lithium ions and their decomposition beneath the surface, respectively. At potentials more negative than 0.80 V *vs.* Li$^+$/Li, particle-like precipitates appeared on the basal plane surface. After the first cycle, the thickness of the precipitate layer was 30 nm. The precipitates were considered to be decomposition of the lithium salt (LiPF$_6$) and solvent molecules (EC and DEC), and to have an important role in suppressing further solvent decomposition on the basal plane.

Key words : surface film, graphite, lithium-ion battery, AFM, SEI

요 약 흑연 음극 표면상에 형성되는 필름의 생성 기구를 규명하기 위하여, 1 몰의 LiPF$_6$가 함유된 탄산에틸렌과 탄산디에칠의 혼합 용액 중에서 고배향성 열분해 흑연을 0.5 mV s^{-1} 의 느린 속도로 전위주사하면서 원자력간 현미경을 이용하여 전극표면을 in-situ 관찰하였다. 전해질 용액의 분해반응은 전극의 스텝 모서리 상에서 우선적으로 진행되었으며, 전극 전위 2.15 V (*vs.* Li$^+$/Li) 에서 시작되었다. 0.95-0.8 V (*vs.* Li$^+$/Li) 의 전위 영역에서 전극 표면의 특정 부분이 평탄하게 부풀어오르는 현상과, 타원형의 돌기 구조가 관찰되었다. 이러한 형상 변화에 있어서 전자는 용매화된 리튬 이온이 흑연 층간에 삽입되며 나타나는 구조 변화이며, 후자는 삽입된 용매화 리튬이 환원 분해되어 생성된 것으로 추정된다. 0.8 V (*vs.* Li$^+$/Li) 보다 음의 전위 영역에서는 입자상의 침전물이 전극 표면에 형성되었다. 1 사이클 후, 측정된 침전층의 두께는 30 nm 이었다. 이러한 침전물은 리튬염(LiPF$_6$)과 용매 분자(EC 및 DEC)들이 분해되어 생성된 것이며, 전극 표면에서 계속적으로 전해질 용액이 분해되는 반응을 억제하는 중요한 역할을 하고 있는 것으로 생각된다.

1. Introduction

Graphite is used as a negative electrode in

commercially available lithium-ion batteries due to its relatively high specific reversible capacity (theoretically 372 mAh g^{-1}), small irreversible capacity and good cycleabilty. When a graphite electrode is polarized to negative potentials during the first charging in an ethylene carbonate (EC)-based solution, EC reductively decomposes on the graphite surface to form a stable surface film[1,2]. The passivating film, called solid

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electrolyte interphase (SEI)[3], suppresses further solvent decomposition and plays a beneficial role in improving the safety and cycleability of lithium-ion batteries. The SEI formation on graphite negative electrode thus a prerequisite for its stable charging and discharging; however, it is the primary cause for bringing about irreversible capacity through consumption of a considerable amount of charge.

Many researchers have made efforts in search for good electrolyte systems that give superior SEI with a minimal consumption of charge[4-6]. For this purpose, understanding of the nature of SEI is very important, and has long been a focus of much work over the last decade. However, despite extensive work, the properties such as the morphology, the thickness, and the chemical composition, of the surface film and the role of the anions in electrolyte solution has not been clearly understood. The present work aimed at clarifying the mechanism for surface film formation in a LiPF$_6$-based solution and understanding the role of lithium salt in the surface film formation.

The SEI formation is a very complicated interfacial phenomenon occurring at the graphite/electrolyte interface. In studies on electrode surfaces in lithium-ion batteries, in-situ experimental techniques are very important because the electrodes are highly reactive and unstable in the air. Electrochemical scanning probe microscopy (SPM) is a useful tool for direct visualizing electrode/solution interfaces at which various electrochemical reactions occur under potential control[7]. In the present work, the mechanism for surface film formation and understanding the role of anions was studied by in-situ electrochemical atomic force microscopy (AFM) observation of a highly oriented pyrolytic graphite (HOPG) basal plane in 1 mol dm^{-3} (M) LiPF$_6$/EC + DEC.

2. Experimental

Freshly cleaved HOPG (Advanced Ceramics, ZYH grade, Mosaic Spread: 3.5 ± 1.5°) blocks were used as model graphite negative electrodes for CV and AFM observations. AFM observation was carried out with an AFM system (Molecular Imaging, PicoSPM^{TM},

USA) equipped with a potentiostat (Molecular Imaging, PicoStatTM) and a laboratory-made fluid cell. Pyramidal silicon nitride tips were used for AFM measurements. CV was performed at a sweep rate of 0.5 mV s^{-1} between 2.9 and 0.0 V. AFM images were continuously obtained at an interval of 150 mV during CV measurements. The geometric surface area of the electrode was fixed at 1.2 cm^2 using a Viton^{TM} O-ring, by which only the basal plane was brought into contact with electrolyte solution. The electrolyte solution was 1 M LiPF$_6$ dissolved in a 1:1 (by volume) mixture of EC and diethyl carbonate (DEC) (Kishida Chemical Co., Battery Grade, Japan). The water content in the solution was less than 20 ppm. The counter and reference electrodes were lithium foil. All potentials were referred to as volts vs. Li$^+$/Li. All measurements were carried out at room temperature in an argon-filled glove box (Miwa, MDB-1B + MM3-P60S) at a dew point < −60℃.

3. Results and Discussion

3.1 Electrochemical potential cycling of HOPG basal plane

Figure 1 shows the first and second cyclic voltammograms of a freshly cleaved HOPG basal plane in 1 M LiPF$_6$/EC + DEC. In the first cycle, a minor reduction current began to flow at about 2.2 V, and two major reduction peaks appeared at about 0.8 and 0.5 V. These reduction peaks, including small current between 2.2 and 0.8 V, disappeared in the second cycle and hence are attributed to irreversible decomposition reactions of the electrolyte solution that are closely related to SEI formation[8-9]. A large reduction current was observed at potentials lower than 0.4 V, which may be assigned partly to lithium intercalation because of the corresponding oxidation peak assigned to lithium de-intercalation at around 1.0 V. However, the charge consumed for the reduction current was much larger than that for the oxidation peak, and hence, a substantial fraction of the reduction current at potentials < 0.4 V was consumed by irreversible processes such as direct electrolyte decomposition on the HOPG surface.
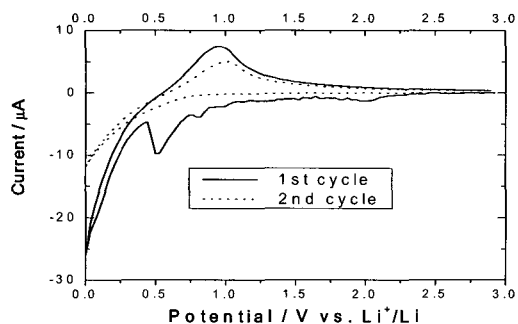
Fig 1. Cyclic voltammograms of the HOPG basal plane in 1 M LiPF$_6$/EC + DEC.

Fig 2. AFM images (5 × 5 μm^2) of the HOPG basal plane surface obtained at (a) 2.9 V before CV, (b) 2.15-2.00 V, (c) 0.95-0.80 V, (d) 0.80-0.65 V during the first cycle at 0.5 mV s^{-1} in 1 M LiPF$_6$/EC + DEC.

3.2 Morphology changes of HOPG basal plane during the first cycle

To obtain information about SEI formation, morphology changes of the HOPG basal plane were observed during a slow scan CV using electrochemical AFM. Figure 2 shows surface morphology changes of a 5 × 5 μm area of the HOPG basal plane obtained simultaneously during the first cycle shown in Fig. 1. Figure 2(a) shows an AFM image obtained at 2.9 V before potential cycling. The surface consisted of atomically flat terraces separated by several steps, which is a typical structure of the HOPG basal plane. At this potential, the step-and-terrace structure of the basal plane was stable for several hours, which confirms that HOPG surface was quite inert and neither deposition nor intercalation reaction took place.

During the first cathodic sweep, no topographical changes appeared between 2.9 and 2.15 V. Morphology changes began at a potential around 2.15 V shown in Fig. 2(b). Figure 2(b) shows an AFM image obtained in the potential ranges of 2.15-2.00 V. The arrows in parentheses denote the direction of raster of the microcantilever; for example, the bottom and top scanning lines of Fig. 2(b) were obtained at 2.15 and 2.00 V, respectively. Some reaction products were observed from the step edges. This is little different from that observed in LiClO$_4$-based electrolyte solution, in which no morphology changes were observed in the potential range[10].

Figure 2(c) shows AFM image obtained in the potential ranges of 0.95-0.80 V. Dramatic changes of surface morphology began at about 0.9 V in Fig. 2(c),
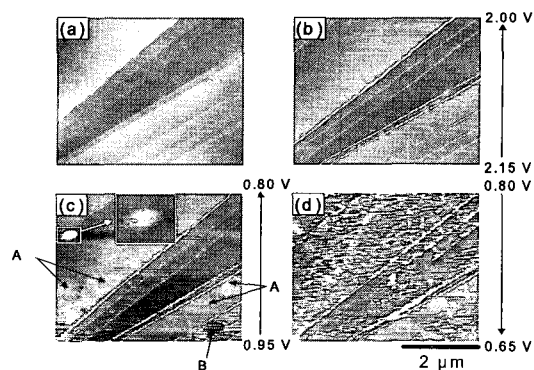
and peculiar structures designated as A appeared with a complicated pattern on the basal plane. They can be identified as hill-like structures formed by the intercalation of solvated lithium ions[8-10]. At potentials close to 0.80 V, a swelling of the surface, which is shown by a square at the upper left of Fig. 2(c), appeared. The height of these swelling was 220 nm, and much higher than that of the hills. It should be noted from the expanded image of the swelling that a line of step edge is clearly seen running on the swelling. This fact clearly indicates that the swelling was an interior structure formed beneath the surface. That is, it was formed by accumulation of decomposition products of solvated lithium ions between graphite layers. From these morphology changes, the reduction current peak around 0.8 V can be related to the intercalation of solvated lithium ions and their decomposition between graphene layers. In addition to hill and swelling formation, distinctive feature seen in Fig. 2(c) is that part of the step edge designated as B exfoliated around 0.9 V. Although the details for the exfoliation is not clear at present, tone plausible reason is the formation of gaseous product upon decomposition of solvated lithium ions.

At potentials more negative than 0.80 V in Fig. 2(d), particle-like precipitates appeared on the HOPG surface. The precipitates are considered to be decomposition products of solvent molecules. The number of the precipitates increased with lowering the

potential down to 0.0 V (not shown here). This indicates that the current rise at potentials close to 0.0 V in Fig. 1 is attributed not only to lithium intercalation, but also to solvent decomposition on the basal plane.

3.3 Estimation of the thickness of precipitate layer

After the images in Fig. 2 obtained, AFM observation was continued during the reverse potential sweep to 2.9 V. The precipitate layer formed at lower potentials gradually disappeared during the reverse sweep. This phenomenon is due to surface scrapping of the AFM tip because AFM observation was performed in the contact-mode. It is widely known that contact-mode AFM is very useful to scrape off a thin organic layer deliberately by careful surface scratching[11-13]. When materials are weakly attached to the sample surface, the AFM tip physically pushes them in the scanning direction in the contact mode, which results in surface scraping. Figure 3 shows how the AFM tip scraped off the precipitates. The precipitate layer disappeared gradually after repeated scanning. Almost all precipitate layer was removed after 18th scan. After the precipitate layer was removed in the manner, an expanded area of 8 × 8 μm was observed at 2.9 V. Figure 4 shows an AFM image and a height profile of an expanded area (8 × 8 μm) including the 5 × 5 μm area of Fig. 2 observed during the first cycle. Many precipitates are clearly seen on the surface outside the 5 × 5 μm area, although they are missing inside the 5 × 5 μm area. From the height profile. the thickness of the precipitate layer in Fig. 4 was roughly estimated to be 30 nm. This value is smaller than that obtained from a LiClO4-based electrolyte solution, in which 40 nm thickness layer was formed on graphite surface[10]. This indicates that the electrochemical reactions involving surface layer formation on graphite is affected by the anion in electrolyte solution. The rectangular hole confirmed strong surface scraping during AFM observation. It is clear that the precipitate layer has a role in suppressing further reductive decomposition of solvent molecules on the basal plane.

The results of AFM observation in the present study revealed that passivating film formation on graphite negative electrodes involves the following two different processes: (i) the intercalation of solvated lithium ions and their decomposition beneath the surface and (ii) direct decomposition of solvents on the basal plane to form a precipitate layer.
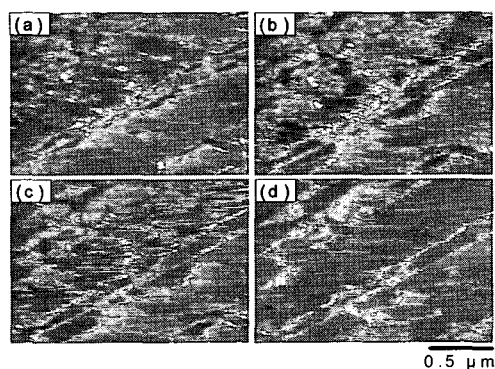

Fig 3. AFM images (2 × 2 μm^2) of the HOPG basal plane surface obtained at 2.9 V (a) the first, (b) the 5th, (c) the 12th and (d) the 18th AFM scans after the first cycle of CV at 0.5 mV s^{-1} in 1 M LiPF6/EC + DEC.
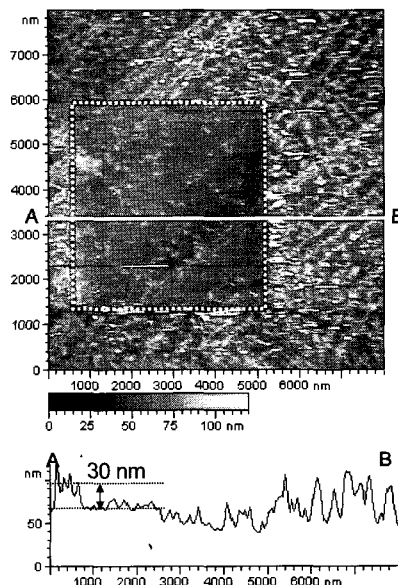

Fig 4. AFM image of an expanded area (8 × 8 μm^2) and a height profile of the HOPG basal plane surface obtained at 2.9 V after the first cycle of CV. The dotted square shows the area observed during the first cycle in Fig. 2.

4. Conclusions

In-situ AFM observation of HOPG basal plane was performed during CV at a slow scan-rate in a LiPF$_6$-based electrolyte solution, 1 M LiPF$_6$/EC + DEC. Surface morphology changes began at a potential around 2.15 V on step edges by the decomposition of the electrolyte solution. In the potential range of 0.95-0.8 V, the formation of the hill-like structures and swelling were observed, which confirmed that the intercalation of solvated lithium ions and their decomposition took place in this potential range. At potentials more negative than 0.65 V, particle-like precipitates appeared on the basal plane surface of HOPG. After the first cycle, the thickness of the precipitate layer was 30 nm. The precipitates were considered to be the decomposition of the salts and solvent molecules and to have an important role in suppressing further solvent decomposition on the basal plane. The electrochemical and morphological behaviors observed in the present study suggested that the anions in solution take part in surface film formation, which is the reason for various salt effects that are unique to graphite negative electrodes.

Acknowledgements

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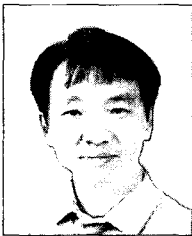
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<Areas studied>
Primary/Secondary Batteries, Fuel Cells, SPM