

Safety Improvement of Lithium Ion Batteries by Fluorine Compounds

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Abstract Thermal stability, electrochemical oxidation stability and charge/discharge characteristics of natural graphite powder were investigated by mixing of five fluoro-carbonates with 1 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.). DSC study revealed that thermal stability of the electrolyte solution was improved by mixing of fluoro-carbonates by 10.0-33.3 vol.%. Electrochemical oxidation stability was also improved. Oxidation currents for Pt electrode were significantly decreased by mixing of fluoro-carbonates. In the fluoro-carbonate-mixed electrolyte solutions, electrochemical reduction of PC decreased with increasing concentration of fluoro-carbonate and current density. As a result, first coulombic efficiency for natural graphite electrode increased, that is, irreversible capacity decreased in the fluoro-carbonate-mixed solutions.

1. Introduction

Lithium ion batteries have a possibility of firing and/or explosion at high temperatures, by short circuit, by overcharging and so on since they employ flammable organic solvents. High oxidation stability of lithium ion batteries is one of the most important issues for their application to hybrid cars and electric vehicles. In order to improve the oxidation stability of lithium ion batteries, new additives or solvents for electrolyte solutions have been investigated [1-44]. Phosphorus compounds were mainly examined as flame retardant additives. Thermal stability and electrochemical properties were investigated in detail for various phosphorus compounds. Our recent study revealed that fluoro-carbonates and fluoro-ethers are able to be used as nonflammable solvents for lithium ion batteries [39, 40]. Fluorine substitution of organic compounds improves their oxidation stability [39, 40, 44]. However, the fluorine substitution simultaneously increases reduction potentials of organic compounds, i.e. causes electrochemical decomposition at higher potentials than those for organic solvents such as EC (ethylene carbonate), PC (propylene carbonate), DEC (diethyl carbonate) etc. [39, 40]. If electrochemical reduction of organo-fluorine compounds continues without forming a protective surface film (Solid

Electrolyte Interphase or Interface: SEI) on carbon anode, irreversible capacity highly increases. However, if decomposed products quickly form SEI on carbon electrode, such fluorine compounds can be used as nonflammable solvents for lithium ion batteries. Mixing of fluoro-carbonates with 1 mol/L LiClO₄-EC/DEC significantly improved the oxidation stability without decrease in charge capacities and first coulombic efficiencies for natural graphite (NG) electrodes [39]. The results show that many fluorine compounds with high oxidation stability can be used for EC-based solvents such as EC/DEC as nonflammable solvents [39]. However, it is difficult to use high crystalline graphite such as natural graphite in PC-mixed electrolyte solutions due to the continuous decomposition of PC. EC with a high melting point, 36°C should be used for such high crystalline graphite electrode for the quick formation of SEI. Therefore if PC with a low melting point, -55°C can be used for graphite, lithium ion batteries are used in a wide range of temperature. For example, the melting points of 1 mol/L LiClO₄-EC/DEC (1:1 vol.) and EC/DEC/PC (1:1:1 vol.) are -1°C and -31°C, respectively [40]. It was found in a previous study that mixing of cyclic and linear fluoro-carbonates with 1 mol/L LiClO₄-EC/DEC/PC highly increased not only oxidation stability of electrolyte solutions but also first coulombic efficiencies for natural graphite electrodes [39]. This result indicates that electrochemically reduced fluoro-carbonates quickly form SEI on graphite electrode. It is therefore an additional advantage for organo-fluorine compounds that the fluoro-carbonates enable the use of PC-containing solvents for graphite electrode.

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In the present study, thermal and electrochemical oxidation stability of fluoro-carbonate-mixed electrolyte solutions was investigated by differential scanning calorimetry (DSC) and oxidation current measurements, and charge/discharge characteristics of natural graphite electrode were evaluated using the same electrolyte solutions as functions of mixing ratio of fluoro-carbonates and current density.

2. Experimental

2.1 Fluorine compounds

Five fluoro-carbonates (purity: 99.9%, H₂O: <10 ppm), synthesized in Daikin Industries, Ltd., were used in the present study (Fig. 1). Viscosities and specific conductivities of fluorine compounds, A and C were 4.79 and 0.80 cP at 20°C, and 5.5×10^{-3} and 8.9×10^{-4} S/cm at room temperature, respectively. Those for EC/DEC were 0.50 cP at 20°C and 2.8×10^{-3} S/cm at room temperature.

2.2 Thermal stability by DSC measurements

Thermal stability of fluoro-carbonate-mixed electrolyte solutions was examined by differential scanning calorimetry (DSC-60, Shimadzu). DSC measurement was carried out using a mixture of 0.90, 0.78 or 0.67 mol/L LiClO₄-EC/DEC/PC (A, B, C, D, or E) (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) and lithiated or delithiated graphite (NG15 μm) between room temperature and 300°C at a temperature increasing rate of 5°C/min. Fully lithiated and delithiated graphite samples were electrochemically prepared after 3 cycles. Electrolyte solution (3 μL) and lithiated or delithiated graphite (0.8-1.0 mg) were sealed in an airtight Al cell to examine the thermal stability.

2.3 Electrochemical oxidation stability by oxidation current measurements

Oxidation currents for 0.90, 0.78 or 0.67 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and 0.90, 0.78 or 0.67 mol/L LiClO₄-EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) were measured by linear sweep of potential at 0.1 mV/s between 4 and 10 V vs Li/Li⁺ using Pt wire electrode (diameter: 0.3 mm, geometrical surface area: 0.22 cm²) (Hokuto Denko, HZ-5000). Counter and reference electrodes were lithium foil.

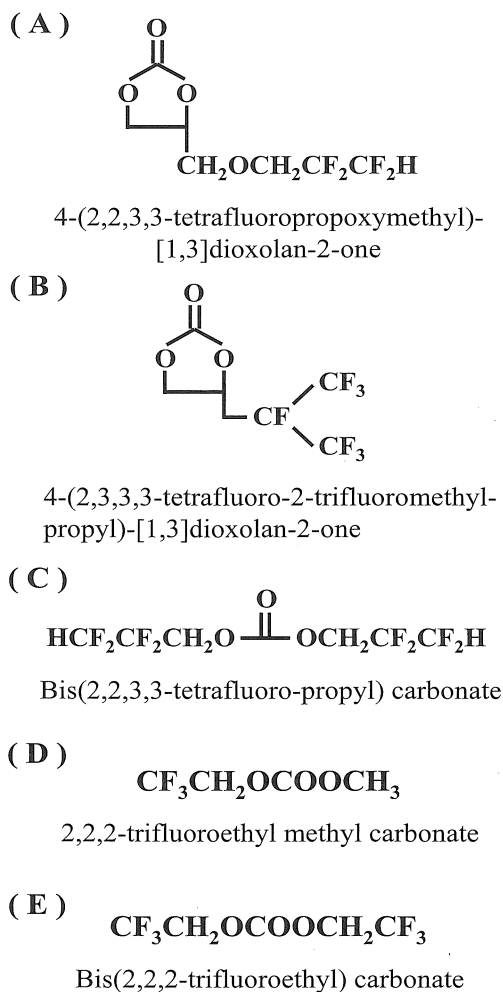


Fig. 1 Fluorine compounds used in the present study.

2.4 Charge/discharge characteristics for NG15 μm electrode in fluorine compound-containing electrolyte solutions

Natural graphite (purity: >99.95%) with average particle size of 15 μm (abbreviated to NG15 μm) was used as an electrode material. The d_{002} value obtained by X-ray diffractometry (XRD-6100, Shimadzu) was 0.3355 nm. Surface area and meso-pore volume obtained by BET surface area measurement (Tristar 3000, Shimadzu) were 6.9 m²/g, and 0.026 cm³/g. Peak intensity ratios of D-band to G-band ($R=I_D/I_G$) obtained by Raman spectroscopy (NRS-1000, Jasco) with Nd:YVO₄ laser (532 nm) was 0.25.

Three-electrode cell with natural graphite as a working electrode and lithium foil as counter and reference electrodes was used for 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 fluoro-carbonate with 1 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.). The fluoro-carbonates are miscible with 1 mol/L LiClO₄-EC/DEC and EC/DEC/PC in whole range of composition at room temperature. The 0.90, 0.78 or 0.67 mol/L LiClO₄-EC/DEC/PC/(A, B, C, D, or E) (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) was used for galvanostatic charge/discharge experiments. Preparation of 1 mol/L LiClO₄-EC/DEC/PC/(A, B, C, D, or E) (1:1:1:1.5 vol., 33.3 vol.%) can be made at room temperature by dissolving LiClO₄ in 0.67 mol/L LiClO₄-EC/DEC/PC/(A, B, C, D, or E) (1:1:1:1.5 vol., 33.3 vol.%), respectively. However, the 0.90, 0.78 or 0.67 mol/L LiClO₄-EC/DEC/PC/(A, B, C, D, or E) (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) was used for charge/discharge cyclings to simplify the experiments. Galvanostatic charge/discharge cyclings were performed using NG15 μm at current densities of 60, 150 and 300 mA/g between 0 and 3 V relative to Li/Li⁺ reference electrode at 25°C (Hokuto Denko, HJ1001 SM8A).

3. Results and discussion

3.1 Thermal stability of fluorine compound-mixed electrolyte solutions

Thermal stability of fluoro-carbonate-mixed electrolyte solutions was evaluated by differential scanning calorimetry (DSC) under various conditions as a function of mixing ratio of fluoro-carbonate with 1 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.). **Fig. 2** shows DSC curves for the mixtures of 0.67, 0.78 or 0.90 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and delithiated graphite. Exothermic reactions started above 260°C. Exothermic peaks were found at 280°C, 289°C and >300°C, increasing with decreasing concentration of LiClO₄ from 0.90 to 0.67 mol/L, which suggests that the exothermic reactions are caused by decomposition of not only organic solvents and SEI but also LiClO₄. Mixtures of fluoro-carbonate-mixed solution (33.3 vol.%) and delithiated graphite showed the similar exothermic curves to those in **Fig. 2** though exothermic reactions started at slightly lower temperatures between 250°C and 260°C (**Fig. 3**). No exothermic peaks were found below 250°C in both **Figs. 2** and **3**. Reactions of lithiated graphite with electrolyte solution and SEI are very important for the safety of lithium ion

batteries. **Fig. 4** shows DSC curves for lithiated graphite with SEI obtained after 3 cycles. DSC measurements were made using only lithiated graphite without electrolyte solution. Lithiated graphite obtained in 0.78 mol/L LiClO₄-EC/DEC/PC gave a weak exothermic peak at 128°C and another strong one at 164°C while only one exothermic peak was observed at 162°C for lithiated graphite prepared in 0.67 mol/L LiClO₄-EC/DEC/PC. These exothermic peaks would be due to the reaction of deintercalated lithium with SEI because lithiated graphite is decomposed by temperature increase to ~200°C [45-50]. It was reported that LiC₆ decomposes to LiC₁₂ by temperature increase to 120°C and Li-intercalated graphite completely decomposes at around 200°C [50]. The main reactions of deintercalated Li with main components of SEI were also reported: $2\text{Li} + (\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4$, $2\text{Li} + 2\text{CH}_3\text{OLi} \rightarrow 2\text{Li}_2\text{O} + \text{CH}_3\text{CH}_3$ [50]. Strong exothermic peaks shifted to higher temperatures than 162-164°C or almost disappeared for lithiated graphite samples (Li_{0.94-0.98}C₆) prepared in 0.78 mol/L LiClO₄-EC/DEC/PC/(A, B, C and D) (**Fig. 4(a)**), and for those (Li_{0.92-0.95}C₆) prepared in 0.67 mol/L LiClO₄-EC/DEC/PC/(A, B and C) (**Fig. 4(b)**), though exothermic peaks were observed at 130 and 137°C for the electrolyte solutions containing fluoro-carbonate B. Thus no significant difference was found between the reactions of deintercalated Li with surface films (Solid Electrolyte Interphase: SEI) prepared in the electrolyte solutions with and without fluorine compounds probably because main reactive species with Li in surface film (Solid Electrolyte Interphase: SEI) are lithium alkyl carbonates and lithium alkoxides such as ROCO₂Li and ROLi, respectively [50]. **Fig. 5** shows DSC curves obtained for mixtures of electrolyte solution and lithiated graphite. Mixtures of 0.90, 0.78 or 0.67 mol/L LiClO₄-EC/DEC/PC and lithiated graphite yielded three exothermic peaks at 148-153°C (medium peaks), 194-203°C (weak peaks) and 284-288°C (strong peaks). The medium and weak peaks at 148-153°C and 194-203°C, respectively, would be due to the reactions of deintercalated Li with SEI and electrolyte solutions. The medium peaks at 148-153°C may arise from the decomposition of LiC₆, and weak peaks at 194-203°C are probably due to the decomposition of high stage lithiated graphite as mentioned above [50]. The strong peaks at 284-288°C would be due to the decomposition of electrolyte solutions. Reactions of deintercalated Li with SEI and electrolyte solutions changed depending on the used fluoro-carbonates and their concentrations as shown in **Fig. 5**. With increase in the concentrations of fluoro-carbonates, exothermic peaks at around 150°C and 200°C disappeared or

shifted to higher temperatures. When fluoro-carbonates were mixed with 1 mol/L LiClO₄-EC/DEC/PC by 10.0 vol.% (Fig. 5(a)), fluoro-carbonate C gave the highest effect. The exothermic peak at 148°C disappeared by mixing of fluoro-carbonate C. A strong peak shifted to higher temperature in the solution with fluoro-carbonate D though the solution containing fluoro-carbonate B gave an exothermic peak at 124°C. When the amount of mixed fluoro-carbonate increased to 21.7 vol.%, improvement of thermal stability was clearly seen as shown in Fig. 5(b). The exothermic peaks due to the reaction with deintercalated Li were suppressed for the electrolyte solutions containing fluoro-carbonates B, C and D. In case of the solution with fluoro-carbonate A, the exothermic peak shifted to higher temperature, 167°C. However, very broad exothermic peak was observed in the electrolyte solution containing fluoro-carbonate E. Fig. 5(c) indicates DSC curves obtained when fluoro-carbonates were mixed with 1 mol/L LiClO₄-EC/DEC/PC by 33.3 vol.%. With mixing of fluoro-carbonate by 33.3 vol.%, the reaction of deintercalated lithium with SEI and electrolyte solution was more pronouncedly suppressed for the solutions containing fluoro-carbonates A, B, C and D. Even in case of the solution with fluoro-carbonate E, the exothermic peak shifted to 191°C. Exothermic peaks due to the decomposition of electrolyte solutions were observed between 278 and 296°C for the solutions with fluoro-carbonates A, C, D and E. It was above 300°C in the fluoro-carbonate B-mixed electrolyte solutions. Thus five fluoro-carbonates used in the study improve the thermal stability of electrolyte solution. The amounts of fluoro-carbonates needed to suppress the reaction of deintercalated lithium with SEI and electrolyte solution are 10 vol.% for fluoro-carbonate C, 21.7 vol.% for fluoro-carbonates B and D, and 33.3 vol.% for fluoro-carbonates A and E. It was reported that reduction products in the SEI contain lithium alkyl carbonates (ROCO₂Li) and lithium alkoxides (ROLi) and Li₂CO₃ is formed by the reaction of deintercalated Li with (ROCO₂Li)₂ in SEI [50, 51]. Fluorine atoms with electron-withdrawing ability reduce electron densities of oxygen atoms in carbonate type fluorine compounds, which would suppress the reaction of Li with carbonates yielding lithium alkyl carbonates and lithium alkoxides. Fig. 4 clearly shows that the reactions of deintercalated Li with EC, DEC and PC and SEI are significantly reduced by coexistence of fluorine compounds.

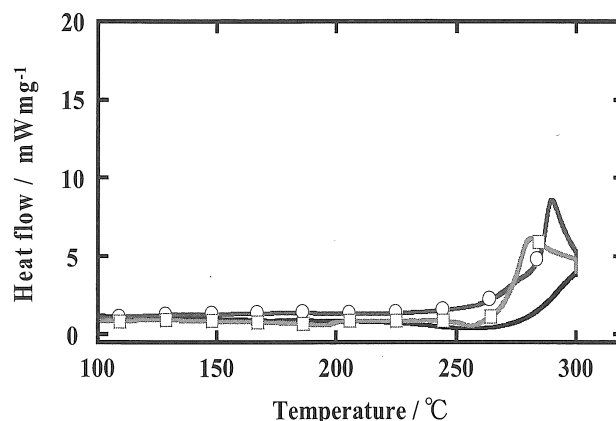


Fig. 2 DSC curves for 0.67, 0.78 and 0.90 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and delithiated graphite.
 — 0.67 mol/L —○— 0.78 mol/L —□— 0.90 mol/L

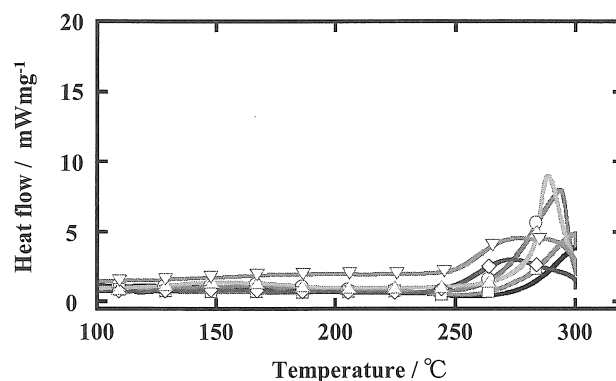


Fig. 3 DSC curves for 0.67 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) or 0.67 mol/L LiClO₄-EC/DEC/PC/(A, B, C, D or E) (1:1:1:1.5 vol., 33.3 vol.) and delithiated graphite.
 — EC/DEC/PC, —○— EC/DEC/PC/A, —□— EC/DEC/PC/B, —◇— EC/DEC/PC/C, —△— EC/DEC/PC/D, —▽— EC/DEC/PC/E

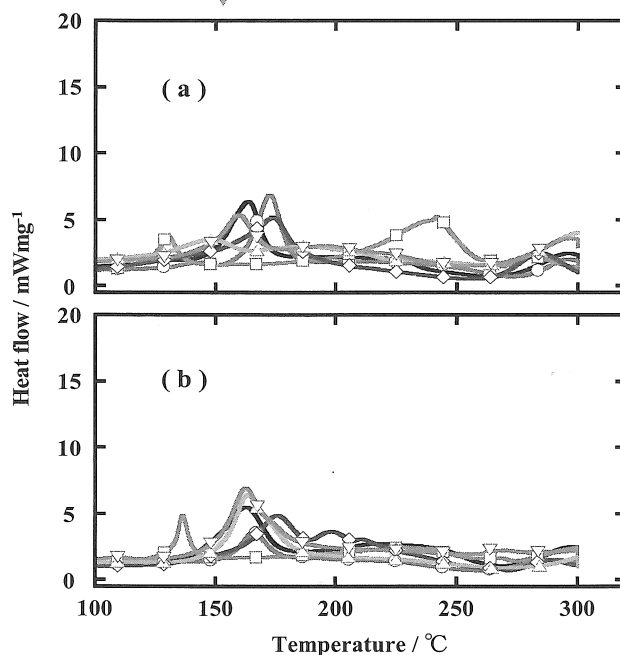


Fig. 4. DSC curves for lithiated graphite ($\text{Li}_{0.92-0.98}\text{C}_6$) with SEI film.

(a) $\text{Li}_{0.94-0.98}\text{C}_6$ prepared in 0.78 mol/L LiClO_4 -EC/DEC/PC (1:1:1 vol.) or EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.83 vol., 21.7 vol.%).

(b) $\text{Li}_{0.92-0.95}\text{C}_6$ prepared in 0.67 mol/L LiClO_4 -EC/DEC/PC (1:1:1 vol.) or EC/DEC/PC/(A, B, C, D or E) (1:1:1:1.5 vol., 33.3 vol.%).

— EC/DEC/PC, —○— EC/DEC/PC/A,
—□— EC/DEC/PC/B, —◇— EC/DEC/PC/C,
—△— EC/DEC/PC/D, —▽— EC/DEC/PC/E

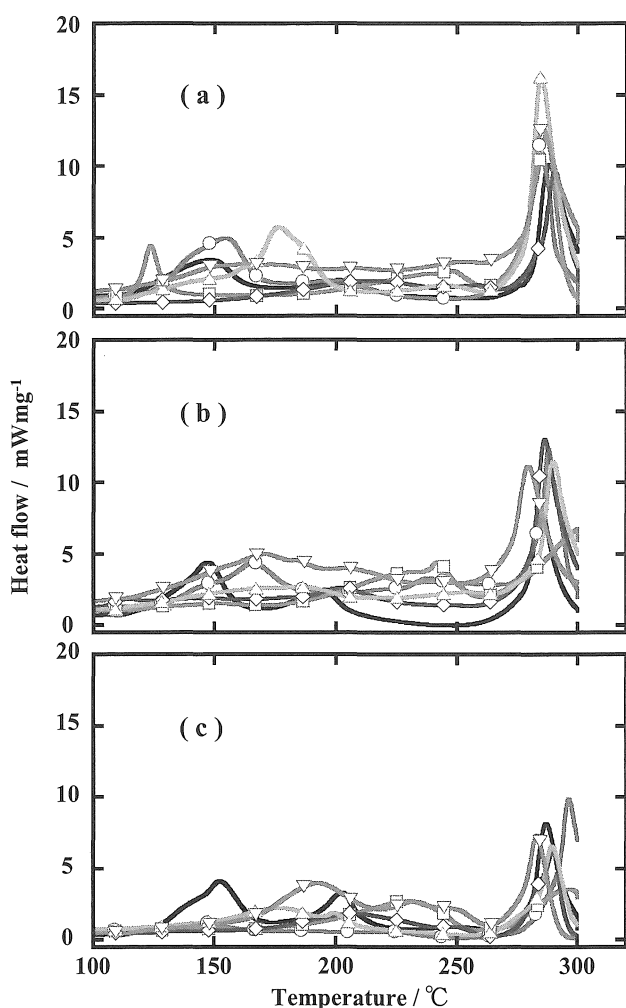


Fig. 5. DSC curves for mixtures of fluoro-carbonate containing electrolyte solution and lithiated graphite ($\text{Li}_{0.92-0.98}\text{C}_6$).

(a) 0.90 mol/L LiClO_4 -EC/DEC/PC (1:1:1 vol.) or EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.33 vol., 10.0 vol.%) and $\text{Li}_{0.96-0.98}\text{C}_6$.

(b) 0.78 mol/L LiClO_4 -EC/DEC/PC (1:1:1 vol.) or EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.83 vol., 21.7 vol.%) and $\text{Li}_{0.96-0.97}\text{C}_6$.

(c) 0.67 mol/L LiClO_4 -EC/DEC/PC (1:1:1 vol.) or

EC/DEC/PC/(A, B, C, D or E) (1:1:1:1.5 vol., 33.3 vol.%) and $\text{Li}_{0.92-0.96}\text{C}_6$.

— EC/DEC/PC, —○— EC/DEC/PC/A
—□— EC/DEC/PC/B, —◇— EC/DEC/PC/C,
—△— EC/DEC/PC/D, —▽— EC/DEC/PC/E

3.2 Electrochemical oxidation stability of fluorine compound-mixed electrolyte solutions

Electrochemical oxidation stability of electrolyte solutions was evaluated by oxidation current measurements as shown in **Fig. 6**. Small oxidation currents were observed from 5.8 V, increasing after 6.0 V vs. Li/Li^+ in the EC/DEC/PC solvents. Very small currents below 5.8 V were not detected probably because Pt wire electrode had a small surface area. Oxidation currents were significantly reduced with increase in the amounts of mixed fluoro-carbonates. In the electrolyte solutions containing fluoro-carbonates A, B and C by 21.7 and 33.3 vol.%, oxidation currents were much lower than those in EC/DEC/PC and the solutions containing fluoro-carbonates D and E. Reduction of oxidation currents may be caused due to decrease in surface area of Pt electrode by adsorption of stable fluorine compounds at high potentials. It has been found that mixing by 21.7 vol.% is enough for fluoro-carbonates A, B and C to reduce oxidation currents. However, mixing by 33.3 vol.% is necessary for fluoro-carbonates D and E. The results show that mixing of fluoro-carbonates well improves electrochemical oxidation stability of electrolyte solutions.

3.3 Charge/discharge characteristics of NG15 μm in fluorine compound-mixed electrolyte solutions

Charge/discharge characteristics of natural graphite electrode were investigated in low potential region because fluorine compounds generally show high oxidation stability but they are electrochemically reduced at higher potentials than EC, DEC, PC etc. It was already reported that electrochemical reduction of fluoro-carbonates start between 1.9 and 2.7 V vs Li/Li^+ [39, 40], which are higher potentials than those of EC (1.4 V), DEC (1.3 V) and PC (1.0-1.6 V) [52, 53]. As stated in the **Introduction**, EC-based solvents should be used for high crystalline graphite such as natural graphite to reduce irreversible capacity by the quick formation of SEI on the electrode. Many fluorine-containing compounds can be used for EC/DEC solvents because EC easily forms SEI on natural graphite electrodes [39]. Several examples are given in **Table 1**, which indicates that the first coulombic efficiencies obtained in

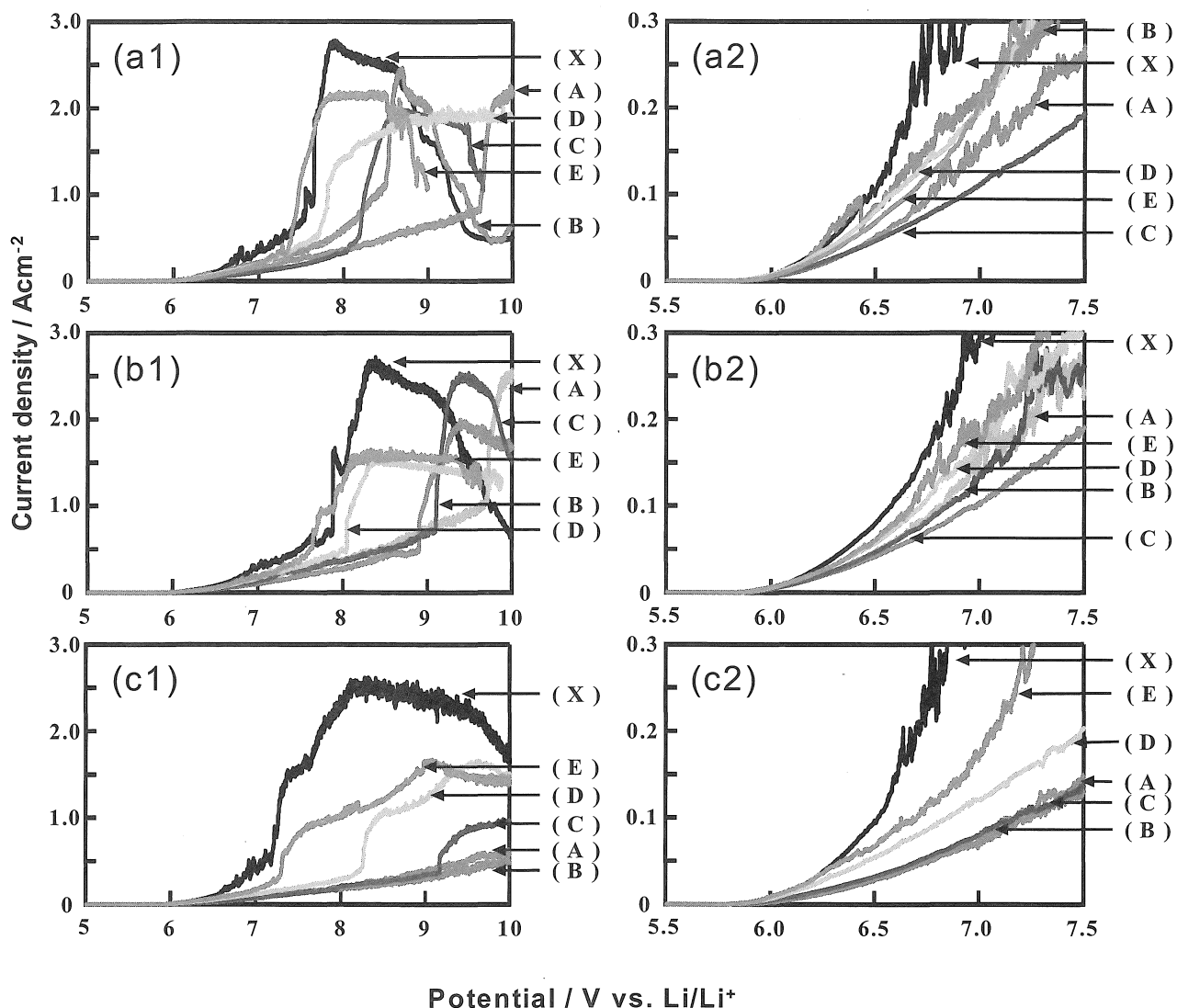


Fig. 6. Linear sweep voltammograms for Pt wire electrode in fluoro-carbonate containing electrolyte solutions.
 (a1) and (a2): 0.90 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.33 vol., 10.0 vol.%).
 (b1) and (b2): 0.78 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.83 vol., 21.7 vol.%).
 (c1) and (c2): 0.67 mol/L LiClO₄-EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/(A, B, C, D or E) (1:1:1:1.5 vol., 33.3 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

Table 1 First coulombic efficiencies for natural graphite electrodes in 0.67 mol/L LiClO₄-EC/DEC (1:1 vol.) and EC/DEC/(A, B or C) (1:1:1 vol., 33.3 vol.%) at 60 mA/g.

Natural graphite	First coulombic efficiency / %			
	EC/DEC	EC/DEC/A	EC/DEC/B	EC/DEC/C
NG5 μm	75.1	76.3	74.4	72.3
NG10 μm	78.0	77.9	80.3	80.3
NG15 μm	77.7	75.9	84.4	84.0
NG25 μm	85.6	82.7	82.0	86.2
NG40 μm	85.7	87.1	88.4	87.5

In ref.39, data are not given as Table.

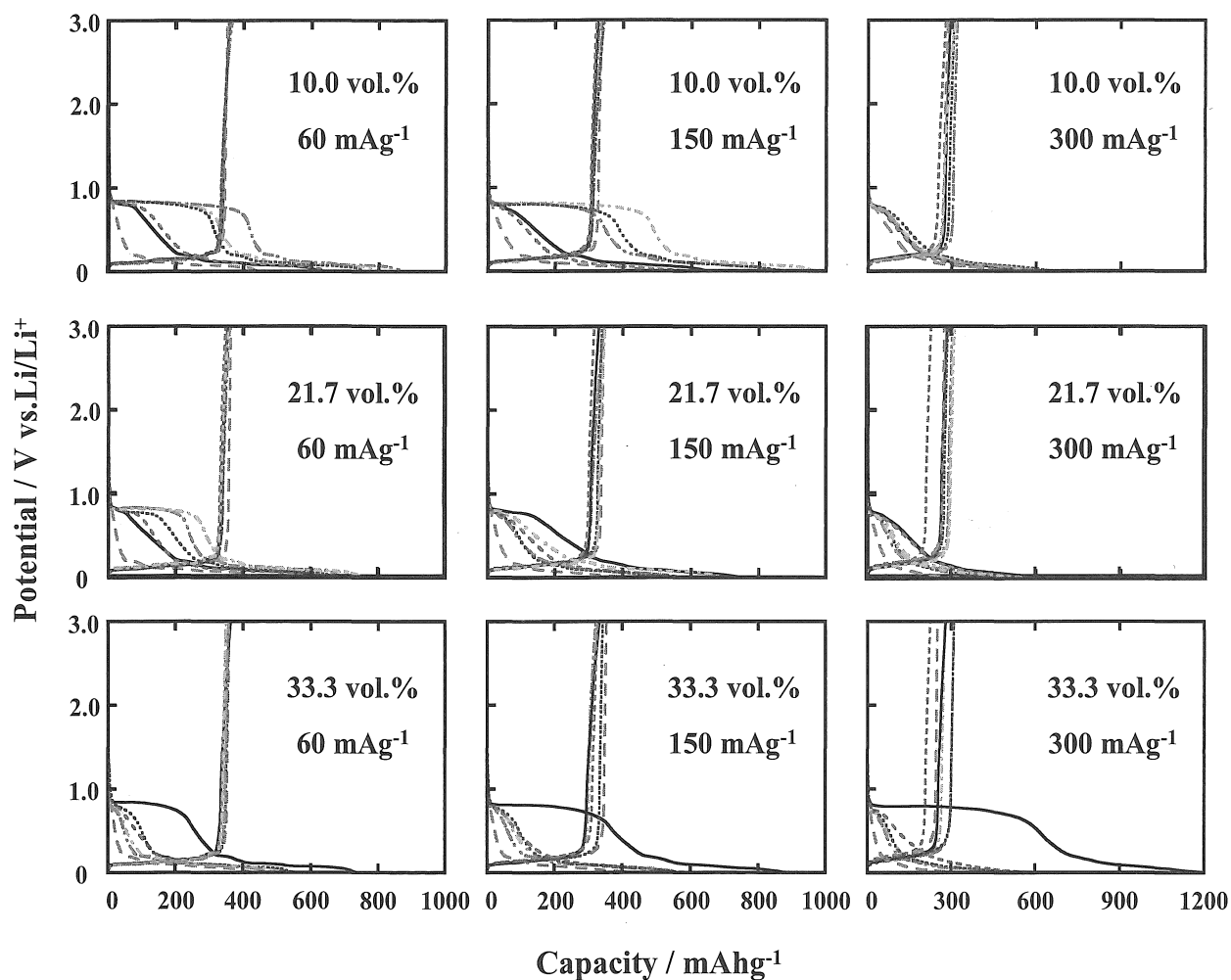


Fig. 7. First charge/discharge curves of NG15 μm electrode in 0.90, 0.78 and 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC}$ (1:1:1 vol.) and 0.90, 0.78 and 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC/(A, B, C, D or E)}$ (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) as functions of concentration of fluoro-carbonate and current density.

— EC/DEC/PC - - - - - EC/DEC/PC/A - · - · - · EC/DEC/PC/B
 ····· EC/DEC/PC/C - - - - - EC/DEC/PC/D - - - - - EC/DEC/PC/E

Table 2 First coulombic efficiencies (%) for NG15 μm electrode in 0.90, 0.78 or 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC}$ (1:1:1 vol.) and 0.90, 0.78 or 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC/(A, B, C, D or E)}$ (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively).

Solvent	Concentration of fluoro-carbonate / vol.%								
	10.0			21.7			33.3		
	Current density / mA/g								
	60	150	300	60	150	300	60	150	300
EC/DEC/PC	57.4	50.7	50.7	56.9	43.3	45.5	49.6	37.9	23.5
EC/DEC/PC/A	55.8	55.1	56.1	59.1	53.3	38.7	63.2	54.6	37.9
EC/DEC/PC/B	79.8	73.3	57.9	84.1	76.1	70.3	84.1	80.0	73.7
EC/DEC/PC/C	47.3	39.3	46.4	51.9	57.6	52.9	65.9	59.6	55.2
EC/DEC/PC/D	45.5	35.5	48.9	47.6	50.0	54.5	70.9	57.2	55.1
EC/DEC/PC/E	42.2	38.4	49.0	53.0	58.2	54.7	75.0	58.6	53.2

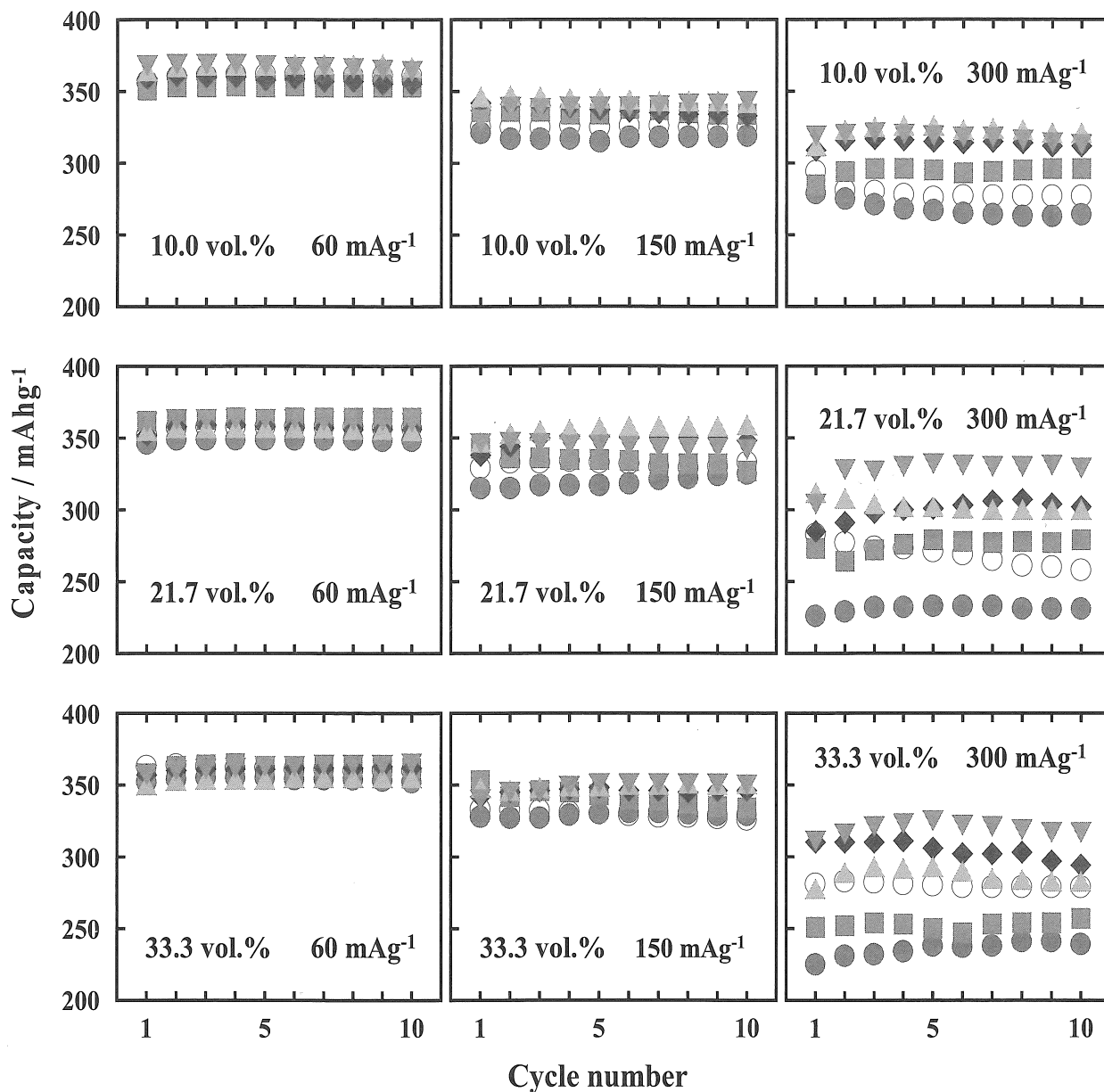


Fig. 8. Charge capacities of NG15 μm electrode in 0.90, 0.78 and 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC}$ (1:1:1 vol.) and 0.90, 0.78 and 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC}$ /(A, B, C, D or E, 1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) as functions of concentration of fluoro-carbonate and current density.

○ EC/DEC/PC, ● EC:DEC/PC/A, ■ EC/DEC/PC/B, ◆ EC/DEC/PC/C, ▲ EC/DEC/PC/D, ▼ EC/DEC/PC/E

fluoro-carbonate-mixed electrolyte solutions are nearly the same as or slightly higher than those obtained in EC/DEC without fluorine compounds. It means that the fluorine compounds can be used in EC/DEC solvents. If decomposed products of fluorine compounds quickly form SEI on graphite electrode, PC-containing solvents with low melting points can be also used. **Fig. 7** shows first charge/discharge curves obtained in EC/DEC/PC (1:1:1 vol.) and EC/DEC/PC/(A, B, C, D or E) (1:1:1:0.33, 0.83 or 1.5 vol., 10.0, 21.7 or 33.3 vol.%, respectively) as functions of concentration of fluoro-carbonate

and current density. The potential plateaus at 0.8 V vs Li/Li^+ in **Fig. 7** indicates the reduction decomposition of PC. In EC/DEC/PC solvent without fluorine compound, the potential plateau lengthened with decreasing concentration of LiClO_4 from 0.90 to 0.67 mol/L and increasing current density from 60 to 300 mA/g. Particularly long potential plateaus were observed in 0.67 mol/L $\text{LiClO}_4\text{-EC/DEC/PC}$. According to this change in potential plateau, first columbic efficiency in EC/DEC/PC solvent decreased with decreasing concentration of LiClO_4 and increasing current density as given in **Table 2**. On the other

hand, in the fluoro-carbonate-mixed electrolyte solutions, the potential plateau was shortened with increasing concentration of fluoro-carbonate from 10.0 to 33.3 vol.% and current density from 60 to 300 mA/g. The difference in EC/DEC/PC with and without fluorine compound was clearly observed when fluoro-carbonate was mixed by 33.3 vol.%, where the electrode potentials were quickly lowered. As shown in **Table 2**, first coulombic efficiency in EC/DEC/PC/(**A**, **B**, **C**, **D** or **E**) solvent increased, that is, irreversible capacity decreased with increasing concentration of fluoro-carbonate and current density. **Table 2** indicates that fluoro-carbonate **B** is the best among five fluoro-carbonates examined, giving much higher first coulombic efficiencies, i.e. lower irreversible capacities than others. For other fluoro-carbonates except **B**, much higher first coulombic efficiencies than those in EC/DEC/PC solvent were also obtained by mixing of fluoro-carbonates by 33.3 vol.%. **Fig. 8** shows charge capacities of NG15 μm electrode as a function of cycle number. Charge capacities were nearly the same as each other in the electrolyte solutions with and without fluoro-carbonates at 60 mA/g. There was not a large difference in the capacities at 150 mA/g. A large difference in the charge capacities was observed at 300 mA/g. Particularly fluoro-carbonate **A**-mixed solution gave the lowest charge capacities because **A** is a viscous material.

3. Conclusions

Thermal stability, electrochemical oxidation stability and charge/discharge behavior of natural graphite (NG15 μm) were investigated using fluoro-carbonate-mixed electrolyte solutions. DSC study revealed that thermal stability was improved by mixing of five fluoro-carbonates with 1 mol/L LiClO_4 -EC/DEC/PC (1:1:1 vol.). The amounts of fluoro-carbonates needed to suppress the reaction of Li with electrolyte solution and SEI are 10 vol.% for fluoro-carbonate **C**, 21.7 vol.% for fluoro-carbonates **B** and **D**, and 33.3 vol.% for fluoro-carbonates **A** and **E**. Electrochemical oxidation stability was also significantly improved by mixing of fluoro-carbonates. To decrease the oxidation current, mixing by 21.7 vol.% is necessary for fluoro-carbonates **A**, **B** and **C**, and mixing by 33.3 vol.% for fluoro-carbonates **D** and **E**. In the fluoro-carbonate-mixed electrolyte solutions, reduction decomposition of PC decreased with increasing concentration of fluoro-carbonate from 10.0 to 33.3 vol.% and current density from 60 to 300 mA/g. As a result, first coulombic efficiency increased, that is, irreversible capacity decreased in the

fluoro-carbonate containing electrolyte solutions. Fluoro-carbonate **B** is the best compound among five fluoro-carbonates, giving much higher first coulombic efficiencies, i.e. lower irreversible capacities than others in PC-containing solvent. Much higher first coulombic efficiencies than those in EC/DEC/PC solvent were also observed for other fluoro-carbonate-mixed solutions by 33.3 vol.%.

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