リチウムイオン電池用黒鉛の電極特性へのフッ素エステルの添加効果
Effect of fluoroester on the electrode behavior of graphite for lithium ion battery

中島　剛[†]，ラマサミ　チャンドラセカラン[†]，大澤善美[†]，高　明天[††]，青山博一[††]

T. Nakajima[†], R. Chandrasekaran[†], Y. Ohzawa[†], M. Koh[††] and H. Aoyama[††]

Abstract　Effect of fluoroadditive on the electrode characteristics of natural graphite samples with average particle sizes of 5, 10 and 15 μm (NG5μm, NG10μm and NG15μm, respectively) has been investigated at 25°C and -10°C in 1 mol dm^{-3} LiClO$_4$ – ethylene carbonate (EC) / diethyl carbonate (DEC) / propylene carbonate (PC) (1:1:1 in volume). Addition of CHF$_2$COOCH$_3$ increased both first coulombic efficiencies and charge capacities at -10°C for three graphite samples.

1. Introduction

Graphite with high crystallinity is mainly employed as a host of lithium in secondary (rechargeable) lithium battery. As electrolyte solutions, mixtures of organic carbonates such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and propylene carbonate (PC) are currently used. Among them, EC is an essentially important solvent forming the surface film (Solid Electrolyte Interface: SEI) on graphite anode. We have investigated the effect of fluoroadditives on the low temperature electrode characteristics of natural graphite powder (NG7, average particle size: 7 μm, BET surface area: 4.8 m^2 g^{-1}) in 1 mol dm^{-3} LiClO$_4$ – EC/DEC and – EC/DEC/PC mixtures[1-3]. Among fluoroesters examined, methyl difluoroacetate (CHF$_2$COOCH$_3$) – added solvents showed the higher capacities than others at low temperatures[1, 2]. The effect of addition of fluorine compound was shown by the result that graphite electrode had the higher capacity in CHF$_2$COOCH$_3$ containing EC/DEC than in CH$_3$COOCH$_3$-added one at 0°C[3]. Addition of some fluoroethers having slightly higher reduction potentials than that of EC (0.6 V vs Li/Li$^+$) also increased the capacities of graphite electrode in EC/DEC at 0°C[2]. Quantum calculation of HOMO/LUMO energies indicated that reduction potentials of fluorine containing esters and ethers increase with decrease in the LUMO levels[2, 3]. It was suggested that decomposed products containing hydrophobic CF$_2$ and CF$_3$ groups incorporated in SEI layers facilitated the easy diffusion of Li$^+$ ion due to the low friction of hydrophobic C-F groups. In PC containing solvent, a carbonaceous electrode with high disorder is preferable for the quick formation of surface film (SEI) by the decomposition of a small amount of solvent, which leads to the low irreversible capacity, i.e. high first coulombic efficiency and capacity. In the present study, electrode characteristics of three natural graphite samples with different particle sizes and high disorder have been investigated in fluoroester containing EC/DEC/PC mixtures at 25°C and −10°C, and the effect of addition of fluoroester to the solvents has been discussed.

2. Experimental

Graphite samples used in the present study were powdery natural graphites with average particle sizes of 5, 10 and 15 μm (abbreviated to NG5μm, NG10μm and NG15μm, respectively, purity: >99.95%) supplied by SEC Co., Ltd. BET surface areas of these graphite samples were 12.1, 7.2 and 5.3 m^2 g^{-1}, and R values obtained by the peak intensity ratio of D-band to G-band in Raman spectrum were 0.24, 0.28 and 0.27 for NG5μm, NG10μm and NG15μm, respectively. Fluoroadditive examined was CHF$_2$COOCH$_3$ (difluoromethyl acetate). The electrolyte solution was 1 mol dm^{-3} LiClO$_4$ – EC/DEC/PC (1:1:1 in volume) (50 ml), to which the fluoroester (2.5 ml) was added. For the electrochemical measurements, three-electrode cell with natural graphite as a working electrode and metallic lithium as counter and reference electrodes was used. Preparation of a graphite electrode was described in a previous paper[1]. Cyclic voltammetry measurement was made at a scan speed of 0.1 mVs^{-1} between 0 and 2 V vs Li/Li$^+$. Galvanostatic charge/discharge cycling was performed at a current density of 60 mAg^{-1} between 0 and 3 V vs Li/Li$^+$. The electrochemical measurements were done at 25°C and -10°C.

3. Results and discussion

Fig. 1 shows the cyclic voltammograms obtained at 25°C for NG5μm, NG10μm and NG15μm in 1 moldm^{-3} LiClO$_4$ – EC/DEC/PC and – EC/DEC/PC/CHF$_2$COOCH$_3$ solutions. The reduction current was larger in 1st cycle than 5th cycle between 2 and 0 V vs Li/Li$^+$. In the 1st reduction curves obtained in

[†]Department of Applied Chemistry, Aichi Institute of Technology (Toyota)
[††]Daikin Industries, Ltd. (Settsu)

EC/DEC/PC, reduction peaks were observed at 0.71 V (Fig. 1a), 0.75 and 0.68 V (Fig. 1c), and 0.75 and 0.70 V (Fig. 1e) for NG5μm, NG10μm and NG15μm, respectively. The peaks at 0.75 V would correspond to the reduction of PC and those at0.68 and 0.70 V at lower potentials would be due to the reduction of EC. The reduction peak at 0.71 V in Fig. 1a may be an overlapped one of two peaks. Thus two reduction peaks were separately observed and the peak currents increased with increasing particle size of natural graphite. This means that the decomposition of PC and EC increased with increasing particle size, that is, with decreasing surface area of graphite sample. The area of edge plane, where desolvation and reduction of PC

and EC and insertion of Li$^+$ ion occur, decreases with decreasing surface area, i.e. from NG5μm to NG15μm. In addition, the ratio of edge plane to total surface area decreases with increasing particle size. Desolvation and reduction of the solvent molecules and subsequent formation of solid electrolyte interface (SEI) may smoothly proceed in NG5μm with the larger area of edge plane. However, decomposition of larger amounts of PC and EC may occur in NG10μm and NG15μm because the insertion of desolvated Li$^+$ ion into the smaller areas of edge plane is somewhat difficult. This may be the reason why the smallest reduction peak of the solvents was observed in NG5μm. In CHF$_2$COOCH$_3$-added EC/DEC/PC
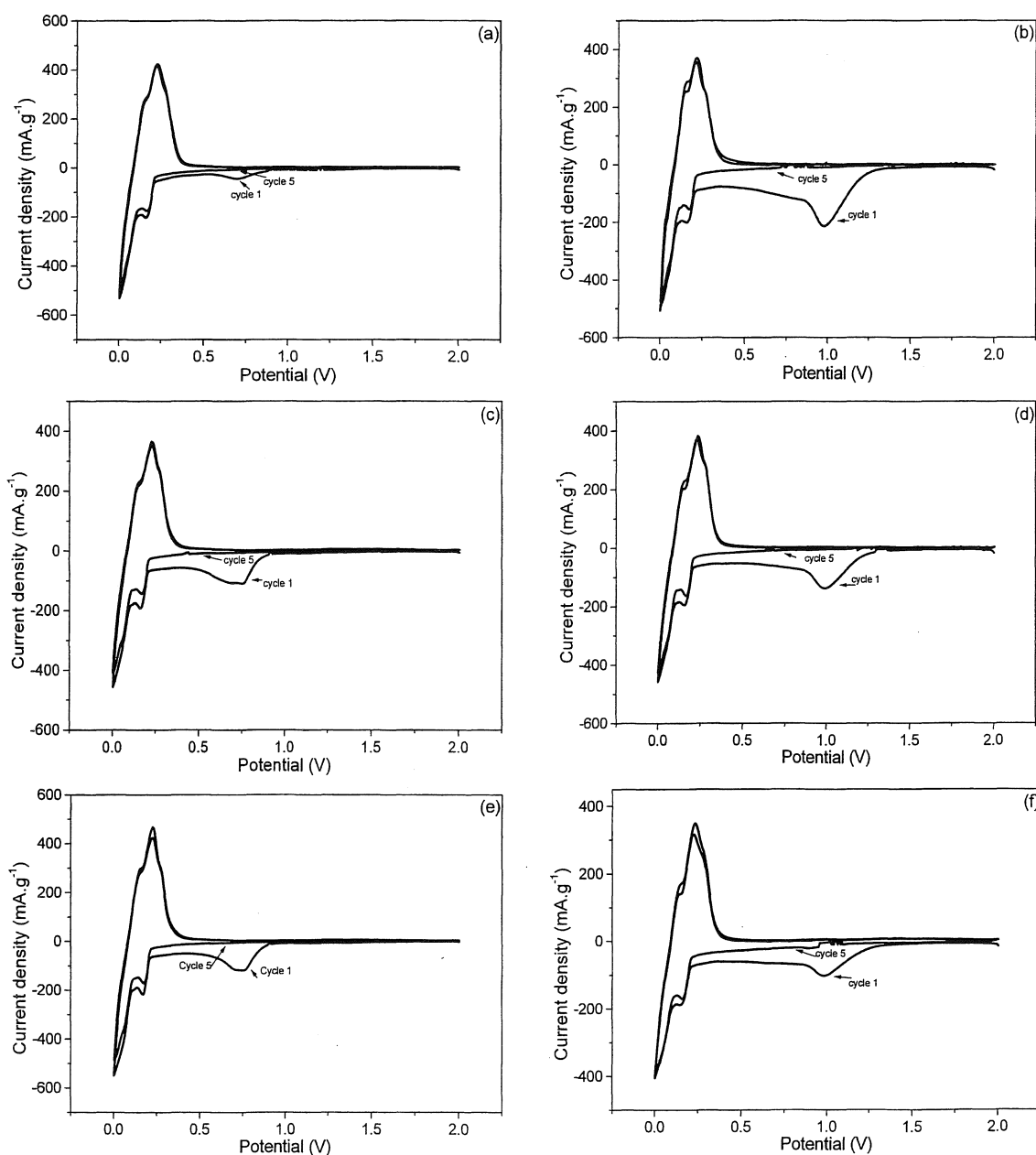

Fig. 1. Cyclic voltammograms for NG5μm, NG10μm and NG15μm, obtained at 25°C in 1 mol.dm^{-3} LiClO$_4$ − EC/DEC/PC and − EC/DEC/PC/CHF$_2$COOCH$_3$. (a) NG5μm in EC/DEC/PC, (b) NG5μm in EC/DEC/PC/CHF$_2$COOCH$_3$, (c) NG10μm in EC/DEC/PC, (d) NG10μm in EC/DEC/PC/CHF$_2$COOCH$_3$, (e) NG15μm in EC/DEC/PC, (f) NG15μm in EC/DEC/PC/CHF$_2$COOCH$_3$.

Effect of fluoroster on the electrode behavior of graphite for lithium ion battery

solutions, the reduction peaks were found at 0.99-1.00 V higher than the decomposition potentials of PC and EC for three graphite samples (Fig. 1b, 1d and 1f), indicating the electrochemical decomposition of CHF_2COOCH_3[1]. The current of the reduction peak decreased from NG5μm to NG15μm, i.e. with decreasing BET surface area. Li^+ ions would not be solvated by a small amount of added CHF_2COOCH_3, but preferentially solvated by PC and EC molecules with high dielectric constants in the solutions. Therefore the electrochemical reduction of added CHF_2COOCH_3 would have occurred in proportion to the total surface area of graphite sample. The reversibility of Li^+ ion intercalation and

deintercalation into and from graphite was good both in EC/DEC/PC and EC/DEC/PC/CHF_2COOCH_3 solutions at 25°C.

Fig. 2 shows the cyclic voltammograms obtained at -10°C. The reduction peaks observed at 0.69 V and 0.56 V in Fig. 2a are attributed to the reduction of PC and EC. The strong reduction peaks at 0.67 V (Fig. 2c) and 0.66 V (Fig. 2e) are due to the reduction of PC. The reduction currents for PC were larger than those observed at 25°C in EC/DEC/PC solution, increasing with increasing particle size from NG5μm to NG15μm (Figs. 2a, 2c and 2e) probably because the formation rate of SEI is slow at -10°C. In CHF_2COOCH_3-added
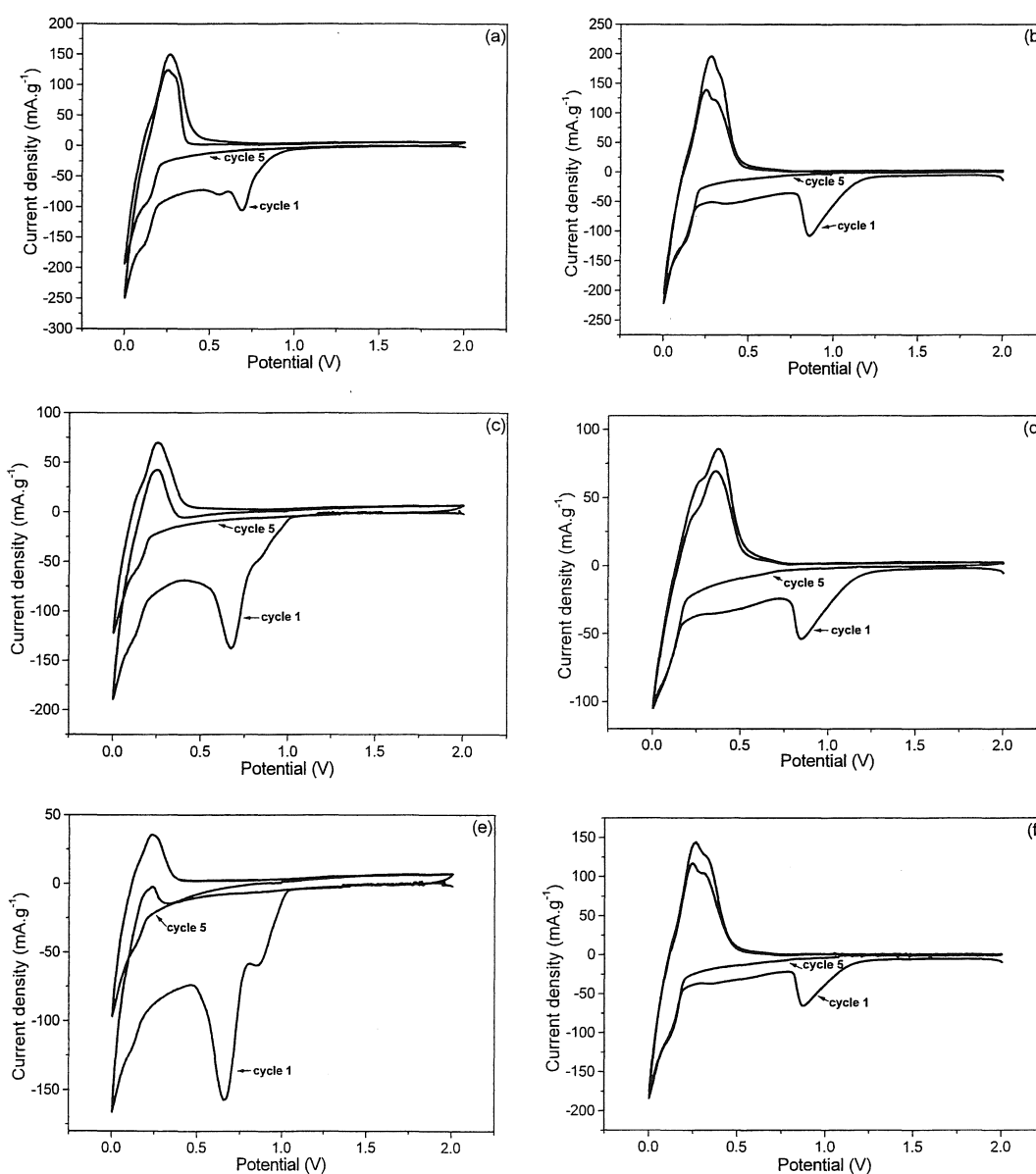

Fig. 2. Cyclic voltammograms for NG5μm, NG10μm and NG15μm, obtained at -10°C in 1 mol.dm^{-3} LiClO$_4$ – EC/DEC/PC and – EC/DEC/PC/CHF_2COOCH_3. (a)-(f) are the same as those in Fig. 1

EC/DEC/PC solution, the reduction of CHF$_2$COOCH$_3$ was observed at 0.84-0.88 V (Figs. 2b, 2d and 2f). All reduction peaks for CHF$_2$COOCH$_3$, PC and EC were thus shifted to the lower potentials probably due to the low diffusion rates at -10°C. The peak currents indicating the reduction of CHF$_2$COOCH$_3$ were smaller than those at 25°C, decreasing with decreasing surface area of graphite. Decomposed product of CHF$_2$COOCH$_3$ would be less soluble in EC/DEC/PC at -10°C than at 25°C, which may lead to the SEI formation by the decomposition of a less amount of CHF$_2$COOCH$_3$. The peak currents for reduction and oxidation of graphite at 1st cycle significantly decreased due to the low diffusion rate of

Li$^+$ ion at -10°C. The reversibility of Li$^+$ ion intercalation and deintercalation into and from graphite was also low particularly in EC/DEC/PC solutions without additives (Figs. 2a, 2c and 2e). Only very small oxidation currents were observed at 1st cycle for NG10μm and NG15μm in EC/DEC/PC mixtures (Figs. 2c and 2e). It is clearly observed in Fig. 2 that the reversibility of Li$^+$ ion intercalation and deintercalation was highly improved at -10°C by the addition of a small amount of CHF$_2$COOCH$_3$ to EC/DEC/PC.

Fig. 3 shows the galvanostatic charge/discharge curves for NG5μm, NG10μm and NG15μm, obtained at -10°C in EC/DEC/PC and EC/DEC/PC/CHF$_2$COOCH$_3$ solutions at a
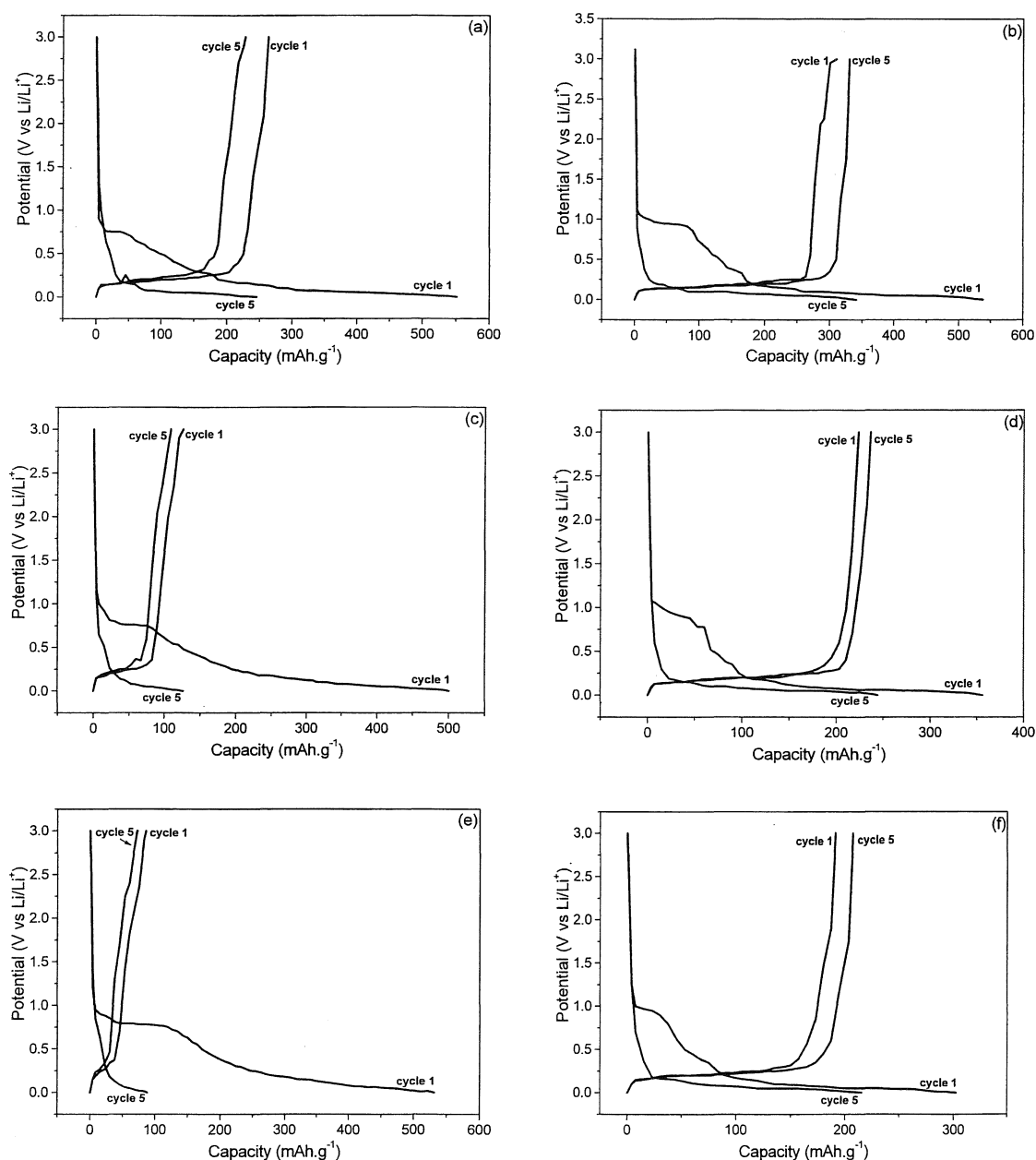
Fig. 3. Charge/discharge curves for NG5μm, NG10μm and NG15μm, obtained at -10°C in 1 mol.dm^{-3} LiClO$_4$ – EC/DEC/PC and – EC/DEC/PC/CHF$_2$COOCH$_3$. (a)-(f) are the same as those in Fig. 1.

current density of 60 mAg^{-1}. The decomposition of PC and EC largely occurred in EC/DEC/PC. The decomposition of the solvents increased and charge capacity decreased with increasing particle size of graphite powder (Figs. 3a, 3c and 3e). However, in CHF$_2$COOCH$_3$-added solvents, three graphite electrodes exhibited much better behavior as suggested by cyclic voltammograms shown in Fig. 2,. The much higher charge capacities were observed in CHF$_2$COOCH$_3$-added solvents as shown in Figs. 3b, 3d and 3f. The current indicating the decomposition of CHF$_2$COOCH$_3$ and solvents decreased

with increasing particle size of graphite, i.e. with decreasing surface area. The result suggests that the decomposition of CHF$_2$COOCH$_3$ well contribute to the SEI formation at -10°C.

Coulombic efficiencies and charge capacities obtained at 25°C and -10°C in EC/DEC/PC and EC/DEC/PC/CHF$_2$COOCH$_3$ solutions are summarized in Tables 1 and 2, respectively. Addition of CHF$_2$COOCH$_3$ to EC/DEC/PC is not effective at 25°C (Table 1). In cases of NG5μm and NG10μm, first coulombic efficiencies were decreased by the addition of CHF$_2$COOCH$_3$ probably because CHF$_2$COOCH$_3$ is

Table 1   Coulombic efficiencies (%) and charge capacities (mA.h.g^{-1}) for natural graphite samples (NG5μm, NG10μm and NG15μm) in 1 mol.dm^{-3} LiClO$_4$ – EC/DEC/PC and – EC/DEC/PC/CHF$_2$COOCH$_3$ at 25°C.

Solvent	Cycle number							
Graphite	1	2	3	4	5	6	7	8
EC/DEC/PC								
NG5μm (%)	70.5	90.3	93.4	94.3	94.0	-	-	-
(mA.h.g^{-1})	356	354	352	347	342	-	-	-
NG10μm (%)	60.5	86.7	90.0	91.7	93.0	93.0	93.9	93.9
(mA.h.g^{-1})	290	279	278	278	278	278	277	276
NG15μm (%)	44.0	89.9	92.6	93.6	94.7	-	-	-
(mA.h.g^{-1})	331	320	312	307	304	-	-	-
EC/DEC/PC/CHF$_2$COOCH$_3$								
NG5μm (%)	28.4	75.7	81.1	83.3	85.5	-	-	-
(mA.h.g^{-1})	309	302	301	300	300	-	-	-
NG10μm (%)	45.6	79.5	83.1	84.9	85.5	87.9	88.3	89.4
(mA.h.g^{-1})	309	302	300	299	296	298	295	296
NG15μm (%)	47.6	79.6	83.8	85.3	87.5	88.3	88.8	89.6
(mA.h.g^{-1})	325	324	326	325	328	326	326	326

Table 2   Coulombic efficiencies (%) and charge capacities (mA.h.g^{-1}) for natural graphite samples (NG5μm, NG10μm and NG15μm) in 1 mol.dm^{-3} LiClO$_4$ – EC/DEC/PC and – EC/DEC/PC/CHF$_2$COOCH$_3$ at -10°C.

Solvent	Cycle number							
Graphite	1	2	3	4	5	6	7	8
EC/DEC/PC								
NG5μm (%)	42.1	87.1	92.4	92.3	94.5	-	-	-
(mA.h.g^{-1})	263	251	242	229	224	-	-	-
NG10μm (%)	25.2	73.0	79.2	82.1	86.5	89.1	87.9	89.4
(mA.h.g^{-1})	126	122	114	110	109	106	102	101
NG15μm (%)	16.2	64.6	71.0	80.1	81.8	-	-	-
(mA.h.g^{-1})	86	84	76	76	71	-	-	-
EC/DEC/PC/CHF$_2$COOCH$_3$								
NG5μm (%)	57.6	92.0	94.5	96.0	96.5	-	-	-
(mA.h.g^{-1})	310	321	326	328	329	-	-	-
NG10μm (%)	62.6	92.3	93.7	95.5	96.7	95.5	96.3	97.5
(mA.h.g^{-1})	228	228	233	236	236	234	235	235
NG15μm (%)	63.2	91.7	94.4	95.4	96.3	96.3	95.4	96.7
(mA.h.g^{-1})	191	199	204	206	207	208	206	208

decomposed at the higher potential than those for PC and EC and decomposed products may be soluble in the solution at 25°C since CHF_2COOCH_3 contains only two hydrophobic C-F bonds. The effect of CHF_2COOCH_3 addition was clearly observed at -10°C (Table 2). The first coulombic efficiencies and charge capacities were very low at -10°C in EC/DEC/PC, decreasing with decreasing surface area from NG5μm to NG15μm. Both coulombic efficiencies and charge capacities were highly increased by the addition of CHF_2COOCH_3. Decomposition of CHF_2COOCH_3 may facilitate the formation of SEI because CHF_2COOCH_3 is reduced at the higher potential than PC and EC and decomposed product may be less soluble in the electrolyte solution at -10°C than at 25°C.

4. Conclusion

Effect of addition of a small amount of fluoroester or fluoroether to EC/DEC/PC has been examined at 25°C and -10°C using natural graphite samples with average particle sizes of 5, 10 and 15 μm (NG5μm, NG10μm and NG15μm). It was found that addition of CHF_2COOCH_3 was not effective at 25°C, but increased both first coulombic efficiencies and charge capacities of three graphite samples at -10°C. CHF_2COOCH_3 is electrochemically reduced at around 1.0 V vs Li/Li$^+$ close to the reduction potential of PC, and probably contributes to the formation of SEI at -10°C. On the other hand,

the addition of fluoroethers to EC/DEC/PC somewhat increased first coulombic efficiencies and charge capacities at both 25°C and -10°C. Decomposed products of fluoroethers are probably less soluble in EC/DEC/PC than that of CHF_2COOCH_3 because fluoroethers have a larger number of hydrophobic C-F groups, therefore being able to contribute to the SEI formation even at 25°C.

References

1) T. Nakajima, K. Dan, M. Koh, "Effect of fluoroesters on the low temperature electrochemical characteristics of graphite electrode", J. Fluorine Chem. **87**, 221-227 (1998).
2) T. Nakajima, K. Dan, M. Koh, T. Ino, T. Shimizu, "Effect of addition of fluoroethers to organic solvents for lithium ion secondary batteries", J. Fluorine Chem. **111**, 167-174 (2001).
3) T. Nakajima, "Fluorine-containing energy conversion materials", J. Fluorine Chem. **105**, 229-238 (2000).

（受理　2006 年 5 月 2 日）