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Electrochemical Properties of Nonflammable Organo-Fluorine Compounds for Lithium Ion Batteries

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Abstract Electrochemical behavior of organo-fluorine compounds with high oxidation stability has been investigated. Oxidation currents of fluorine compound-containing EC/DEC solutions were much smaller than those of EC/DEC and EC/DEC/PC at the higher potentials than 6 V vs Li/Li$^+$. Electrochemical reduction of fluorine compounds started at ca. 2 V vs Li/Li$^+$ higher than those for EC, DEC and PC. However, first coulombic efficiencies for natural graphite electrodes in fluorine compound-containing EC/DEC mixtures were nearly the same as those in EC/DEC without increase in irreversible capacities. Furthermore first coulombic efficiencies in fluorine compound-containing EC/DEC/PC mixtures were much larger than those in EC/DEC/PC itself. The results show that the fluorine compounds used in the present study can be used as non-flammable solvents for lithium ion batteries.

1. Introduction

Lithium ion batteries are currently used as important electric sources for many electronic instruments such as computers, mobile phones, watches and so on. Recently the demand as electric sources for electric vehicles is rapidly increasing. Lithium ion batteries with high power densities are especially requested for this purpose. 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 differently from other secondary batteries with aqueous electrolyte solutions. The safety problem is one of the most important issues for the practical use of lithium ion batteries. To increase the thermal and oxidation stability of lithium ion batteries, new additives or solvents have been investigated1)-23). Most of them are phosphorus compounds (phosphates) having flame retardant properties. It was shown that the phosphorus compounds improved thermal stability of lithium ion batteries. However, battery performance was lowered in most of the cases.

In addition to phosphorus compounds, organo-fluorine compounds have high stability against oxidation because introduction of fluorine atoms into organic compounds reduces HOMO/LUMO energies. Decrease in HOMO energies gives high anti-oxidation ability to organo-fluorine compounds. Therefore organo-fluorine compounds are different type candidates as flame retardant solvents for lithium ion batteries. However, the decrease in LUMO energies due to introduction of fluorine atoms into organic compounds simultaneously elevates reduction potentials of organic compounds24), which facilitates electrochemical decomposition of fluorine compounds. If electrochemical reduction of fluorine compounds continues for a long time without forming protective surface film (Solid Electrolyte Interface: SEI) on carbonaceous anode, irreversible capacity unfortunately increases. However, if decomposed products quickly forms SEI, such fluorine compounds can be used as solvents. Another important problem is miscibility of fluorine compounds with polar solvents for lithium ion batteries such as EC (ethylene carbonate), PC (propylene carbonate), DEC (diethyl carbonate) and so on. In the present study, electrochemical redox reactions of fluorine compounds were investigated and charge/discharge characteristics of natural graphite electrodes were evaluated in fluorine compound-containing solvents for the application of organo-fluorine compounds to flame retardant solvents for lithium ion batteries.

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2. Experimantal

Natural graphite powder samples (purity: >99.95%) with average particle sizes of 5, 10, 15, 25 and 40 μm (abbreviated to NG5μm, NG10μm, NG15μm, NG25μm and NG40μm) were used for cyclic voltammetry and charge/discharge cycling. The d_{002} values obtained by X-ray diffractometry were 0.3355, 0.3354, 0.3355, 0.3358 and 0.3358 nm for NG5μm, NG10μm, NG15μm, NG25μm and NG40μm, respectively. Surface structure of natural graphite samples were investigated by BET surface area measurement and Raman spectroscopy with Nd:YVO_4 laser (532 nm).

The following fluorine compounds with carbonate structures (purity: 99.9%, H_2O<10 ppm), synthesized in Daikin Industries, Ltd., were used in the present study.

A: 4-(2,2,3,3-Tetrafluoropropoxymethyl)-[1,3]dioxolan-2-one
B: 4-(2,3,3,3-Tetrafluoro-2-trifluoromethyl-propyl)-[1,3] dioxolan-2-one
C: Bis-(2,2,3,3-tetrafluoro-propyl) carbonate
D: Bis-(2,2,3,3,3-pentafluoro-propyl) carbonate

HOMO and LUMO energies of fluorine compounds **A**, **B**, **C** and **D** were calculated by Spartan'06 semi-empirical method using AM1, being compared with those for the same type compounds consisting of C, H and O (**A**-H, **B**-H, **C**-H and **D**-H).

Oxidation currents for 0.67 mol/ℓ $LiClO_4$ – EC/DEC (1:1 by volume), EC/DEC/PC (1:1:1 by volume) and EC/DEC/(**A**, **B** or **C**) (1:1:1 by volume) 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 were used for cyclic voltammetry study and galvanostatic charge/discharge experiments. Electrolyte solutions were prepared by mixing the fluorine compound **A**, **B**, **C** or **D** with 1 mol/ℓ $LiClO_4$ – EC/DEC (1:1 by volume) and/or 1 mol/ℓ $LiClO_4$ – EC/DEC/PC (1:1:1 by volume). Fluorine compounds **A**, **B** and **C** are mixed with EC/DEC and EC/DEC/PC in whole range of composition at room temperature while the solubility of **D** is ca. 10 vol% in both solvent mixtures. For cyclic voltammetry study, 0.5 mol/ℓ $LiClO_4$ – EC/DEC/(**A**, **B** or **C**) (1:1:2 by volume) and 0.91 mol/ℓ $LiClO_4$ – EC/DEC/**D** (1:1:0.2 by volume) were used. Cyclic voltammograms were obtained using NG5μm at a scan rate of 0.1 mV/s for EC/DEC/(**A**, **B** or **C**) and 1.0 mV/s for EC/DEC/**D**. For galvanostatic charge/discharge experiments, the mixing ratios of solvents were 1:1:1 by volume in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/(**A**, **B** or **C**) and 1:1:1:1.5 by volume in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC/(**A**, **B** or **C**). Galvanostatic charge/discharge cyclings were performed at a current density of 60 mA/g between 0 and 3 V relative to the Li/Li^+ reference electrode in a glove box filled with Ar at 25°C.

3. Results and discussion

3.1. Surface structure of natural graphite samples

Surface areas were 13.9, 9.2, 6.9, 3.7 and 3.2 m^2/g for NG5μm, NG10μm, NG15μm, NG25μm and NG40μm, respectively. Change in the pore volume has the same trend. In mesopore size distributions, NG5μm, NG10μm and NG15μm have the larger peaks at a diameter of 2.3 nm while NG25μm and NG40μm show the smaller peaks at a diameter of 2.0 nm. Raman spectra of five natural graphite samples had strong G-bands (1580 cm^{-1}) and very weak D-bands (1360 cm^{-1}). The peak intensity ratio of D-band to G-band is defined as R value ($=I_D/I_G$) indicating the degree of surface disorder of carbon materials. R values of five natural graphite samples were in the range of 0.23 to 0.27, which shows that surface disorder of five samples is similar to each other.

3.2. HOMO and LUMO energies of fluorine compounds

Substitution of fluorine for hydrogen increases anti-oxidation ability of organic compounds. HOMO energies are the lower in fluorine compounds **A**, **B**, **C** and **D** than **A**-H, **B**-H, **C**-H and **D**-H, respectively. It suggests that fluorine compounds **A**, **B**, **C** and **D** are stronger against electrochemical oxidation than **A**-H, **B**-H, **C**-H and **D**-H, respectively. However, LUMO energies are simultaneously decreased by fluorine introduction into organic compounds. It also suggests that the compounds **A**, **B**, **C** and **D** are electrochemically reduced at higher potentials than **A**-H, **B**-H, **C**-H and **D**-H, respectively.

3.3. *Electrochemical oxidation of fluorine compounds*

Fig. 1 shows oxidation currents measured for 0.67 mol/ℓ $LiClO_4$ – EC/DEC, EC/DEC/PC and EC/DEC/(**A**, **B** or **C**) solutions. Oxidative decomposition started at ca. 6 V vs Li/Li^+ for all solutions. Gas evolution was also observed above 6 V. However, the oxidation currents were much smaller in EC/DEC/(**A**, **B** or **C**) than in both EC/DEC and EC/DEC/PC at the higher potentials than 6 V. The decrease in the oxidation currents by mixing of fluorine compounds with EC/DEC was much larger than the mixing ratio of fluorine compounds, i.e. 33.3 vol%, which would have been caused by decrease in the electrode area due to adsorption of stable fluorine compounds on Pt electrode surface. Thus the mixing of organo-fluorine compounds with EC/DEC highly increases oxidation stability of electrolyte solutions.

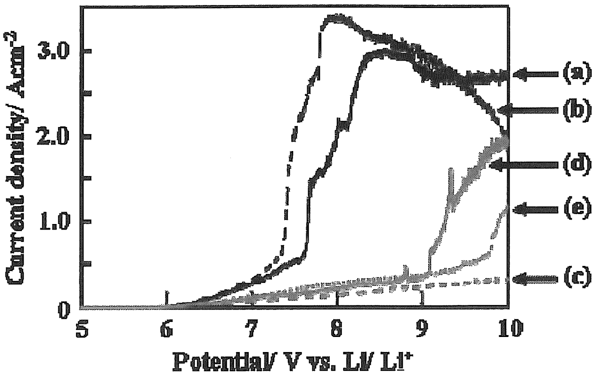


Fig. 1 Linear sweep voltammograms for Pt wire electrode in 0.67 mol/ℓ $LiClO_4$ – EC/DEC (1:1 vol), EC/DEC/PC (1:1:1 vol) and EC/DEC/(**A**, **B** or **C**) (1:1:1 vol).
(a) EC/DEC, (b) EC/DEC/PC, (c) EC/DEC/**A**, (d) EC/DEC/**B**, (e) EC/DEC/**C**.

3.4. *Electrochemical reduction of fluorine compounds*

Cyclic voltammograms obtained in fluorine compound-containing solvents show the large reduction currents indicating the decomposition of fluorine compounds **A**, **B** and **C** while the reduction current for **D** was very small because of its low solubility in EC/DEC. The electrochemical reduction of **A**, **B**, **C** and **D** started at 2.0, 2.2, 1.9 and 2.3 V and their reduction current peaks were observed at 1.0, 1.1, 0.55 and 2.1 V vs Li/Li$^+$, respectively. The reduction current increased in the order of **A**, **B** and **C** (**A**<**B**<**C**). On the other hand, the reduction current peak for EC was located at 0.68 V as usual. Since the reduction of EC, DEC and PC starts at 1.4, 1.3 and 1.0-1.6 V[25), 26)], respectively, all fluorine compounds used in the present study are reduced at the higher potentials than EC, DEC and PC as suggested by molecular orbital calculation.

3.5. *Charge/discharge behavior of natural graphite samples in fluorine compound-containing solvents*

In 0.67 mol/ℓ $LiClO_4$ – EC/DEC and EC/DEC/(**A**, **B** or **C**) solutions, charge/discharge capacities and coulombic efficiencies at 1st cycle were similar to each other. Charge capacities at 1st cycle were in the range of 358-329 mAh/g in both EC/DEC and EC/DEC/(**A**, **B** or **C**), slightly decreasing from NG5μm to NG40μm, i.e. with increasing average particle size. First coulombic efficiency increased from 75.1% (NG5μm) to 85.7% (NG40μm) with decreasing surface area of natural graphite though the actual current density increases with decreasing surface area. It means that SEI is quickly formed on natural graphite powder by the decomposition of EC and fluorine compound **A**, **B** or **C**. In EC/DEC/(**A**, **B** or **C**), first coulombic efficiencies were in the range of 76.3-87.1%, 74.4-88.4% and 72.3-87.5%, respectively, also increasing from NG5μm to NG40μm. In the case of NG15μm, first coulombic efficiencies slightly increased by the addition of **B** and **C** to EC/DEC. The results show that fluorine compounds **A**, **B** and **C** well contribute to the SEI formation without increase in irreversible capacity. First charge capacities somewhat decreased with increasing average particle size of natural graphite probably due to the slow Li diffusion in graphene layers.

Table 1 First coulombic efficiencies for natural graphite samples in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC (X) and EC/DEC/PC/(**A**, **B** or **C**).

Graphite	First coulombic efficiency (%)			
	X	X/A	X/**B**	X/C
NG5μm	72.1	71.7	72.4	73.0
NG10μm	61.9	69.8	77.8	65.1
NG15μm	58.0	69.4	81.6	63.0
NG25μm	54.1	75.7	82.0	80.3
NG40μm	54.3	69.6	87.7	78.3

SEI formation on high crystalline natural graphite is slow in PC-containing solvents, which normally causes large increase in irreversible capacity. In fact, first coulombic efficiency decreased from 72.1% (NG5μm) to 54.3% (NG40μm) with decreasing surface area, i.e. with increasing actual current density in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC. However, discharge capacities at 1st cycle were decreased by addition of the fluorine compounds to EC/DEC/PC except NG5μm. The decrease in first discharge capacities for NG10μm, NG15μm, NG25μm and NG40μm were in the range of 76-127 mAh/g, 93-220 mAh/g and 42-188 mAh/g in EC/DEC/PC/(**A**, **B** or **C**), respectively, increasing from NG10μm to NG40μm. On the other hand, charge capacities were similar to each other in both EC/DEC/PC and EC/DEC/PC/(**A**, **B** or **C**) in most of the cases (charge capacities: 349-314 mAh/g in EC/DEC/PC; 350-314 mAh/g in EC/DEC/PC/**A**; 347-317 mAh/g in EC/DEC/PC/**B**; 354-331 mAh/g in EC/DEC/PC/**C**). Consequently first coulombic efficiencies were increased by mixing of fluorine compounds with EC/DEC/PC except NG5μm as shown in **Table 1**. Addition of fluorine compounds was not effective for increasing first coulombic efficiencies of NG5μm probably because of its large surface area where actual current density was relatively small. Nevertheless, the results clearly show that the fluorine compounds **A**, **B** and **C** can be used as solvents for all natural graphite samples including NG5μm because no increase in irreversible capacity was observed. The increase in first coulombic efficiency by mixing of fluorine compound was larger as the surface area of natural graphite decreased, i.e. from NG10μm to NG40μm, which suggests that high values of first coulombic efficiencies can be obtained also at high current densities. These results mean that addition of **A**, **B** and **C** to EC/DEC/PC mixture highly facilitates SEI formation on natural graphite electrodes of NG10μm – NG40μm. Among three fluorine compounds examined, **B** was the best for increasing first coulombic efficiencies of natural graphite electrodes. The same phenomena are also seen in first charge/discharge potential curves obtained in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC and EC/DEC/PC/(**A**, **B** or **C**) solutions (**Fig. 2**). In 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC, potential plateaus indicating the electrochemical reduction of PC are observed at 0.8 V. The potential plateau became longer with decreasing surface area from NG5μm to NG40μm, being consistent with decrease in first coulombic efficiency. The potential plateaus showing the reduction of PC almost disappeared by mixing of fluorine compounds **A**, **B** or **C** with EC/DEC/PC except NG5μm as shown in **Fig. 2**. In the case of NG5μm, no change in the potential curves was observed by the addition of fluorine compounds. **Fig. 3** shows charge capacities and coulombic efficiencies as a function of cycle number, obtained in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC/(**B**). Cyclability was good in all cases and coulombic efficiencies approached 100% after several cycles. First coulombic efficiencies were increased by addition of fluorine compounds **A**, **B** and **C** to EC/DEC/PC except for NG5μm. This trend was more evident with increasing average particle size of natural graphite. Even after 1st cycle, coulombic efficiencies were higher in EC/DEC/PC/(**A**, **B** or **C**) solutions than in EC/DEC/PC itself in many cases. In the case of NG10μm and NG15μm, the charge capacities were slightly lower in EC/DEC/PC/(**A**, **B** or **C**) solutions than in EC/DEC/PC in most of the cases, which could be due to increase in the resistances of SEI films containing fluorine groups because SEI resistance was increased by the introduction of fluorine groups into SEI while charge transfer resistance was reduced27). The results obtained show that mixing of fluorine compounds **A**, **B** and **C** with EC/DEC/PC not only improves oxidation stability of electrolyte solutions but also increases first coulombic efficiencies, i.e. reduces irreversible capacities.

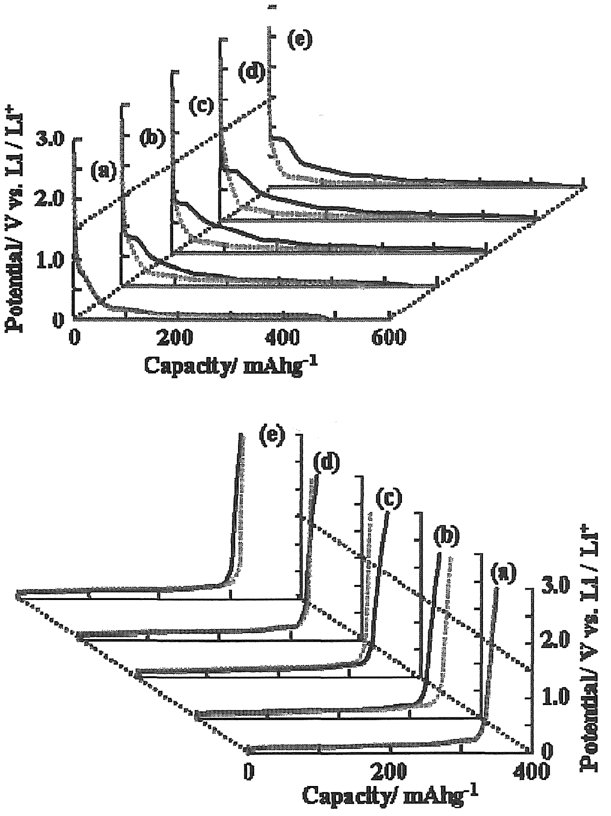
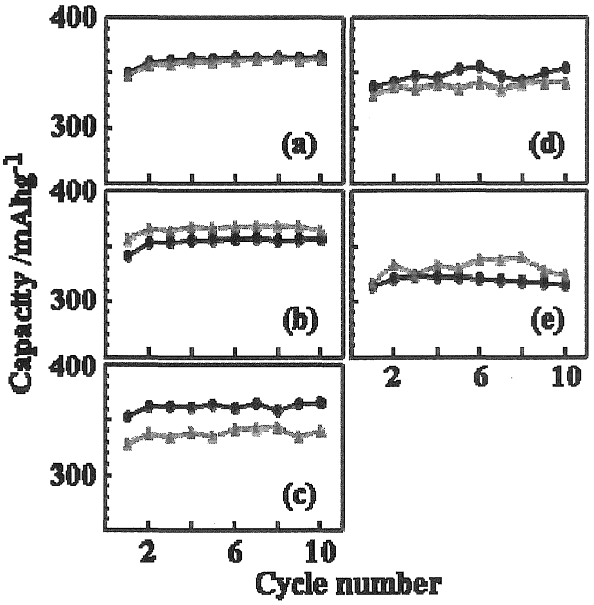


Fig. 2 First charge/discharge potential curves for natural graphite samples in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC (1:1:1 vol) and EC/DEC/PC/(**A**, **B** or **C**) (1:1:1:1.5 vol).

(a) NG5μm, (b) NG10μm, (c) NG15μm, (d) NG25μm, (e) NG40μm.

——: EC/DEC/PC, ············: EC/DEC/PC/(**A**, **B** or **C**).



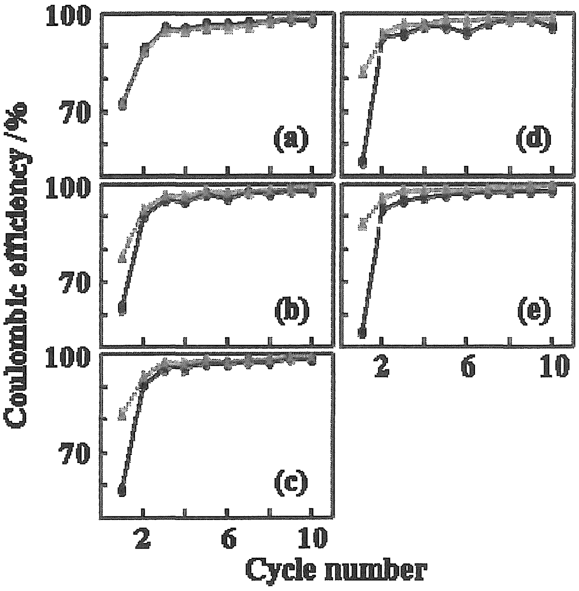


Fig. 3 Charge capacities and coulombic efficiencies for natural graphite samples in 0.67 mol/ℓ $LiClO_4$ – EC/DEC/PC (1:1:1 vol) and EC/DEC/PC/**B** (1:1:1:1.5 vol).

(a) NG5μm, (b) NG10μm, (c) NG15μm, (d) NG25μm, (e) NG40μm.

——•——: EC/DEC/PC, ········▲········: EC/DEC/PC/**B**.

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