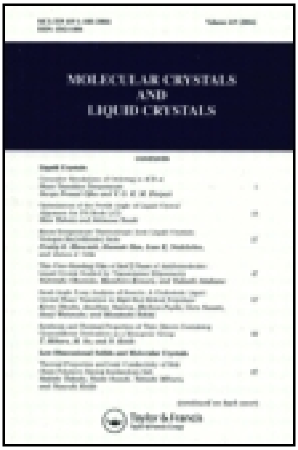

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SEI Film Formation On Graphite Anode Surfaces In Lithium Ion Battery

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SEI Film Formation On Graphite Anode Surfaces In Lithium Ion Battery

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In Situ Electrochemical Atomic Force Microscope (AFM) was used to study Solid Electrolyte Interphase (SEI) film formation on the graphite anode surfaces in lithium ion battery. SEI film formation was clearly observed on the surface of KS-44 synthetic graphite composite electrode in 1M $LiClO_4$ Ethylene carbonate (EC) -based electrolyte under galvanostatic discharge. Together with quantitative analytical results of SEI films formed in several different electrolytes, we have concluded that direct electron transfer from the surface of graphite to solvated lithium ion caused the SEI film formation on graphite anodes in EC-based electrolytes.

Keywords: Atomic Force Microscope; SEI; Graphite; Anode; Lithium Ion Battery

INTRODUCTION

Lithium ion batteries have a great attention since they have very high energy density. Typical lithium ion battery system is using graphite anode and transition metal oxide cathode. Non-aqueous organic electrolyte need to be used because an average potential difference between the anode and the cathode during charge and discharge is approximately 3.6 - 3.7 V. Aqueous electrolytes often used in most of primary and secondary battery system are decomposed under such high electrochemical potential. It is known that even organic electrolytes are decomposed during first lithium intercalation into graphite to form Solid Electrolyte Interphase (SEI) film on the graphite anode surfaces. Recently Aurbach et al. reported that the compositions of the SEI films on graphite anodes were very similar to those of well-known SEI films on lithium metal anodes [1]. We successfully introduced electrochemical AFM to explore the surface reactions on graphite anodes recently [2]. In this paper, we will discuss the SEI film formation mechanism based on quantitative analytical results of lithium contents in the SEI film and real time observations of SEI film formation using in situ electrochemical AFM on the graphite anodes.

EXPERIMENTAL

KS-44 synthetic graphite (TIMCAL) / polyvinylidene difluoride (Kureha) composite electrode and Highly Oriented Pyrolytic Graphite (HOPG, Advanced Ceramics Corp.) were used in this study. Preparation of the KS-44/ PVDF composite electrode was reported elsewhere [2]. The electrolytes used were ethylene carbonate (EC)+ ethyl methyl carbonate (EMC) solution or ethylene carbonate (EC)+ diethyl carbonate (DEC) solution (1:1 by volume) containing 1M $LiClO_4$., $LiPF_6$ or lithium bistrifluoromethylsulfonyl imide (LiTFSI) (Mitsubishi Chemical Corp.). Lithium contents in the SEI films formed on one KS-44 composite electrodes (12.5 mm ϕ, approximately 10 mg) at the first discharge and charge cycle were analyzed by atomic absorption spectroscopy after washing the electrodes by diethyl carbonate several times to remove electrolyte components in argon-filled grove box. The electrodes were dried in vacuo before the atomic absorption spectroscopy analysis. All AFM images were obtained using the AFM contact mode of an SPM-3700 Scanning Probe Microscope (Seiko Instruments Inc.) enclosed in a glove box in conjunction with the galvanostat (Hokuto Denko HA-501). Detailed AFM experimental conditions were published elsewhere [2]. In this paper, discharging is defined as the intercalation of lithium into the graphite electrode, and charging is defined as the deintercalation of lithium from the graphite electrode.

RESULTS AND DISCUSSION

Li Content in SEI Films

Irreversible capacity loss is observed during first lithium intercalation into graphite. The irreversible capacity is the difference between the first discharge capacity and the first charge capacity. It is believed that the part of the irreversible capacity loss is caused by the SEI film formation on the graphite anodes. TABLE 1 shows lithium contents in the SEI films formed on one KS-44 synthetic graphite composite electrode at the first discharge and charge cycle in 3 different electrolytes. There were good agreement between lithium contents analyzed by atomic absorption spectroscopy and lithium contents calculated from the electrochemical irreversible capacity based on one electron reaction process. From these results, it is concluded that all of consumed charge was used to form lithium contained SEI films. One electron reduction process as shown in FIGURE 1 seems to be the main reaction of irreversible reaction at the first lithium intercalation into graphite electrodes.

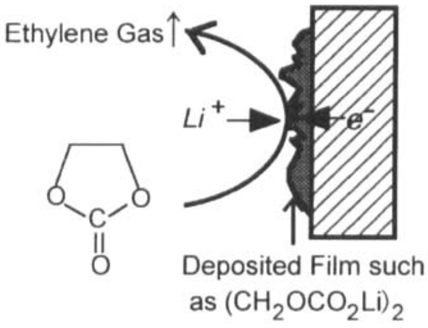

FIGURE 1 One electron reduction of carbonate solvent on graphite anode

Electrochemical AFM Study

In AFM experiments, the electrochemical cell was connected to a galvanostat, and the system was allowed to equilibrate until a constant open circuit voltage (OCV) was reached. Left AFM image of Figure 2 shows typical

TABLE 1 Irreversible Capacity and Li Content in SEI Films
*1M Li-salt EC/DEC=1/1 ** μmol Li in 1 graphite sheet electrode (approximately 10mg, 12.5mmϕ), after 1st charge and discharge

Li Salts*	Irreversible Capacity**	Li Content**
LiPF6	248	246
LiClO4	262	262
LiTFSI	290	279
Method	Charge-Discharge Test	AAS Analysis

1 x 1 μm AFM image of the KS-44 graphite composite anode surface initially at OCV state (approximately 2.9 V vs. Li/Li^+) in 1M $LiClO_4$ EC/EMC (1:1) electrolyte. Several distinct graphite crystal boundaries are visible in the chosen scanning area. When a current density of 0.255 mA/cm^2 was applied, sharp decrease of electrochemical potential was occurred at the early stages of constant current discharging from OCV state as shown in Figure 2. Between 2.0 V and 0.9 V vs. Li/Li^+, trace deposition along graphite step edges was detected. In this sample, film deposition was observed preferentially around the graphite crystal edges below 2 V vs. Li/Li^+. It appeared that at a potential of approximately 1.0 V vs. Li/Li^+ a film-like covering begins to form quickly on the surface of the electrode (center AFM image of Figure 2). Below approximately 0.4 V vs. Li/Li^+, a thick film formation covered a large proportion of the previously visible graphite edge detail and contained numerous island-like structures as shown in the right AFM image in Figure 2. These island-like formations remained until approximately 0.27 V vs. Li/Li^+ when a large change in topography possibly resulting from gas evolution due to the electrochemical reduction of electrolyte solvent as shown in FIGURE 1, resulted in uncontrollable noise in the images, and the later movement of the

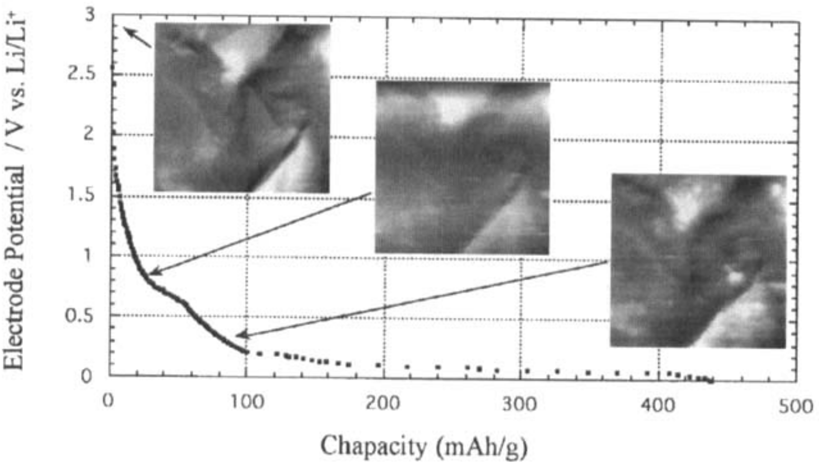

FIGURE 2 SEI film formation on KS-44 synthetic graphite electrode in 1M $LiClO_4$ EC + EMC (1:1 by volume)

laser out of the range of detection at approximately 0.2 V vs. Li/Li$^+$ in this experiment. Several bubbles were visible after disassembling the electrochemical AFM cell. This evidence agreed with one electron reduction SEI film formation scheme that we mentioned above. Furthermore, dendritic lithium deposition on SEI film formed on the HOPG graphite electrode was also observed after keeping the electrode potential 0 V vs. Li/Li$^+$ for several minutes. New SEI film remained stable with dendritic lithium shape even after dissolution of deposited lithium metal.

SEI Film Formation Mechanism

Besenhard et al. proposed solvent co-intercalation / decomposition mechanism for SEI film formation on graphite anodes using dilatometry [3]. According to their mechanism, ternary solvated graphite-lithium intercalation compounds (GICs) are formed, then ternary GICs decompose and build up SEI layer on the graphite anodes. Inaba et al. also supported their proposal since they observed hill-like structure at 1.1 V vs. Li/Li$^+$ using electrochemical scanning tunneling microscopy (STM) [4]. However, we have not observed such hill-like structure in our electrochemical AFM study. We have observed quick SEI film coverage on the entire graphite anode surfaces within 1 minute under 0.9

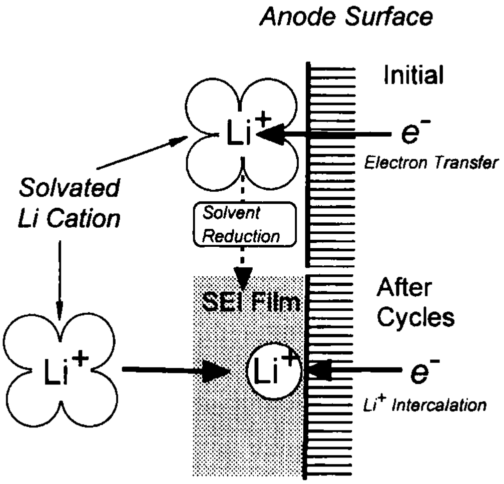

FIGURE 3 SEI Film Formation Mechanism on Graphite Anodes

V vs. Li/Li$^+$. We think that it is unlikely to happen the quick materials transfer from graphite edges to basal planes, if we assume the SEI films can only form on the graphite edge via solvent co-intercalation / decomposition process. Based on above considerations, we propose that direct electron transfer from graphite anode surfaces including both edge and basal plane to solvated lithium ion triggers the decomposition of solvents to form SEI films as shown in FIGURE 3. After SEI film formation on the graphite anodes, lithium ions are de-solvated during transportation in SEI films to intercalate into graphite hosts without further solvent decompositions.

CONCLUSIONS

We have shown that the lithium contents in the SEI films formed on KS-44 synthetic graphite composite electrode in three different electrolytes analyzed by atomic absorption spectroscopy were agreed with lithium contents calculated from the electrochemical irreversible capacity based on one electron reaction process. We have demonstrated that SEI film formation on KS-44 synthetic graphite composite anode using in situ electrochemical AFM in EC-based non-aqueous electrolytes. After constant current discharging, a very thin SEI film, initially detected below 2 V vs. Li/Li$^+$ along crystal boundaries on KS-44 composite electrode was visible. Below 0.9 V vs. Li/Li$^+$, a thicker SEI film formation containing island-like structures was observed over the entire surface of the KS-44 composite electrode. We have proposed that direct electron transfer from graphite anode surfaces including both edge and basal plane to solvated lithium ion triggers the decomposition of solvents to form SEI films. This mechanism explains in situ electrochemical AFM observations.

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