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Surface Film Formation on Graphite Negative Electrodes in Rechargeable Lithium Batteries

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SUMMARY: The choice of solvent is quite important to obtain good protecting surface film on graphite negative electrodes in rechargeable lithium batteries. A subtle difference of the molecular structure of solvent greatly affects the easiness of surface film formation. In order to understand the solvent effects and to elucidate the mechanism of surface film formation, morphology changes of the basal plane of highly oriented pyrolytic graphite were studied using electrochemical scanning tunneling microscopy (EC-STM). In this article, our recent results of EC-STM observation in different solvent systems are reviewed.

Introduction

Carbonaceous materials have been extensively studied for use as negative electrodes in rechargeable lithium batteries (lithium-ion cells).[1) The charge (lithium intercalation) and discharge (deintercalation) reactions of carbon negative electrodes take place at extremely negative potentials close to Li^+/Li (-3.045 V vs. NHE), and thereby nonaqueous solutions are used instead of aqueous solutions. Even nonaqueous solvents should not be thermodynamically stable at such negative potentials. It is generally believed that a kind of passive film, called solid electrolyte interface (SEI) by Peled,[2) is formed on carbon negative electrode in the initial stage of charging. The presence of SEI prevents further solvent decomposition and improves the safety and cycleability of lithium-ion cells. The composition of SEI layer on carbon electrode has been extensively studied by FT-IR,[3-5) electron energy loss spectroscopy (EELS) coupled with transmission electron microscopy (TEM),[6,7) temperature programmed decomposition mass spectroscopy (TPD-MASS),[8) etc. For example, these studies have reported the presence of Li_2CO_3 and lithium alkylcarbonates ($ROCO_2Li$) in SEI layer formed on carbon electrodes in EC-based solvent systems. However, the mechanism of SEI formation is still the subject of much debate.

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It is widely known that the choice of solvent is very important to obtain good SEI for carbon electrodes, in particular highly graphitized ones, in lithium-ion cells. When graphite is charged in a 4-methyl-1,3-dioxolan-2-one (propylene carbonate, PC) electrolyte solution, the potential is kept at ca. 0.9 V vs. Li^+/Li and the electrode gradually deteriorates by exfoliation of graphite layers so that lithium ions are not intercalated.9,10) Such phenomena are generally believed to be due to the decomposition of PC.9) This problem has been overcome by the use of 1,3-dioxolan-2-one (ethylene carbonate, EC)-based solvent systems,11) and they are now used in commercially available lithium-ion cells. Other interesting solvent effects have been also reported. For example, the addition of 1,4,7,10-tetraoxacyclododecane (12-crown-4) to PC12,13) or the use of 4-trifluoromethyl-1,3-dioxolan-2-one (trifluoropropylene carbonate, TFPC) in place of PC14) is effective to prevent solvent decomposition and the exfoliation of graphite layers, and hence enables lithium ions to be intercalated within graphite. These facts imply that not only the stability of solvent against reduction, but also some unknown factors determine the easiness of SEI formation on carbon anodes. Thus the understanding of the above-mentioned solvent effects on SEI formation is a clue to clarify the mechanism for SEI formation.

We have employed electrochemical scanning tunneling microscopy (EC-STM) to understand the solvent effects peculiar to graphite negative electrode.15-19) Electrochemical STM is a powerful new technique for detailed structural and topographical characterization of electrode/electrolyte interfaces.20) Knowledge of surface structures could be crucial to the understanding of surface film formation that is taking place at the electrode surface. As a test carbon material, HOPG was used because an atomically flat basal plane can be obtained easily by cleaving the surface layers with an adhesive tape. In this article, results of our recent studies using different kinds of solvent systems are reviewed.

Charge/Discharge Characteristics

Panels (a)-(d) in Fig. 1 show the first charge and discharge curves of electrodes made of natural graphite powder (Kansai, Coke and Chemicals, NG-7) in 1 M (M = mol dm^{-3}) $LiClO_4$ dissolved in a 1:1 (by volume) mixture of EC and diethyl carbonate (DEC), PC, PC containing 0.5 M 12-crown-4, and TFPC, respectively. In EC+DEC, the potential dropped rapidly after subtle retardation at ca. 0.8 V at Li^+/Li upon the first charging. The main intercalation and deintercalation of lithium ions take place at potentials < 0.25 V.1) The charge consumed by the first charging (ca. 400 mA h g^{-1}) was not fully recovered by the following discharging. The capacity that cannot be recovered is called "irreversible capacity" (Q_{irr}), 65 mA h g^{-1} in this case, which is generally considered to be consumed by SEI formation. The reversible capacity Q_{rev} was 335 mA h g^{-1}. In PC, the potential was kept nearly constant at about 0.9 V up to 2000 mA h g^{-1}, and then dropped suddenly to 0 V (Fig. 1b). The whole charge was consumed by solvent decomposition and exfoliation of graphite, and the electrode did not have any appreciable discharge capacity. The addition of 0.5 M 12-crown-4, which selectively coordinates Li$^+$ ion, enables Li$^+$ ions to be intercalated within graphite (Fig. 1c). The reversible capacity (340 mA h g^{-1}) was comparable with that in EC+DEC, whereas Q_{irr} was twice as large as that in EC+DEC. The use of TFPC in place of PC also enables lithium intercalation (Fig. 1d). However, Q_{rev} was smaller (275 mA h g^{-1}) and Q_{irr} was much bigger (335 mA h g^{-1})

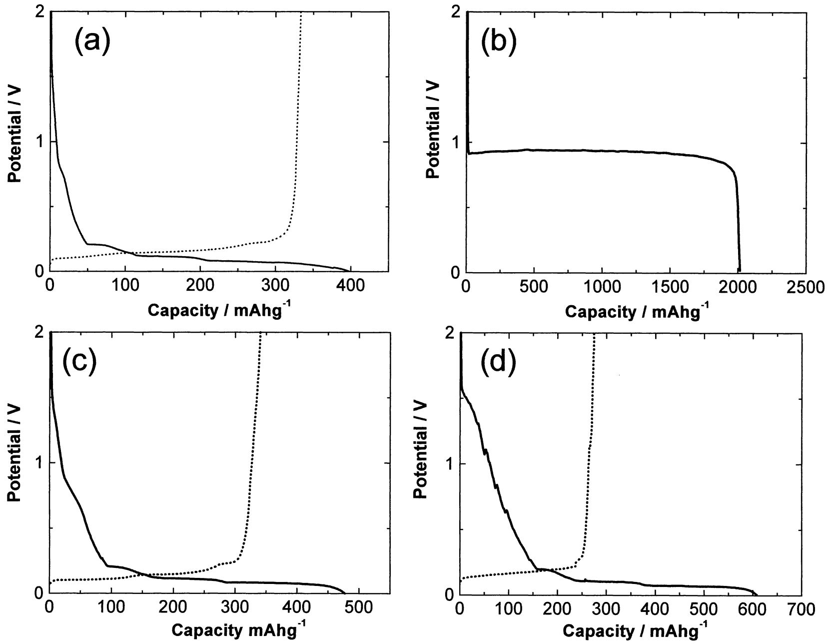

Fig. 1: First charge and discharge curves of natural graphite powder (NG-7) in (a) 1 M $LiClO_4$ dissolved in (a) EC+DEC (1:1 by volume), (b) PC, (c) PC + 0.5 M 12-crown-4, and (d) TFPC. Solid and dotted lines show charge and discharge curves, respectively. The potential was refereed to as volts vs. Li$^+$/Li.

STM observation in EC-based solvent systems

STM images were obtained with an STM unit placed in an argon glove box, in which the dew point is <-60°C. A typical STM image of HOPG basal plane is shown in Fig. 2a, which was obtained at 2.8 V vs. Li^+/Li obtained in a 1 M solution of $LiClO_4$ dissolved in a mixture of EC and DEC (1:1 by volume).[15,16] A clear step of 3-nm height is seen horizontally in the image, which corresponds nine layers of graphite sheets. When the potential was stepped to 1.1 V (Fig. 2b), two "hill-like" features appeared at the upper part of the image and in the vicinity of the step edge. The height of both hills was 0.8-1 nm, and the hilltop was atomically flat. The shape of the latter hill at the step edge clearly indicates that it was formed from the step edge and then spread out. When the hilltop was observed with an atomic resolution, typical atomic images of graphite basal plane, in which every other atom on the hexagonal carbon network of the graphite sheet as bright spots spaced by ca. 0.25 nm on a two-dimensional triangular lattice, were obtained.[21] This fact indicates that the top surface consisted of graphite sheets of ABAB.... stacking, and thereby the hill was a structure raised by insertion of something beneath the surface.[16] The observed height of the hill-like structure, ca. 1 nm, is comparable to the interlayer spacings of stage-1 ternary GICs of alkali metal with organic solvent molecules, such as tetrahydrofuran and dimethoxyethane, prepared by a solution method.[22] It was thus suggested that solvated lithium ions are intercalated between graphite sheets at this potential to form the hill-like structures. Besenhard et al.[23] studied the crystal expansion of HOPG during electrochemical reduction in an EC-based solution by dilatometry, and observed a drastic expansion of the graphite matrix (> 150%) at potentials more negative

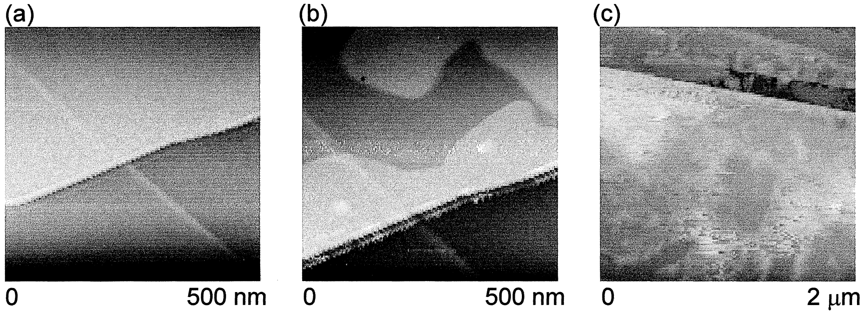

Fig. 2: Electrochemical STM images of HOPG basal plane at (a) 2.8, (b)1.1 V, and (c) after potential was stepped to 0.75 V for 1 min in 1 M $LiClO_4$/EC+DEC.[15,16] Images (a) and (b) are of nearly the same position, but image (c) was obtained for a different sample. The tip potential was kept at 3.0 V.

than 1.0 V. They attributed this expansion to solvent co-intercalation, and concluded that the intercalated solvent further decomposes to form an immobile product that remains between the graphene layers and this reduction product prevents further solvent intercalation and the exfoliation of graphite layers. The observed hill-like structure supports the solvent-cointercalation model proposed by Basenhard *et al.* After the potential was kept at 0.75 V, a significant change in surface morphology was observed as shown in Fig. 2c.51) Large blisters in irregular shapes were formed on the surface. The maximum height of the blisters was ca. 20 nm, which was much higher than that of the hills (ca. 1 nm). These blisters seem to have been formed by accumulation of decomposition products of the solvated lithium ions that had been intercalated beneath the surface. Similar blisters were observed in 1 M $LiClO_4$ dissolved in EC + dimethoxyethan (DME) solvent system.16)

STM observation in other solvent systems

In contrast to the above results in the EC-based solvent systems, morphology changes in a 1 M solution of $LiClO_4$ dissolved in PC were quite different as shown in Fig. 3.17) Neither hill-like structures nor blisters were formed in 1 M $LiClO_4$/PC, but only rapid exfoliation and rupturing of graphite layers occurred. At 0.7 V, the original step structure was completely ruined (Fig. 3c). Since the exfoliation of graphite sheets leads to regeneration of fresh edge planes, stable SEI should not be formed. Although it is not clear why such vigorous exfoliation of graphite layers occurs in PC solution, the intercalation of $Li(PC)_n^+$ may cause partial decomposition of $Li(solv)_n^+$ involving gas evolution11,13) or cause a substantial stress between graphite layers because of the larger molecular size of PC.17)

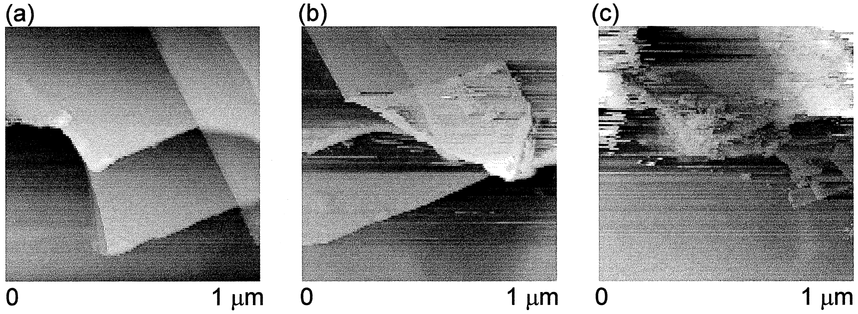

Fig. 3: Electrochemical STM images of HOPG basal plane after the potential was stepped to (a) 1.1 V, (b) 0.95, and (c) 0.7 V for 30 s in 1 M $LiClO_4$/PC.17) The tip potential was kept at 3.0 V.

Figure 4 shows STM images obtained in 1 M $LiClO_4$/PC + 12-crown-4 [18] The addition of 12-crown-4 into PC greatly suppressed the exfoliation. After potential was kept at 0.9 V, atomically flat, hill-like structures with an enhanced height of 1 nm appeared on the surface (Fig. 4b). When the potential was kept below 0.8 V, part of the hills was swelled and changed to irregular-shaped structures (blisters) with an enhanced height of 20-30 nm. Blister formation became more significant as the potential was lowered (Fig. 4c). The observed morphology changes were very similar to those observed in EC+DEC shown in Fig. 2; hence, these hills and blisters are also considered to have been formed by the intercalation of solvated Li^+ ions and their decomposition, respectively. It should be noted that the solution *did* contain PC molecules; nevertheless, stable SEI was formed in the presence of 12-crown-4. According to the solvent co-intercalation model, whether stable SEI is formed or not should depend on the kind of solvent molecules that solvate Li^+ ion. In this case, Li^+ is selectively coordinated with 12-crown-4 so that Li^+/12-crown-4 complexes were intercalated within graphite. The presence of 12-crown-4 hence prevents PC from being co-intercalated within graphite and suppresses the exfoliation of graphite layers.

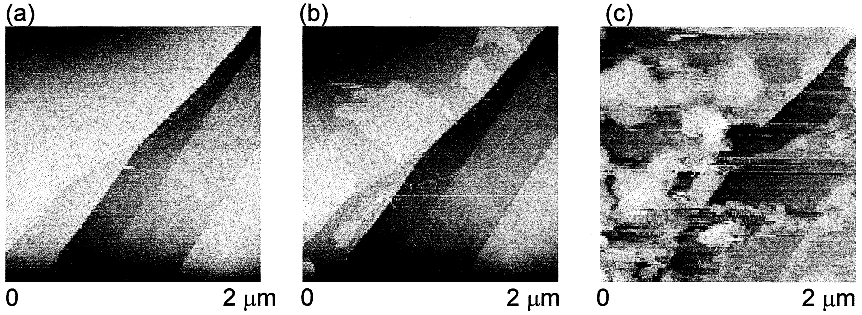

Fig. 4: STM images of HOPG basal plane surface observed at 2.8 V after the potential was kept at (a) 1.0 V, (b) 0.9 V, and (c) 0.3 V for 1 min in 1 M $LiClO_4$/PC + 0.5 M 12-crown-4. The tip potential was kept at 3.0 V.

Figure 5 shows morphology changes in 1 M $LiClO_4$/TFPC.[19] Exfoliation of graphite layers was observed at potentials around 0.9 V (Fig. 5b); however, it was not so severe as that observed in 1 M $LiClO_4$/PC (Fig. 3). Below 0.8 V, such exfoliation was terminated by the formation of swelling along the newly formed step edges (Fig. 5c). The observed exfoliation indicates that the intercalation of TFPC-solvated lithium ions causes a substantial stress between graphite layers or causes partial decomposition involving gas evolution, and thereby $Li(TFPC)_n^+$ cannot be accommodated steadily in the interlayer space as is the case in PC. However, the degree of the exfoliation in TFPC is not as vigorous as that observed in PC; hence, it does not cause fatal deterioration of the host graphite during charging. TFPC should be more vulnerable to reduction than EC or PC because it has electron-withdrawing fluorine atoms. It should be noted that the swellings observed in Fig. 5c were formed only in quite a narrow area along the step edges on HOPG. This fact implies that TFPC-solvated lithium ions decompose as soon as being intercalated. This rapid decomposition can leave immobile products that work as stable SEI along step edges. Consequently, the instability of TFPC against reduction enables rapid SEI formation and suppresses further exfoliation.

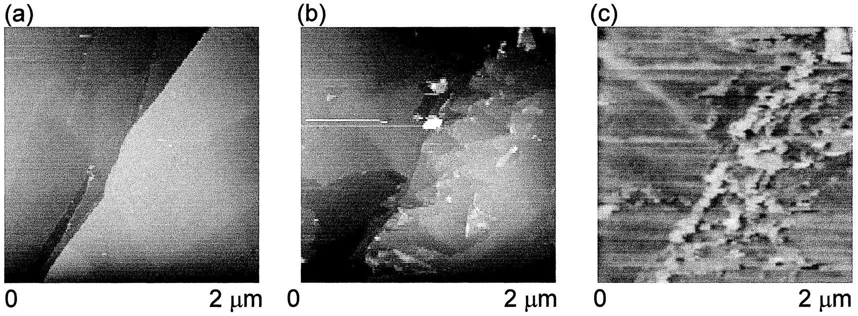

Fig. 5: STM images of HOPG basal plane surface obtained at (a) 1.2, (b) 1.0, and (c) 0.5 V in 1 M $LiClO_4$/TFPC.[19)] The tip potential was kept at 3.0 V.

Conclusions

A subtle difference of the molecular structure of solvent greatly affects the surface reaction when graphite negative electrode is polarized below 1.0 V vs. Li^+/Li in different solvent systems. *In situ* observation of the surface morphology changes of HOPG test samples using EC-STM gave us useful information about the mechanism of SEI formation on graphite. It was found that SEI formation is triggered by the intercalation of solvated Li^+ ions, and whether stable SEI is formed or not depends greatly on the kind of solvent molecules that solvate Li^+ ions. The observed morphology changes in different solvent systems lead us to conclude that at least the following three factors determine whether stable SEI is formed or not on graphite: (i) the easiness of $Li(solv)_n^+$ intercalation between graphite layers, (ii) the magnitude of the interlayer stress caused by $Li(solv)_n^+$ intercalation or gas evolution, in other words, to what extent the graphite host withstands the stress, and (iii) the stability of solvent [or $Li(solv)_n^+$] against reduction. These factors are intricately involved in the SEI formation on graphite, which would be the reason for the complexity and inconsistency in the solvent effects for carbon negative electrodes reported so far

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