Oxidation Stability and Electrochemical Properties of Organo-Fluorine Compounds

for Lithium Ion Batteries

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Abstract   Differential scanning calorimetry (DSC) study demonstrated that mixing of fluoro-ethers and fluoro-carbonates improved the thermal stability of 0.67 mol/L LiClO$_4$-EC (ethylene carbonate) / DEC (diethyl carbonate) / PC (propylene carbonate) (1:1:1 vol.). Oxidation currents were smaller in the fluorine compound-mixed electrolyte solutions than in 0.67 mol/L LiClO$_4$-EC/DEC/PC, which shows also high stability of the fluorine compound-mixed electrolyte solutions against electrochemical oxidation. Electrochemical reduction of fluorine compounds took place at the higher potentials than EC, DEC and PC as suggested by HOMO and LUMO energies of fluorine compounds. However, charge/discharge experiments using natural graphite electrodes showed that the fluorine compounds increased first coulombic efficiencies due to quick formation of SEI on natural graphite in PC-containing solvents.

1. Introduction

Lithium ion batteries with high rate charge and discharge are urgently requested for their application to hybrid cars and electric vehicles. However, lithium ion batteries have a possibility of firing and/or explosion at high temperatures, by short circuit, by overcharging and so on since they use flammable organic solvents. The high safety is one of the most important issues for the practical use of lithium ion batteries, especially for the application to hybrid cars and electric vehicles. In order to improve the thermal and oxidation stability of lithium ion batteries, new additives or solvents for electrolyte solutions have been investigated[1)-34)]. Most of them are phosphorus compounds (phosphates) having flame retardant properties. Several papers were quite recently published for the effect of organo-fluorine compounds on the electrochemical oxidation stability and charge/discharge behavior[31)-34)]. It was found in our previous study that cyclic and linear fluoro-carbonates can be used as nonflammable solvents for lithium ion batteries[34)].   Mixing of the fluoro -

carbonates with 1 mol/L LiClO$_4$ – EC (ethylene carbonate) / DEC (diethyl carbonate) significantly improved the oxidation stability without decrease in charge capacities and first coulombic efficiencies for natural graphite (NG) electrodes, and furthermore mixing of the same fluoro-carbonates with 1 mol/L LiClO$_4$-EC/DEC/PC(propylene carbonate) highly increased not only oxidation stability of electrolyte solutions but also first coulombic efficiencies for the same natural graphite electrodes[34)]. Fluoro-carbonates used are very stable against electrochemical oxidation at high potentials. They are electrochemically reduced at the higher potentials than EC, DEC and PC, easily forming protective surface film (Solid Electrolyte Interphase or Interface: SEI) on graphite electrode. EC with a high melting point, 36°C should be used for high crystalline graphite for the quick formation of SEI. Therefore it is desirable to use PC with a low melting point, −55°C. According to our measurement, the melting points of 1 mol/L LiClO$_4$-EC/DEC (1:1 vol.) and EC/DEC/PC (1:1:1 vol.) were −1°C and ca. −31°C, respectively. However, it is difficult to use graphite in PC-based electrolyte solutions due to the continuous decomposition of PC. It is therefore an additional advantage that the fluoro-carbonates enable the use of PC-containing solvents for graphite electrode. Fluorine substitution of organic compounds reduces HOMO/LUMO levels[34),35)]. Organo-fluorine compounds are new type candidates as nonflammable solvents for lithium ion batteries because the

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decrease in HOMO levels gives high oxidation stability to fluorine compounds. However, the decrease in LUMO levels due to fluorine substitution simultaneously increases reduction potentials of organic compounds, which causes electrochemical decomposition of fluorine compounds. If electrochemical reduction of fluorine compounds continues without forming SEI on carbon anode, irreversible capacity largely increases. However, if decomposed products quickly form SEI, such fluorine compounds can be used as nonflammable solvents. Other important problems are miscibility of fluorine compounds with polar solvents for lithium ion batteries such as EC, PC and DEC, and solubilities of inorganic electrolytes. The fluoro-carbonates examined in a previous paper[34] solved these problems, meeting the request as nonflammable solvents for lithium ion batteries. In the present study, thermal stability and electrochemical reactions of fluoro-ethers, fluoro-ester and fluoro-carbonates were investigated and charge/discharge characteristics of natural graphite electrodes were studied in the fluorine compound-mixed electrolyte solutions to develop new nonflammable solvents for lithium ion batteries.

2. Experimantal

Natural graphite samples (purity: >99.95%) with average particle sizes of 15 and 25 μm (abbreviated to NG15 μm and NG25 μm) were used for cyclic voltammetry and charge/discharge cycling. The d_{002} values obtained by X-ray diffractometry were 0.3355 and 0.3358 nm for NG15 μm and NG25 μm, respectively. Surface areas and meso-pore volumes obtained by BET surface area measurement were 6.9 and 3.7 m^2/g, and 0.026 and 0.009 cm^3/g for NG15 μm and NG25 μm, respectively. Peak intensity ratios of D-band to G-band ($R=I_D/I_G$) obtained by Raman spectroscopy with Nd:YVO$_4$ laser (532 nm) were nearly the same as each other (0.25 and 0.26. for NG15 μm and NG25 μm, respectively).

The ether, ester and carbonate type fluorine compounds (purity: 99.9%, H_2O: <10 ppm) were used in the present study (Fig. 1). Among them, the compounds, I-III were used only for differential scanning calorimetry (DSC) measurement because their electrochemical properties were already reported in a previous paper[34]. HOMO and LUMO energies of fluorine compounds **A, B, C, D, E** and **F** were calculated by Spartan'06 semi-empirical method using AM1, being compared with those for the same type compounds without F. HOMO/LUMO energies for fluorine compounds, I-III and the corresponding compounds without F, were reported in a previous paper[34].

Thermal stability of fluorine compound-mixed electrolyte solutions was examined by differential scanning calorimetry (DSC). DSC measurement was carried out using an Al cell containing a mixture of 0.67 mol/L LiClO$_4$–EC/DEC/PC (1:1:1 vol.) or EC/DEC/PC(**A, B, C, D, E, F, I, II** or **III**) (1:1:1:1.5 vol.) and NG15 μm between room temperature and 300°C or 310°C (for mixtures with **I, II** or **III**) at a temperature scan rate of 5°C/min. Electrolyte solution (3 μL) and NG15 μm (0.8 mg) were sealed in an airtight Al cell in air to effectively examine the thermal stability.

Oxidation currents for 0.67 mol/L LiClO$_4$–EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/(**A, B, C, D, E** or **F**: Organo-Fluorine Compound (**OFC**)) (1:1:1:1.5 vol.) were measured by linear sweep of potential at 0.1 mV/s using Pt wire electrode. Counter and reference electrodes were lithium foil.

Three-electrode cell with natural graphite as a working electrode and lithium foil as counter and reference electrodes was used for cyclic voltammetry study and galvanostatic charge/discharge experiments. Natural graphite electrode was prepared as follows. Natural graphite powder was dispersed in N-methyl-2-pyrrolidone (NMP) containing 12 wt% poly(vinylidene fluoride) (PVdF) and the slurry was pasted on a copper current collector. The electrode was dried at 120°C under vacuum for half a day. After drying, the electrode contained 80 wt% graphite and 20 wt% PVdF. Electrolyte solutions were prepared by mixing the fluorine compound with 1 mol/L LiClO$_4$–EC/DEC/PC (1:1:1 vol.). Fluorine compounds are miscible with 1 mol/L LiClO$_4$-EC/DEC and EC/DEC/PC in whole range of composition at room temperature. For cyclic voltammetry study, 0.5 mol/L LiClO$_4$–EC/DEC/PC/**OFC** (1:1:1:1.5 vol.) was used. Cyclic voltammograms were obtained using NG15 μm at a scan rate of 0.1 mV/s. The 0.67 mol/L LiClO$_4$–EC/DEC/PC/**OFC** (1:1:1:1.5 vol.) was used for galvanostatic charge/discharge experiments. Preparation of 1 mol/L LiClO$_4$–EC/DEC/**OFC** (1:1:1 vol.) and EC/DEC/PC/**OFC** (1:1:1:1.5 vol.) can be made at room temperature by dissolving LiClO$_4$ in 0.67 mol/L LiClO$_4$–EC/DEC/**OFC** and EC/DEC/PC/**OFC** (1:1:1:1.5 vol.), respectively. However, the 0.67 mol/L LiClO$_4$–EC/DEC/PC/**OFC** (1:1:1:1.5 vol.) was used for charge/discharge cyclings to simplify the experiments. Galvanostatic charge/discharge cyclings were performed using NG15 μm and NG25 μm at a current density of 60 mA/g between 0 and 3 V relative to the Li/Li$^+$ reference electrode in a thermostat at 25°C.
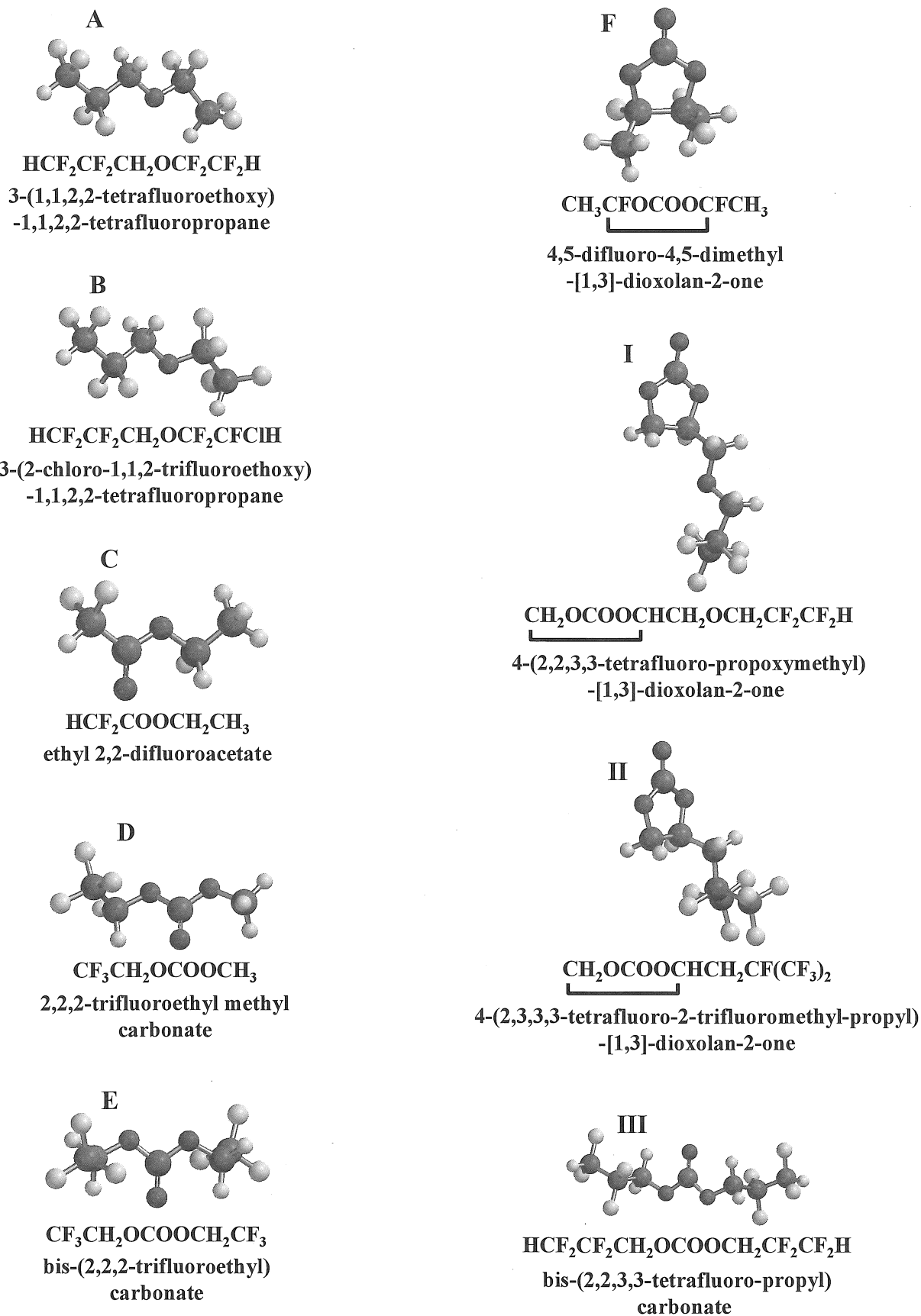
A

$HCF_2CF_2CH_2OCF_2CF_2H$

3-(1,1,2,2-tetrafluoroethoxy)
-1,1,2,2-tetrafluoropropane

B

$HCF_2CF_2CH_2OCF_2CFClH$

3-(2-chloro-1,1,2-trifluoroethoxy)
-1,1,2,2-tetrafluoropropane

C

$HCF_2COOCH_2CH_3$

ethyl 2,2-difluoroacetate

D

$CF_3CH_2OCOOCH_3$

2,2,2-trifluoroethyl methyl
carbonate

E

$CF_3CH_2OCOOCH_2CF_3$

bis-(2,2,2-trifluoroethyl)
carbonate

F

$CH_3CFOCOOCFCH_3$

4,5-difluoro-4,5-dimethyl
-[1,3]-dioxolan-2-one

I

$CH_2OCOOCHCH_2OCH_2CF_2CF_2H$

4-(2,2,3,3-tetrafluoro-propoxymethyl)
-[1,3]-dioxolan-2-one

II

$CH_2OCOOCHCH_2CF(CF_3)_2$

4-(2,3,3,3-tetrafluoro-2-trifluoromethyl-propyl)
-[1,3]-dioxolan-2-one

III

$HCF_2CF_2CH_2OCOOCH_2CF_2CF_2H$

bis-(2,2,3,3-tetrafluoro-propyl)
carbonate

Fig. 1 Fluorine compounds used in the study.

3. Results and discussion

3.1. HOMO and LUMO energies of fluorine compounds.

Both HOMO and LUMO levels were decreased by fluorine substitution. The decrements in the HOMO and LUMO energies are qualitatively proportional to the numbers of substituted fluorine atoms. The result suggests that oxidation stability of organic compounds is improved by fluorine substitution, however, their reduction simultaneously becomes easy, i.e. their reduction potentials are elevated.

3.2. Thermal stability of fluorine compound-mixed electrolyte solutions.

Thermal stability of fluorine compound-mixed electrolyte solutions with NG15 μm was evaluated by DSC measurement as shown in Fig. 2. The 0.67 mol/L LiClO₄-EC/DEC/PC had an endothermic peak at 265°C, followed by an exothermic peak at 281°C. The endothermic peak would be due to the evaporation of DEC with the lower boiling point, disappearing by mixing the fluorine compounds. Exothermic peaks for fluoro-ethers, **A** and **B**-mixed solutions were observed both at a slightly higher temperature of 286°C. Fluoro-ester, **C**-mixed solution gave an exothermic peak at a similar temperature of 284°C. Fluoro-carbonates, **D** and **E**-mixed solutions showed the better thermal stability, i.e. provided their exothermic peaks at 300°C< and 296°C, respectively. However, thermal stability of **F**-mixed solution is slightly inferior, i.e. an exothermic peak was situated at 279°C. Fluoro-carbonates, **I-III**-mixed solutions demonstrated the higher thermal stability than 0.67 mol/L LiClO₄-EC/DEC/PC. Exothermic peaks were observed at 301°C, 310°C< and 300°C for fluoro-carbonates, **I**, **II** and **III**, respectively. DSC measurement showed that fluoro-carbonates, **I**, **II** and **III** are good candidates as nonflammable solvents for lithium ion batteries.

3.3. Electrochemical oxidation of fluorine compound-mixed electrolyte solutions.

Fig. 3 shows oxidation currents for 0.67 mol/L LiClO₄–EC/DEC/PC and EC/DEC/PC/OFC. No oxidation current was observed until 6.0 V vs Li/Li⁺. After 6 V, the larger oxidation currents flowed in 0.67 mol/L LiClO₄–EC/DEC/PC than in fluorine compound-mixed solutions. In particular, oxidation current abruptly increased at 7.3 V in 0.67 mol/L LiClO₄–EC/DEC/PC. Much smaller oxidation currents were observed in fluoro-ethers, **A** and **B**-mixed solutions, which shows that fluoro-ethers, **A** and **B** have high stability against electrochemical oxidation. Fluoro-carbonates, **D** and **F**-mixed

solutions also showed high oxidation stability. Oxidation currents observed in fluoro-ester, **C** and fluoro-carbonate, **E**-mixed solutions were relatively larger than in other fluorine compound-mixed ones, abruptly increasing at 7.3 V Li/Li⁺. Electron-withdrawing CF₂H group is directly bonded to ester group, −C=O(O)− in fluoro-ester, **C**, and two CF₃ groups are bonded to carbonate group, −OC=O(O)− from both sides in fluoro-carbonate, **E**. These structures probably weaken the chemical bonds, compared with other compounds.
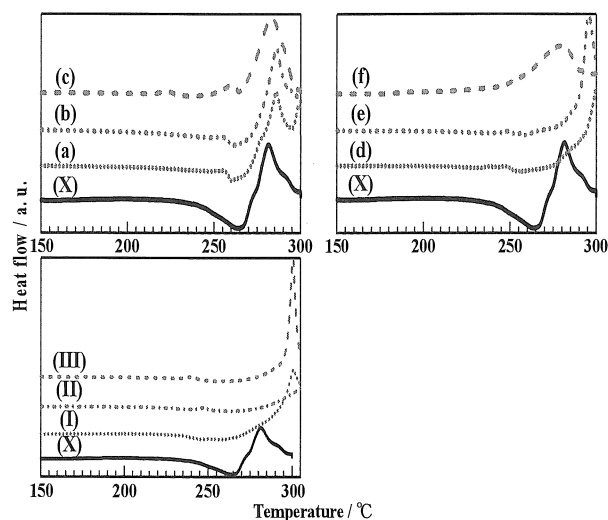

Fig. 2 DSC profiles for mixtures of 0.67 mol/L LiClO₄ - EC/DEC/PC (1:1:1 vol.) or EC/DEC/PC/(**A**, **B**, **C**, **D**, **E**, **F**, **I**, **II** or **III**) (1:1:1:1.5 vol.) and NG15 μm. (X): EC/DEC/PC, (a): EC/DEC/PC/**A**, (b): EC/DEC/PC/**B**, (c): EC/DEC/PC/**C**, (d): EC/DEC/PC/**D**, (e): EC/DEC/PC/**E**, (f): EC/DEC/PC/**F**, (I): EC/DEC/PC/**I**, (II): EC/DEC/PC/**II**, (III): EC/DEC/PC/**III**.
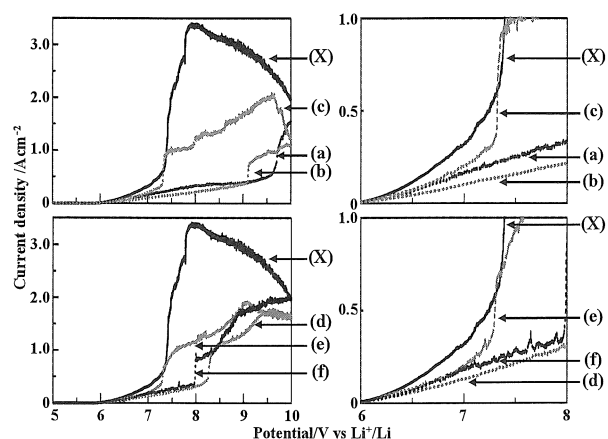

Fig. 3 Linear sweep voltammograms in 0.67 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/OFC (1:1:1:1.5 vol.). (X): EC/DEC/PC, (a): EC/DEC/PC/**A**, (b): EC/DEC/PC/**B**, (c): EC/DEC/PC/**C**, (d): EC/DEC/PC/**D**, (e): EC/DEC/PC/**E**, (f): EC/DEC/PC/**F**.

3.4. Electrochemical reduction of fluorine compound-mixed electrolyte solutions.

Fluorine substitution of organic compounds reduces LUMO levels, i.e. elevates their reduction potentials. Cyclic voltammograms were obtained for 0.67 mol/L LiClO$_4$–EC/DEC/PC and EC/DEC/PC/**OFC**. Reduction currents started to flow at 2.1, 2.3, 2.6, 2.7, 2.7 and 2.4 V vs Li/Li$^+$ for 0.67 mol/L LiClO$_4$–EC/DEC/PC/**OFC**, respectively. Since electrochemical reduction of EC, DEC, and PC starts at 1.4, 1.3 and 1.0-1.6 V, respectively[36),37)], fluorine compounds, **A-F** electrochemically decompose at the higher potentials than those for EC, DEC and PC. Fluoro-ether, **A** is electrochemically stable and **B** is also stable at a higher potential than 1 V vs Li/Li$^+$, where only small reduction currents similar to that in 0.67 mol/L LiClO$_4$–EC/DEC/PC were observed. Fluoro-ester, **C** easily decomposed between 1.0 and 2.6 V, where the larger current flowed. Electrochemical reduction of linear fluoro-carbonates, **D** and **E** started both at 2.7 V, however, the reduction currents were smaller than **C** between 1.0 and 2.7 V. On the other hand, cyclic fluoro-carbonate, **F** had a reduction current peak at 1.2 V. The reduction potentials obtained by cyclic voltammetry are not proportional to the LUMO energies in their order probably because the fluorine compounds are of different type in their structures. Decrease in HOMO/LUMO levels by fluorine substitution of organic compounds qualitatively shows the increase in oxidation stability and reduction potentials.

3.5. Charge/discharge characteristics of NG samples in fluorine compound-mixed electrolyte solutions.

First charge/discharge curves shown in Fig. 4 clearly indicate that potential plateaus at 0.8 V due to the electrochemical reduction of PC were reduced and the electrode potentials were quickly lowered, approaching that of lithium-intercalated graphite by mixing of fluorine compounds with 0.67 mol/L LiClO$_4$–EC/DEC/PC, which suggests that the fluorine compounds electrochemically decompose prior to the decomposition of PC and facilitate SEI formation. Fluoro-ethers, **A** and **B**, and fluoro-carbonates, **E** and **F** were quite effective for the quick formation of SEI on graphite electrodes. In the electrolyte solutions containing the fluorine compounds, **A**, **B**, **E** and **F**, first coulombic efficiencies increased by 17-31% as summarized in Table 1. Even in the solutions with fluorine compounds, **C** and **D**, first coulombic efficiencies increased by 6-16%. It was also shown that first discharge capacities were largely reduced by mixing of fluorine compounds. The decrements of first discharge capacities were
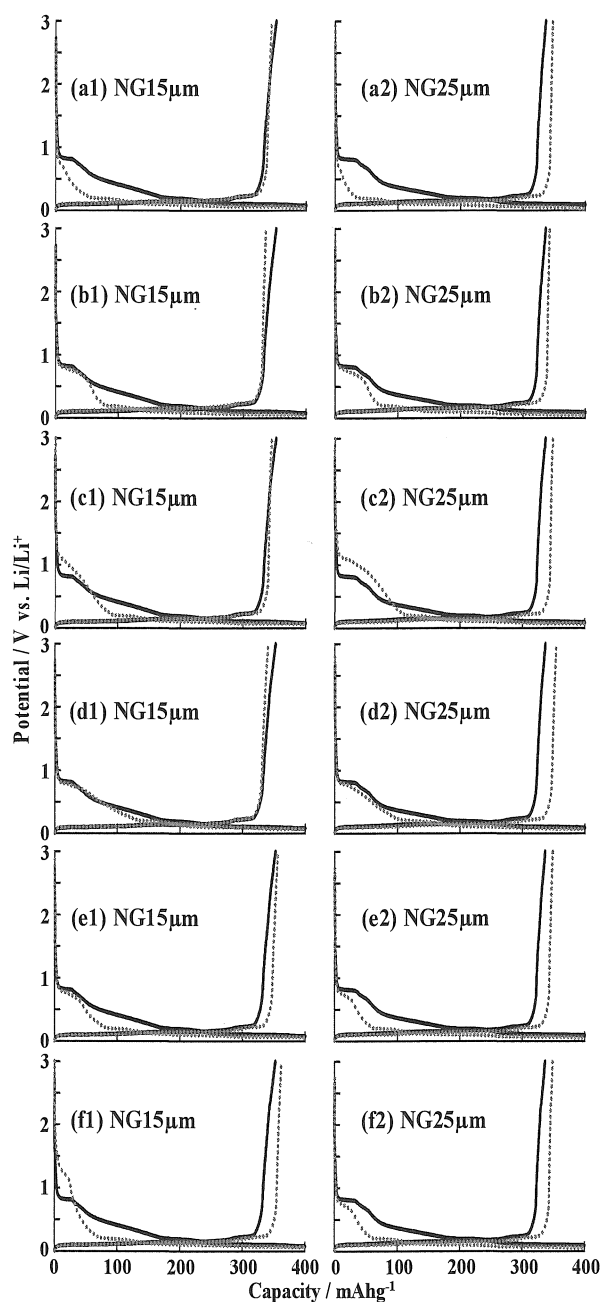

Fig. 4 First charge/discharge potential curves for natural graphite samples in 0.67 mol/L LiClO$_4$–EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/**OFC** (1:1:1:1.5 vol.).
(a1), (a2): EC/DEC/PC/**A**, (b1), (b2): EC/DEC/PC/**B**, (c1), (c2): EC/DEC/PC/**C**, (d1), (d2): EC/DEC/PC/**D**, (e1), (e2): EC/DEC/PC/**E**, (f1), (f2): EC/DEC/PC/**F**.
——: EC/DEC/PC, ··········: EC/DEC/PC/**OFC**.

79-180 and 105-215 mAh/g for NG15 μm and NG25 μm, respectively, which is the main reason for the increase in first coulombic efficiencies. Thus fluorine compounds decompose at the higher potentials than PC, EC and DEC, contributing to the formation of SEI on graphite. The charge capacities for NG15

μm were similar to each other in the solutions with and without fluorine compounds. Those for NG25 μm were slightly increased by mixing of fluorine compounds. This is consistent with the previous results that the charge capacities of graphite was significantly increased by the addition of organo-fluorine compounds at low temperatures (0, −5°C and −10°C)[35]. Fluorine-containing chemical species may be incorporated in the SEI by the reduction of fluorine compounds. Diffusion of Li$^+$ ion may be facilitated in SEI containing fluorine species because surface free energies of organo-fluorine compounds with C-F covalent bonds are low. Since surface area of NG25 μm is smaller than that of NG15 μm, actual current density would be larger for NG25 μm than NG15 μm. The higher kinetics for NG25 μm may have increased the first charge capacities. Charge capacities and coulombic efficiencies for NG15 μm are shown in Fig. 5 as a function of cycle number. Cycleability for NG samples was good and coulombic efficiencies quickly approached 100% after first cycle. Coulombic efficiencies obtained in 0.67 mol/L LiClO$_4$-EC/DEC/PC/**OFC** were higher than those in 0.67 mol/L LiClO$_4$–EC/DEC/PC even after first cycle except the data obtained for NG15 μm in 0.67 mol/L LiClO$_4$–EC/DEC/PC/**F**, in which coulombic efficiencies were the same as those in 0.67 mol/L LiClO$_4$–EC/DEC/PC. The results revealed that the fluorine compounds examined in the study contributed to quick formation of SEI on natural graphite electrodes, increasing first coulombic efficiencies. Taking the thermal and electrochemical oxidation stability into account, good candidates as nonflammable solvents for lithium ion batteries are fluoro-ethers, **A** and **B**, and fluoro-carbonates, **D**, **E**, **I**, **II** and **III** (see ref. 34 on the electrochemical oxidation stability and charge/discharge characteristics of fluoro-carbonate, **I**, **II** or **III**-mixed electrolyte solutions).

Table 1 First coulombic efficiencies for natural graphite electrodes in 0.67 mol/L LiClO$_4$ – EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/**OFC** (1:1:1:1.5 vol.).

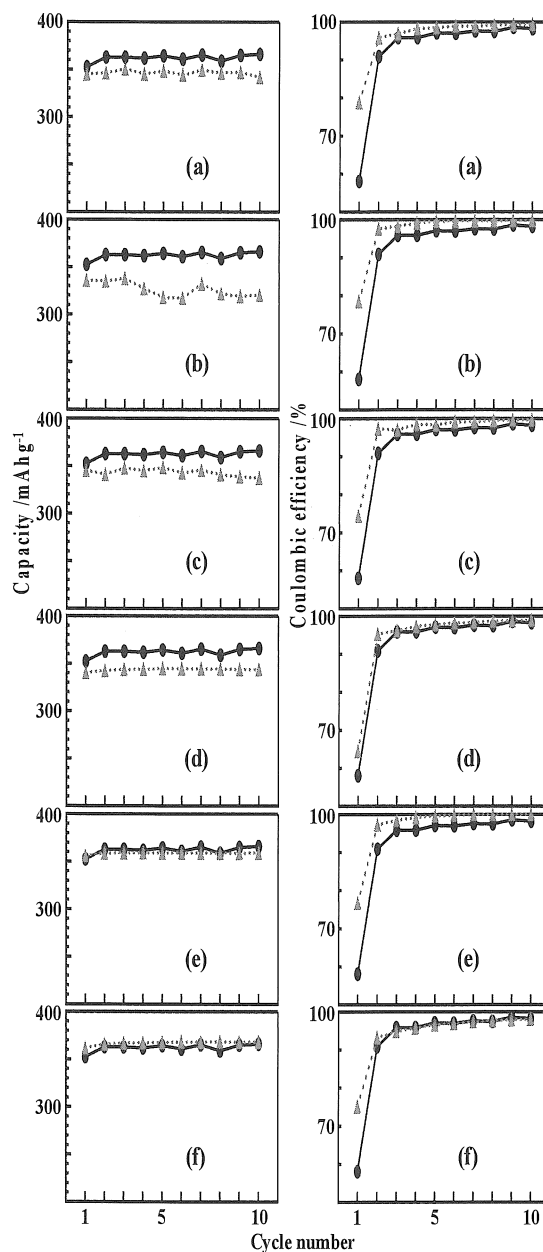| Electrolyte solution	First coulombic efficiency (%)	
	NG15 μm	NG25 μm
EC/DEC/PC	58.0	54.1
EC/DEC/PC/**A**	78.8	85.4
EC/DEC/PC/**B**	78.5	79.3
EC/DEC/PC/**C**	74.4	69.7
EC/DEC/PC/**D**	64.4	68.4
EC/DEC/PC/**E**	76.7	80.8
EC/DEC/PC/**F**	75.1	78.7

Fig. 5 Charge capacities and coulombic efficiencies for NG15 μm in 0.67 mol/L LiClO$_4$–EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/**OFC** (1:1:1:1.5 vol.).
(a): EC/DEC/PC/**A**, (b): EC/DEC/PC/**B**, (c): EC/DEC/PC/**C**,
(d): EC/DEC/PC/**D**, (e): EC/DEC/PC/**E**, (f): EC/DEC/PC/**F**.
——•——: EC/DEC/PC, ········ ▲ ········: EC/DEC/PC /**OFC**.

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