

**In Situ Probe Microscopic Studies on
Graphite Electrodes for Lithium-ion Batteries**

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Preface

This thesis is a compilation of “In Situ Probe Microscopic Studies on Graphite Electrodes for Lithium-ion Batteries”, which was carried out at Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University during 2013-2016.

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General Introduction

Background of the work

1. Graphite as a negative electrode in lithium-ion batteries

Graphite is a crystalline carbonaceous material that has layer structures by stacking graphene layers along the *c*-axis, which are weakly bonded by van der Waals force. Various chemical species such as metal ions and molecules can be accommodated between graphene layers by chemical or electrochemical processes [1]. Lithium ions can intercalate into graphite to form lithium-graphite intercalation compounds (Li-GICs) by both chemical and electrochemical methods. In electrochemical method, lithium-ion intercalation reaction occurs at graphite electrode at potentials between 0.25 and 0.0 V vs. Li^+/Li [2-5]. This simple reaction has been used as a superior negative electrode reaction in most practical lithium-ion batteries (LIBs). In general, LIB consists of graphite and lithium-transition metal oxide (LiCoO_2 , LiMn_2O_4 , etc) as negative and positive electrodes, respectively, with an organic electrolyte solution between these electrodes. Figure 1 shows the charge and discharge processes of LIB. During the charge process, lithium ion de-intercalates from the positive electrode and then intercalates into the negative electrode through the electrolyte solution. During the discharge process, the opposite lithium-ion transfer occurs.

As mentioned above, lithium-ion intercalation reaction into graphite takes place at extremely lower potentials. Under this strongly reductive condition, almost all organic electrolyte solutions must be reductively decomposed. Therefore, during lithium-ion intercalation process at graphite electrode, the reductive reaction of organic electrolyte solutions firstly occurs at higher potentials than ca. 1.0 V vs. Li^+/Li and this reaction should continue to occur until organic electrolyte solutions are consumed. Based on this thermodynamic aspect, the lithium-ion intercalation reaction into graphite cannot be expected to proceed in organic electrolyte solutions. However, lithium-ion intercalation reaction into graphite can take place. This is because the reductive decomposition products of organic electrolyte solutions formed on graphite can serve as

a surface protective film to suppress the further reductive reaction of organic electrolyte solutions. This surface protective film is known as a solid electrolyte interphase (SEI) [6, 7] and has a key role of graphite negative electrodes in LIBs.

2. Solid electrolyte interphase at graphite negative electrode of lithium-ion batteries

Peled claimed the formation of SEI on Li metal electrodes in non-aqueous electrolyte solutions for the first time [8]. Metallic cation can be deposited on metal electrode through the SEI during electrochemical process because the SEI has only cation conductivity but not electronic conductivity. This Schottky lattice defects model for deposition and dissolution of metal cation is shown in Fig. 2. Solvated-metal cation ($M^+(\text{sol})_n$) penetrates into SE (solid electrolyte) and M^+ migrates in SE, and finally, electron-transfer reaction occurs at SE/metal interface. Since lithium-ion intercalation reaction is not simple electron-transfer process, the SEI formation mechanism would be different between the metals and graphite electrode. However, the Peled's SEI model has been also applied to graphite negative electrode in LIB. The SEI on the graphite negative electrode in LIBs is believed to be lithium-ion conductive but not electron conductive. The SEI formation process consumes electricity because this process is an irreversible reaction. The electricity loss due to the irreversible reaction is called an irreversible capacity. The irreversible capacity at graphite negative electrode must be compensated by the excess positive electrode material in battery, which brings to the extra cost and the difficulty in battery design. Therefore, this irreversible capacity must be minimized. In addition, the SEI is one of the paths for lithium-ion transfer in LIBs and should influence the LIBs' performance. Based on these facts, the formation mechanism and physicochemical properties of SEI have been extensively investigated.

2.1 SEI formation process in common electrolyte solutions

In the practical LIBs, organic solvents containing lithium salt are used as electrolyte solutions. The organic solvents are predominantly decomposed at graphite negative electrode and form lithium alkyl carbonate, lithium alkoxide, and lithium carbonate, etc, which are thought to be the components of SEI [6, 7]. It has been considered that the SEI properties are strongly affected by such solvent decomposition

products. Ethylene carbonate (EC) is an organic solvent which gives effective SEI to graphite negative electrode during initial charge process [2, 6, 9]. Accordingly, EC-based electrolyte solution has been mainly used in commercial LIBs. Propylene carbonate (PC), which is used in lithium primary batteries, is more attractive solvent since the melting point ($-49\text{ }^{\circ}\text{C}$) is lower than that of EC ($34\text{ }^{\circ}\text{C}$), leading to the use of LIBs in colder areas [10]. However, the lithium-ion intercalation reaction at graphite negative electrode cannot take place in PC-based electrolyte solutions. Instead of the lithium-ion intercalation reaction, the exfoliation of graphite only occurs at 0.9 V vs. Li^+/Li in PC-based electrolyte solutions [11, 12]. The difference of EC and PC has been understood by considering a co-intercalation process. It has been known that graphite can accept not only ionic species but also various molecules. Solvent molecules can also intercalate with lithium ion into graphite to form ternary $\text{Li}(\text{solv})_y\text{-GIC}$, which is more stable than binary Li-GIC thermodynamically [1, 13-17]. This intercalation reaction both lithium ion and solvent molecules is called a co-intercalation reaction. The difference of charge-discharge profiles in EC- and PC-based electrolyte solutions is shown in Fig. 3. As shown in Fig. 3, the reversible charge-discharge profile is obtained in EC-based electrolyte solution by forming Li-GIC but only potential plateau is observed in PC-based electrolyte solution corresponding to the formation of ternary $\text{Li}(\text{solv})_y\text{-GIC}$ and reductive decomposition of electrolyte solutions. This result indicates that SEI was formed in only EC-based electrolyte solutions.

Besenhard et al. studied the co-intercalation reaction of solvated-lithium ion at a highly oriented pyrolytic graphite (HOPG) in EC-based electrolyte solution during electrochemical measurement and found that the co-intercalation reaction was irreversible by dilatometry. They suggested SEI formation mechanism as shown in Fig. 4 [18]. Solvated-lithium ion is intercalated into graphite to form $\text{Li}(\text{solv})_y\text{C}_n$ at about 1.0 V vs. Li^+/Li , which is decomposed rapidly within graphene layers. After that, the decomposition reaction takes place on the surface of graphite and SEI is formed. This mechanism was clarified by Inaba et al. They investigated the morphology change of HOPG basal plane at certain potential in EC-based electrolyte solution by *in-situ* electrochemical scanning probe microscopy (SPM) [19-21]. The *in-situ* SPM images confirmed that hill-like structure ($1\text{-}2\text{ nm}$) at about 1 V vs. Li^+/Li and blister ($15\text{-}20\text{ nm}$) at about 0.8 V vs. Li^+/Li caused by co-intercalation and decomposition reactions of

solvated-lithium ion within graphene layers. The surface film was formed on HOPG basal plane below 0.65 V vs. Li^+/Li (Fig. 5). In addition, they revealed that exfoliation of graphite was observed at 0.95 V vs. Li^+/Li , caused by co-intercalation reaction, and further, deterioration of graphite was confirmed at 0.7 V Li^+/Li by *in-situ* scanning tunneling microscopy images of HOPG basal plane in PC-based electrolyte solution (Fig. 6) [22].

A question, why the presence of methyl- group in PC suppresses the formation of the SEI still remains unsolved. One of the explanations claimed by Aurbach et al. is as follows: they reported that $(\text{CH}_2\text{OCO}_2\text{Li})_2$ (lithium ethylene dicarbonate, LEDC) and $\text{CH}_3\text{CH}(\text{OCO}_2\text{Li})\text{CH}_2\text{OCO}_2\text{Li}$ (lithium propylene dicarbonate, LPDC) are major decomposition products accompanied by ethylene and propylene gas in EC and PC-based electrolyte solution, respectively [23-26]. And, they suggested that the main reason of irreversibility of graphite negative electrode is attributes to different lithium alkyl carbonate from that of EC and internal pressure of propylene gas in PC-based electrolyte solution. The reduction pathways of EC and PC on graphite negative electrode were shown in Fig. 7. Interestingly, in the case of other low crystallized carbonaceous materials such as soft carbons and hard carbons, lithium-ion intercalation reaction can take place in PC-based electrolyte solutions [2, 3, 61-64]. The crystallinity of carbonaceous materials also plays an important role on SEI formation. Although it has not been clearly understood about the SEI formation in soft and hard carbon negative electrodes, this result indicates that SEI can be formed on the graphite when co-intercalation reaction is suppressed in PC-based electrolyte solution.

2.2 SEI formation in PC-based electrolyte solution by additives

As described in the previous section, the key of SEI formation in PC-based electrolyte solutions is the suppression of the co-intercalation reaction. The simple method to avoid the co-intercalation reaction is to form SEI at higher potentials than the co-intercalation reaction potentials. Based on this strategy, various substances have been investigated as SEI formation additives. The demands for SEI formation additives are 1) additives are reduced at higher than 0.9-1.0 V vs. Li^+/Li , 2) the reductive decomposition products act as SEI. Several additives have been suggested such as vinylene carbonate (VC), fluoroethylene carbonate (FEC), and ethylene sulfite (ES), etc [27-31]. Zhang et

al. investigated the reduction potentials of EC, PC, diethyl carbonate (DEC), dimethyl carbonate, and VC and found that the reduction potential of VC is higher than those of EC, PC and DEC [27]. The co-intercalation reaction was effectively suppressed in PC-based electrolyte solution by the addition of VC. This is because the reduction decomposition products of VC acted as the effective SEI to suppress the co-intercalation reaction of PC-solvated lithium ion. Jeong et al. investigated the surface film in PC-based electrolyte solution containing VC, FEC, and ES by *in-situ* atomic force microscopy (AFM) [32]. Figure 8 shows the cyclic voltammograms and the AFM images of HOPG in these electrolyte solutions. At any cases, reduction peaks were confirmed above 1.0 V vs. Li^+/Li during the first cycle and the peaks disappeared during the second cycle, indicating irreversible reactions should be related with the SEI formation. In addition, surface films caused by the reduction of the additives were observed above 1.0 V vs. Li^+/Li and the co-intercalation reaction of PC-solvated lithium ion was not recognized below 1.0 V vs. Li^+/Li . These results indicate that the decomposition products of the additives effectively suppressed co-intercalation reaction of PC-solvated lithium ion, and that they act as the effective SEI. In addition, it is also reported that the effective SEI can be formed by using pure PC containing lithium bis(oxalato)borate (LiBOB) salt [33-36]. In this case, BOB^- anion participates in the SEI formation process, and BOB^- derived decomposition product serves as the effective SEI together with the decomposition product from organic solvent.

2.3 Unusual SEI formation in PC-based electrolyte solution by co-intercalation reaction of co-solvent

The co-intercalation reaction of solvated-lithium ion commonly occurs at graphite negative electrode as well as PC in the case of using organic solvents which have relatively high donor number because of strong interaction between lithium ion and organic solvents [13-17]. Dimethylsulfoxide (DMSO) has a higher donor number (29.8) than PC (15.1) [38]. Consequently, DMSO-solvated lithium ion intercalates into graphite at about 1.5 V vs. Li^+/Li in DMSO-based electrolyte solution [39]. Interestingly, in the case of using PC and DMSO-mixed electrolyte solution, the co-intercalation reaction of PC-solvated lithium ion is suppressed and the reversible intercalation and de-intercalation reactions of lithium ion take place as shown in Fig. 9 [40]. In this

binary solvent system, DMSO preferentially coordinates to lithium ion due to the stronger electron donicity than PC. Also, it is considered that DMSO-solvated lithium ion is intercalated and decomposed within graphene layers at more positive potential than PC co-intercalation potential and this decomposition product may act as an effective SEI to suppress co-intercalation reaction of PC-solvated lithium ion. However, DMSO cannot be considered as a SEI forming reagent because continual co-intercalation reaction occurs in the single DMSO-based electrolyte solution. The reason for the unique electrochemical phenomenon has been unclear.

3. New strategy of forming SEI in PC-based electrolyte solutions

3.1 SEI formation in highly concentrated lithium salt PC-based electrolyte solutions

The use of SEI forming additives is effective and practical. However, the content of SEI forming additives should be minimized from the view of cost. SEI forming additive is completely consumed at certain cycles. And when the additive-derived SEI is broken, the PC-based electrolyte solution cannot be used anymore. Therefore, other strategy that does not depend on the SEI forming additives must be designed.

Jeong et al. reported that the reversible lithium-ion intercalation and de-intercalation at graphite take place in concentrated electrolyte solution using pure PC as shown in Fig. 10 [41, 42]. Lithium ion is coordinated by 4 or 5 PC molecules, and a lot of free PC molecules exist in non-concentrated electrolyte solution (i.e.; molar ratio of lithium ion/PC is roughly calculated to be 1/12 for ca 1 mol dm⁻³ (0.83 mol kg⁻¹) LiClO₄/PC). But, in the case of concentrated electrolyte solution, it was confirmed that most of PC molecules coordinate to lithium ion by Raman spectroscopy. From Fig. 10, it was clarified that when lithium ion/PC is over 1/3 (3.27 mol kg⁻¹), the reversible lithium-ion intercalation and de-intercalation at graphite occurred. And in the concentrated electrolyte solution, it was confirmed that the solvation number of solvated-lithium ion was decreased [44]. As a result, the solvation structure is drastically changed at certain concentration [41, 43]. In addition, thin SEI on HOPG basal plane was confirmed in 3.27 mol kg⁻¹ LiN(SO₂C₂F₅)₂/PC by *in-situ* AFM [42]. Based on this concept, various concentrated electrolyte solutions have been investigated

and lithium-ion intercalation reaction into graphite was found in various solvents in which lithium-ion intercalation cannot occur in the normal concentration, ex. 1 M [44-47, 54-57].

Meanwhile, the solvation structure is related with the interaction between lithium ion and solvent molecules. Therefore, this interaction should be controlled in order to make effective SEI in graphite negative electrode. In addition, the interaction between lithium ion and anion is not negligible, because anion interacts with lithium ion in concentrated electrolyte solutions. Henderson clarified ionic association such as solvent separated ion pair (SSIP), contact ion pair (CIP) and aggregate (AGG) in various organic electrolyte solutions containing lithium salt, which is affected by ionic association strength between cation and anion [48-52]. Thus, solvent and anion interacts with lithium ion competitively in concentrated organic electrolyte solution [53]. Yamada et al. showed that fast intercalation reaction of lithium ion in highly concentrated acetonitrile (AN) or 1,2-dimethoxyethane (DME) electrolyte solutions as shown in Fig. 11 [54, 55]. In the normal concentration of AN- or DME-based electrolyte solutions, lithium-ion intercalation reaction does not occur, similarly to PC. They suggested that lowest unoccupied molecular orbital (LUMO) level of anion become lower than that of solvent by salt concentration and anion-derived decomposition products are mainly confirmed on graphite after cycles [54, 56, 57]. From the view of anion decomposition product derived SEI, these electrolyte solutions should be categorized to the same group as LiBOB system. Although the content of lithium salt is huge as compared with SEI forming additives, the consumption of anion should be considered. However, this salt concentrated electrolyte solution suggested that the effect of anion cannot be ignored and the interaction of lithium ion and anion should be also considered as a significant factor to determine solvation structures as well as solvent.

3.2 Control of solvation structure by stronger Lewis acid in PC-based electrolyte solution

Based on the above work, a new approach was suggested for controlling solvation structure. Takeuchi et al. investigated electrochemical properties of graphite in PC-based electrolyte solution containing both of lithium salt and divalent cation salt (calcium or magnesium) [58-60]. Figure 12 shows charge and discharge profiles in

lithium bis(trifluoromethane sulfonyl)amide (LiTFS)/PC containing different molality of calcium ion. Reversible intercalation and de-intercalation reactions of lithium ion are confirmed in 1.72 mol kg^{-1} , whereas only co-intercalation reaction of PC-solvated lithium ion takes place in 1.63 mol kg^{-1} . Lithium and calcium ions can be considered as a Lewis acid, which interact with organic solvent as a Lewis base. In these cases, PC prefers to coordinate to calcium ion in PC-based electrolyte solution containing lithium and calcium ions, which is attributed to stronger Lewis acid nature of calcium ion than lithium ion. Accordingly, solvation number in solvated-lithium ion decreases and lithium ion can be intercalated into graphite in 1.72 mol kg^{-1} electrolyte solution. This result indicates that solvation structure of solvated-lithium ion is drastically changed by the addition of stronger Lewis acid than lithium ion. The threshold of lithium-ion intercalation reaction was different between calcium salt and magnesium salt. Therefore, these results imply that the Lewis acidity is an important factor. In these electrolyte solutions, there is no information of SEI formation process.

Outline of the work

Based on the background as described above, SEI plays a vital role for lithium-ion intercalation at graphite negative electrode in PC-based electrolyte solutions. However, the nature and formation process of SEI have not been fully understood. In the case of using SEI forming additives, acceptable SEI formation mechanism was suggested; however, there is no detail investigation in the unique electrolyte solution systems. It is also considered that the SEI is greatly affected by interaction among lithium ion, divalent cation, solvent molecules, and anion in electrolyte solutions. Therefore, a factor related in the interaction should be clarified to understand the SEI formation process. In the organic electrolyte solution, lithium ion and cation are Lewis acids and solvent molecules and anion are Lewis bases, therefore, Lewis acid and base theory was focused to clarify the interaction among electrolyte solution species. In this study, SEI formation process was investigated at graphite negative electrode in PC-based electrolyte solutions with various solvation environments for lithium ion.

In chapter 1, effect of the addition of diethyleneglycol dimethyl ether (diglyme) on co-intercalation reaction of PC-solvated lithium ion at graphite negative electrode was

investigated by electrochemical measurement and *in-situ* AFM. The addition of small amount of diglyme (diglyme:PC=1:20 by volume ratio) enabled lithium-ion intercalation. This phenomenon was discussed on the basis of the *in-situ* AFM results. Diglyme worked as stronger Lewis base than PC and interacted with lithium ion preferentially. Diglyme-solvated lithium ion played an important role in SEI forming process.

In chapter 2, co-solvents' and anions' Lewis basicity on SEI formation process were investigated by charge and discharge measurements and *in-situ* AFM. The co-solvents' Lewis basicity was investigated by using glymes with different chain length (diglyme, triethyleneglycol dimethyl ether (triglyme), and tetraethyleneglycol dimethyl ether (tetraglyme)). The addition of tetraglyme increased the reversible capacity. The anions' Lewis basicity was investigated by using lithium bis(fluorosulfonyl)amide (LiFSA) and LiCF_3SO_3 in PC+tetraglyme. It can be explained that reactivity of solvated-lithium ion is lower caused by strong interaction between solvated-lithium ion and CF_3SO_3^- anion compared with FSA anions. The SEI formation process was discussed by the results of *in-situ* AFM

In chapter 3, *in-situ* Raman spectroscopy was performed to investigate electrolyte solution structure at the vicinity of graphite negative electrode. As SEI forming electrolyte solutions, $\text{LiClO}_4/\text{EC}+\text{DEC}$ (1:1 by volume ratio) and $\text{LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$ (20:1 by volume ratio) were used and $\text{LiCF}_3\text{SO}_3/\text{PC}$ was used as continuous co-intercalation system. In the SEI forming electrolyte solutions, vibrational frequency shifts to higher wavenumber in free solvents and anion were observed during the first charge process. In contrast, any vibrational frequency shifts was not confirmed in $\text{LiCF}_3\text{SO}_3/\text{PC}$. The difference of Raman spectra and the SEI formation process were discussed.

In chapter 4, SEI formation processes in $\text{LiTFSA}+\text{Ca}(\text{TFSA})_2/\text{PC}$, $\text{LiTFSA}+\text{Mg}(\text{TFSA})_2/\text{PC}$, and concentrated LiTFSA/PC were investigated by *in-situ* AFM. Effective SEI is formed at graphite irrespective of solutions, resulting in the reversible intercalation and de-intercalation of lithium ion. In $\text{LiTFSA}+\text{Ca}(\text{TFSA})_2/\text{PC}$

and concentrated LiTFSA/PC, co-intercalation type SEI formation was observed. On the contrary, LiTFSA+Mg(TFSA)₂/PC gave surface decomposition type SEI formation. Based on the SEI formation processes, the lithium-ion intercalation and de-intercalation reaction was discussed.

In chapter 5, *in-situ* AFM carried out to understand SEI formation process on glassy carbon in EC and PC-based electrolyte solutions, respectively. Thin SEI film was observed on glassy carbon and SEI formation process was not co-intercalation system. This indicates that SEI formation process is significantly different between non-graphitic and graphitic carbons.

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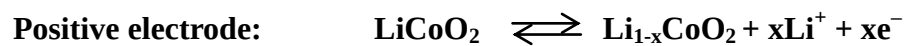
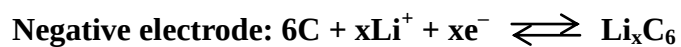
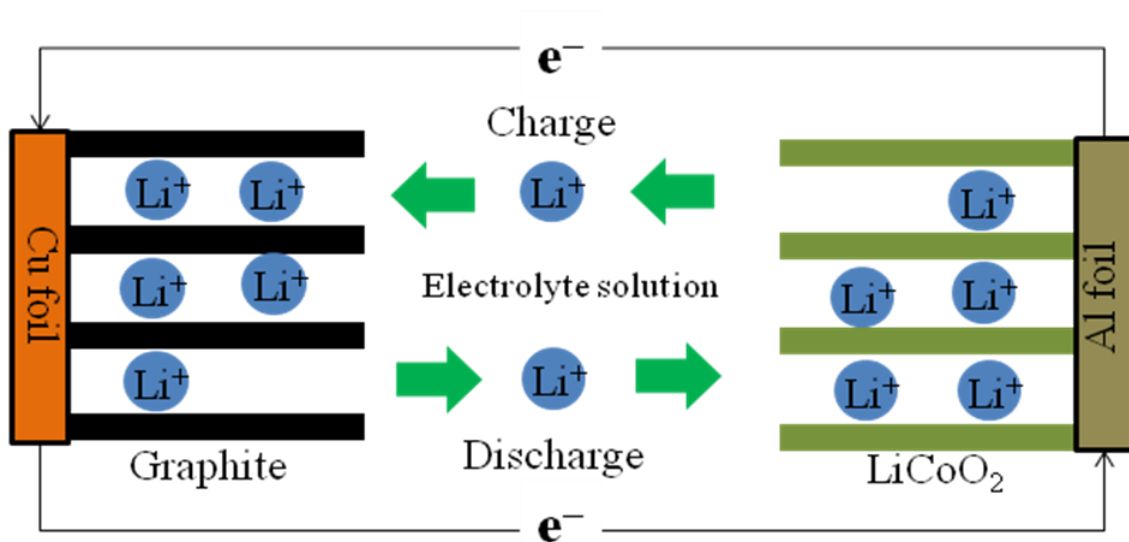


Fig. 1. Reaction principle of a lithium-ion battery (graphite/ LiCoO_2 system). Intercalation and de-intercalation reactions of lithium ion occur during charging and discharging.

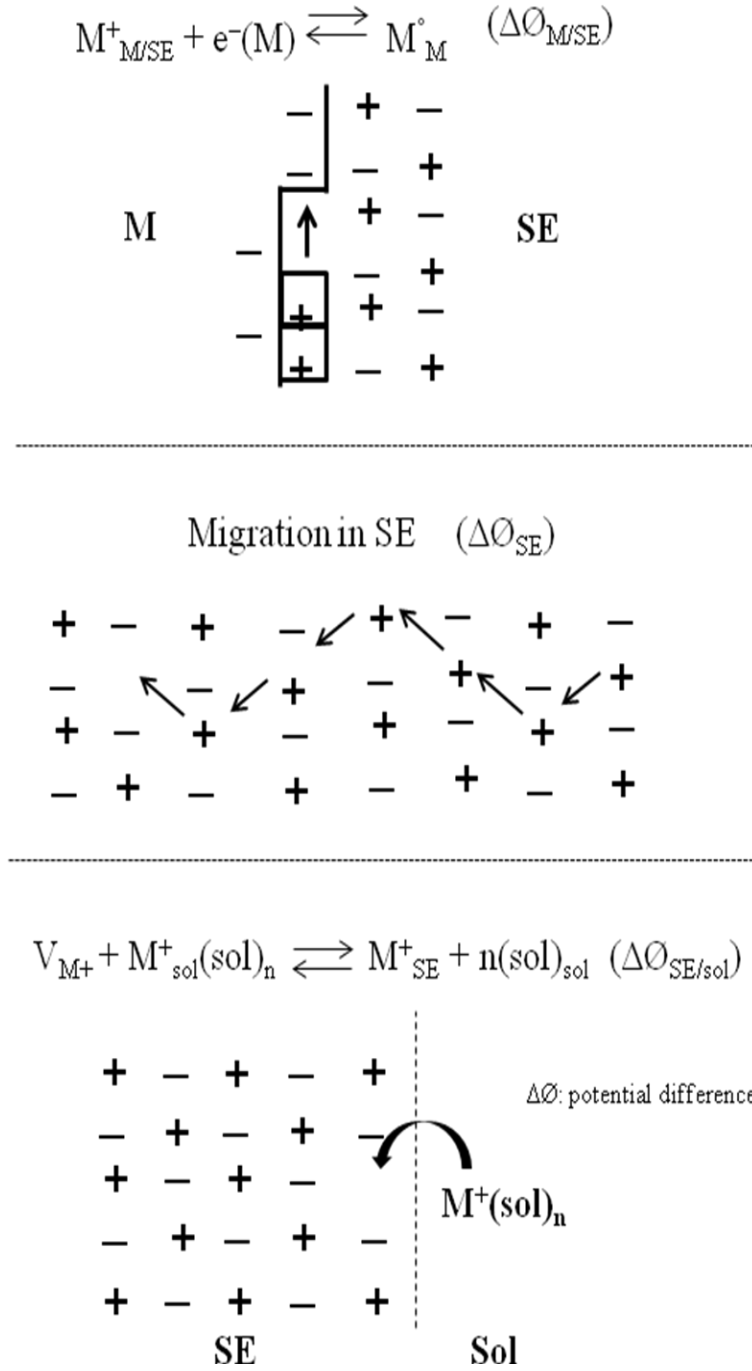


Fig. 2. A schematic model of the deposition and dissolution process on metal electrode through SEI in non-aqueous electrolyte solution. [[8] E. Peled, *J. Electrochem. Soc.*, **126**, 2047-2051 (1979).]

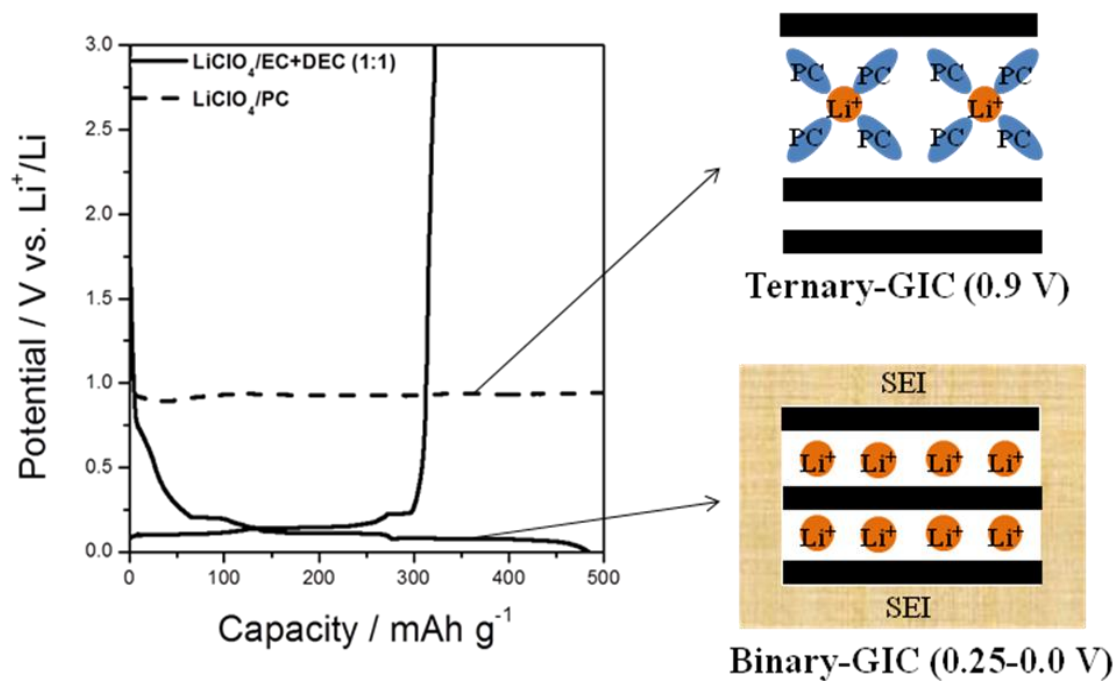


Fig. 3. Typical potential profiles of graphite negative electrodes in EC and PC-based electrolyte solutions and two kinds of GIC formed at different potentials.

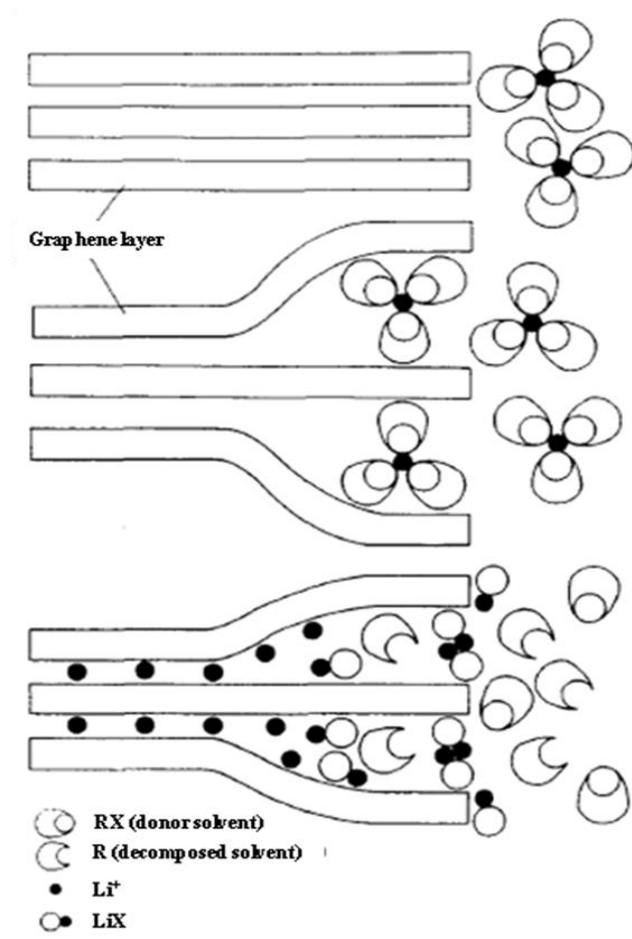


Fig. 4. A schematic model of SEI formation mechanism at graphite negative electrode via decomposition of $\text{Li}(\text{Solv})_y\text{C}_n$ in EC-based electrolyte solution. [[18] J.O. Besenhard et al., *J. Power Sources*, **54**, 228-231, (1995).]

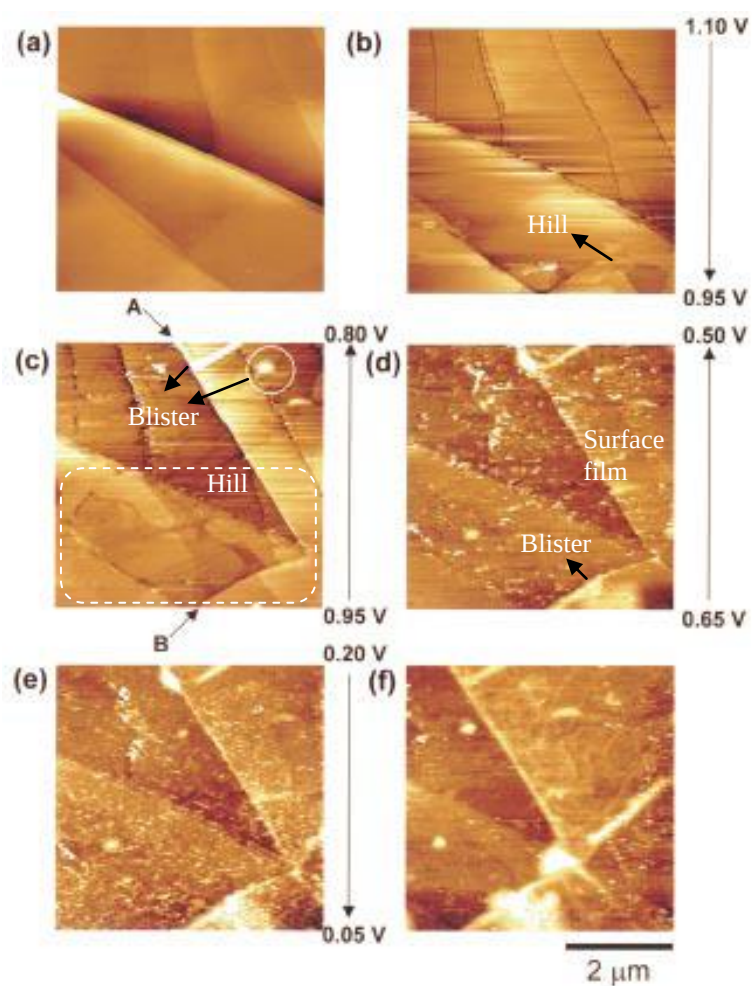


Fig. 5. *In-situ* AFM images of the HOPG basal plane obtained at (a) 2.9 V before CV, (b) 1.10–0.95 V, (c) 0.95–0.80 V, (d) 0.65–0.50 V, (e) 0.20–0.05 V during the first cycle, and (f) 2.9 V after the first cycle in 1 mol dm⁻³ LiClO₄/EC+DEC (1:1 by vol.). [[20] S. K. Jeong et al., *J. Electrochem. Soc.*, **148**, A989-A993 (2001).]

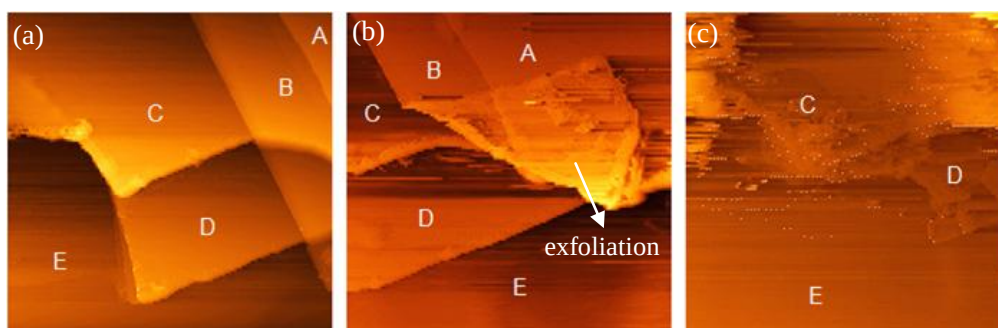


Fig. 6. STM images of HOPG basal plane after the potential was stepped to at (a) 1.1 V, (b) 0.95 V, and 0.7 V for 30 s in 1 mol dm⁻³ LiClO₄/PC. [[22] M. Inaba, et al., *J. Power Sources*, **68**, 221-226 (1997).]

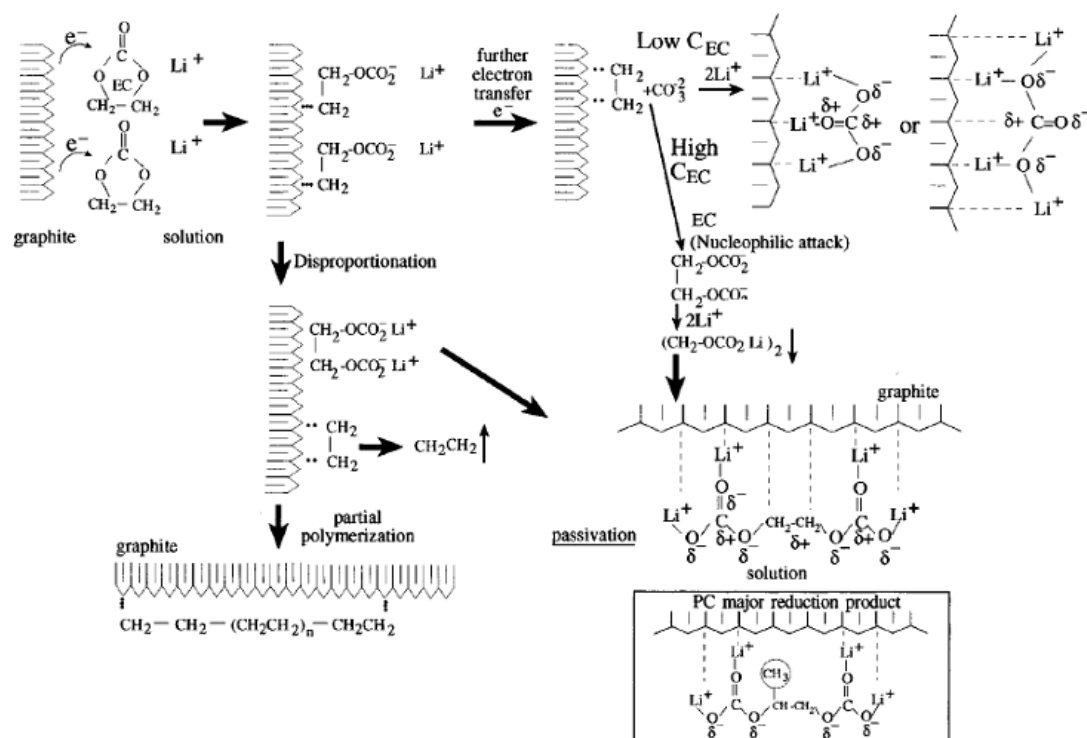


Fig. 7. Reduction pathways of cyclic carbonates on graphite negative electrode and major decomposition products. [[25] D. Aurbach et al., *Electrochim. Acta*, **45**, 67-86 (1999).]

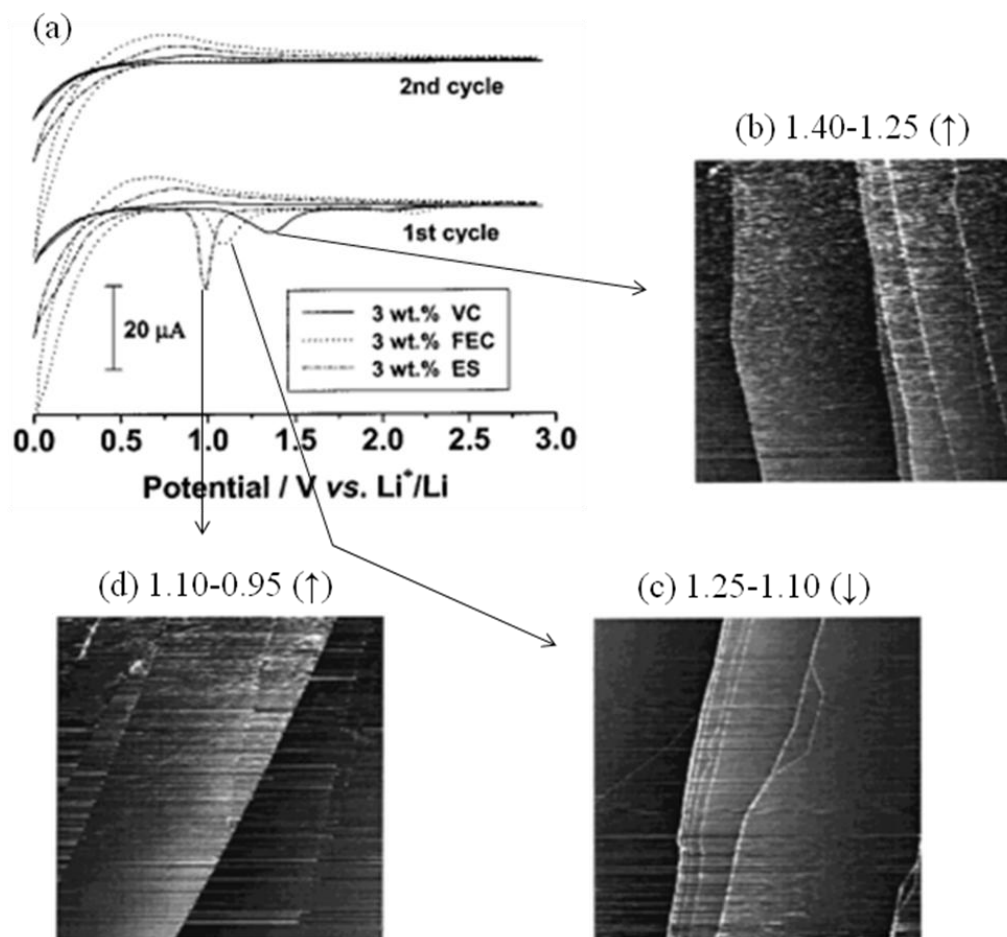


Fig. 8. (a) Cyclic voltammograms and AFM images of HOPG basal plane at the reduction potentials in $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ contained (b) VC, (c) FEC, and (d) ES, respectively. [[19] S. K. Jeong et al., *Langmuir*, **17**, 8281-8296 (2001).]

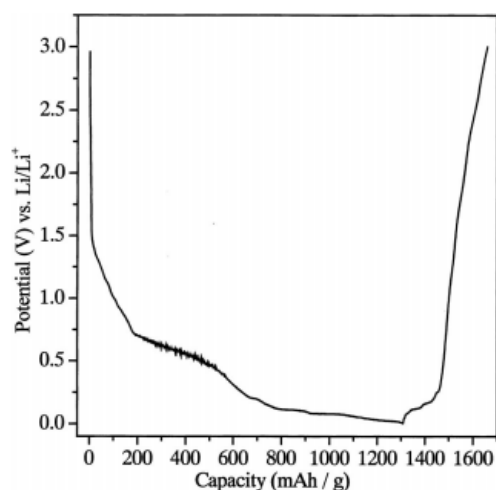


Fig. 9. Charge and discharge curves of graphite negative electrode during the first cycle in $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$ containing $0.5 \text{ mol dm}^{-3} \text{ DMSO}$. [[40] T. Abe et al., *J. Electrochem. Soc.*, **150**, A257-A261 (2003).]

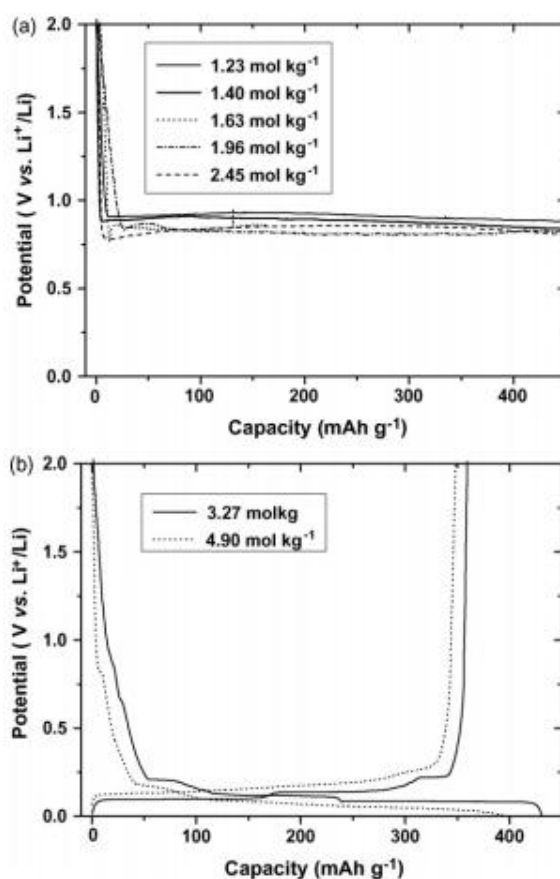


Fig. 10. Charge and discharge curves of natural graphite for the first cycle in PC containing relatively (a) low concentrations of $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ and (b) high concentrations of $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$. [[42] S. K. Jeong et al., *J. Power Sources*, **175**, 540-546 (2008).]

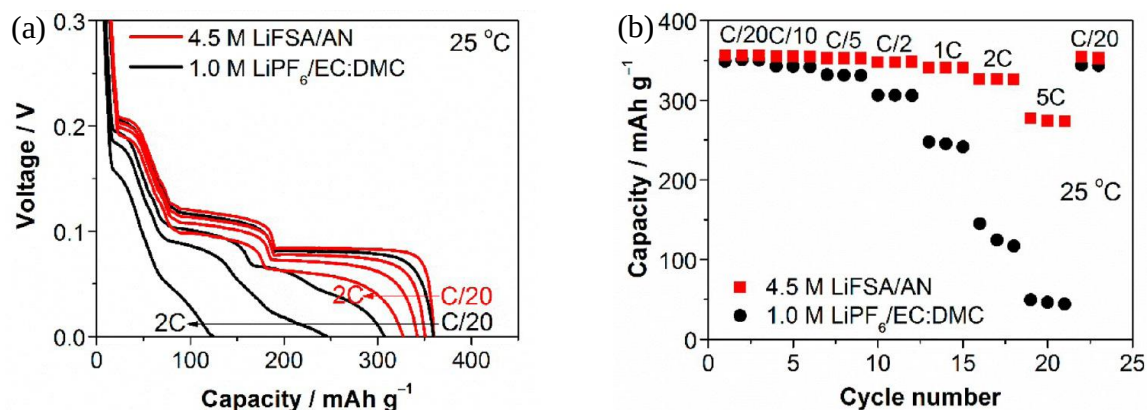


Fig. 11. (a) Lithium intercalation voltage curves of a natural graphite/lithium metal half cell with superconcentrated 4.5 mol dm⁻³ LiFSA/AN and commercial 1.0 mol dm⁻³ LiPF₆/EC:DMC (1:1 by volume ratio) electrolytes at various C-rates. (b) Reversible capacity of natural graphite in the two electrolytes at various C-rates. [[54] Y. Yamada et al., *J. Am. Chem. Soc.*, **136**, 5039-5046 (2014).]

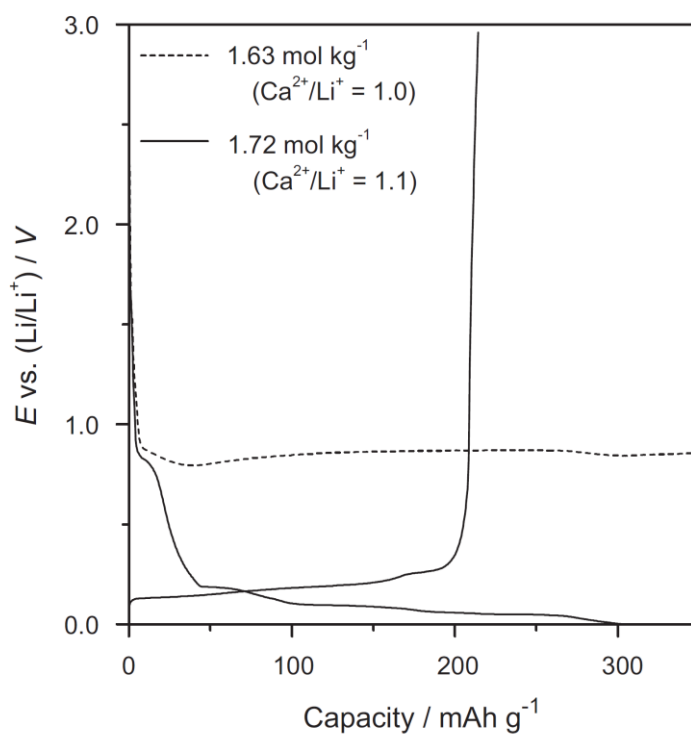


Fig. 12. Charge and discharge curves of natural graphite in 1.63 and 1.72 mol kg⁻¹ LiTFSA and Ca(TFSA)₂/PC. [[58] S. Takeuchi et al., *Electrochim. Acta*, **56**, 10450-10453 (2011).]

Chapter 1

Suppression of Co-intercalation Reaction of Propylene Carbonate and Lithium Ion into Graphite Negative Electrode by Addition of Diglyme

1.1 Introduction

Graphite is used as an active negative electrode material in practical lithium-ion batteries (LIB). Lithium-ion intercalation/de-intercalation into/from the graphite proceeds during the charge/discharge process as a negative electrode reaction. This reaction undergoes at near 0 V vs. Li^+/Li and organic solvents should be reduced at this potential thermodynamically. However, a surface film known as solid electrolyte interphase (SEI), that is lithium-ion conductive and electron non-conductive, is formed on the surface of graphite during the 1st charge process in proper electrolyte solutions [1]. SEI enables lithium ion to intercalate into the graphite without further reduction of electrolyte solutions. As a proper organic solvent, ethylene carbonate (EC) is widely used. In EC-based electrolyte solutions, reductive decomposition products of EC act as SEI [2-7]. Hence, EC is used as a main organic solvent in practical LIBs.

Propylene carbonate (PC) is known as a main organic solvent in primary lithium batteries. A melting point of PC ($-49\text{ }^{\circ}\text{C}$) is lower than that of EC ($34\text{ }^{\circ}\text{C}$). Considering LIBs in cold areas, PC is the suitable solvent since the melting point of EC is lower than ambient temperature in the cold areas and will freeze even for the cryoscopy phenomenon by lithium salt. However, in PC-based electrolyte solutions, lithium-ion intercalation into the graphite cannot proceed and only exfoliation of the graphite occurs. This is why only EC-based electrolyte solutions can be used in practical LIBs. There are some explanations for the reason of the exfoliation of the graphite [3, 8-10]. Our group has shown that the co-intercalation reaction of PC-solvated lithium ion and subsequent reduction of the PC-solvated lithium ion in graphene layers is the main reason for the exfoliation of the graphite by using the *in-situ* scanning probe microscope (SPM) technique [10]. For now, this proposed mechanism seems to be reasonable.

Based on this mechanism, some strategies of the use of PC in LIBs have been proposed, that is, how we suppress the co-intercalation reaction. One is to use additives that can be reduced at higher potential than the co-intercalation reaction potential and whose reductive decomposition products can act as SEI [11-14], the second is to use highly-concentrated lithium-salt electrolyte solutions [15,16], and the third is the addition of multivalent-cation salts as Lewis acid [17, 18]. From the view of scientific aspect, the second and the third strategies are quite important since solvated-lithium ion structure was drastically changed in bulk electrolyte solutions and the changed solvated-lithium ion structure played important role in a lithium-ion transfer process at the interface between the graphite and the electrolyte solution. However, both electrolyte solutions are highly viscous and a new breakthrough is needed to be used in practical LIBs. On the contrary, additives are quite convenient from the view of practical use, since additives themselves make the SEI irrespective of PC. Vinylene carbonate (VC) is one of the most popular additives [11, 12]. VC is reduced at higher potential than co-intercalation reaction potential at the surface of the graphite. In this case, a formation mechanism of SEI is simple and many similar additives have been reported. However, the SEI formation mechanism of some additives is unknown. In the case of dimethyl sulfoxide (DMSO), when DMSO was used as a single organic solvent, the co-intercalation reaction of DMSO and lithium ion only proceeds and lithium-ion intercalation does not occur as well as PC. However, lithium-ion intercalation can proceed in the PC-DMSO mixed electrolyte solution [19, 20]. This is an unexplained phenomenon and the reason was not clarified, therefore, the detail investigation should be carried out. However, DMSO is toxic and hardly used in practical LIBs, therefore we focused on diethylene glycol dimethyl ether (diglyme) as an alternate to DMSO, since a donor number of diglyme would be higher than that of PC as well as DMSO. Moreover, diglyme is not toxic and inexpensive. In this chapter, the effect of the addition of diglyme in the PC-based electrolyte solution on electrochemical behavior including the SEI formation and lithium-ion intercalation was investigated by using the *in-situ* SPM and the *in-situ* Raman spectroscopy.

1.2 Experimental

Charge and discharge measurements were performed by a coin-type cell. A natural graphite (SNO-15) composite electrode was used as a working electrode (SNO-15: polyvinylidene difluoride = 90:10 wt%) and lithium foil was used as a counter electrode. In this chapter, the charge denotes the intercalation and the discharge denotes the de-intercalation. Electrolyte solutions were PC, diglyme, and PC+diglyme (1:2, 2:1, and 20:1 by volume ratio) containing 1 mol dm⁻³ lithium bis(trifluoromethane sulfonyl)amide (LiTFSA). The *in-situ* SPM observation was carried out by a specialized three-electrode cell. A working electrode was a highly oriented pyrolytic graphite (HOPG) and counter and reference electrodes were lithium foil. Hereafter, electrode potential was referred to Li⁺/Li in the case of the three-electrode cell. Observation mode was contact mode (atomic force microscope; AFM mode) in an Ar-filled glove box [4, 5, 16]. Electrode potential was swept from 3.07 to 0.1 V at 2 mV s⁻¹ to observe the surface morphology of the HOPG. Also, potential was kept at 0.9 V to investigate the co-intercalation reaction at the HOPG. In addition, the *in-situ* Raman spectroscopy was carried out to investigate the intercalation behavior of lithium ion. The Raman spectra were excited by using a 514.5 nm line of an argon ion laser, and the scattered light was collected in a backscattering geometry. A SNO-15 composite electrode was used as a working electrode and lithium foils were used as a counter and counter and reference electrodes were lithium foil. The *in-situ* Raman cell with optical polished pyrex[®] glass window was fabricated and sealed in the Ar-filled glove box. All electrochemical measurements were carried out at 25 °C.

1.3 Results and discussion

1.3.1 Charge and discharge properties in PC-diglyme mixed electrolyte solutions

Figure 1.1 shows charge and discharge profiles in PC and diglyme containing LiTFSA. The large potential plateau was observed at about 0.9 V in PC (Fig. 1.1a). This result has been reported in many researches and the degradation of the graphite is owing to the vigorous co-intercalation and decomposition reaction of PC-solvated lithium ion inside the graphite [3, 8-10]. In contrast, the reversible reaction took place in diglyme (Fig. 1.1b). It was reported that the intercalation and de-intercalation of lithium ion into/from the graphite occur below 0.25 V with the staging phenomenon [21]. But, in

this case, a significant discharge reaction occurred above 0.7 V, although potential reached to 0 V during the charge process. In previous works, ternary Li^+ -solvent-graphite intercalation compounds (GIC) were formed chemically in various ether-based electrolyte solutions because of the strong interaction between lithium ion and these solvent, such as dimethoxyethane, diethoxyethane, and tetrahydrofuran [22]. Similarly we confirmed that the ternary Li^+ -solvent-GIC was formed by chemical method in the diglyme solution. Therefore, based on the discharge reaction at high voltage, the reversible intercalation and de-intercalation reaction of diglyme-solvated lithium ion took place in diglyme.

Charge and discharge measurements were performed to understand the effect of volume ratio of PC+diglyme (Fig. 1.2). In all of cases, the intercalation and de-intercalation reaction of lithium ion took place below 0.25 V in PC+diglyme different from diglyme, although the large irreversible capacity was observed at the first cycle. Therefore, it is found that the addition of diglyme to PC is effective to the intercalation and de-intercalation reactions of lithium ion. The reason might be explained as follows. One lithium ion should be coordinated by two diglymes in PC+diglyme, because diglyme is bidentate oxygen ligand and would have higher donor number than PC. In literature, it is reported that the addition of PC into the diglyme- LiCF_3SO_3 complexes did not significantly affect the coordination of the diglyme-solvated lithium ion [23]. Therefore, most of lithium ions would be coordinated to diglyme in PC+diglyme (1:2 and 2:1), because the molar ratio of Li^+ /diglyme was 1/4.72 and 1/2.36, respectively. But, all of lithium ions can't be coordinated by diglyme in PC+diglyme (20:1), because the molar ratio of Li^+ /diglyme is 2.97/1. In this case, two kinds of solvated-lithium ions would exist; those are diglyme-solvated lithium ion and PC-solvated lithium ion. However, some of diglyme in diglyme-solvated lithium ions might be replaced by PC. It is reported that when PC was added to the solvated ionic liquid (equimolar mixture of LiTFSa and glymes (triethylene glycol dimethyl ether or tetraethylene glycol dimethyl ether)), glyme in glyme-lithium ion complex cation was replaced by PC [24]. Although glyme species and concentration are different, similar phenomenon might occur. Therefore, in this study, the term “diglyme-solvated lithium ion” includes diglyme-PC-solvated lithium ion. These solvated-lithium ions should participate in the interfacial reaction between

the graphite and the electrolyte solution. Diglyme-solvated lithium ion intercalates into graphite first, because the co-intercalation reaction potential was higher in LiTFSA/diglyme than in LiTFSA/PC as shown in Fig. 1.1. Consequently, the decomposition products from diglyme-solvated lithium ion was formed within graphite, and acted as the SEI and suppressed the co-intercalation reaction of PC-solvated lithium ion. In addition, the reversible capacity increased with decreasing of the volume of diglyme, in spite of the largest irreversible capacity in PC+diglyme (20:1). Based on this result, diglyme is thought to act as SEI-forming additive in PC. In the next section, we investigated the effect of diglyme in detail.

1.3.2 Investigation of morphology change and intercalation behavior during the first cycle by *in-situ* SPM and Raman spectroscopy

AFM images are shown in Figs. 1.3 (PC) and 1.4 (PC+diglyme (20:1)). The potential was kept at 0.9 V during AFM observation after sweeping from 3 to 0.9 V. It was confirmed that there was no change until 2.76 V. Typical step and terrace structures of the pristine HOPG surface were only observed. In PC and PC+diglyme, hill like structures with the height of 1–2 nm were observed between 0.98 and 0.9 V. Also, the higher swelling was observed at about 0.9 V. These changes caused by the co-intercalation reaction of solvated-lithium ion into the HOPG. In previous AFM results in EC-based electrolyte solutions, the SEI was formed at about 0.6 V resulting from the decomposition reaction of electrolyte solution [4]. In PC, considerable change in HOPG basal plane was observed owing to the consecutive co-intercalation reaction of PC-solvated lithium ion while holding the potential at 0.9 V (Figs. 1.3(b)–(f)). As a result, the height of HOPG basal plane became higher by 48 nm with increasing holding time. On the other hand, there was no significant change in PC+diglyme while holding the potential at 0.9 V (Figs. 1.4(b)–(f)). From AFM observation, it was evident that the co-intercalation of PC-solvated lithium ion was suppressed by the addition of diglyme. Figure 1.5 shows the potential profile and *in-situ* Raman spectra of SNO-15 in PC+diglyme (20:1) during the first charge process. Several potential plateaus were observed above 0.25 V during the first charge process. In the Raman spectra, the G-band at 1583 cm^{-1} did not change from OCV to 0.66 V. Hardwick, et al. reported that E_{2g2} (boundary)-band appear from 0.9 V due to the co-intercalation reaction of

solvated-lithium ion in EC+PC (1:1 by weight ratio) containing LiClO₄ [25]. This result suggests that the co-intercalation reaction of PC-solvated lithium ion at about 0.9 V was suppressed effectively by the addition of diglyme. This is good agreement with above AFM results. Moreover, the G-band shifted upward and appeared shoulder at about 1600 cm⁻¹ from 0.5 to 0.25 V. These results indicate that the co-intercalation reaction of PC-solvated lithium ion was not fully suppressed because the passivation ability of SEI from diglyme was not perfect. However, the co-intercalation potential was lowered to 0.66 V, which is lower than typical co-intercalation potential of PC-solvated lithium ion. Therefore, morphology change of HOPG at higher potential in PC+diglyme (20:1) was investigated. Cyclic voltammogram and *in-situ* SPM images were shown in Fig. 1.6. Several cathodic peaks related with the reduction of electrolyte solution were observed between 1.5 and 0.5 V (Fig. 1.6(a)). Only step and terrace structures of the HOPG were observed between 2.58 and 2.06 V (Fig. 1.6(b)). Small cathodic current starts to flow at about 1.5 V, and morphology change at vicinity of HOPG edge plane was observed owing to the co-intercalation reaction between 1.54 and 1.03 V (Fig. 1.6(c)). Since this potential was higher than the co-intercalation potential of PC-solvated lithium ion (Fig. 1.6(d)), it should be considered that the co-intercalation reaction of diglyme-solvated lithium ion proceeded. And diglyme-solvated lithium ion was decomposed within the graphite below 0.95 V and formed SEI which suppressed the co-intercalation reaction of PC-solvated lithium ion at 0.9 V. It was confirmed that the co-intercalation reaction of PC-solvated lithium ion proceeded below 0.66 V from *in-situ* Raman spectra. But, this reaction was suppressed at lower potential. This indicates that the decomposition product of co-intercalated PC-solvated lithium ion strengthened the previously formed SEI and suppressed the further co-intercalation of PC-solvated lithium ion. After SEI was strengthened, the morphology change was not observed below 0.51 V (Fig. 1.6(e)). After the first cycle, SPM scan was carried out to investigate thickness of formed SEI on HOPG basal plane in extended scan range (Fig. 1.7). In this case, SEI was removed physically at the position repeated scan during the first cycle. Difference between the repeated position during the first cycle and the unrepeatd position was measured. After the first cycle, thickness of SEI on HOPG basal plane was estimated to be 12 nm. This value is thinner than that of EC-based electrolyte solutions (40 nm) [4].

1.4 Conclusions

The effects of the addition of diglyme in PC electrolyte solution were investigated and interfacial reactions, such as the co-intercalation reaction of solvated-lithium ion and the formation reaction of SEI were discussed. The co-intercalation reaction of PC-solvated lithium ion was effectively suppressed by addition of the small amount of diglyme. This means that effective decomposition product was formed at the graphite by the decomposition of diglyme-solvated lithium ion. Consequently, the reversible intercalation and de-intercalation reactions at the graphite negative electrode proceeded in PC+diglyme. In the case of PC+diglyme (20:1 by volume ratio), the co-intercalation reaction of small amount of PC-solvated lithium ion took place below 0.66 V. But, this co-intercalation reaction can be suppressed by effective SEI that formed from PC-solvated lithium ion. In addition, thinner SEI film was formed on HOPG basal plane in PC+diglyme (20:1) compare with that of EC-based electrolyte solutions.

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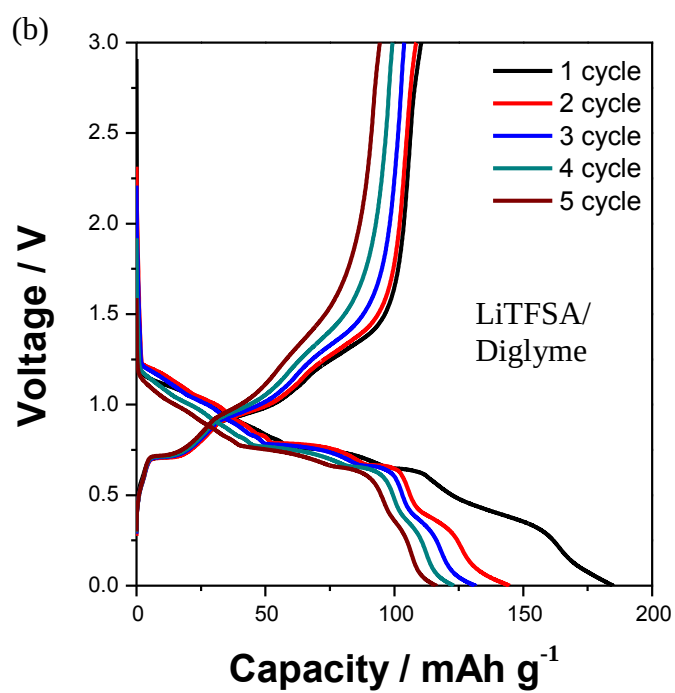
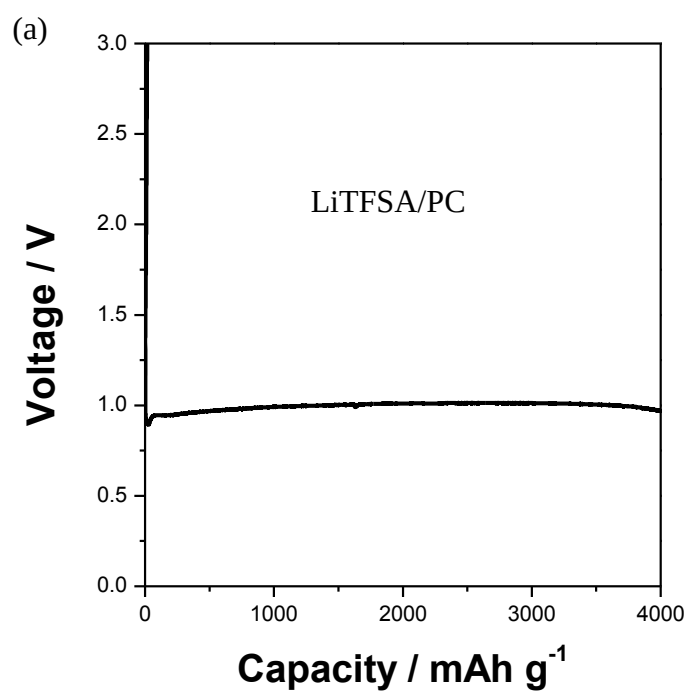


Fig. 1.1. Charge and discharge curves of SNO-15 in (a) LiTFSA/PC and (b) LiTFSA/diglyme. C-rate: 1/12 C.

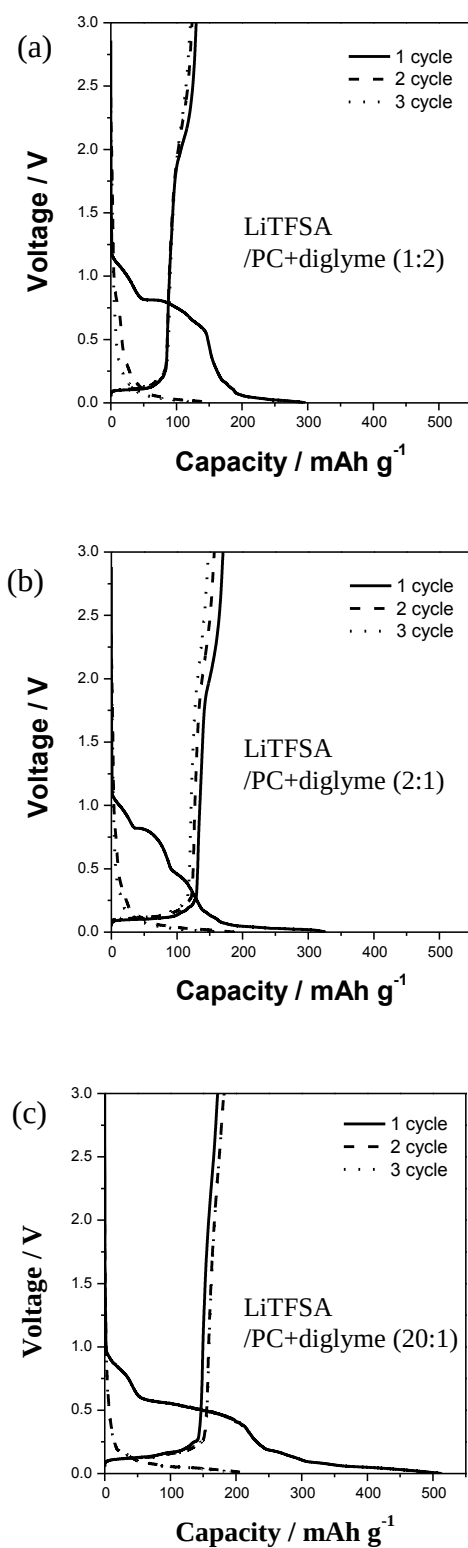


Fig. 1.2. Charge and discharge curves of SNO-15 in LiTFSA/PC+diglyme. The volume ratio of PC/diglyme is (a) 1/2, (b) 2/1, and (c) 20/1. C-rate: 1/12 C.

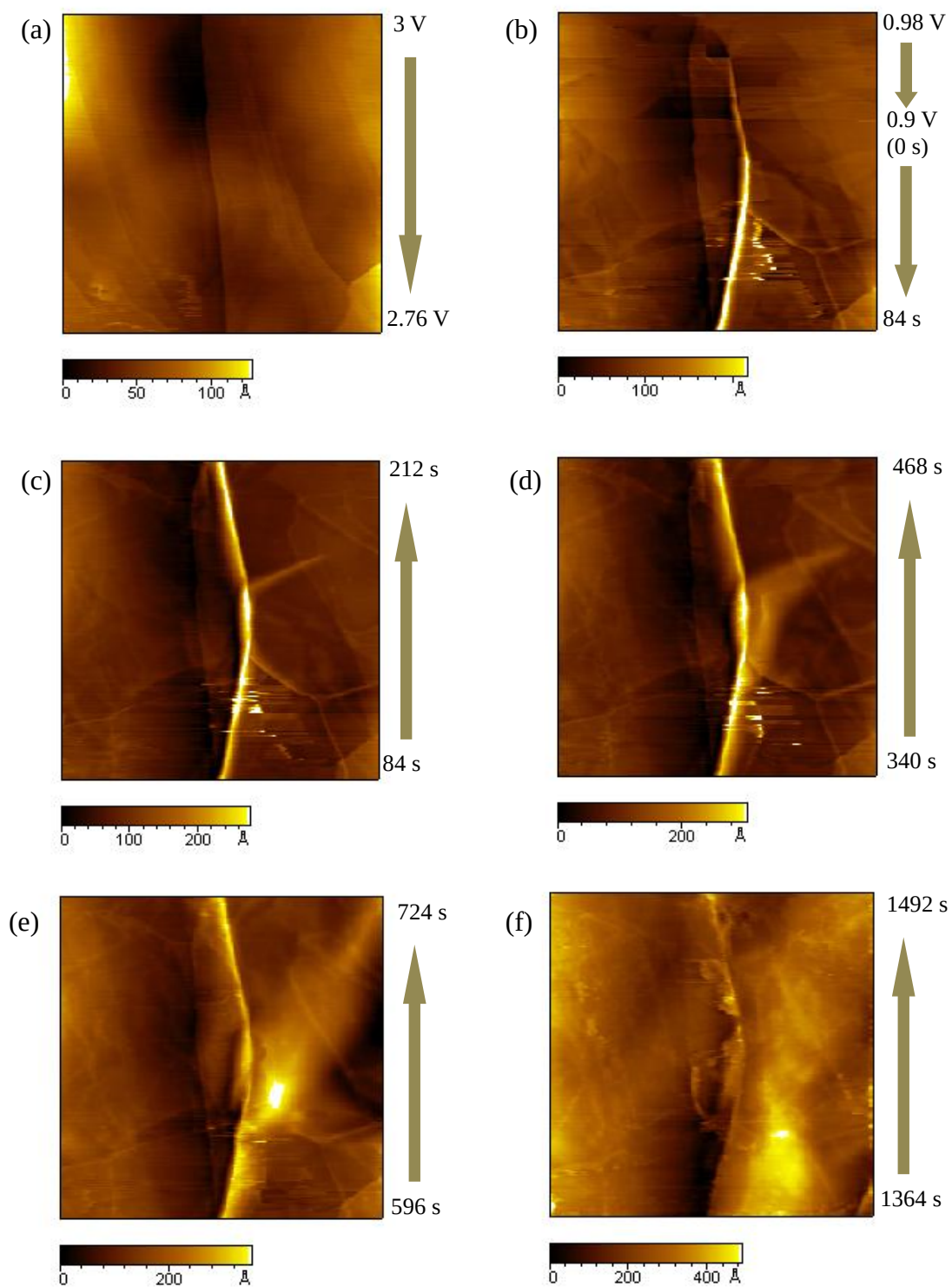


Fig. 1.3. *In-situ* SPM images of HOPG basal plane (5 $\mu\text{m} \times 5 \mu\text{m}$) at 0.9 V in LiTfSA/PC. The potential was kept at 0.9 V after be swept from OCV to 0.9 V.

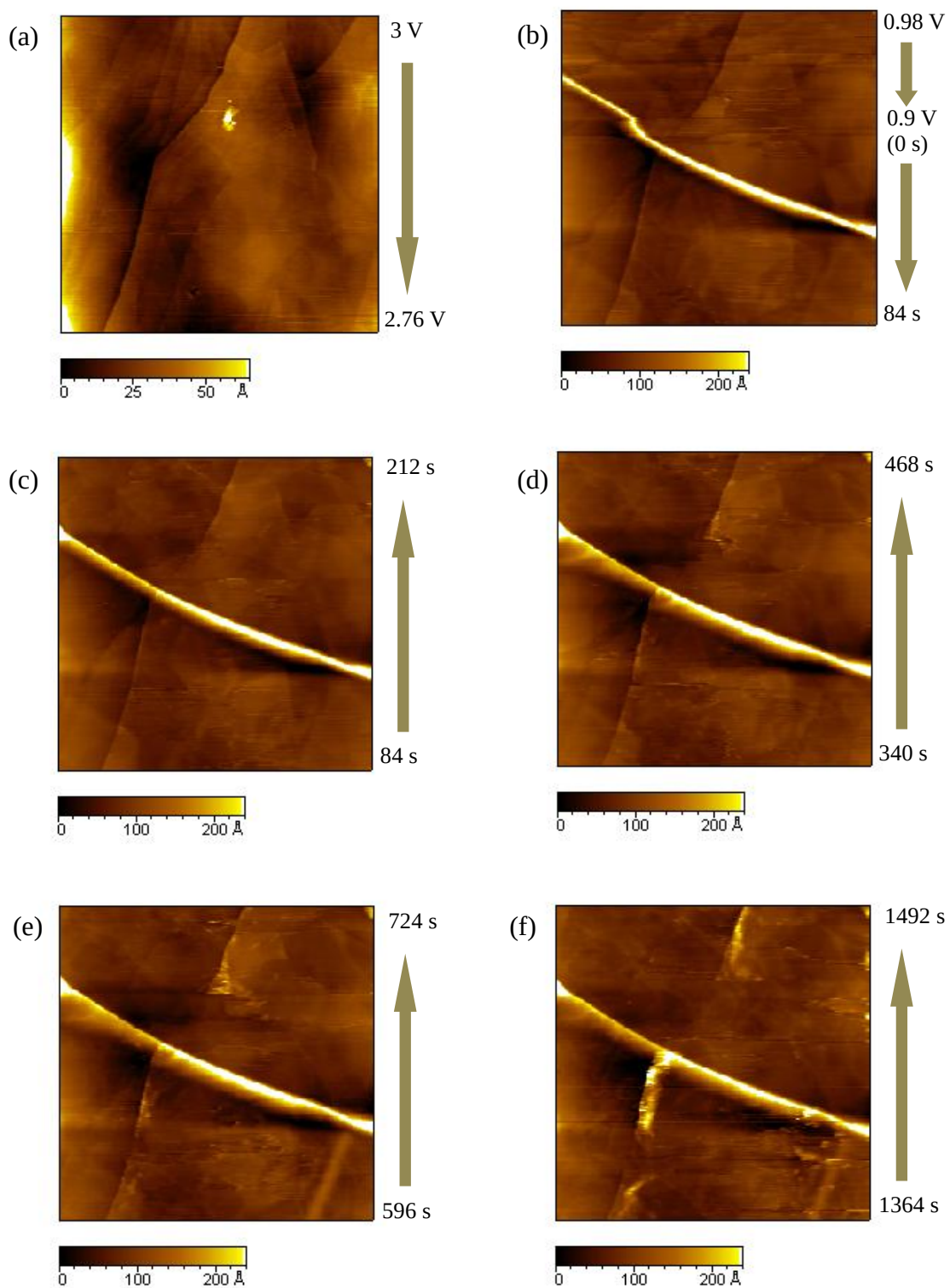


Fig. 1.4. *In-situ* SPM images of HOPG basal plane ($5\ \mu\text{m} \times 5\ \mu\text{m}$) at 0.9 V in LiTFS/PC+diglyme (20:1 by volume ratio). The potential was kept at 0.9 V after be swept from OCV to 0.9 V.

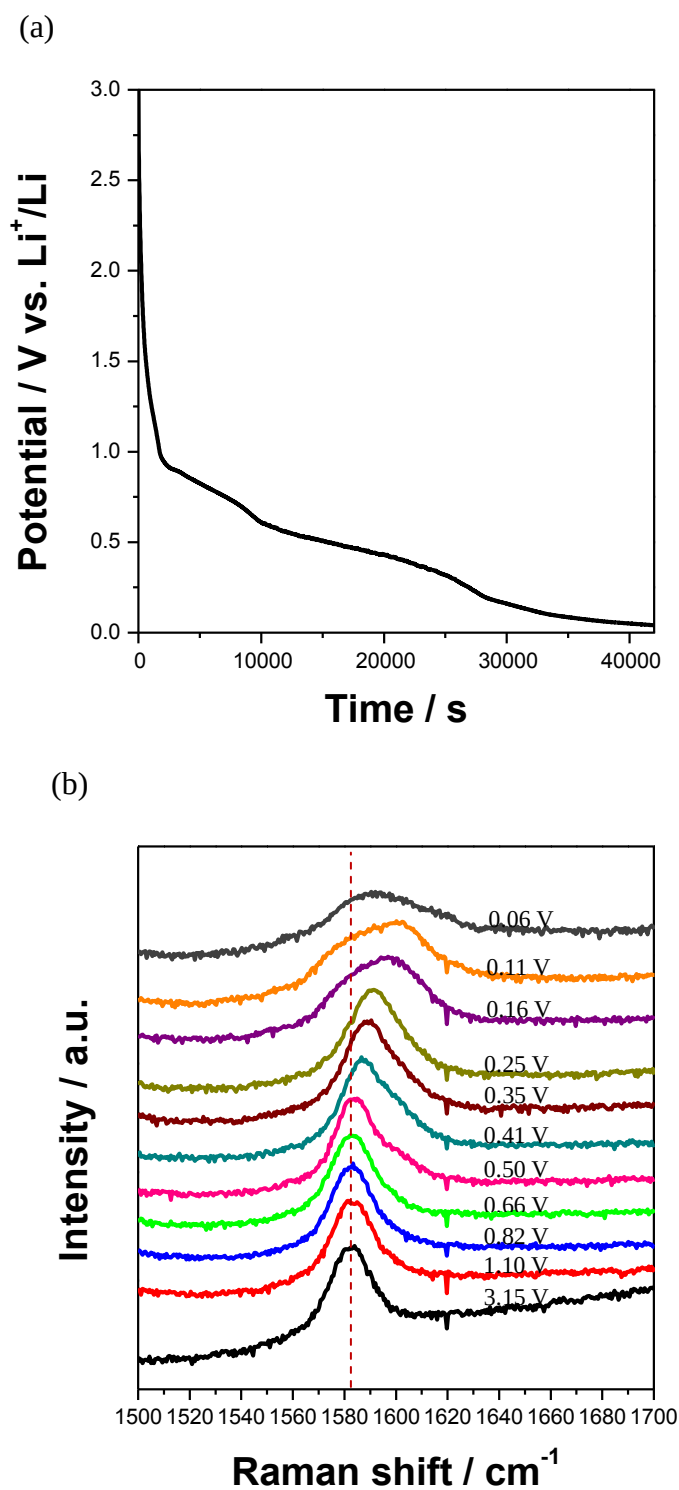


Fig. 1.5. (a) Potential profile and (b) *in-situ* Raman spectra of SNO-15 in LiTFS/PC+diglyme (20:1). C-rate: 0.1 C.

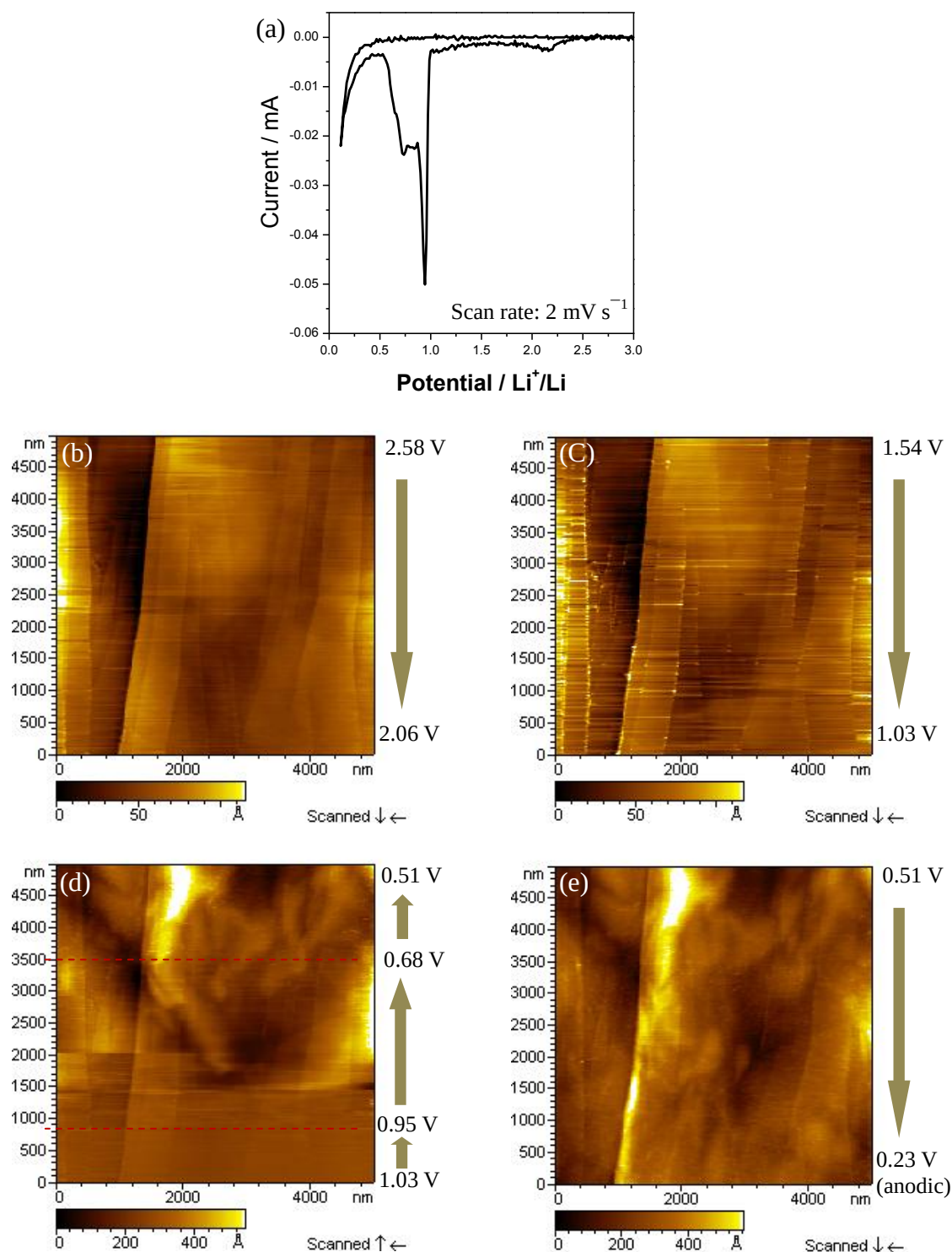


Fig. 1.6. (a) Cyclic voltammogram and *in-situ* SPM images of HOPG basal plane (5 $\mu\text{m} \times 5 \mu\text{m}$) at (b) 2.58–2.06 V, (c) 1.54–1.03 V, (d) 1.03–0.51 V, and (e) 0.51–^{anodic}0.23 V in LiTFS/PC+diglyme (20:1). Scan rate: 2 mV s^{-1} .

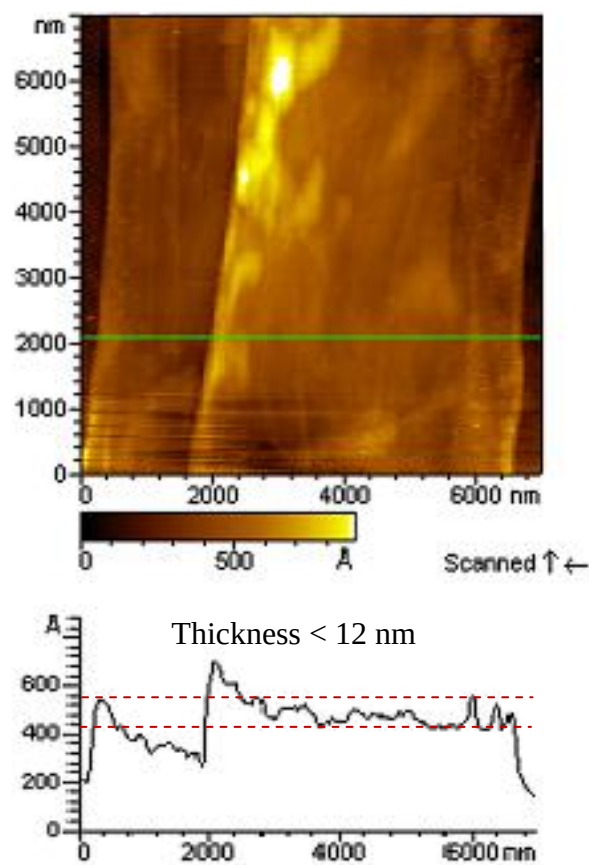


Fig. 1.7. SPM image of HOPG basal plane ($7\ \mu\text{m} \times 7\ \mu\text{m}$) after the first cycle in LiTFSA/PC+diglyme (20:1).

Chapter 2

Solid Electrolyte Interphase Formation in Propylene Carbonate-based Electrolyte Solutions for Lithium-ion Batteries Based on the Lewis Basicity of the Co-solvent and Counter Anion

2.1 Introduction

The formation of a solid electrolyte interphase (SEI) by decomposition of an organic electrolyte solution during initial charging influence the electrochemical performance of the graphite negative electrodes in lithium-ion batteries (LIBs) [1-5]. At the graphite electrode, co-intercalation of solvated lithium ions proceeds at a higher potential than intercalation of the lithium ions alone [6-13]. However, once an effective SEI is formed, it further inhibits co-intercalation and decomposition of the electrolyte species. As a consequence, reversible intercalation and de-intercalation of the lithium ions can kinetically proceed. Hence, effective SEI formation is indispensable for suppressing the co-intercalation of solvated lithium ions.

It is widely known that these co-intercalation reactions continue to take place in propylene carbonate (PC)-based electrolyte solutions and that effective SEI cannot be formed [1, 2, 14-16]. PC-based electrolyte solutions are very attractive for use in cold areas owing to the low melting point of PC ($-49\text{ }^{\circ}\text{C}$) and much research has been conducted on the use of PC-based electrolyte solutions [17-21]. In previous study, it was reported that a PC-based electrolyte solution with a high lithium salt content exhibited reversible lithium-ion intercalation/de-intercalation due to the decrease in the PC-solvation number of the lithium ions [18, 19]. This result indicated that the solvation structure of PC-solvated lithium ions is a significant factor in the formation of an effective SEI and inhibition of co-intercalation reactions. Based on these results, we developed a new strategy wherein the addition of a stronger Lewis acid causes the transfer of PC molecules from the PC-solvated lithium ions to the new, stronger Lewis acid; also, the PC-solvation number of the lithium ions decreased. Our group reported that the addition of calcium ions as a Lewis acid to a PC-based electrolyte solution

facilitated the intercalation/de-intercalation of lithium ions [22, 23]. Inspired by these results, we turned our focus to using a Lewis base in the electrolyte solution as a means to control the solvation structure of PC-solvated lithium ions.

The co-solvent and counter anion are considered as the Lewis bases in the PC-based electrolyte solution. Co-solvents influence the solvation structure of PC-solvated lithium ions by directly interacting with the lithium ion. Conversely, lithium ions form aggregates with counter anions in electrolyte solutions [24-27]. Thus, counter anions also influence the solvation structure of PC-solvated lithium ions. Therefore, it is possible that the formation of an effective SEI between the graphite negative electrode and electrolyte solution may be facilitated by exploiting the Lewis basicity of the co-solvent and counter anion in the system. Thus, it is important to understand the effect of the Lewis basicity of the co-solvent and counter anion upon the SEI formation process in order to improve the performance of LIBs.

In this chapter, we focused on the Lewis basicity of the co-solvent and counter anion in a PC-based electrolyte solution. In chapter 1, we have reported that reversible intercalation and de-intercalation of lithium ions take place in PC-based electrolyte solutions upon addition of diethylene glycol dimethyl ether (diglyme), which exhibits stronger Lewis basicity than PC [32]. In this chapter, the effect of the Lewis basicity of the solvent in a PC-based electrolyte solution was investigated by adding different glymes, and the effect of the Lewis basicity of the counter anion was investigated using different lithium salts. SEI formation was investigated by *in-situ* scanning probe microscopy (SPM).

2.2 Experimental

Charge and discharge measurements were carried out using a 2032 coin-type cell with 1/12 C ($1C = 372 \text{ mA g}^{-1}$). A composite electrode on copper foil was used as a working electrode. The slurry was prepared by mixing natural graphite (SNO-15) as an active material and polyvinylidene difluoride (PVdF) as a binder (90:10 wt%), which was coated onto copper foil and dried at 80 °C for 12 h. Lithium foil was used as the counter electrode. To investigate the effect of co-solvent Lewis basicity, 1 mol dm^{-3} lithium bis(trifluoromethanesulfonyl)amide (LiTFSa) in either PC and triethylene glycol dimethyl ether (triglyme) or PC and tetraethylene glycol dimethyl ether

(tetraglyme) (20:1 by volume ratio) were used as electrolyte solutions. Furthermore, 1 mol dm⁻³ lithium bis(fluorosulfonyl)amide (LiFSA) or lithium trifluoromethanesulfonate (LiOTf) in PC and tetraglyme (20:1 by volume ratio) were used to investigate the effect of the Lewis basicity of the counter anion.

SEI formation was investigated with *in-situ* SPM in contact mode (i.e., atomic force microscope (AFM) mode) using a specialized three-electrode cell [10, 11, 18, 19, 32]. Highly oriented pyrolytic graphite (HOPG) and lithium foils were used as the model working electrode, and counter and reference electrodes, respectively. Hereafter, the electrode potential was referred to Li⁺/Li. The electrolyte solutions comprised 1 mol dm⁻³ LiFSA or LiOTf in PC and tetraglyme (20:1 by volume ratio). The molar ratio of lithium salt/PC/tetraglyme was fixed at 4.63/51.76/1. Cyclic voltammetry was carried out between 3.07 and 0.1 V at 2 mV s⁻¹ during SPM observation in an Ar-filled glove box. The reason of the cut off potential of 0.1 V is to avoid the lithium metal deposition on the HOPG and this potential region is enough to observe the SEI formation process. All electrochemical measurements were performed at 25 °C.

2.3 Results and discussion

2.3.1 Effect of glyme chain length

Figure 2.1 shows the charge and discharge curves for SNO-15 in PC+triglyme and PC+tetraglyme containing LiTFSA. In chapter 1, which concerned a LiTFSA/PC+diglyme electrolyte, it was confirmed that the reversible intercalation and de-intercalation of lithium ions took place, although the co-intercalation of PC-solvated lithium ion occurred at about 0.5 V [32]. In this case, the diglyme-solvated lithium ions were primarily co-intercalated and decomposed within the graphite layers, which prevented the co-intercalation of PC-solvated lithium ions at about 0.9 V. As a result, the co-intercalation voltage for PC decreased. Similarly, co-intercalation of solvated lithium ions at about 0.5 V and intercalation and de-intercalation of lithium ions are observed in LiTFSA/PC+triglyme and LiTFSA/PC+tetraglyme, as shown in Fig. 2.1. Co-intercalation at about 0.5 V is suppressed by the decomposition of PC at a lower voltage. Although the reversible capacities were smaller than that of the theoretical capacity of graphite (372 mA h g⁻¹) due to the partially exfoliation of graphite, the reversible capacities become larger with increasing glyme chain length. This indicates

that a more effective SEI is formed by adding a longer chain glyme. Lewis basicity of the glymes increases with increasing chain length. Thus, the Lewis basicity of the glymes changes the solvation structure of the solvated lithium ions, with tetraglyme being more effective than the other glymes. Hence, tetraglyme was employed as the co-solvent in all subsequent experiments.

2.3.2 Effect of anion Lewis basicity

Lewis basicity of the FSA anion is lower than that of the TFSA anion owing to the stronger electron withdrawal of fluorine compared to that of trifluoromethane group. The OTf anion tends to interact with lithium ions more strongly than FSA and TFSA anions in electrolyte solutions, acting as a stronger Lewis base owing to the large negative charge on the oxygen atoms and the asymmetrical charge distribution [24-30]. Therefore, the FSA anion was used as a weak Lewis base, and the OTf anion was used as a strong Lewis base.

Charge and discharge profiles are shown in Fig. 2.2. In the 1st cycle, the charge and discharge properties in LiFSA/PC+tetraglyme are clearly different from those in LiOTf/PC+tetraglyme. The co-intercalation of PC-solvated lithium ions occurs at about 0.5 V in LiFSA/PC+tetraglyme similarly to the LiTFSA system (Fig. 2.2(a)). Conversely, the co-intercalation reaction at 0.5 V is significantly inhibited in LiOTf/PC+tetraglyme, as shown in Fig. 2.2(b). These electrolyte solutions are prepared using the same molar ratio of Li^+ /PC/tetraglyme (4.63/51.76/1); therefore, the only difference between them is the anion. Thus, these results indicate that SEI formation and co-intercalation are greatly affected by the Lewis basicity of the anion in the system. Therefore, the difference of charge and discharge profiles was investigated from the view of SEI formation process by *in-situ* SPM.

In-situ SPM was performed to investigate SEI formation in LiFSA/PC+tetraglyme and LiOTf/PC+tetraglyme. Figure 2.3 shows the cyclic voltammograms obtained from the *in-situ* cell using these electrolyte solutions. In the both cyclic voltammograms, some cathodic peaks were observed. The cathodic current at about 2.2 V and 0.1 V is due to the reduction reaction of water in the electrolyte solutions and the intercalation of lithium ions, respectively. However, the clear anodic current due to the de-intercalation of lithium ions was not observed since the cut off

potential was limited to 0.1 V. The cathodic currents above 0.25 V for LiFSA/PC+tetraglyme and LiOTf/PC+tetraglyme are different. From 1.5 to 0.7 V, which is related to the reaction of tetraglyme-solvated lithium ions, the cathodic current for LiFSA/PC+tetraglyme is larger than that for LiOTf/PC+tetraglyme, suggesting that LiFSA/PC+tetraglyme is more reactive than LiOTf/PC+tetraglyme. Lithium ions are coordinated by PC and tetraglyme molecules in these electrolyte solutions, but the reactivity of the solvated lithium ions is different because the Lewis basicity of the counter anions surrounding the solvated lithium ions is different. The interaction between FSA anions and solvated lithium ion is weaker than that with the OTf anion, and thus the reactivity of the solvated lithium ion in LiFSA/PC+tetraglyme is stronger than in LiOTf/PC+tetraglyme.

The change in the morphology of the HOPG basal plane was observed at each potential during the 1st cycle in these electrolyte solutions (Figs. 2.4 and 2.5). In LiFSA/PC+tetraglyme, no morphology change is observed until 2.06 V (Fig. 4(b)). In this case, two kinds of solvated lithium ions exist, i.e., tetraglyme- and PC-solvated lithium ions. The co-intercalation and decomposition of tetraglyme-solvated lithium ions proceeds before that of PC-solvated lithium ions [32]. Significant change is observed at the HOPG edge owing to the co-intercalation of tetraglyme-solvated lithium ions from 1.80 to 1.28 V (Figs. 2.4(c) and (d)), and co-intercalated tetraglyme-solvated lithium is decomposed at about 1.28 V (Fig. 2.4(d)). Furthermore, the co-intercalation of PC-solvated lithium ions at about 0.9 V is not observed due to the SEI formed from the decomposition products of tetraglyme-solvated lithium ions. Furthermore, drastic morphological change is observed at 0.77 V. Below 0.77 V, blistered structures caused by the decomposition of PC-solvated lithium ions within the graphite layers are observed. As a result, decomposition products were observed as an SEI after the cathodic sweep (Fig. 2.4(f)). Conversely, morphological change is not observed until 1.03 V in the LiOTf/PC+tetraglyme system (Figs. 2.5(a)–(d)), although sharp cathodic currents are observed between 1.5 and 1.0 V in Figure 2.3(b). Based on the cyclic voltammograms, co-intercalation and decomposition of tetraglyme-solvated lithium ions occurs in both LiFSA/PC+tetraglyme and LiOTf/PC+tetraglyme above 1.0 V (Figs. 2.3(a) and (b)). However, more vigorous co-intercalation and decomposition occurs from 1.80 to 1.03 V in LiFSA/PC+tetraglyme, which indicates that the reactivity of the

tetraglyme-solvated lithium ions in LiFSA/PC+tetraglyme is higher than in LiOTf/PC+tetraglyme. This indicates that the interaction between tetraglyme-solvated lithium ions is weaker in the presence of FSA anions than OTf anions. Hill-like structures due to the co-intercalation of PC-solvated lithium ions into the graphite layers are observed between 1.03 and 0.92 V (Fig. 2.5(e)). The height of the hill-like feature is estimated to be 14 nm at about 1.03 V. The height of the hill-like structure has been reported to be 1–2 nm in EC-based electrolyte solutions [10, 31]. In our case, larger PC-solvated lithium ions are intercalated within the graphite layers, indicating the intercalation of lithium-PC-OTf anion complexes. Furthermore, blister structures are observed below 0.92 V, which would suppress the further co-intercalation of PC-solvated lithium ions. Decomposition products are observed at 0.77 and 0.62 V in LiFSA/PC+tetraglyme and LiOTf/PC+tetraglyme, respectively. This indicates that the co-intercalation potential of PC-solvated lithium ions is influenced by the counter anion. In other words, PC-solvated lithium ions are more stable due to their interaction with the OTf anion being stronger than that with FSA anions; therefore, a lower reduction potential is required to decompose PC-solvated lithium ions. When the electrode potential reaches the reduction potential, the PC-solvated lithium ions interacting with the OTf anions are immediately decomposed in the graphite layer and form SEI (Figs. 2.5(e) and (f)). This hypothesis is supported by the charge and discharge profiles in Fig. 2.2. The voltage plateau below 0.6 V for LiFSA/PC+tetraglyme is larger than that for LiOTf/PC+tetraglyme, and reversible capacity is large in LiOTf/PC+tetraglyme. This means that the SEI is formed immediately without degradation of the graphite electrode in LiOTf/PC+tetraglyme. Based on the *in-situ* SPM analysis, the cathodic current at 0.5 V in cyclic voltammograms (Fig. 2.3) can be assigned to the reaction of PC-solvated lithium ions.

In addition, the thickness of the SEI was estimated. Figure 2.6 shows AFM images of the HOPG basal plane in LiFSA/PC+tetraglyme and LiOTf/PC+tetraglyme after the 1st cycle. In these cases, a wider scan range was used to investigate thickness of SEI [10]. The decomposition product was physically cleaned from a small area by cantilever after the 1st cycle. The thicknesses of the SEI after the 1st cycle were estimated to be 32 and 8 nm in LiFSA/PC+tetraglyme and LiOTf/PC+tetraglyme, respectively. This corresponds well with previous studies. Based on these results, it is

clear that the Lewis basicity of the counter anion plays an important role in the formation of an effective SEI on the graphite negative electrode, and this concept will be useful for research into the enhancement of LIB performance.

2.4 Conclusions

The effect of the Lewis basicity of the co-solvent and counter anion on SEI formation process in PC-based electrolyte solutions was investigated. The addition of diglyme, triglyme, and tetraglyme indicated that reversible capacities increased with the increasing chain length of the glyme. However, the co-intercalation of PC-solvated lithium ions at about 0.5 V was not adequately suppressed in PC-based electrolyte solutions. The co-intercalation of PC-solvated lithium ions was more significantly suppressed in a mixed PC and tetraglyme electrolyte solution containing LiOTf compared with one containing LiFSA. This difference was explained by the reactivity of the solvated lithium ion interacting with the counter anion. The Lewis basicity of the OTf anion is stronger than that of the FSA anion; therefore, PC-solvated lithium ions were stabilized by the OTf anion. The stability of the PC-solvated lithium ions was found to be an important factor in the formation of an effective SEI, and this stability is influenced by the counter anion.

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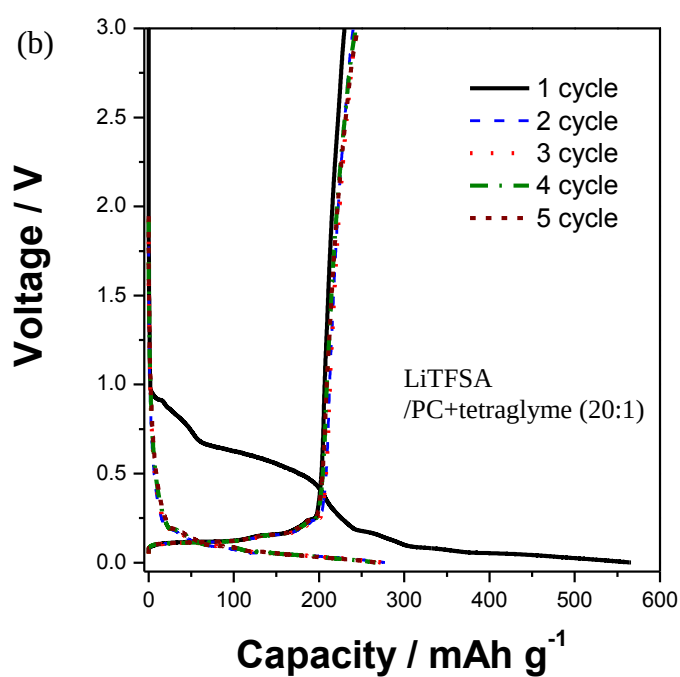
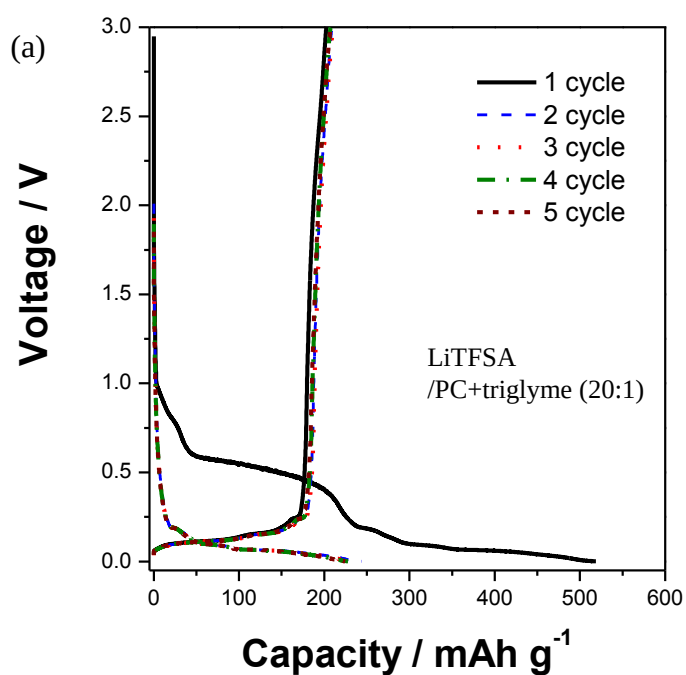


Fig. 2.1. Charge and discharge profiles of natural graphite (SNO-15) in 1 mol dm⁻³ LiTFSA/PC+(a) triglyme and (b) tetraglyme (20:1 by volume ratio). C-rate: 1/12 C.

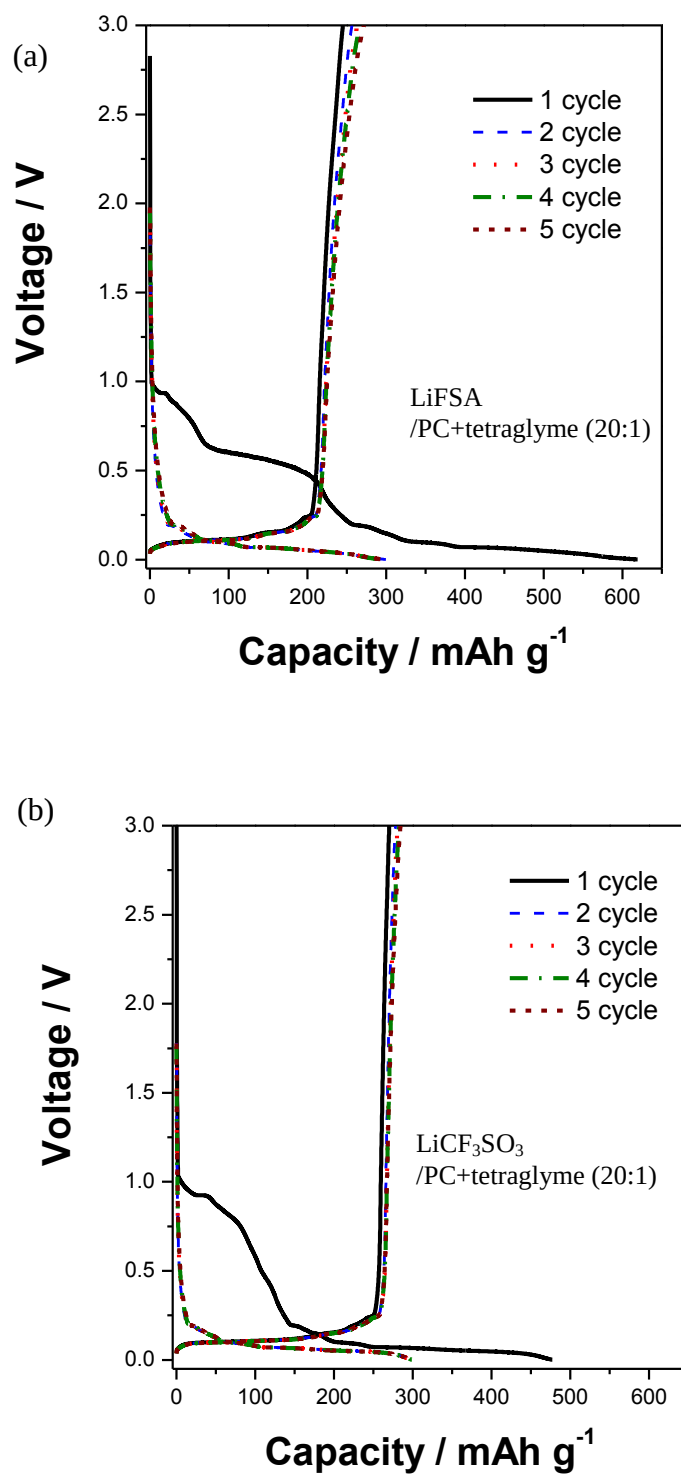


Fig. 2.2. Charge and discharge profiles of natural graphite (SNO-15) in 1 mol dm⁻³ (a) LiFSA and (b) LiCF₃SO₃/PC+tetraglyme (20:1 by volume ratio). C-rate: 1/12 C.

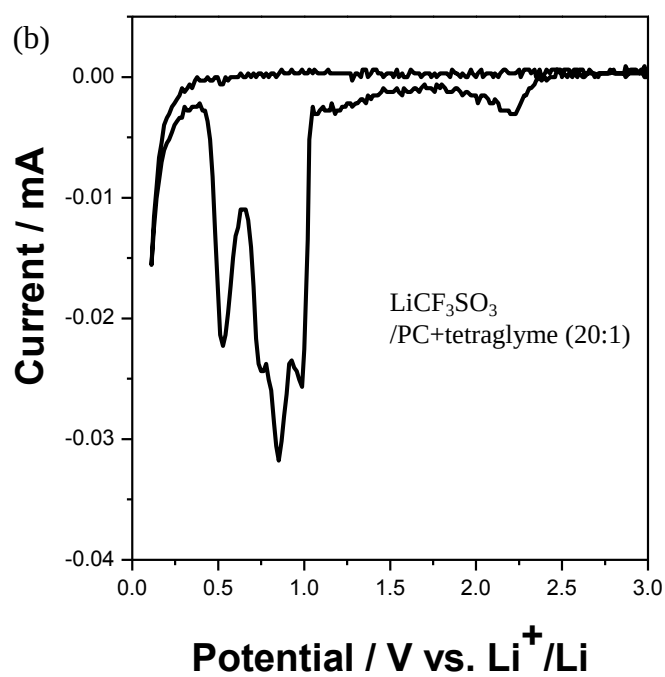
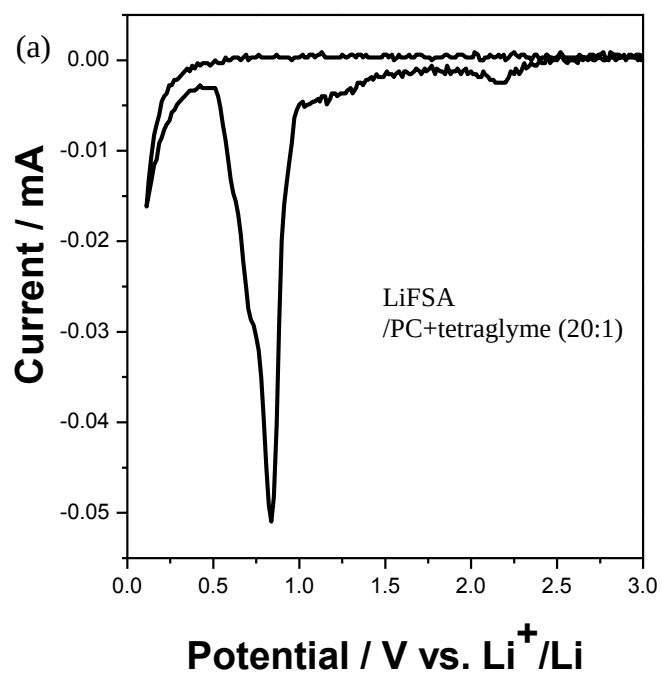


Fig. 2.3. Cyclic voltammograms of HOPG in 1 mol dm^{-3} (a) LiFSA and (b) LiCF_3SO_3 /PC+tetraglyme (20:1 by volume ratio). Scan rate: 2 mV s^{-1} .

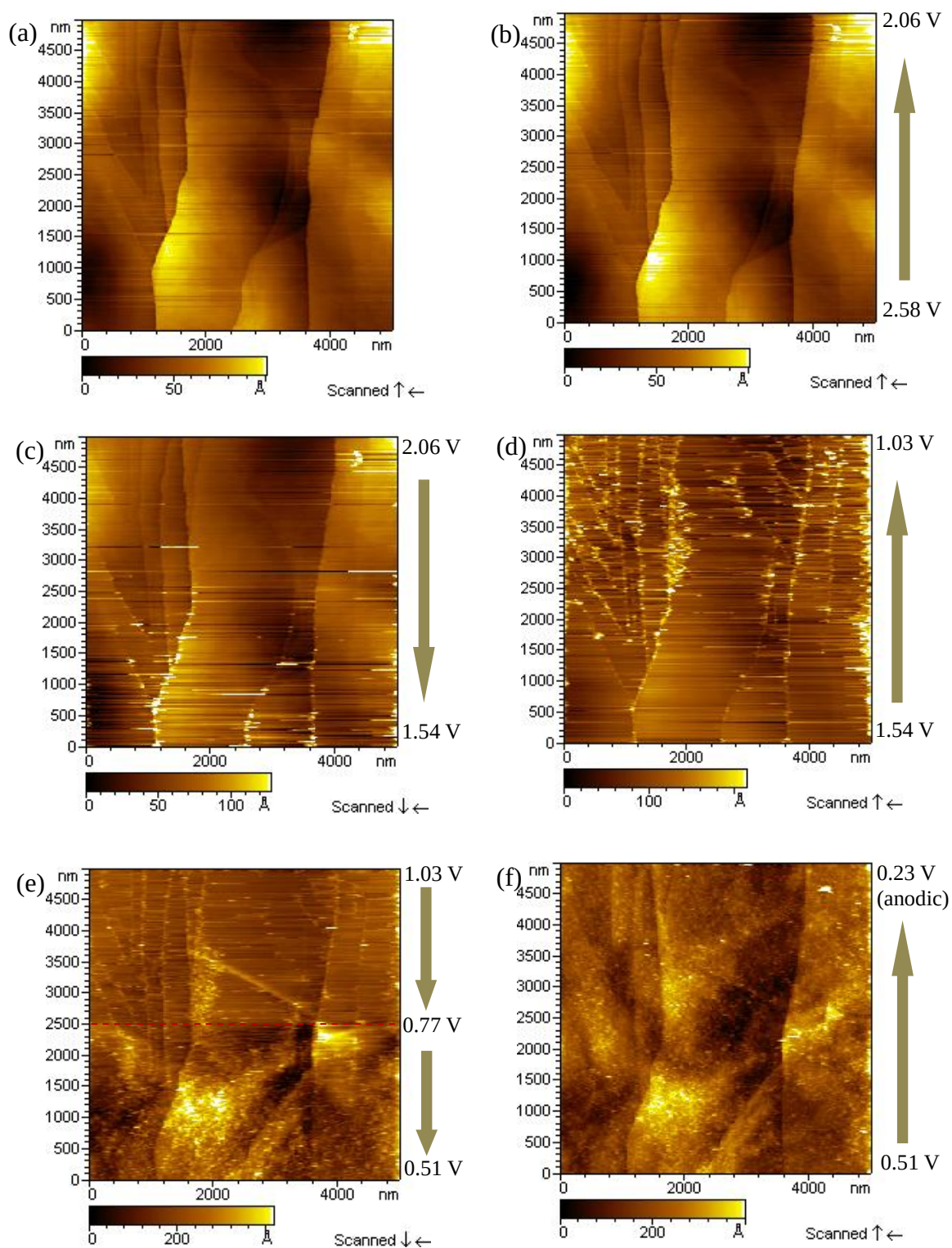


Fig. 2.4. *In-situ* SPM images of the HOPG basal plane (5 $\mu\text{m} \times 5 \mu\text{m}$) at (a) pristine, (b) 2.58–2.06 V, (c) 2.06–1.54 V, (d) 1.54–1.03 V, (e) 1.03–0.51 V, and (f) 0.51–^{anodic}0.23 V in 1 mol dm^{-3} LiFSA/PC+tetraglyme (20:1 by volume ratio).

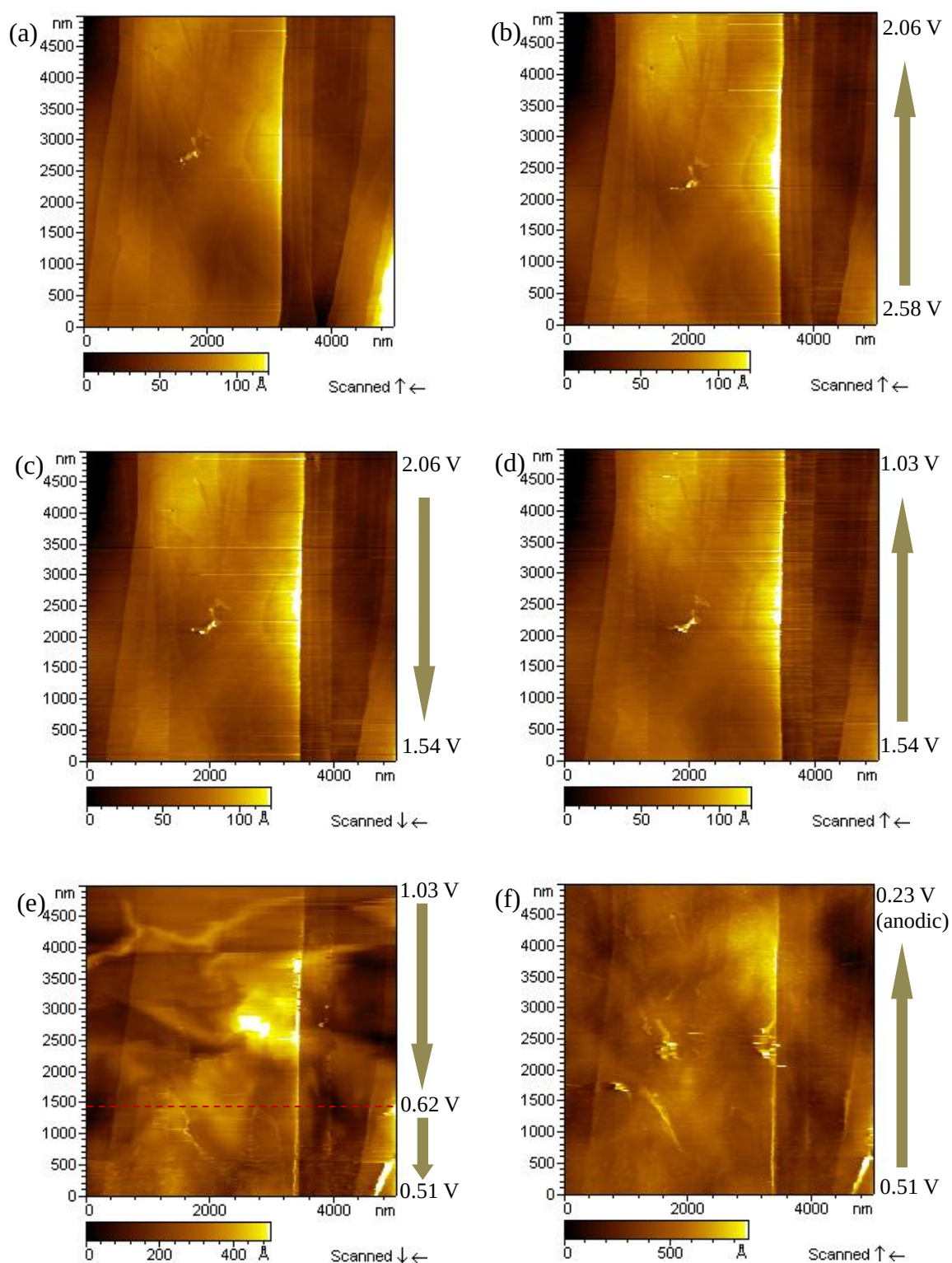


Fig. 2.5 *In-situ* SPM images of the HOPG basal plane ($5\ \mu\text{m} \times 5\ \mu\text{m}$) at (a) pristine, (b) 2.58–2.06 V, (c) 2.06–1.54 V, (d) 1.54–1.03 V, (e) 1.03–0.51 V, and (f) 0.51–^{anodic}0.23 V in $1\ \text{mol dm}^{-3}\ \text{LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$ (20:1 by volume ratio).

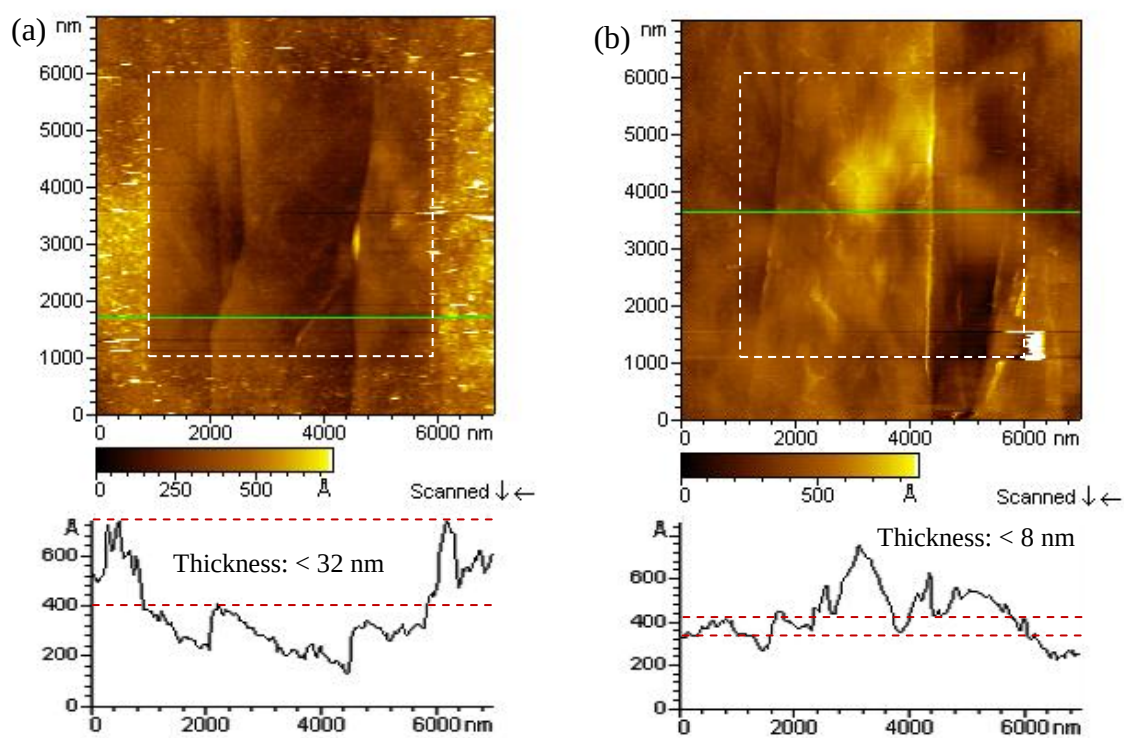


Fig. 2.6. SPM images of the HOPG basal plane ($7\ \mu\text{m} \times 7\ \mu\text{m}$) after the first cycle in $1\ \text{mol dm}^{-3}$ (a) LiFSA and (b) LiCF₃SO₃/PC+tetraglyme (20:1 by volume ratio).

Chapter 3

***In-situ* Raman Investigation of Electrolyte Solutions at the Vicinity of the Graphite Negative Electrodes**

3.1 Introduction

In lithium-ion batteries (LIB), graphite is a still desirable negative electrode material owing to the superior reversibility compared with other negative electrode materials such as disordered carbon, Si-based materials, and so on [1-3]. Intercalation and de-intercalation reactions of lithium ions take place at graphite negative electrodes during the charge and discharge processes [4-6]. Since reduction potentials of the organic electrolyte solutions are higher than that of the lithium-ion intercalation reaction, the reductive reaction of the organic electrolyte solutions should continue thermodynamically. However, at the 1st intercalation process, the reductive decomposition products formed from organic electrolyte solutions act as the solid electrolyte interphase (SEI) and the further reductive reaction of the organic electrolyte solutions can be suppressed [1, 7-10]. As a result, lithium ions can intercalate into graphite in organic electrolyte solutions kinetically. Ethylene carbonate (EC) has been used as an essential organic solvent in LIBs because the reductive decomposition products of EC-based electrolyte solutions act as the SEI. On the other hand, propylene carbonate (PC) that is similar structure with EC cannot be used since the reductive decomposition products of PC-based electrolyte solutions cannot act as SEI and lithium ions cannot intercalate into graphite. In both EC- and PC- based electrolyte solutions, the co-intercalation reaction of solvated-lithium ions into graphite occurs at first, and then, the intercalated solvated-lithium ions decompose within graphite layers. Interestingly, EC-solvated lithium ions can form SEI during the reductive decomposition reaction but PC-solvated lithium ions exfoliate graphite [11, 12]. However, various researches revealed that the tuning of solvation structure of PC-solvated lithium ions enabled lithium-ion intercalation to occur [13-17]. These

results have been understood based on the bulk structure of electrolyte solutions [13-19]. So far, the solvation structures of ions such as solvated ion, solvated separated ion pair (SSIP), contact ion pair (CIP), and aggregate (AGG) in bulk electrolyte solutions have been identified by Raman spectroscopy, NMR, and so on [13, 15, 19, 20-24]. Based on the above results, it suggests that the solvation structures in bulk electrolyte solutions must play important roles in the SEI formation process in PC-based electrolyte solutions. In chapter 2, the addition of small amount of tetraethylene glycol dimethyl ether (tetraglyme) to PC (1:20 by volume ratio) enabled lithium-ion intercalation to occur [25]. In this case, the amount of added tetraglyme was too small to change the solvation structures in the bulk electrolyte solution. Moreover, it was reported that only co-intercalation reaction proceeded in the triethylene glycol dimethyl ether (triglyme)-based electrolyte solution [26]. This result indicates that triglyme cannot act as the SEI forming additive that decomposes at the surface of graphite like vinylene carbonate [27]. Similarly, tetraglyme is thought not to be the SEI forming additive. Therefore, it should be thought that the added tetraglyme influenced with the electrolyte solution at the interface between the graphite and the electrolyte solution. Hence, the structure of electrolyte solution at the interface between the graphite and the electrolyte solution should be clarified. In addition, a large electric field is usually applied at the electrode and electrolyte interface; therefore, the information of PC-solvated lithium ion structure under applied potential must be considered.

However, it has been difficult to obtain the solvation structure of electrolyte solution at the electrode and electrolyte interface. Abe successfully detected concentration change of the lithium ion and the change of the structure of electrolyte solution as a function of distance from negatively polarized lithium metal electrode by ultrafine fiber Raman probe [28]. This finding supports our hypothesis that solvation structures at the interface should be different from that in the bulk electrolyte solution. However, this ultrafine fiber Raman probe is a professional technique and it is not easy to apply to graphite composite electrode. Therefore, we tried to detect the solvation structures at the interface by the conventional *in-situ* Raman spectroscopy.

In this chapter, *in-situ* Raman spectroscopy was performed to investigate the change of the structure of electrolyte solutions at the vicinity of the graphite composite electrode by using a practical three-electrode cell. The difference of the change of the

structure of electrolyte solutions among EC-based electrolyte solution, PC-based electrolyte solution, and PC-based electrolyte solution containing tetraglyme was investigated.

3.2 Experimental

The electrochemical cell for *in-situ* Raman spectroscopy was fabricated in order to decrease effect of the bulk electrolyte solution with attaching working electrode to Pyrex glass window directly as shown in Fig. 3.1. A composite electrode of natural graphite (SNO-15) coated on copper foil was used as a working electrode (SNO-15:PVdF = 9:1 by weight ratio). Lithium metal was used as a reference and a counter electrode respectively. Hereafter, all potentials are referred to Li^+/Li . As electrolyte solutions, 1 mol dm^{-3} $\text{LiClO}_4/\text{EC}+\text{diethyl carbonate (DEC)}$ (1:1 by volume ratio) and 1 mol dm^{-3} $\text{LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$ (20:1 by volume ratio) as SEI formation electrolyte solutions and 1 mol dm^{-3} $\text{LiCF}_3\text{SO}_3/\text{PC}$ as no SEI formation electrolyte solution were selected. The electrochemical cell was assembled in Ar-filled glove box. Argon ion laser with 514.5-nm line (CVI Melles Griot, 543-GS-A03) was scattered at the interface between graphite and electrolyte solution and a spectrum was obtained at each potential for 200 s during the 1st reduction process. Raman spectra were collected by a triple monochromator (Jobin-Yvon, T64000) equipped with a CCD detector. Potential profiles were obtained under constant current of 37.2 mA g^{-1} .

3.3 Results and discussion

3.3.1 Structure of electrolyte solution at the vicinity of graphite in $\text{LiClO}_4/\text{EC}+\text{DEC}$

Figure 3.2 shows a potential profile of the graphite composite electrode during the 1st reduction process in 1 mol dm^{-3} $\text{LiClO}_4/\text{EC}+\text{DEC}$. It has been generally accepted that SEI is formed during initial reduction process. Consequently, two potential plateaus were observed above 0.25 V leading to the SEI formation process. Based on the literatures, the co-intercalation and the decomposition reactions within graphite layers took place from 1.1 to 0.8 V and decomposition reaction on the graphite surface occurred at about 0.65 V after suppression of co-intercalation reaction [7, 8].

In-situ Raman spectra were shown in Fig. 3.3. The Raman band at 716 cm^{-1} is attributed to the C=O bending mode of EC and the shoulder at 730 cm^{-1} is related in the interaction of EC and lithium ion (Fig. 3.3(a)) [29, 30]. It was confirmed that the band at 716 cm^{-1} was shifted to 719 cm^{-1} below 1.25 V, but there was no change in the band at 730 cm^{-1} . So far, this phenomenon has not been reported. This result indicates that vibrational frequency shift of free EC occurs during co-intercalation reaction. In addition, the symmetry stretch band of ClO_4^- anion at 933 cm^{-1} was also shifted to higher wavenumber during co-intercalation reaction at 1.02 V, despite of no shift in the ring breathing band of EC at 897 cm^{-1} (Fig. 3.3(b)). Generally, anion interacts with cation and solvent molecules in organic electrolyte solutions and form SSIP, CIP, or AGG, which can be identified by Raman shift [20-23]. Based on the above solvation structures, these results indicate that anion interacts with free ECs at the vicinity of the graphite during the co-intercalation reaction and probably forms the SSIP since the Raman shift was smaller than that of the CIP and AGG (these are larger than 936 cm^{-1}). Interestingly, the C=O bending mode of EC and the symmetry stretch mode of ClO_4^- anion were shifted to downward below 0.14 V where the lithium-ion intercalation reaction occur as shown in Fig. 3.4. These back band shifts indicate that the formed SSIP was broken after the co-intercalation reaction. This SSIP formation during the co-intercalation reaction is a unique phenomenon. The detail relation between the reaction mechanism and the Raman shift is discussed in the next section with comparison in PC-based electrolyte solutions.

3.3.2 Structure of electrolyte solutions at the vicinity of graphite in $\text{LiCF}_3\text{SO}_3/\text{PC}$ and $\text{LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$

Potential profiles of SNO-15 in $1\text{ mol dm}^{-3}\text{ LiCF}_3\text{SO}_3/\text{PC}$ and $1\text{ mol dm}^{-3}\text{ PC}+\text{tetraglyme}$ were shown in Fig. 3.5. Although the potential profiles were almost same until 0.9 V, the potential never drop below 0.9 V in $\text{LiCF}_3\text{SO}_3/\text{PC}$. At this potential, PC-solvated lithium ions are intercalated within graphite layers and this reaction continue until the complete deterioration of graphite. In contrast, the electrode potential dropped below 0.25 V in $\text{LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$. In chapter 2, PC-based electrolyte solution containing tetraglyme, the co-intercalation of tetraglyme-solvated lithium ions occurred first and pre-SEI was formed. The co-intercalation reaction of PC-solvated

lithium ions was partially suppressed by this pre-SEI and finally SEI was formed at graphite, which leads to the reversible intercalation and de-intercalation reactions of lithium ions [25]. Figure 3.6 shows the *in-situ* Raman spectra of LiCF₃SO₃/PC at the vicinity of the graphite during the 1st reduction process. In contrast to the above result in EC-based electrolyte solution, any changes in the PC ring deformation and the CF₃ deformation bands were not observed during the co-intercalation reaction of PC-solvated lithium ions at about 0.9 V [31-34]. Based on this result, there was no unique interaction between free PCs and anion at the vicinity of the graphite. On the other hand, in LiCF₃SO₃/PC+tetraglyme, the vibrational frequency shifts to higher wavenumber in the PC ring deformation and the CF₃ deformation were observed below 1.41 V (Fig. 3.7(a)) and these peaks were shifted downward at lower potential (Figs. 3.7(b) and (c)). These behaviors are similar to those in EC-based electrolyte solution (Figs. 3.3 and 3.4). This result suggested that free PCs interacted with anion during the co-intercalation reaction and SSIP was formed at the vicinity of graphite and then the formed SSIP was broken.

Finally, the reason of the formation of SSIP and the relation between SSIP formation at the vicinity of the graphite and SEI formation process were summarized. In LiClO₄/EC+DEC, the co-intercalation reaction of solvated-lithium ions and the reductive decomposition reaction of solvent molecules at the vicinity of graphite would occur competitively. The decomposition product of solvent molecules would moderate the exfoliation of graphite layers by the reductive decomposition of solvated-lithium ions within graphite layers. As a result, the local lithium-salt concentration was increased due to the dissipation of solvent molecules and SSIP was formed at the vicinity of the graphite. In LiCF₃SO₃/PC, the co-intercalation reaction of the PC-solvated lithium ions might be fast and the reductive decomposition reaction of the PC-solvated lithium ions within graphite layers accompanied by the exfoliation of graphite might occur simultaneously. Therefore, SSIP was not formed and not observed in Raman spectra. In LiCF₃SO₃/PC+tetraglyme, the pre-SEI was formed by the reductive decomposition of the co-intercalated tetraglyme-solvated lithium ions and this pre-SEI brought the reduction in the co-intercalation rate of the PC-solvated lithium ions. Instead, the reductive decomposition reaction of solvent molecules at the vicinity of graphite would occur competitively. As a result, the local lithium-salt concentration

was increased and SSIP was formed at the vicinity of the graphite as show in the case of $\text{LiClO}_4/\text{EC}+\text{DEC}$. Based on the above consideration, the key of SEI formation at graphite would be the reduction in the co-intercalation reaction rate. Jeong et al. reported that lowering the reaction temperature such as $-15\text{ }^\circ\text{C}$ made lithium-ion intercalation in $1\text{ mol dm}^{-3}\text{ LiClO}_4/\text{PC}$ possible [35]. Our results would be related with the Jeong's result from the view of the reduction in the co-intercalation reaction rate. The detection of resulting SSIP formation at the vicinity of graphite by *in-situ* Raman spectroscopy would be useful information to design the electrolyte solution compatible with graphite negative electrode.

3.4 Conclusions

The structures of electrolyte solutions of $1\text{ mol dm}^{-3}\text{ LiClO}_4/\text{EC}+\text{DEC}$, $1\text{ mol dm}^{-3}\text{ LiCF}_3\text{SO}_3/\text{PC}$, and $1\text{ mol dm}^{-3}\text{ LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$ at the vicinity of graphite composite electrode were investigated by *in-situ* Raman spectroscopy. The change of electrolyte species at the vicinity of graphite during reduction process was interesting. In the case of $\text{LiCF}_3\text{SO}_3/\text{PC}$ in which lithium-ion intercalation reaction fail, there was no change in free PC and anion in Raman spectra. On the contrary, in the case of $\text{LiClO}_4/\text{EC}+\text{DEC}$ and $\text{LiCF}_3\text{SO}_3/\text{PC}+\text{tetraglyme}$ in which lithium-ion intercalation reaction proceed, free EC, free PC, and anion showed positive shift during only the co-intercalation reaction of EC- or PC-solvated lithium ions in spite of the different SEI formation processes. These shifts would suggest that solvated separated ion pair (SSIP) was formed at the vicinity of graphite due to the dissipation of solvent molecules. The dissipation of solvent molecules would be brought by the reductive decomposition of solvent molecules at the vicinity of graphite instead of rate reduced co-intercalation reaction. Based on this work, the reduction in the co-intercalation reaction rate should be the key of successful lithium-ion intercalation when SEI is formed by the co-intercalation reaction process.

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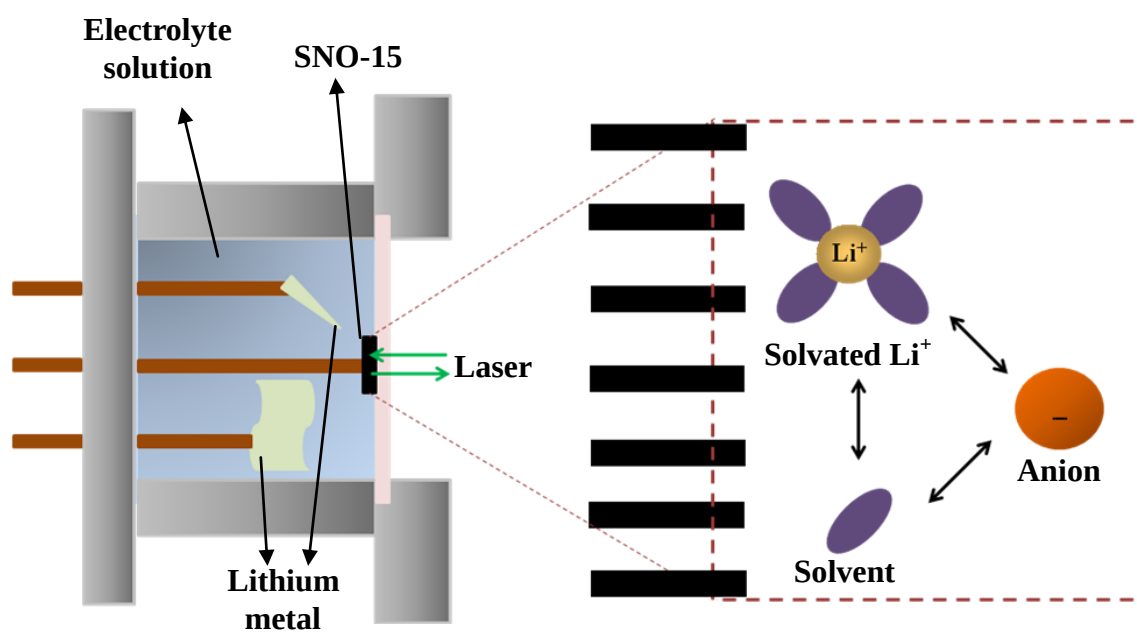


Fig. 3.1. An electrochemical three-electrode cell for *in-situ* Raman spectroscopy.

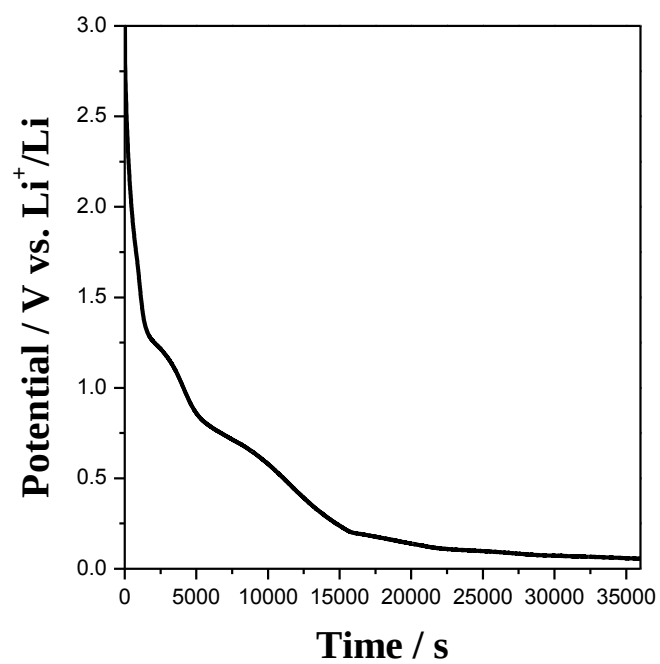


Fig. 3.2. Potential profile of SNO-15 in $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC}+\text{DEC}$ (1:1 by volume ratio) during the first reduction process. Current was 0.1C.

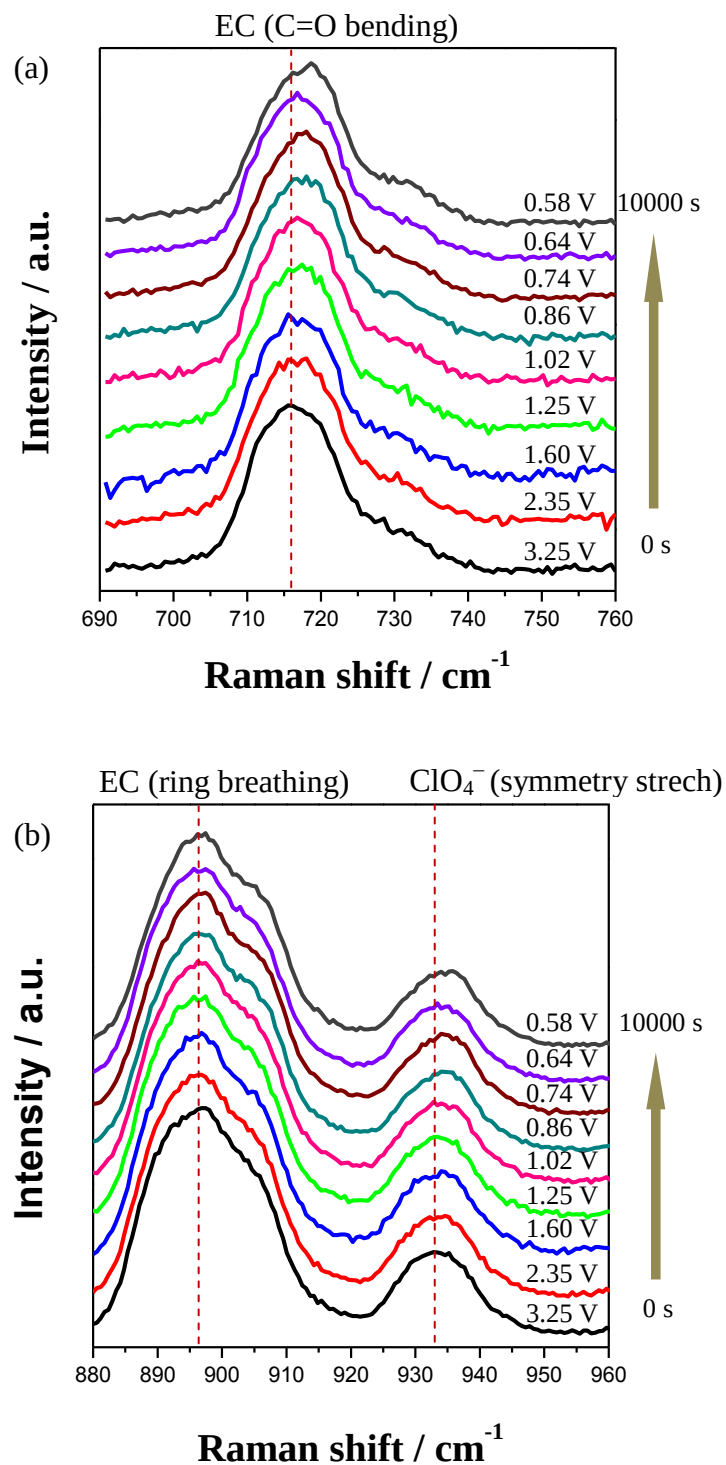


Fig. 3.3. *In-situ* Raman spectra of 1 mol dm⁻³ LiClO₄/EC+DEC (1:1 by volume ratio) from 3.25 to 0.58 V. (a) C=O bending mode of EC, and (b) ring breathing mode of EC and symmetry stretch mode of ClO₄⁻ anion.

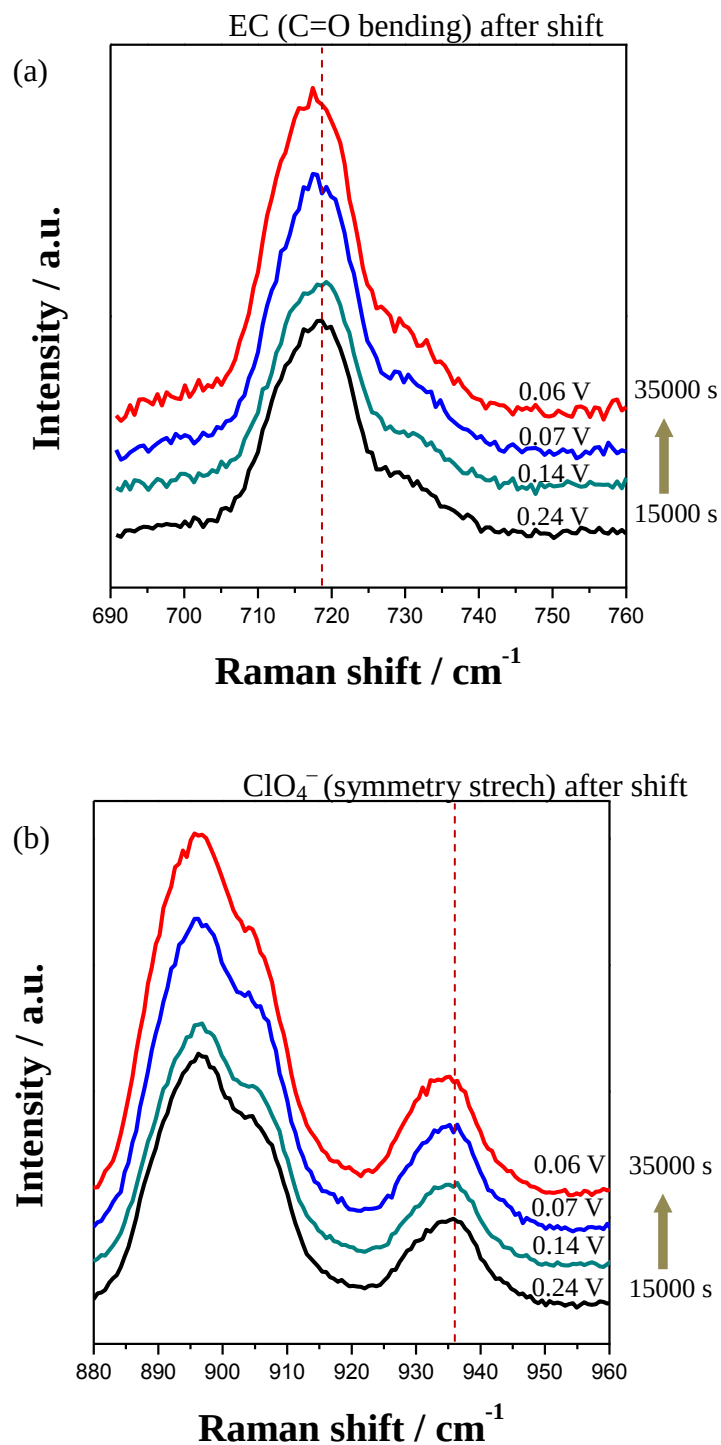


Fig. 3.4. *In-situ* Raman spectra of 1 mol dm^{-3} $\text{LiClO}_4/\text{EC}+\text{DEC}$ (1:1 by volume ratio) from 0.24 to 0.06 V. (a) C=O bending mode of EC, and (b) ring breathing mode of EC and symmetry stretch mode of ClO_4^- anion.

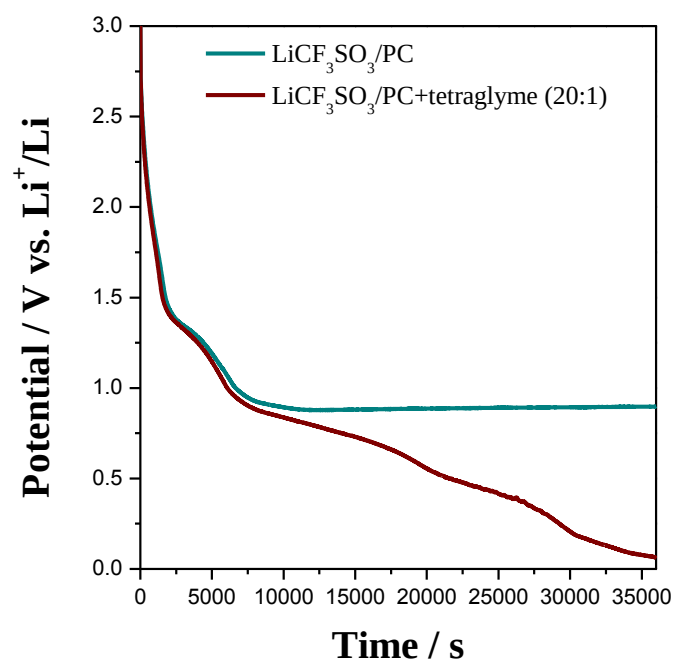


Fig. 3.5. Potential profiles of SNO-15 in 1 mol dm⁻³ LiCF₃SO₃/PC and PC+tetraglyme (20:1 by volume ratio) during the first charge process. C-rate: 0.1 C.

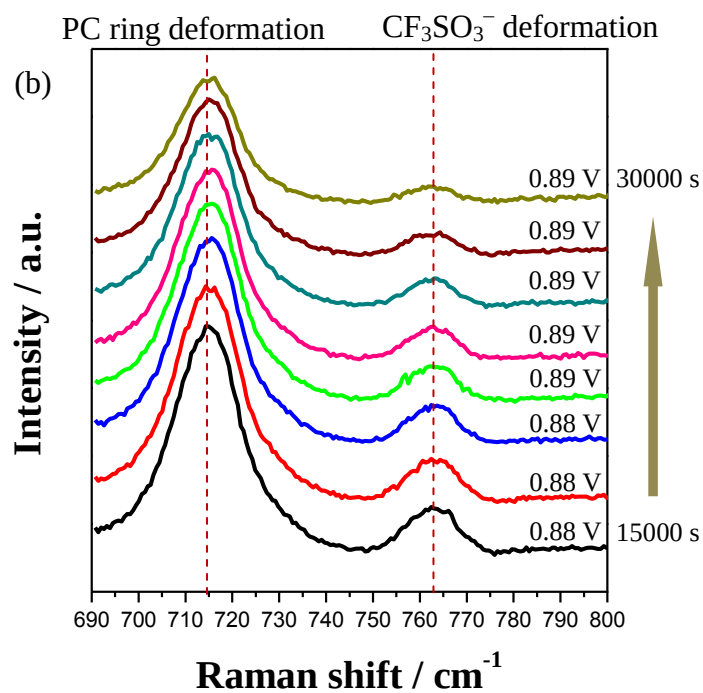
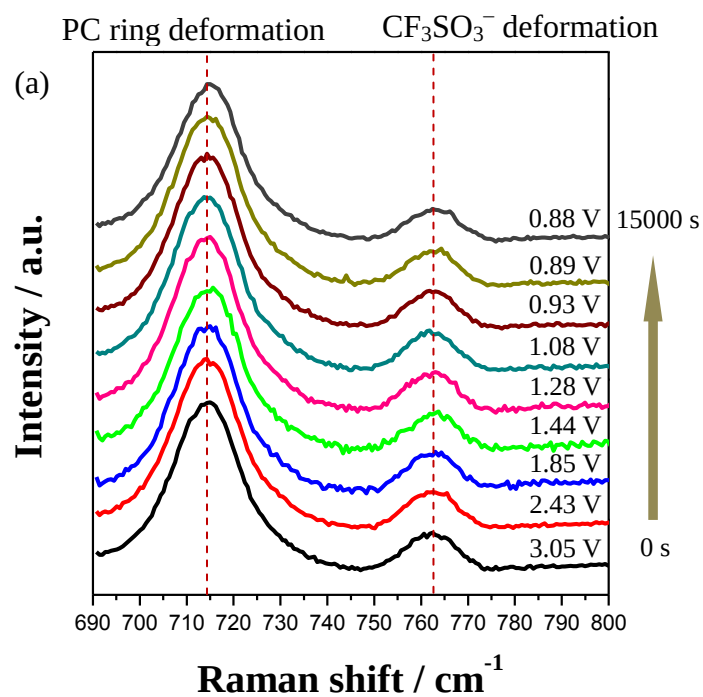
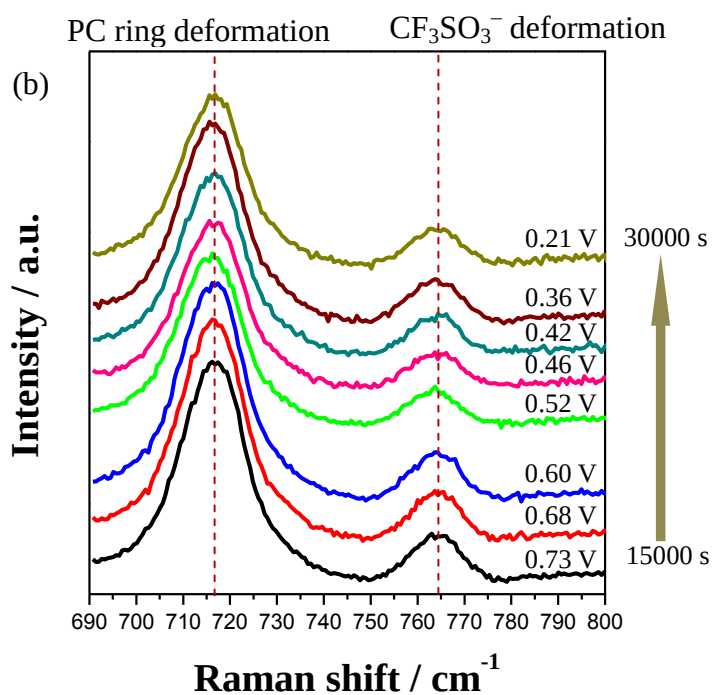
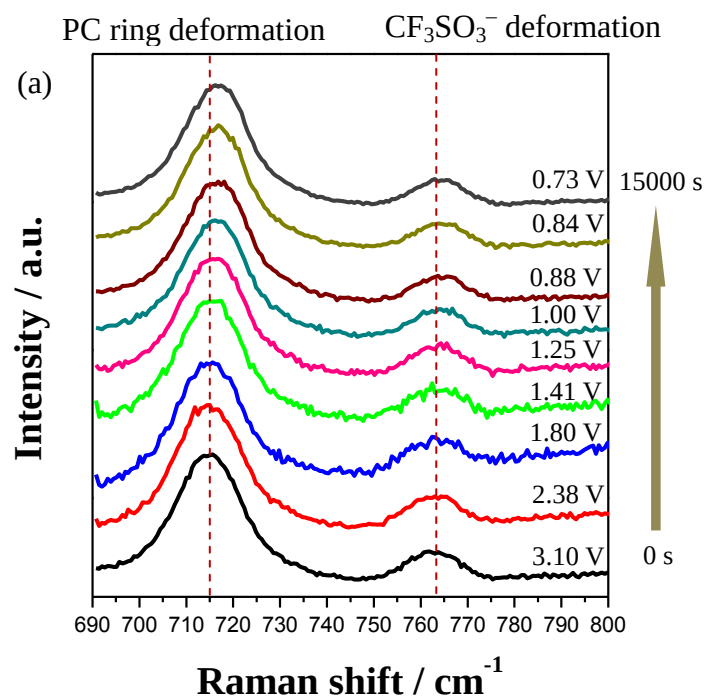


Fig. 3.6. *In-situ* Raman spectra for ring deformation mode of PC and CF_3 deformation mode of CF_3SO_3^- anion in $1 \text{ mol dm}^{-3} \text{LiCF}_3\text{SO}_3/\text{PC}$ at (a) 3.05-0.88 V and (b) 0.88-0.89 V.



be continued

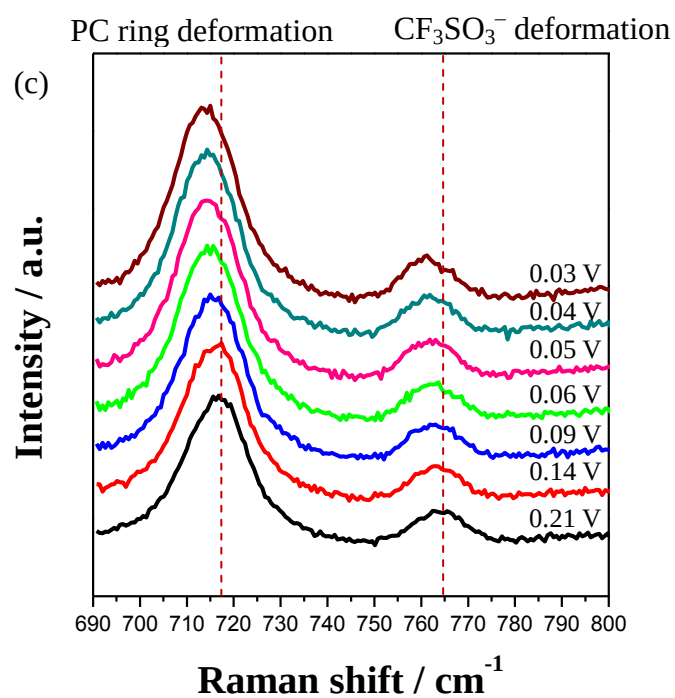


Fig. 3.7. *In-situ* Raman spectra for ring deformation mode of PC and CF_3 deformation mode of CF_3SO_3^- anion in $1 \text{ mol dm}^{-3} \text{LiCF}_3\text{SO}_3/\text{PC} + \text{tetraglyme}$ (20:1 by volume ratio) at (a) 3.10-0.73 V, (b) 0.73-0.21 V, and (c) 0.21-0.03 V.

Chapter 4

***In-situ* AFM Observation of Surface Morphology of Highly Oriented Pyrolytic Graphite in Propylene Carbonate-based Electrolyte Solutions Containing Lithium and Bivalent Cations**

4.1 Introduction

In spite of the huge expansion of the research for post lithium-ion batteries (LIBs) [1-5], the superiority of LIBs in the industrial use is unchallenged currently. Therefore, enhancement of the performance of LIBs must be achieved although the remained issues in LIBs are quite challenging [6-12]. One of the issues is a low-temperature performance which attributing in the non-selectivity of an electrolyte solvent. Ethylene carbonate (EC) is essential in conventional electrolyte solutions since EC is the only practical solvent in which the graphite negative electrodes can work [13, 14]. However, the melting point of EC (34 °C) is higher than ambient temperature. Therefore, the use of EC causes the deterioration of its ionic conductivity in cold area. From this point, EC-free electrolyte solutions with high melting point are expected. One way is to replace EC with other solvents such as propylene carbonate (PC) with a low melting point of -49 °C. However, the intercalation/de-intercalation of lithium ions at the graphite negative electrodes cannot proceed in the conventional PC-based electrolyte solutions without additives. This is because a stable solid electrolyte interphase (SEI) is not formed on the graphite negative electrodes and only the exfoliation of the graphite occurs in the conventional PC-based electrolyte solutions [15]. So far, various SEI forming additives have been investigated [16-22], but they are consumable materials in the LIBs and the use of the solvent that can form SEI from itself is desirable. In previous study, the lithium-ion intercalation/de-intercalation at the graphite negative electrodes occurred in the lithium salt-concentrated PC without SEI forming additives [23, 24]. Moreover, our group has reported that the lithium-ion intercalation in the conventional PC-based electrolyte solutions was facilitated by the

addition of the bivalent cation such as calcium ion and magnesium ion [25-29]. They attributed these behaviors to the solvated-lithium ion structure and suggested that when the PC-solvation number in the solvated-lithium ion was decreased lithium ions can intercalate. However, the influence of the bivalent cations with the SEI formation process has not been clarified. Apart from our group's studies, Yamada et al, reported that the SEI was formed by the "sacrificial anion reduction mechanism" in the highly concentrated lithium bis(trifluoromethanesulfonyl)amide (LiTFSA)/acetonitrile (AN) [30]. This report indicates that the SEI formation process in salt-concentrated electrolyte solution should be different from that in the conventional electrolyte solutions and motivated us to investigate the SEI formation process in the PC-based electrolyte solutions containing both lithium ion and bivalent cations.

One of the powerful tools to investigate the SEI formation process on the graphite negative electrodes is an *in-situ* atomic force microscopy (AFM) [16, 31-41]. By using *in-situ* AFM, the SEI formation process on the graphite negative electrodes can be clarified in detail. In this chapter, the SEI formation process on a highly oriented pyrolytic graphite (HOPG) as a model of the graphite negative electrode in the PC-based electrolyte solutions containing both lithium ion and bivalent cation (calcium ion or magnesium ion) was investigated by *in-situ* AFM.

4.2 Experimental

Electrolyte solutions were prepared from LiTFSA, Mg(TFSA)₂, Ca(TFSA)₂, and PC, all of which were purchased from Kishida Chemical Co., Ltd. In previous studies, the threshold of successful lithium-ion intercalation reaction was 0.9 (Mg²⁺/Li⁺) and 1.1 (Ca²⁺/Li⁺) [25, 29]. Therefore, the concentration of LiTFSA in PC was fixed at 1 mol dm⁻³ and the molar ratio of Mg(TFSA)₂ or Ca(TFSA)₂ to LiTFSA were set to be 1.2. In addition, 4 mol dm⁻³ LiTFSA/PC was also used. Residual water in the electrolyte solutions was removed using molecular sieves, resulting in water content below 100 ppm confirmed by means of a Karl-Fischer moisture titrator.

A three-electrode cell was used for cyclic voltammetry. A composite electrode of natural graphite powder (SNO-15, SEC carbon) and polyvinylidene difluoride (PVdF) at a weight ratio of 9:1 and an HOPG (ZYH grade) was used as a working electrode. Lithium foils were used as counter and reference electrodes. Hereafter, all

potentials are referred to Li^+/Li . Cyclic voltammetry was conducted at 0.1 mV s^{-1} between 3 V and 0 V.

In-situ AFM was conducted by using a specialized three-electrode cell, as in our group's previous papers [16, 31-35]. A working electrode was an HOPG and counter and reference electrodes were lithium foils. The observation mode was a contact mode in an Ar-filled glove box (MIWA MDB-1B+MS-P60SN, dew point $< -76^\circ\text{C}$). Hereafter, electrode potential refers to Li^+/Li . The electrode potential was swept between the open circuit potential (ca. 3 V) and 0.1 V at 2 mV s^{-1} to observe the surface morphology change of the basal plane of the HOPGs.

4.3 Results and discussion

Figure 4.1 shows the cyclic voltammograms of the graphite composite electrodes in (a) $\text{LiTFSA}+\text{Ca}(\text{TFSA})_2/\text{PC}$, (b) $\text{LiTFSA}+\text{Mg}(\text{TFSA})_2/\text{PC}$, and (c) LiTFSA/PC . As shown in Figs. 4.1(a) and (b), clear redox peaks were observed near 0 V. Since the calcium-ion and magnesium-ion intercalations into the graphite have not been known so far and the magnesium and calcium metal deposition reactions did not occur in these electrolyte solutions, these redox peaks must be due to the lithium-ion intercalation/de-intercalation reaction. In Fig. 4.1(c), the similar redox peaks were observed. In all figures, the irreversible reduction peaks were observed at 0.7 V at only the 1st cycle, leading to the formation of SEI. In addition, almost the same electrochemical behaviors were observed in cyclic voltammograms of HOPGs (Figs. 4.1(d)–(f)). In the case of HOPGs, the de-intercalation potential in LiTFSA/PC was lower than that in $\text{LiTFSA}+\text{Ca}(\text{TFSA})_2/\text{PC}$ and $\text{LiTFSA}+\text{Mg}(\text{TFSA})_2/\text{PC}$. In addition, the redox peak current of LiTFSA/PC was larger than others. The viscosities of LiTFSA/PC , $\text{LiTFSA}+\text{Ca}(\text{TFSA})_2/\text{PC}$, and $\text{LiTFSA}+\text{Mg}(\text{TFSA})_2/\text{PC}$ are 115 mPa s, 87 mPa s, and 131 mPa s, respectively. It can be thought that viscosities would not influence the electrochemical response since there is no any tendency in viscosities. The large difference among these electrolytes is the concentration of lithium ion. Since lithium-ion transfer resistance is inversely proportional to lithium-ion concentration empirically, the smaller polarization of the de-intercalation reaction and the large redox peak current would be due to the higher lithium-ion concentration in LiTFSA/PC . Similar behavior was also observed in AN- or ether-based superconcentrated electrolyte

solutions [42, 43]. Based on these results, it is confirmed that the electrochemical intercalation and de-intercalation of lithium ions at the graphite composite electrodes and the HOPGs occurs in all electrolyte solutions used in this study. Therefore, it was thought that the HOPG can be served as a model electrode for *in-situ* AFM.

In order to investigate the difference of SEI formation process, *in-situ* AFM was carried out. Figure 4.2 shows the cyclic voltammograms at the 1st and 2nd cycles and *in-situ* AFM images ($5 \times 5 \mu\text{m}^2$) of the HOPG in LiTFSA+Ca(TFSA)₂/PC during potential sweep at the 1st cycle. In each AFM image (Figs. 4.2(b)–(h)), the scan direction (upper arrow or lower arrow) and potential range are described. In the cyclic voltammogram at the 1st cycle, the clear reduction peak was observed at about 0.7 V corresponding to the reduction of electrolyte solution. At the 2nd cycle, this reduction peak disappeared and this phenomenon indicated that the SEI was formed at the 1st cycle. In the AFM images from 3.072 to ca 0.87 V, only step of the HOPG was observed and there is no clear morphology change of the HOPG. However, as shown by arrow in Fig. 4.2(f), the hill-like structure was observed at the vicinity of the step. And decreasing of the electrode potential, the large hill-like structures was observed as shown by dotted arrow, and then, the blisters as shown in dotted circle appeared. This surface morphological change indicated that the co-intercalation of the solvated-lithium ions occurred and they were decomposed within the graphene layers. At 0.1 V, relatively smooth surface was observed as shown in Fig. 4.2(g) and this showed that the stable SEI was formed. During the anodic sweep from 0.1 V, some large precipitates were observed as shown in Figs. 4.2(g) and (h). These would be the further reductive decomposition products of the electrolyte solution at the region with the incomplete SEI. Based on the *in-situ* AFM observation, it clarified that the SEI formation process in LiTFSA+Ca(TFSA)₂/PC was the co-intercalation type as reported in LiClO₄/EC+diethyl carbonate (DEC) [14, 31]. Figure 4.3 shows the cyclic voltammograms at the 1st and 2nd cycles and *in-situ* AFM images ($5 \times 5 \mu\text{m}^2$) of the HOPG in LiTFSA+Mg(TFSA)₂/PC during the potential sweep at the 1st cycle. In the cyclic voltammogram at the 1st cycle, the clear reduction peak was observed at about 0.6 V corresponding to the reduction of the electrolyte solution. At the 2nd cycle, this reduction peak disappeared and this phenomenon indicated that the SEI was formed at the 1st cycle. Similar to LiTFSA+Ca(TFSA)₂/PC, there is no morphological change

from 3.072 to ca 0.89 V (as shown by the dotted horizontal line). However, at 0.89 V, the drastic morphological change was observed, that is, small precipitates covered the HOPG. And after the potential sweeping, there is no clear change. In the case of LiTFSA+Mg(TFSA)₂/PC, the SEI formation process was not the co-intercalation type but the surface decomposition type. The surface decomposition type was observed in LiClO₄/PC containing vinylene carbonate (VC) as the film forming additive and the formed SEI was reported to be thinner than that in LiClO₄/EC+DEC [16]. And it is revealed that the surface film formed on the glassy carbon (GC) in LiClO₄/PC was thinner than that in LiClO₄/EC+DEC [35]. In the case of GC, the surface film formation process proceeds by the surface decomposition type because the co-intercalation reaction does not occur at the GC. Therefore, the thickness of the SEI formed in LiTFSA+Mg(TFSA)₂/PC is presumed to be thin. However, unfortunately, the viscosities of electrolyte solutions in this study are too large and we could not estimate the thickness of the SEI by using the surface scratching method. Finally, same analysis was carried out against LiTFSA/PC. The results are shown in Fig. 4.4. In the case of LiTFSA/PC, the hill-like structures and the blisters were observed at the low electrode potential. These results are similar to those in LiTFSA+Ca(TFSA)₂/PC. Therefore, the SEI formation process in LiTFSA/PC would be the co-intercalation type.

Based on the above SEI formation processes, we interpret the difference of the charge–discharge properties between LiTFSA+Ca(TFSA)₂/PC and LiTFSA+Mg(TFSA)₂/PC. In the previous literature, the irreversible capacity and the reversible capacity at the 1st cycle in LiTFSA+Ca(TFSA)₂/PC ($\text{Ca}^{2+}/\text{Li}^{+}=1.1$) was reported to be ca 100 mA h g⁻¹ and ca 200 mA h g⁻¹, respectively [25]. In the case of LiTFSA+Mg(TFSA)₂/PC ($\text{Mg}^{2+}/\text{Li}^{+}=0.9$), the irreversible capacity and the reversible capacity at the 1st cycle was ca 350 mA h g⁻¹ and ca 300 mA h g⁻¹, respectively [29]. This difference would be related with the SEI formation process. In the both cases, the irreversible capacities were relatively large. This means that the formed SEI could not adequately suppress the reduction reaction of electrolyte solutions. In LiTFSA+Ca(TFSA)₂/PC, the SEI was formed by the co-intercalation type. Considering the small reversible capacity, the formed SEI would not suppress the further co-intercalation reaction and the graphite would be partially exfoliated. As a result, the reversible capacity underran the theoretical capacity (372 mA h g⁻¹). The formed SEI is

supposed to be porous; therefore, the further co-intercalation reaction would not be suppressed adequately. In fact, the reductive decomposition reaction of EC and PC was reported to be accompanied by the gas evolution [44] and would give the porous SEI. For LiTFSA+Mg(TFSA)₂/PC, the SEI was formed by the surface decomposition type. In this case, the reductive decomposition of the electrolyte solution occurred at the surface of the graphite and the exfoliation of the graphite would be suppressed. Therefore, the reversible capacity would be similar value to the theoretical capacity. However, the formed SEI would be dense and thin; therefore, though the further co-intercalation reaction would be suppressed the further reductive decomposition reaction would not be suppressed perfectly. These different SEI properties derived from the different formation process would be the key to determine the charge–discharge properties.

4.4 Conclusions

Lithium-ion intercalation/de-intercalation reactions at the graphite composite electrodes and the HOPGs successfully proceeded in 1 mol dm⁻³ LiTFSA+1.2 mol dm⁻³ Ca(TFSA)₂/PC, 1 mol dm⁻³ LiTFSA+1.2 mol dm⁻³ Mg(TFSA)₂/PC, and 4 mol dm⁻³ LiTFSA/PC. The SEI formation processes on the HOPGs at 1st cycle in all electrolyte solutions were investigated by *in-situ* AFM. The SEI formation process in 1 mol dm⁻³ LiTFSA+1.2 mol dm⁻³ Ca(TFSA)₂/PC and 4 mol dm⁻³ LiTFSA/PC was the co-intercalation type. And the SEI formation process in 1 mol dm⁻³ LiTFSA+1.2 mol dm⁻³ Mg(TFSA)₂/PC was the surface decomposition type. Considering these SEI formation processes and the charge–discharge properties, the SEI in 1 mol dm⁻³ LiTFSA+1.2 mol dm⁻³ Ca(TFSA)₂/PC would be porous, and the SEI in 1 mol dm⁻³ LiTFSA+1.2 mol dm⁻³ Mg (TFSA)₂/PC would be dense and thin. It is revealed that the SEI formation process was changed by the addition of bivalent cations. The different SEI properties would be strongly related with the charge–discharge properties.

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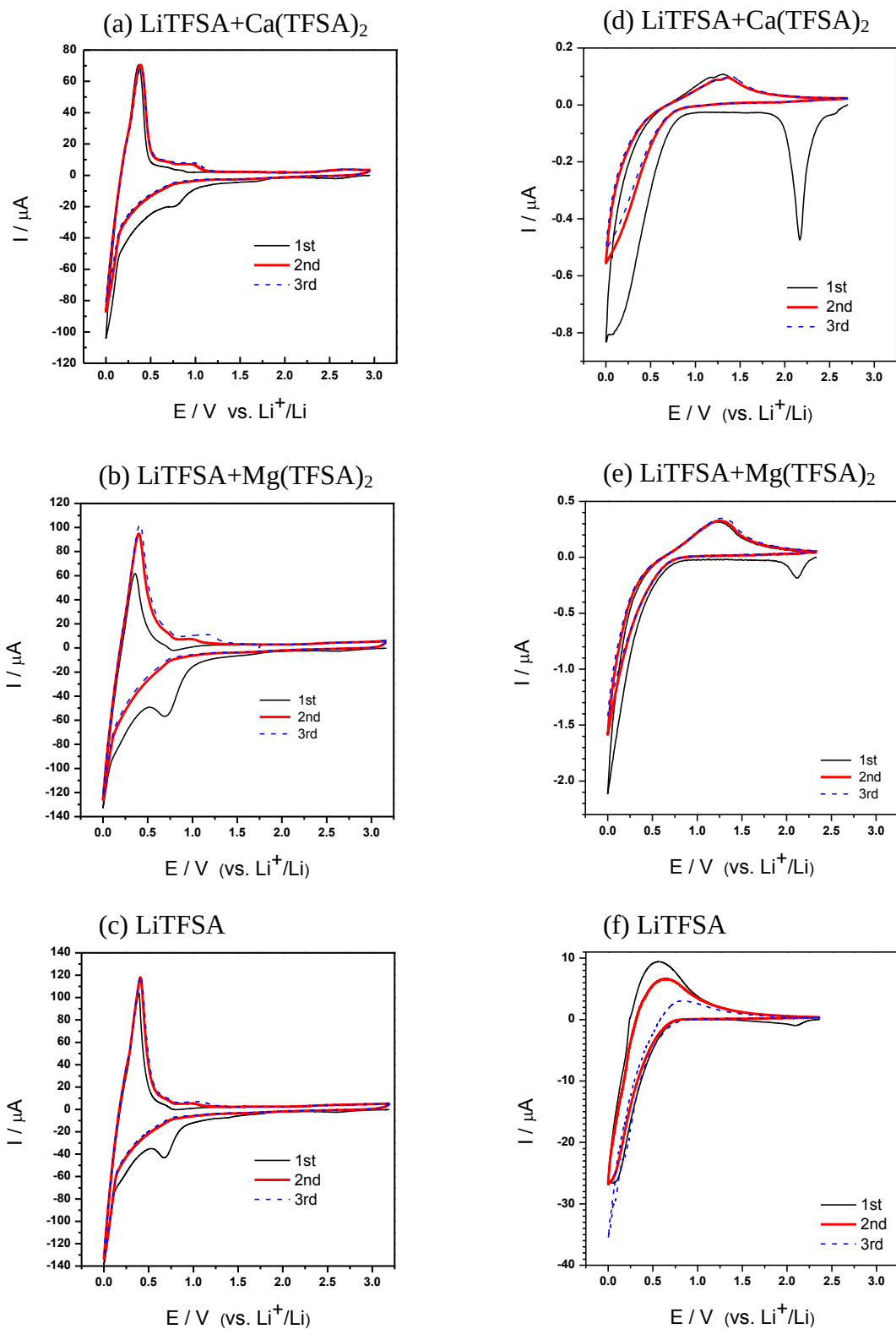


Fig. 4.1. Cyclic voltammograms of graphite composite electrodes or HOPGs in various electrolyte solutions (a) and (d) 1 mol dm^{-3} LiTFSA+ 1.2 mol dm^{-3} Ca(TFSA)₂/PC, (b) and (e) 1 mol dm^{-3} LiTFSA+ 1.2 mol dm^{-3} Mg(TFSA)₂/PC, and (c) and (f) 4 mol dm^{-3} LiTFSA/PC. The sweep rate was 0.1 mV s^{-1} .

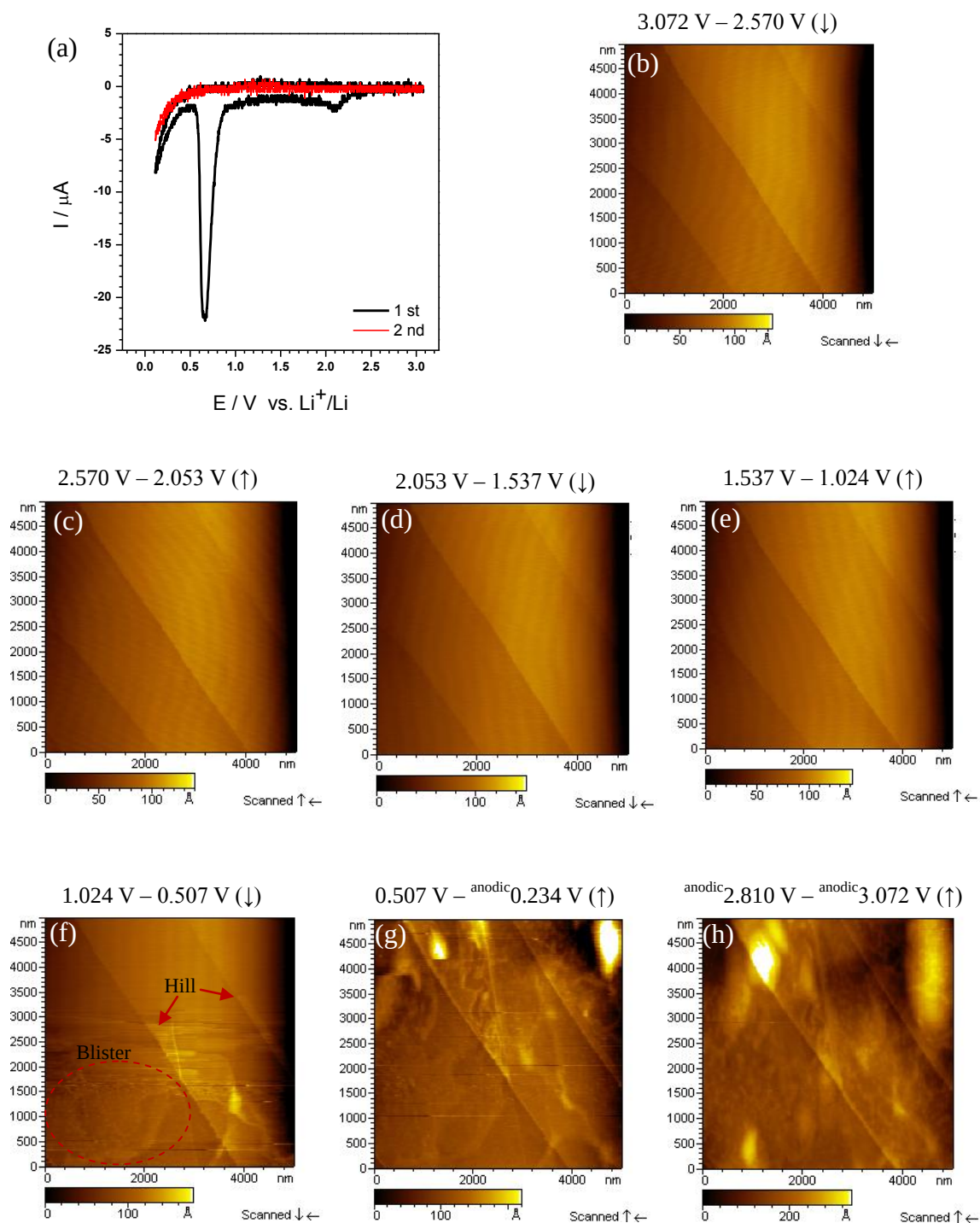


Fig. 4.2. (a) Cyclic voltammograms and *in-situ* AFM images of HOPG basal plane (5 $\mu\text{m} \times 5 \mu\text{m}$) at (b) 3.072–2.570 V, (c) 2.570–2.053 V, (d) 2.053–1.537 V, (e) 1.537–1.024 V, (f) 1.024–0.507 V, (g) 0.507–^{anodic}0.234 V, and (h) ^{anodic}2.810–^{anodic}3.072 V in 1 mol dm^{-3} LiTFSa+1.2 mol dm^{-3} Ca(TFSa)₂/PC during the 1st cycle. Scan rate: 2 mV s^{-1} .

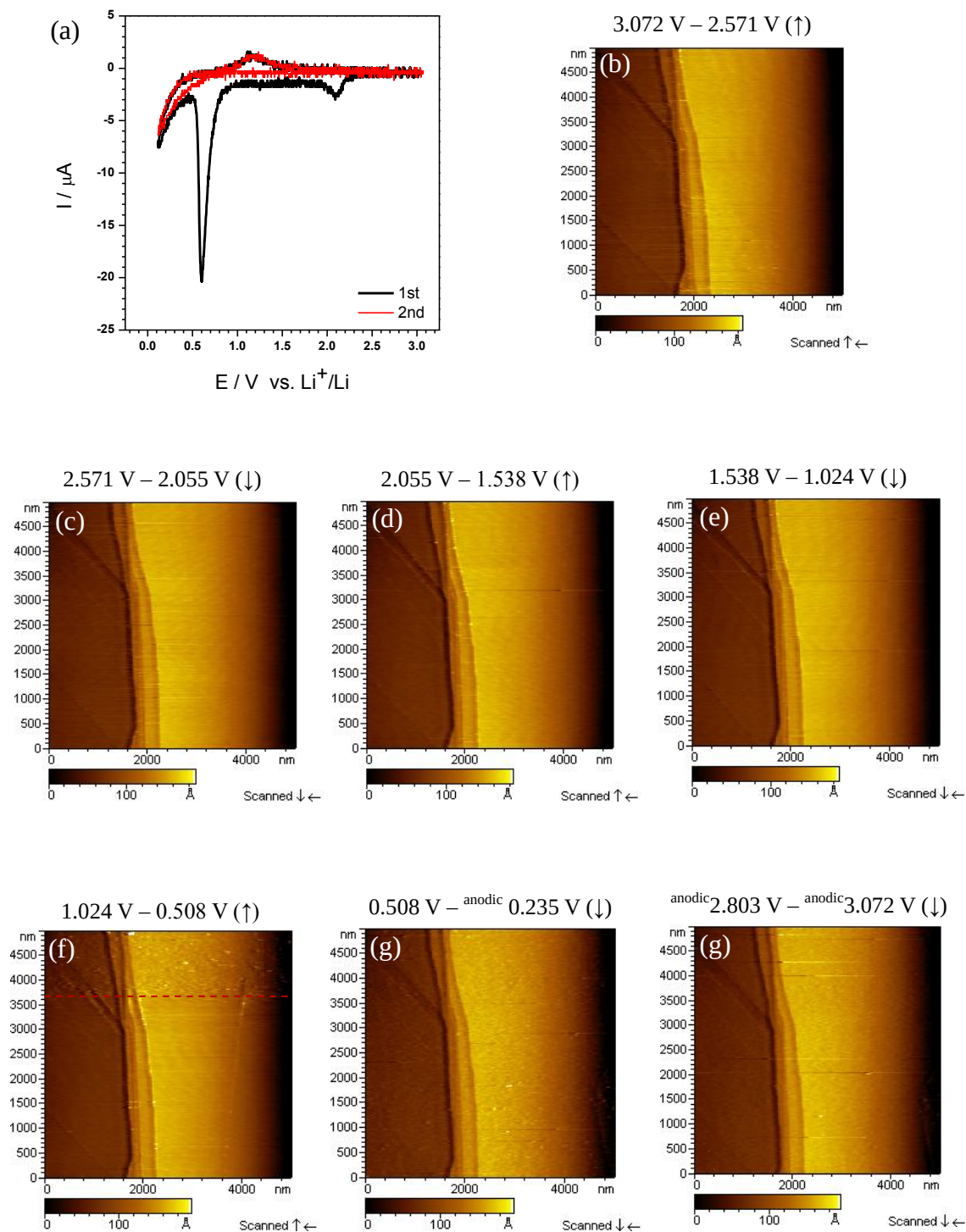


Fig. 4.3. Cyclic voltammograms (a) and *in-situ* AFM images of HOPG basal plane ($5 \mu\text{m} \times 5 \mu\text{m}$) at (b) 3.072–2.570 V, (c) 2.570–2.053 V, (d) 2.053–1.537 V, (e) 1.537–1.024 V, (f) 1.024–0.507 V, (g) 0.507–^{anodic}0.234 V, and (h) ^{anodic}2.810–^{anodic}3.072 V in $1 \text{ mol dm}^{-3} \text{LiTfSA} + 1.2 \text{ mol dm}^{-3} \text{Mg(TfSA)}_2/\text{PC}$ during the 1st cycle. Scan rate: 2 mV s^{-1} .

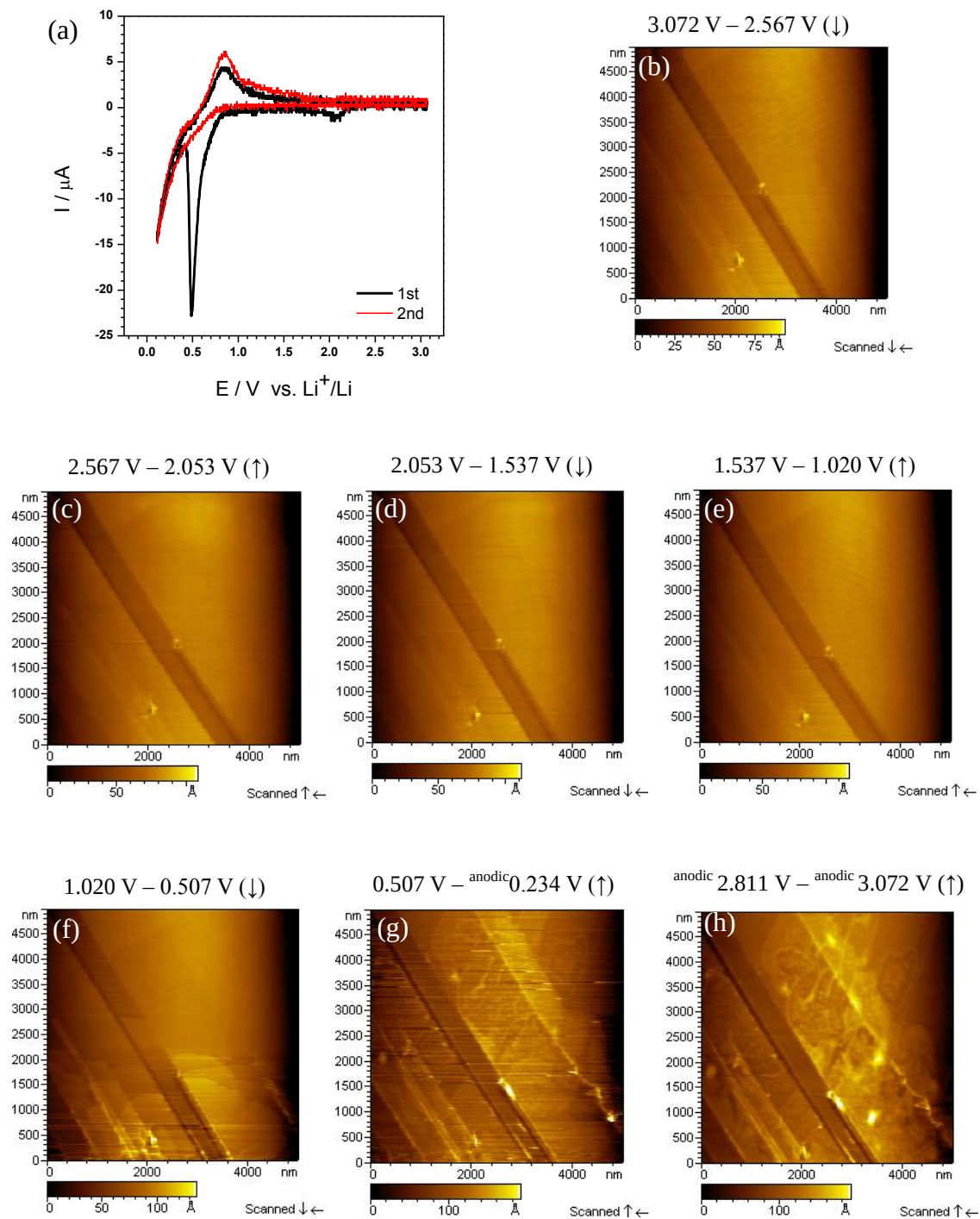


Fig. 4.4. Cyclic voltammograms (a) and *in-situ* AFM images of HOPG basal plane ($5 \mu\text{m} \times 5 \mu\text{m}$) at (b) 3.072–2.570 V, (c) 2.570–2.053 V, (d) 2.053–1.537 V, (e) 1.537–1.024 V, (f) 1.024–0.507 V, (g) 0.507–^{anodic}0.234 V, and (h) ^{anodic}2.810–^{anodic}3.072 V in 4 mol dm^{-3} LiTFS/PC during the 1st cycle. Scan rate: 2 mV s^{-1} .

Chapter 5

Investigation of the Surface Film Forming Process on Nongraphitizable Carbon Electrodes by *In-situ* Atomic Force Microscopy

5.1 Introduction

Nongraphitizable carbon is preferred as a negative electrode in lithium-ion batteries (LIB) for use in electric vehicles (EVs). Compared with the graphitic carbon used in practical LIBs, nongraphitizable carbon shows a large capacity, high-rate performance, and smooth potential profile [1-8]. Among these characteristics, a smooth potential profile is important because monitoring of the battery voltage is compulsory for controlling the state of charge. Although nongraphitizable carbon has already been used in some EVs, it has not been investigated as fundamentally as graphitic carbon. The drawback of nongraphitizable carbon is the formation of surface film. The reaction potential of nongraphitizable carbon is as low as that of graphitic carbon; therefore, a reductive decomposition reaction of an electrolyte solution must occur and a passivation surface film such as the solid electrolyte interphase (SEI) on the graphitic carbon should be formed. However, the surface film formation process on nongraphitizable carbon is not fully understood. Therefore, the composition of the surface film on sucrose-derived nongraphitizable carbon after a charge–discharge cycle was investigated by ex-situ X-ray photoelectron spectroscopy, and the surface film was reported to be thicker than that of a graphitizable carbon [9]. Recently, the surface film formation process on resorcinol formaldehyde-derived nongraphitizable carbon was investigated by *in-situ* small-angle neutron scattering [10]. From the results, the thickness of the surface film was estimated to be 1 nm and a chemical change in the surface film during the lithium-ion insertion process was also suggested [10]. Based on the literature to date, including these two papers, there is no unified explanation about the surface film on nongraphitizable carbon. Our group has been investigating the formation process of SEI

on graphitic carbon (highly oriented pyrolytic graphite; HOPG) by *in-situ* atomic force microscopy (AFM) [11-18]. Using this technique, the formation process and the thickness of the surface film on nongraphitizable carbon can be clarified.

In this chapter, a mirror-polished glassy carbon plate was used as a binder-free model electrode of the nongraphitizable carbon and the surface film formation process on the glassy carbon plate was observed by *in-situ* AFM.

5.2 Experimental

GC20 (Tokai Carbon) heat-treated at 500 °C in air for 1h was used as the mirror-polished glassy carbon plate. In the previous study [19], the lithium-ion transfer process between GC20 and the liquid electrolyte interface was strongly influenced by the heat treatment at 500 °C. The pores of pristine GC20 were closed and the lithium-ion insertion process did not proceed properly, and the heat-treatment process was conducted to obtain the correct electrochemical properties of GC20.

In-situ AFM was conducted using a specialized three-electrode cell, as in our group's previous papers [11-14]. A working electrode was GC20 with or without heat treatment at 500 °C and the counter and reference electrodes were lithium foils. In order to investigate the differences caused by the solvent, the electrolyte solutions were either a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume ratio) or propylene carbonate (PC), both containing 1 mol dm⁻³ lithium perchlorate (LiClO₄) purchased from TOMIYAMA PURE CHEMICAL INDUSTRIES, LTD. and the water content of 20 ppm was guaranteed. The observation mode was a contact mode in an Ar-filled glove box (MIWA MDB-1B+MS-P60SN, dew point < -76 °C). Hereafter, electrode potential refers to Li⁺/Li. The electrode potential was swept from the open circuit potential (ca. 3 V) to 0.1 V at 2 mV s⁻¹ to observe the surface morphology of GC20.

5.3 Results and discussion

As observed via Raman spectroscopy, the X-ray diffraction measurement, and Fourier transform infrared (FT-IR) spectroscopy, there is no obvious change between GC20 with and without heat treatment. Therefore, GC20 with heat treatment can be used as a model electrode for nongraphitizable carbon.

Figure 5.1 shows the cyclic voltammogram during the 1st cycle and *in-situ* AFM images ($5 \times 5 \mu\text{m}^2$) of GC20 in $\text{LiClO}_4/\text{EC}+\text{DEC}$ (1:1) during potential sweep. In each AFM image (Figs. 5.1(b)–(g)), the scan direction (upper arrow or lower arrow) and potential range are described. The dark lines in the AFM images are polishing flaws. Because the position of the dark lines did not change during cyclic voltammetry, it is guaranteed that the same region was observed during the experiment. In the cyclic voltammogram (Fig. 5.1(a)), a clear redox peak below 1 V was observed and this peak is assigned to the lithium-ion insertion/extraction process. Compared with the cyclic voltammogram of HOPG, a clear reduction peak due to electrolyte decomposition was not observed. This behavior is in agreement with previous literature [19, 20]. This result indicates that the reductive decomposition of the electrolyte solution and the surface film formation on nongraphitizable carbon are lesser than those with the graphitic carbon. The formation potential of the surface film was not clear from the electrochemical result; therefore, the formation process of the surface film was investigated by *in-situ* AFM. In the AFM images (Figs. 5.1(b)–(f)), there was no morphological change until the potential reached 0.75 V (dot-line). Below 0.75 V (Fig. 5.1(f)), the number of small deposits (white objects in dot-line circled region) was clearly increased. These deposits would be decomposition products of the electrolyte solution. With the increase in the reduction current in the cyclic voltammogram, the number of deposits increased, and these deposits did not disappear during the anodic scan, as shown in Fig. 5.1(g). Therefore, the deposits were stable and could act as the surface film. Additionally, the formation of the hill or blister due to the co-intercalation reaction reported for HOPG [11–13] was not observed in this study. Therefore, it can be considered that the co-intercalation reaction did not proceed in the case of GC20 as opposed to HOPG. Based on the AFM images (Figs. 5.1(f) and (g)), the surface film formation on GC20 with heat treatment starts from 0.75 V and continues to 0.1 V. Although the surface film formation potential of 0.75 V was lower than the reduction potential of alkyl carbonates proposed by *in-situ* FT-IR (1.5 to 1.0 V) [21], the difference between the reduction potential of alkyl carbonates and formation potential of the surface film is not contradictory because the reductive decomposition products formed at higher potential might be unstable. Our result is in agreement with the result of the *in-situ* small-angle neutron scattering [10].

Figure 5.2 shows the cyclic voltammogram during the 1st cycle and *in-situ* AFM images ($5 \times 5 \mu\text{m}^2$) of GC20 in LiClO_4/PC . Lithium-ion insertion/extraction can occur in PC-based electrolyte solutions in the case of nongraphitizable carbon. Therefore, the surface film formation process in PC-based electrolyte solution would be interesting. There is no clear difference between the cyclic voltammograms obtained in EC-based electrolyte solution and those obtained in PC-based electrolyte solution. This indicates that unlike the behavior of HOPG, the electrochemical behavior of GC20 in PC-based electrolyte solution might be the same as that in EC-based electrolyte solution. However, in the AFM images, although a small clear deposit was observed starting from 0.75 V, the height of deposits at lower potentials (Fig. 5.2(g)) was lower than that in Fig. 5.1(g). This result indicates that the decomposition products of PC-based electrolyte solution formed a thinner surface film than EC-based electrolyte solution. To confirm this hypothesis, the thickness of the surface film was estimated. The procedure of this experiment was reported elsewhere [11-13]. Figure 5.3 shows extended areas ($7 \mu\text{m} \times 7 \mu\text{m}$) of the typical AFM images observed in each solution. In each image, the $5 \mu\text{m} \times 5 \mu\text{m}$ area is seen as a rectangular hole where the deposits were scraped off during repeated scanning. The deposited layer remained outside. From the height profile in Fig. 5.3(a), the thickness of the surface film formed in an EC-based electrolyte solution during the 1st cycle was roughly estimated to be below 14 nm. From Fig. 5.3(b), the thickness of the surface film in PC-based electrolyte solution cannot be estimated, and this result would indicate that the thickness of the surface film formed in PC-based electrolyte solution was considerably thinner than that of the surface film formed in EC-based electrolyte solution. This difference is interesting; however, the reason is not clarified at the present stage. In addition, the thickness of the surface film formed in EC-based electrolyte solution was smaller than that observed for HOPG (40 nm) obtained by the same method [11]. The co-intercalation reaction was not observed by *in-situ* AFM at GC; therefore, it is considered that the morphology of surface film was related with the co-intercalation reaction and surface film formation process without the co-intercalation reaction would give thinner surface film.

5.4 Conclusions

Surface film formation processes on GCs were investigated using *in-situ* AFM.

During the surface film formation process, the co-intercalation reaction of solvated-lithium ion did not occur. The surface film on GC in PC-based electrolyte solution was found to be especially thin compared with surface film on GC in EC-based electrolyte solution. In addition the thickness of the surface film formed on GC was thinner than that of HOPG. This is probably because the surface film formation process on GC is not accompanied by the co-intercalation reaction of solvated-lithium ion.

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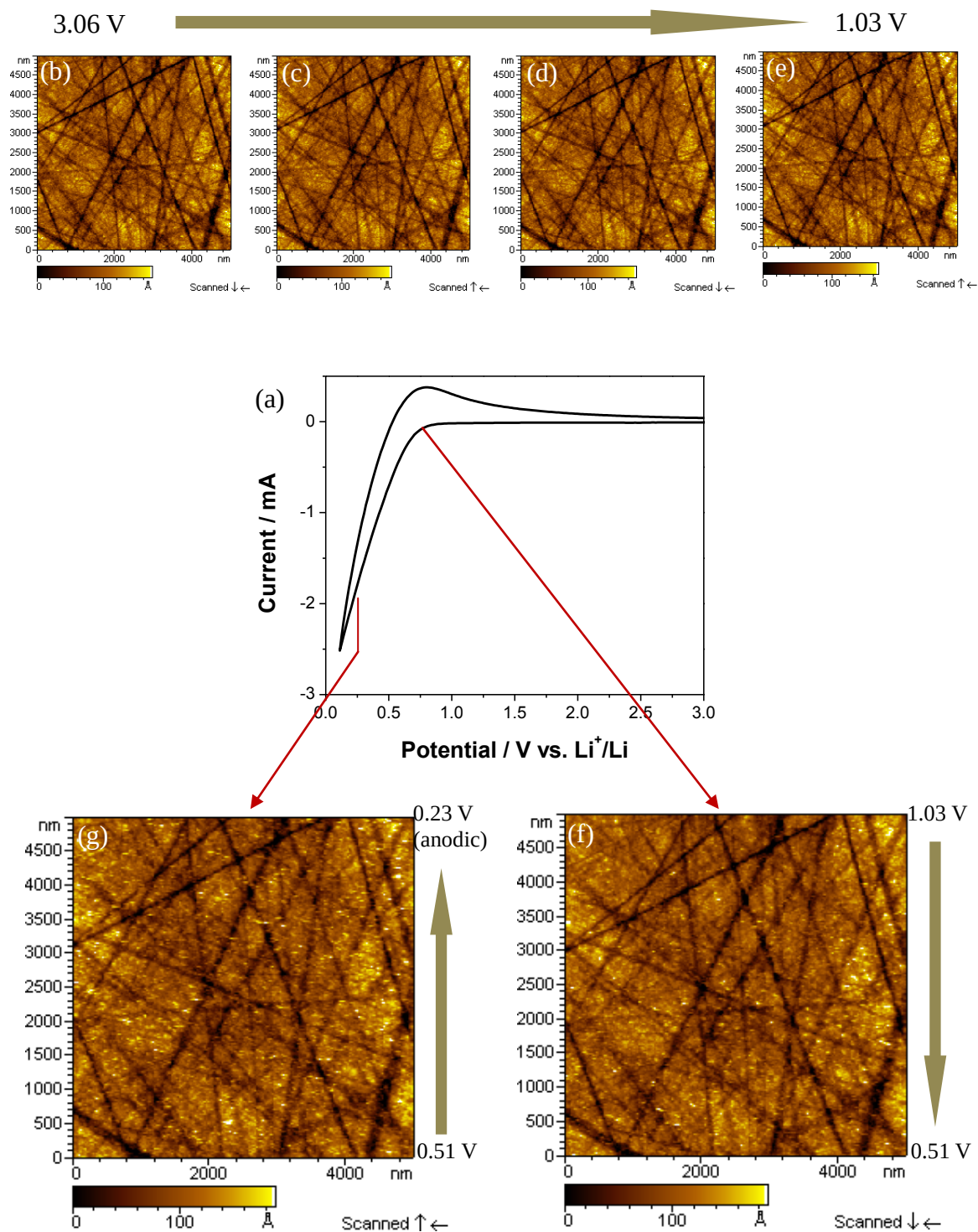


Fig. 5.1. *In-situ* AFM images and cyclic voltammogram of GC20 in 1 mol dm⁻³ LiClO₄/EC+DEC (1:1 by volume ratio). Scan rate: 2 mV s⁻¹.

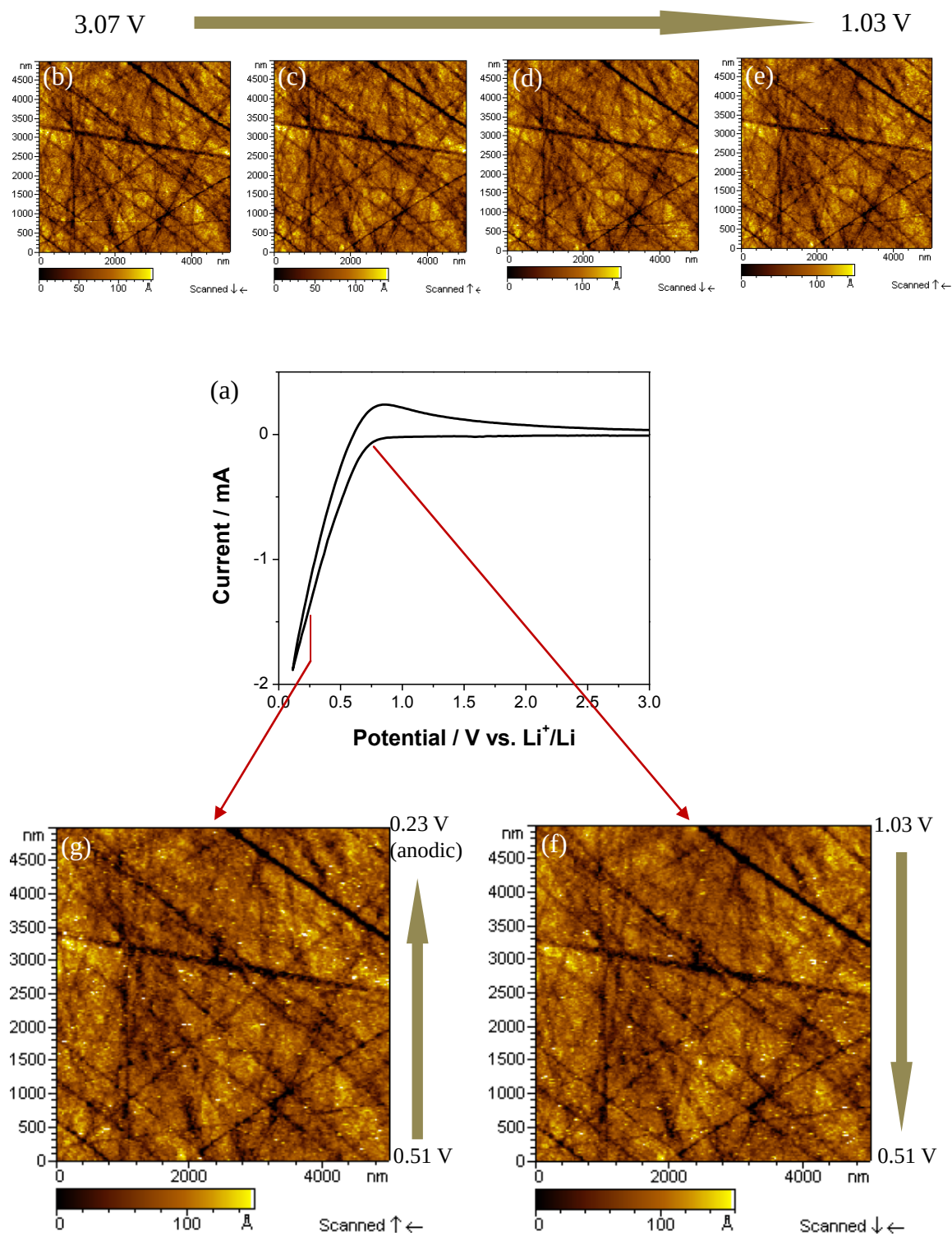


Fig. 5.2. *In-situ* AFM images and cyclic voltammogram of GC20 in 1 mol dm⁻³ LiClO₄/PC. Scan rate: 2 mV s⁻¹.

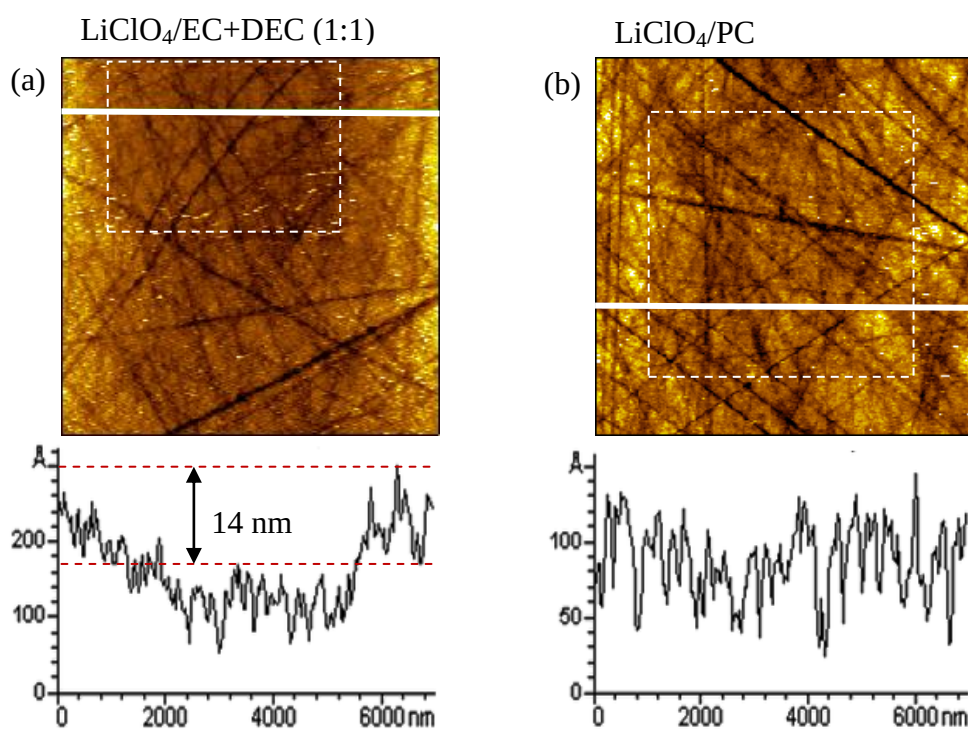


Fig. 5.3. Large area AFM images of GC20 after cyclic voltammetry for 1 cycle in (a) $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC}+\text{DEC} (1:1 \text{ by volume ratio})$ and (b) $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$.

Publication List

Chapter 1

Suppression of Co-intercalation Reaction of Propylene Carbonate and Lithium Ion into Graphite Negative Electrode by Addition of Diglyme

H.-Y. Song, T. Fukutsuka, K. Miyazaki, and T. Abe

Journal of the Electrochemical Society, **163**, A1265-A1269 (2016).

Chapter 2

Solid Electrolyte Interphase Formation in Propylene Carbonate-based Electrolyte Solutions for Lithium-ion Batteries Based on the Lewis Basicity of the Co-solvent and Counter Anion

H.-Y. Song, T. Fukutsuka, K. Miyazaki, and Takeshi Abe

Journal of Applied Electrochemistry, in press (2016).

Chapter 3

***In-situ* Raman Investigation of Electrolyte Solutions at the Vicinity of the Graphite Negative Electrodes**

H.-Y. Song, T. Fukutsuka, K. Miyazaki, and Takeshi Abe

Submitted to *Physical Chemistry Chemical Physics*.

Chapter 4

***In-situ* AFM Observation of Surface Morphology of Highly Oriented Pyrolytic Graphite in Propylene Carbonate-based Electrolyte Solutions Containing Lithium and Bivalent Cations**

T. Fukutsuka, R. Kokumai, H.-Y. Song, S. Takeuchi, K. Miyazaki, and T. Abe

Submitted to *Journal of the Electrochemical Society*.

Chapter 5

Investigation of the Surface Film Forming Process on Nongraphitizable Carbon Electrodes by *In-situ* Atomic Force Microscopy

H.-Y. Song, T. Fukutsuka, K. Miyazaki, and T. Abe

Electrochemistry, in press (2016).

The following paper is not included in this thesis

A Simple Method of Electrochemical Lithium Intercalation within Graphite from A Propylene Carbonate-based Solution

S.-K. Jeong, H.-Y. Song, S. Kim, T. Abe, W. Jeon, R.-Z. Yin, and Y. Kim

Electrochemistry Communications, **31**, 24-27 (2013).