The *in situ* Analysis of Interfacial Reactions between Electrode and Organic Electrolytes III. The Reduction of Electrolytes at Graphite Electrode

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Received December 18, 1997 ; Accepted August 19, 1998

We applied the *in situ* FTIR and AFM measurements for the analysis of interfacial phenomena at graphite electrode in organic electrolytes. The electrolyte solutions used were EC+DEC and EC+EMC each containing 1 mol/dm³ LiPF₆. The different reduction mechanism of solvents was observed in EC+DEC and in EC+EMC. It was confirmed the morphological changes of graphite particles were occurred at 1.0V vs. Li/Li⁺ in the first cathodic polarization by the AFM observation. A larger expansion of graphite particles was observed in EC+DEC than in EC+EMC, and this expansion of graphite would be related to the decomposition of ternary solvated lithium graphite-intercalation compounds.

1 INTRODUCTION

Many groups are studying and investigating about the cathode materials for rechargeable lithium-ion batteries such as LiCoO₂, LiNiO₂ and LiMn₂O₄, and the anode materials such as graphites, cokes and amorphous carbons. But a few groups studies about organic electrolytes of rechargeable lithium-ion batteries¹⁻¹⁰. The interfacial reaction between electrode and electrolyte is the one of the most important factors which influence the battery performances of this battery system. Difficulties of the analysis of the interfacial reactions of lithium ion batteries are that the amount of these products is very small and these products generally form very thin layer and react with H₂O, CO₂ and O₂, which are atmospheric components. Since these reaction products are very instable, it is necessary to conduct *in situ* analysis and experiments in the study of lithium-ion batteries.

Fourier Transform Infrared(FTIR) spectroscopy is one of the useful methods for *in situ* analysis of the interfacial reactions on the electrodes in organic electrolytes. Aurbach *et. al.*, investigated the surface reactions of lithium and graphite electrodes in many organic electrolytes by *in situ* FTIR¹⁻⁸.

Atomic Force Microscopy(AFM) is also regarded as the useful method for *in situ* analysis. We have demonstrated. Technology Laboratory, Matsushita Battery Industrial Co.,LTD., (1, Matsushita-cho, Moriguchi, Osaka 570-8511, Japan)

Key Words: FTIR, AFM, organic electrolyte, graphite electrode

AFM observation is a useful method for *in situ* analysis of lithium surface and for the study of deposition in organic electrolytes¹¹⁻¹³. Yamaguchi *et. al.*, studied the morphological changes of graphite electrodes during discharging by electrochemical AFM^{14,15}, and Ogumi *et. al.*, investigated the surface morphology of graphite electrodes with the polarization by electrochemical STM^{16,17}.

Aurbach reported that ethylmethyl carbonate(EMC) was the promising solvent for rechargeable lithium-ion batteries⁸, because graphite electrodes had long cycle performances with high reversible capacity in the electrolyte using EMC. On the other hand, diethyl carbonate(DEC) was not the suitable solvent⁵⁻⁷. Lithium and graphite electrodes can not be passivated in DEC solutions, because the solvent reduction products are soluble in this solvent. And the performance of lithium or graphite electrode show low cycling efficiency in the solution containing DEC, such as ethylene carbonate(EC)+DEC solution.

In this study we investigate the surface chemistry of in LiPF₆/EC electrolytes, using DEC or EMC as the co-solvent, and compare the effect of co-solvent on the interfacial reactions at graphite electrode. We examined the *in situ* FTIR spectroscopy for the analysis of interfacial reactions and the *in situ* AFM observation for the analysis of the surface morphology of graphite electrodes during lithium intercalation-deintercalation.

2 EXPERIMENTAL

EC, DEC, and EMC(Mitsubishi Chemical) and LiPF_6 (Stella Chemifa) were used as received. The electrolytes used were EC+DEC(1:1 by volume) and EC+EMC(1:1 by volume) each containing 1 mol/dm^3 LiPF_6 , and below 50ppm of water. We examined the two methods of in situ FTIR spectroscopy for the analysis of interfacial reactions at graphite electrodes using a Mattson RS-2 spectrometer¹³. One is Infrared Reflection Absorption Spectroscopy(IRAS) and another is Double Modulation FTIR (DMFTIR) spectroscopy¹⁸. The IRAS spectroscopy using p-polarized IR beam was performed to investigate the reactions of electrolytes at graphite electrodes. The DMFTIR spectroscopy using p-polarized and s-polarized IR beams modulated by photoelastic modulator(PEM-90, Hinds) was performed to investigate the interfacial reactions at graphite electrodes. The DMFTIR spectra data were sampled by the realtime sampling electronics (Mattson) the difference between p-polarized data and s-polarized data as a sample spectrum, and the sum of p- and s-polarized data as a reference spectrum. The center frequency of DMFTIR was set at 1200cm^{-1} in present study. 100 scans were conducted in each measurement, and the resolution was 2cm^{-1} . The test cell for in situ FTIR spectroscopy was performed as same as reported before¹³. The in situ AFM measurement was performed using TMX-1000(Topometrix) as same as reported in our previous papers^{11,12}. A composite graphite working electrode was prepared by a coating of graphite paste on a Cu rode(ϕ 8mm), and it was dried at 110°C under vacuum, and polished with soft clothes. The graphite paste was consisted of Meso Carbon Micro Beads(MCMB, from Osaka gas, mean grain size; $4\mu\text{m}$), styrene-butadiene rubber as binder, carboxymethyl cellulose and water. Lithium was used as a counter electrode and a reference electrode in test cells.

The polarizations with in situ measurements were performed by a potentio/galvanostat system HA-301/HB-104(Hokuto denko). The measurements of FTIR and AFM were performed after the current of the working electrode was decreased under $20\mu\text{A}$. All experiments were performed at room temperature.

3 RESULTS and DISCUSSION

Figure 1 compares DMFTIR spectra of the mixed solvent(EC+DEC, 1a) and electrolyte(1 mol/dm^3 LiPF_6 /EC+DEC, 1b) on graphite electrodes at OCV state, and the difference in these spectra shows as a subtractive spectrum (1c). The major peaks due to the stretching vibration of carbonyl groups($\nu_{\text{C=O}}$) were observed at 1800cm^{-1} (EC), 1772cm^{-1} (EC) and 1736cm^{-1} (DEC) in both spectra (1a and 1b).

The DMFTIR and IRAS spectra of some solvents were measured at the same condition, and the assignments of each peaks of solvents are shown in Table 1. As shown in 1c, increasing new peaks by dissolution of LiPF_6 were observed at 1759 , 1680cm^{-1} ($\nu_{\text{C=O}}$), 1405 , 1298 , 1194 , 1086 , 1045cm^{-1} ($\nu_{\text{C-O}}$) and 841cm^{-1} . We confirmed the changes of spectra related to the solvation of lithium ion were observed increasing peaks around 1190 and around

Fig. 1 Comparison of DMFTIR spectra of solvent and electrolyte at graphite electrodes at OCV. a; solvent (EC+DEC), b; electrolyte(1mol/dm^3 LiPF_6 /EC+DEC), c; subtractive spectrum.

Fig. 2 Comparison of DMFTIR spectra of solvent and electrolyte at graphite electrodes at OCV. a; solvent (EC+EMC), b; electrolyte(1mol/dm^3 LiPF_6 /EC+EMC), c; subtractive spectrum.

Table 1 Assignment of peaks in DMFTIR and IRAS spectra of solvents

	EC DM (IRAS)	DEC DM (IRAS)	EMC DM (IRAS)	DMC DM (IRAS)	DME DM (IRAS)
ν C=O	1800 (1792) 1772 (1765)	1741 (1724)	1746 (1726)	1752 (1728)	— (—)
δ CH, CH ₃	1480 (1480) 1388 (1386)	1467 (1467) 1373 (1370)	1441 (1438) 1368 (1367)	1452 (1446) 1432 (1430)	1452 (1452) 1365 (1365)
ν C-O-C	1230	1251	1258	1271	1245
ν C-O	1158 (1127) 1070 (1040)	1142 (1183) 1090 (1086)	1140 (1164) 1113 (1112) 1088 (1087)	1135 (1178) 1093 (1137)	1190 (1190) 1107 (1110) 1058 (1083)
ν C-C	1029 990 (950) 970 (910)	1017 (960) (897)	1008 970 (983) 932 (920)	— (—) 968 (940)	1023 (1024) 980 (980) 934 (935)
δ CO ₃	(872)	853 (841) (820)	876 (868)	888 (897)	— (—)

DMC: Dimethyl carbonate, DME: Dimethoxy ethane.

800 cm^{-1} and decreasing peaks around 1120 and from 1000 to 860 cm^{-1} in EC+DEC system. Therefore the peak at 1194 cm^{-1} was ascribed to the change due to the solvation, and the peaks at 1680, 1405, 1298 and 1086 cm^{-1} were consistent with those in previous FTIR studies^{3,4)} of lithium alkylcarbonates(ROCO₂Li), which have the peaks at 1680-1640($\nu_{\text{C-O}}$), 1450-1400(δ_{CH} , CH₃), 1350-1300($\nu_{\text{C-O}}$), 1100($\nu_{\text{C-O}}$), 830-820 cm^{-1} (δ_{OCO_2}). Aurbach reported that the FTIR spectra in LiPF₆ solution have pronounced 1030 and 850 cm^{-1} peaks which are assigned to $\nu_{\text{P-O}}$ and $\nu_{\text{P-F}}$, respectively⁵⁻⁷⁾. And XPS studies revealed that the salt reduction products are LiF and Li_xPF_y or Li_xPF_yO_z^{7,19,20)}. Therefore, we think that the peak at 841 cm^{-1} is probably superimposed with the δ_{OCO_2} peak of ROCO₂Li and the $\nu_{\text{P-F}}$ peak of decomposition product of LiPF₆. We think the other peaks at 1759 and 1045 cm^{-1} will be ascribed to another ROCO₂Li, which is also the decomposition product of EC or DEC.

A comparison of DMFTIR spectra of EC+EMC(a) and LiPF₆/EC+EMC(b), as the same in Fig.1, is shown in Fig.2. The peaks at 1800 and 1772 cm^{-1} were assigned to EC, the peak at 1743 cm^{-1} was assigned to EMC, and the peak at 1698 cm^{-1} would be assigned to alkylcarbonate, respectively. As shown in 2c, increasing peaks by dissolution of LiPF₆ were observed at 1765, 1720($\nu_{\text{C-O}}$), 1310, 1194, 1086, 986 cm^{-1} ($\nu_{\text{C-O}}$, $\nu_{\text{C-C}}$) and 841 cm^{-1} . We think these peaks are also ascribed to decomposition products of solvents. The different increasing peaks were observed at 1720, 1310, 986 cm^{-1} , which seem to be ascribed to reduction product of EMC.

Figure 3 shows typical cyclic voltammograms at graphite electrodes in 1 mol/dm³ LiPF₆/EC+DEC and in 1 mol/dm³ LiPF₆/EC+EMC, using a test cell for AFM measurement. At the first cathodic scan(from OCV to 0V vs. Li/Li⁺), the cathodic current was observed below about

2.6V and showed broad peaks around 0.7-0.6V. But at the second and third scans(from 1V to 0V) the cathodic current showed only one peak at around 0V, which was corresponding to lithium intercalation. These results revealed the irreversible cathodic reaction existed at only the first polarization. The peak due to lithium intercalation-deintercalation decreased with cycles, and the reduction of this peak was much more in EC+DEC than that of in EC+EMC. Consequently, it is expected the rechargeability of graphite in EC+EMC are superior to those in EC+DEC. The difference of electrochemical behavior may be caused by the interfacial reaction, thus we examined the morphological changes of graphite electrodes in the polarization by in situ AFM observation.

Fig. 3 Cyclic voltammograms of 1 mol/dm³ LiPF₆/EC+DEC(a) and EC+EMC(b) at graphite electrodes in a test cell for AFM measurement. scan rate; 1mV/s.

Figure 4 shows typical AFM images($20 \times 20 \mu\text{m}$ area) of graphite electrode in $1 \text{ mol/dm}^3 \text{ LiPF}_6/\text{EC}+\text{DEC}$ and in $\text{LiPF}_6/\text{EC}+\text{EMC}$ at various conditions. In the present work AFM images were treated by a leveling process and a modification of the irregular traces in the scanning. Several small particles of MCMB were observed at initial state(OCV) and they enlarged about $0.7 \mu\text{m}$ in height at 0.05V vs. Li/Li^+ in $\text{EC}+\text{DEC}$. On the other hand, the expansion of MCMB particles was about $0.4 \mu\text{m}$ in height at 0.05V in $\text{EC}+\text{EMC}$, and it was smaller than that of in $\text{EC}+\text{DEC}$.

Figure 5 shows AFM images($5 \times 5 \mu\text{m}$ area) of graphite electrode at the first cathodic polarization and the anodic polarization to 1.0V vs. Li/Li^+ . The AFM image at OCV showed that MCMB particle size was in the range of $0.5 \sim 1.2 \mu\text{m}$. Although the result of cyclic voltammogram showed the irreversible reaction existed at $0.6 \sim 0.7 \text{V}$ and the reaction of lithium intercalation occurred below 0.4V , AFM images at 1.5V (5b) and 1.0V (5c) were changed from that of at OCV. The topography of MCMB particles at 1.5V was raised about 140nm . At the potential of graphite

electrode was 0.05V , MCMB particles grew about $0.8 \sim 4.0 \mu\text{m}$ in length and 300nm in height. After these large expansions of MCMB particles had occurred in the first cathodic polarization, the morphological change of MCMB was small in the anodic polarization, even at 1.0V , at which potential lithium de-intercalation would be finished.

The morphological changes of graphite electrode surface over 1.0V were reported by the in situ AFM or STM studies^{14-17,21}. Hirasawa reported that film deposition along graphite step edges was observed below 2V vs. Li/Li^+ in $\text{LiClO}_4/\text{EC}+\text{EMC}$ ¹⁴. Chu also reported that surface species appeared on graphite steps or edge surfaces below 1.6V vs. Li/Li^+ in $\text{LiClO}_4/\text{EC}+\text{DMC}$, and at about 2.0V in $\text{LiPF}_6/\text{EC}+\text{DMC}$ ²¹. On the other hand, Inaba reported that a hill-like structure on graphite surface due to the intercalation of solvated Li^+ ion into graphite was observed at 1.1V in $\text{LiClO}_4/\text{EC}+\text{DEC}$ and $\text{EC}+\text{DME}$ ^{16,17}. Because they used the basal plane of highly ordered pyrolytic graphite(HOPG), the morphological changes occurred at the step edges and reported morphological changes were relatively small. But we observed the surface

Fig. 4 AFM images($20 \times 20 \mu\text{m}$) of graphite electrode at various conditions. a,b; in $1 \text{ mol/dm}^3 \text{ LiPF}_6/\text{EC}+\text{DEC}$, c,d; in $1 \text{ mol/dm}^3 \text{ LiPF}_6/\text{EC}+\text{EMC}$, a,c; at OCV, b,d; at 0.05V vs. Li/Li^+ .

Fig. 5 AFM images($5 \times 5 \mu\text{m}$) of graphite electrode at various potentials in $1 \text{ mol/dm}^3 \text{ LiPF}_6/\text{EC}+\text{DEC}$. a; OCV, b; 1.5V , c; 1.0V , d; 0.05V , e; 1.0V , f; 0.05V vs. Li/Li^+ .

of MCMB particles which was mostly consisted of edge planes, so that our results of morphological changes were larger than other studies. We think these AFM images were obtained clearly, so that they were not affected by the soft depositions, such as binder or reduction products of solvents. Therefore, these results seem to clearly prove that the assumption for the intercalation which solvated Li^+ ions intercalate with solvents into graphite layers and the decomposition of ternary graphite intercalation compounds (GICs)- $\text{Li}(\text{solv})_y\text{C}_n$ which results drastic expansion of the graphite matrix (150~200%)^{22,23}. We think small amount of solvated Li^+ ion were doped into graphite layers and the decomposition of ternary compounds resulted the expansion of edge parts at 1.5V vs. Li/Li^+ .

Figure 6 shows the line-analysis of AFM images of graphite electrode in $\text{LiPF}_6/\text{EC}+\text{DEC}$ at various condition for the analysis in detail. The center figures in Fig.6 are the cross sections of the AFM images(left side) and the triangles in figures mark the same position. It was observed that several graphite particles expanded 90nm in height and 80nm in length at 1.0V vs. Li/Li^+ (6b), and 230nm in height and 410nm in length at 0.05V(6c) from the OCV state(6a). The topography of expanded particles remained by the next anodic polarization to 1.0V(6d).

Because MCMB particle is not a single crystal, we can not precisely estimate the expansion due to the intercalation. The expansion of particles was 4.5 times in height and 1.5 times in length from OCV state.

Next, we investigated the interfacial reaction of graphite electrodes and the decomposition products of (GICs)- $\text{Li}(\text{solv})_y\text{C}_n$ in $\text{LiPF}_6/\text{EC}+\text{DEC}$ and in $\text{LiPF}_6/\text{EC}+\text{EMC}$ by in situ FTIR spectroscopy.

Figure 7 shows IRAS spectra of 1 mol/dm³ $\text{LiPF}_6/\text{EC}+\text{DEC}$ at various potentials in the first cathodic polarization. Each spectrum is obtained by the interferogram of one before as a reference, that is, the spectrum 7a at 2.0V vs. Li/Li^+ is obtained by the interferogram at OCV as a reference, and the spectrum 7b is obtained by the interferogram of 7a as a reference, respectively. Relatively large changes of the spectra were observed at 0.5V(7d) and 0V(7e), and increasing peaks were observed at 1790(EC , $\nu_{\text{C=O}}$), 1717($\nu_{\text{C=O}}$), 1114, 1034, 986, 934 and 898 cm^{-1} . The major increasing peak in 7e was observed at 934 cm^{-1} , which seemed to be ascribed to the C-C stretching vibrations of ether-compounds. The 1717 cm^{-1} peak($\nu_{\text{C=O}}$) was ascribed to lithium alkylcarbonate or ester-compound, but the other increased peaks would be ascribed to ether-compounds.

Fig. 6 Line-analysis of AFM images of the polarized graphite electrode at various potentials in 1 mol/dm³ $\text{LiPF}_6/\text{EC}+\text{DEC}$. a; OCV, b; 1.0V, c; 0.05V, d; 1.0V vs. Li/Li^+ .

Fig. 7 IRAS spectra of 1 mol/dm³ LiPF₆/EC+DEC at various potentials in the first cathodic polarization on graphite electrode. a; 2.0V, b; 1.5V, c; 1.0V, d; 0.5V, e; 0V vs. Li/Li⁺.

The IRAS spectra of 1 mol/dm³ LiPF₆/EC+EMC, as the same in Fig. 7, are shown in Fig. 8. Some changes of the spectra were appeared from 2.0V vs. Li/Li⁺ (8a), the peaks at 1680($\nu_{C=O}$), 1029 and 950cm⁻¹(ν_{C-C}) might be ascribed to lithium alkylcarbonates, such as (CH₂OCO₂Li)₂ reported before¹⁻⁸. The major increasing peaks in 8e(at 0V) were observed at 950 and 915cm⁻¹, which seemed to relate to the C-C stretching vibrations of ether-compounds.

Fig. 8 IRAS spectra of 1 mol/dm³ LiPF₆/EC+EMC at various potentials in the first cathodic polarization on graphite electrode. a; 2.0V, b; 1.5V, c; 1.0V, d; 0.5V, e; 0V vs. Li/Li⁺.

The other peaks, except 1791 and 1717cm⁻¹($\nu_{C=O}$) peaks, also seemed to be ascribed to ether-compounds.

Figure 9 shows IRAS spectra of 1mol/dm³ LiPF₆/EC+DEC at various potentials after the first cathodic polarization. The spectrum 9b(at 0.5V vs. Li/Li⁺) showed the decreasing peaks around 1245cm⁻¹(ν_{C-O-C}) and at 934cm⁻¹(ν_{C-C}) which was increased at 0V. The spectra 9c(at 1.0V) and 9d(at 0.5V) showed the doublet peaks of CO₂(2360

Fig. 9 IRAS spectra of 1 mol/dm³ LiPF₆/EC+DEC at various potentials on graphite electrode. a; 0V, b; 0.5V, c; 1.0V, d; 0.5V, e; 0V vs. Li/Li⁺.

Fig. 10 IRAS spectra of 1 mol/dm³ LiPF₆/EC+EMC at various potentials on graphite electrode. a; 0V, b; 0.5V, c; 1.0V, d; 0.5V, e; 0V vs. Li/Li⁺.

and 2340cm^{-1}) were increased very much. This increase of CO_2 would be corresponding to the decomposition of solvents or lithium alkylcarbonates, by taking account of insufficient airtightness of the test cell. The spectrum 9e obtained at 0V in the second polarization showed the almost same spectrum pattern as 9a.

The IRAS spectra of 1 mol/dm^3 $\text{LiPF}_6/\text{EC}+\text{EMC}$, as the same in Fig. 9, are shown in Fig. 10. The spectrum 10b (at 0.5V vs. Li/Li^+) was looked like the reverse form of the spectrum 10a (at 0V), precisely the peaks increased at 0V, such as 1791 , 1717 , 950 , 915cm^{-1} and around 1120cm^{-1} , were decreased at 0.5V, and the peaks decreased at 0V, such as 1762 , 1688 , 1190 and 803cm^{-1} , were increased at 0.5V. This result indicates that reduction products of solvents in the cathodic polarization were disappeared by the anodic polarization. The increasing of the peaks of CO_2 in the spectrum 10e means the irreversible decomposition of solvents. Therefore, it seemed that the irreversible and reversible reactions exist in the interfacial reaction in $\text{LiPF}_6/\text{EC}+\text{EMC}$.

Figure 11 compares DMFTIR spectra of 1 mol/dm^3 $\text{LiPF}_6/\text{EC}+\text{DEC}$ (a) and $\text{LiPF}_6/\text{EC}+\text{EMC}$ (b) at 0V vs. Li/Li^+ , and the subtractive spectra(c, d) of at 0V and at OCV. The DMFTIR spectrum at 0V (Fig. 11a) showed that the dominant species at the graphite surface was lithium alkylcarbonate (ROCO_2Li) which had a major peak around 1692cm^{-1} . Verily, the subtractive spectrum of $\text{LiPF}_6/\text{EC}+\text{DEC}$ (Fig. 11c) showed the major increasing peak at 1696cm^{-1} ($\nu_{\text{C=O}}$) and the other peaks at 1045 ($\nu_{\text{C-O}}$), 953 ($\nu_{\text{C-C}}$) and 813cm^{-1} , which were ascribed to ROCO_2Li . We think this ROCO_2Li is another reduction product of EC, although Aurbach reported that $(\text{CH}_2\text{OCO}_2\text{Li})_2$ is the major reduction product of EC, having peaks around 1650 ($\nu_{\text{C=O}}$), 1300 ($\nu_{\text{C-O}}$), 1080 ($\nu_{\text{C-O}}$), and 830cm^{-1} (δ_{OCO_2}). On the other hand, the spectra of 11b and 11d in $\text{LiPF}_6/\text{EC}+\text{EMC}$ showed small changes after cathodic polarization. The spectrum 11d showed that increasing peaks at around 1700cm^{-1} ($\nu_{\text{C=O}}$), 1158 , 1070 ($\nu_{\text{C-O}}$) and 817cm^{-1} , and these peaks seemed to be ascribed to ROCO_2Li . Although the major products in cathodic polarization were seemed to ether-compounds in IRAS spectra (Fig. 7~10), the peaks around $910\sim 950\text{cm}^{-1}$ of ether-compounds (except the peak at 953cm^{-1} in 11c) were not clearly observed in DMFTIR spectra at 0V. We think ether-compounds are soluble in electrolytes and not precipitated at electrodes, thus the dominant reduction products at graphite surface are lithium alkylcarbonates (ROCO_2Li) in both systems. The amount of precipitated ROCO_2Li on graphite surface was much higher in EC+DEC than that of in EC+EMC, by a comparison of 11a and 11b, precisely the absorbance of the peak (1692

Fig. 11 DMFTIR spectra of $\text{LiPF}_6/\text{EC}+\text{DEC}$ (a) and $\text{LiPF}_6/\text{EC}+\text{EMC}$ (b) at 0V vs. Li/Li^+ , and subtractive spectra of at OCV and at 0V. a, c; $\text{LiPF}_6/\text{EC}+\text{DEC}$, b, d; $\text{LiPF}_6/\text{EC}+\text{EMC}$, c, d; subtractive spectrum.

cm^{-1}) was increased much higher than that of the solvents in EC+DEC.

In $\text{LiPF}_6/\text{EC}+\text{DEC}$ system, DMFTIR spectra showed the dominant surface product at graphite electrode was ROCO_2Li having a major peak around 1696cm^{-1} after cathodic polarization (at 0V). The IRAS spectra (Fig. 7 and 9) showed the major soluble products in the cathodic polarization were ether-compounds having a major peak around 930cm^{-1} and the other peaks around 1120 , 1034 , 986 and 898cm^{-1} . The amount of CO_2 (the peaks at 2360 and 2340cm^{-1}) in the electrolyte was increased in the second cathodic polarization, and it indicated the decomposition of solvents. These results of FTIR spectroscopy revealed the instability of DEC, that is, DEC was easy to reduce and reduction products of DEC were soluble in electrolyte and not precipitated at the graphite surface. Thereby it seemed that the passivation of the graphite surface was insufficient for the reduction of solvents in EC+DEC.

On the other hand in $\text{LiPF}_6/\text{EC}+\text{EMC}$ system, DMFTIR spectra showed the dominant surface species at graphite electrode were EC and EMC even after cathodic polarization. Although ROCO_2Li having the major peaks around 1700cm^{-1} was increased, the changes of surface species by the polarization was small. The IRAS spectra (Fig. 8 and 10) showed reduction products were ether-compounds, which had the major peaks at 950 and 915cm^{-1} ($\nu_{\text{C-C}}$) and the other peaks around 1120 , 1030 , 872 and 822cm^{-1} . But these peaks ascribed to ether-compounds

were decreased, and the peaks which were decreased at 0V were increased by anodic polarization. Therefore, we think that these peaks may be corresponding to solvation of lithium ion or decomposition of solvents, that is the amount of highly oriented solvent or decomposed solvent increased after lithium intercalation (at 0V), and the amount of this decreased after de-intercalation (at 1V).

4 CONCLUSION

The present study proved the two methods, FTIR spectroscopy and AFM observation, were the effective approaches for in situ analysis even at graphite composite electrodes which were not flat and smooth surface. The morphological changes of graphite electrodes were observed even at 1.5V vs. Li/Li^+ at the first cathodic polarization both in $\text{LiPF}_6/\text{EC}+\text{DEC}$ and in $\text{LiPF}_6/\text{EC}+\text{EMC}$. A larger expansion of graphite particles at 0.05V, such as 4.5 times in height and 1.5 times in length, was observed in $\text{EC}+\text{DEC}$. After this large expansion of graphite had occurred, the morphological changes was small by anodic or cathodic polarizations. The results of AFM observation were consisted with the assumption of solvated lithium intercalation by Besenhard²¹⁾ in the followings;

- 1) The morphological changes start over 1V vs. Li/Li^+ .
- 2) Very large expansion of graphite due to the decomposition of the ternary graphite-intercalation compounds (GICs)- $\text{Li}(\text{solv})_y\text{C}_n$ was observed only at first cathodic polarization.

The DMFTIR spectroscopy, the effective detection for the interfacial reactions, showed that both $\text{EC}+\text{DEC}$ solution and $\text{EC}+\text{EMC}$ solution containing 1 mol/dm³ LiPF_6 were unstable on graphite electrodes even at open circuit state. After cathodic polarization, ROCO_2Li having a peak at 1696cm^{-1} was observed as the dominant surface species in $\text{EC}+\text{DEC}$. This result reveals that the surface chemistry of graphite and the degree of passivation are different in $\text{EC}+\text{EMC}$ from in $\text{EC}+\text{DEC}$. The IRAS spectra showed that major soluble products of solvents were similar ether-compounds which have the major peak at 930cm^{-1} in $\text{EC}+\text{DEC}$, and the peaks at 950 and 920cm^{-1} in $\text{EC}+\text{EMC}$. But the difference of DEC and EMC was appeared at the anodic polarization, as shown in Fig. 9 and 10. This different behavior would be caused by the interfacial reactions of graphite electrodes. We think the surface of graphite was covered by insoluble ROCO_2Li and these insoluble products were more tightly and passivated in $\text{EC}+\text{EMC}$ than in $\text{EC}+\text{DEC}$. The film formation due to the decomposition of $(\text{GICs})-\text{Li}(\text{solv})_y\text{C}_n$ was not clearly observed both in DMFTIR and IRAS spectroscopy.

The authors express their sincere thanks to the New Energy and Industrial Technology Development Organization for their support of this work.

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