



## Effect of organo-fluorine compounds on the thermal stability and electrochemical properties of electrolyte solutions for lithium ion batteries

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### HIGHLIGHTS

- ▶ Reactivity of metallic Li with fluorine compounds is much lower than that of EC/DMC.
- ▶ Reactivity of LiC<sub>6</sub> with fluorine compound-mixed electrolyte solutions containing LiPF<sub>6</sub> is low.
- ▶ Oxidation currents in fluorine-compound-mixed solutions are smaller than those in original ones.
- ▶ First coulombic efficiencies are high in fluoro-ether-mixed electrolyte solutions.

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### ABSTRACT

Thermal stability and electrochemical behavior of fluorine compound-mixed electrolyte solutions have been investigated using 1 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC, 1 molL<sup>-1</sup> LiPF<sub>6</sub>-EC/DMC and 1 molL<sup>-1</sup> LiPF<sub>6</sub>-EC/EMC/PC. DSC study indicates that no exothermic reaction occurs between metallic Li and fluoro-ethers while EC/DMC mixture and fluoro-carbonate start to react with Li at 180 and 226 °C, respectively. In LiClO<sub>4</sub>-containing electrolyte solution, lithiated graphite easily reacts with surface film and electrolyte solutions with and without fluoro-ethers, giving exothermic peaks at 153–162 °C. However, exothermic peaks at 111–137 °C caused by the reaction of lithiated graphite with surface film and electrolyte solutions are weak in LiPF<sub>6</sub>-containing solutions probably because LiF contained in the surface film prevents the reaction with deintercalated Li. Fluoro-carbonate-mixed solution gives the lower reactivity with deintercalated Li than fluoro-ether-mixed ones. Electrochemical oxidation currents are decreased by mixing of fluoro-ethers in both LiClO<sub>4</sub>- and LiPF<sub>6</sub>-containing electrolyte solutions. Charge/discharge experiments indicate that first coulombic efficiencies of natural graphite are mostly high in fluoro-ether-mixed electrolyte solutions, and fluoro-ethers facilitate the formation of surface film on graphite in PC-containing solutions.

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### 1. Introduction

High safety is one of the most important issues for lithium ion batteries since they use flammable organic solvents. It is particularly requested for their application to hybrid cars and electric vehicles. To improve the thermal stability of lithium ion batteries, many kinds of phosphorus compounds such as phosphates were investigated [1–27]. It was shown that they provide flame retarding properties to electrolyte solutions. Other compounds such as phosphazenes, borate, triazines and so on were also examined as flame retardants [28–34]. Organo-fluorine compounds are another

type of candidates as non-flammable solvents because they have normally high oxidation stability. Thermal stability and electrochemical properties were investigated using fluorine-containing ethers, esters and carbonates [35–44]. It was found more than 10 years ago that fluoro-ethers and fluoro-esters improve charge/discharge characteristics of graphite electrode at low temperatures less than 0 °C [45,46]. This work was extended to our recent study on the oxidation stability and electrochemical properties of fluorine compound-mixed electrolyte solutions [39–41]. Fluorine substitution of organic compounds usually improves their oxidation stability and simultaneously elevates reduction potentials. As expected, both HOMO and LUMO levels of fluorine-containing carbonates, esters and ethers are lower than those of the same type compounds without fluorine [39,40]. It was recently reported

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that mixing of organo-fluorine compounds with electrolyte solutions improves oxidation stability [35–44]. However, it is also important to investigate charge/discharge behavior of graphite electrode in low potential region because fluorine-containing carbonates, esters and ethers are electrochemically reduced at higher potentials than usually employed organic solvents such as EC (ethylene carbonate), PC (propylene carbonate), DMC (dimethyl carbonate), EMC (ethyl methyl carbonate) and DEC (diethyl carbonate). Synthetic and natural graphites are normally used as anode materials [39–41]. For these graphites with high crystallinity, EC-based solvents should be employed for the quick formation of surface film (Solid Electrolyte Interphase: SEI). Since EC has a high melting point (36 °C), it is desirable to use PC with a low melting point (–55 °C). However, it is difficult to use PC for graphite with high crystallinity because electrochemical reduction continues on graphite, which gives a large irreversible capacity. Therefore, fluorine compounds are very useful if they facilitate SEI formation on graphite electrode. The advantage of fluorine-containing carbonates and ethers for the SEI formation was shown in our previous papers [39–41].

In the present study, thermal stability and electrochemical oxidation stability of fluoro-ether-mixed electrolyte solutions have been investigated using 1 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC, 1 molL<sup>-1</sup> LiPF<sub>6</sub>-EC/DMC and 1 molL<sup>-1</sup> LiPF<sub>6</sub>-EC/EMC/PC. Fluoro-carbonate-mixed solution was also used for comparison. To confirm the influence of electrochemical reduction of fluorine compounds, charge/discharge behavior of natural graphite powder has been evaluated in the fluorine compound-mixed electrolyte solutions.

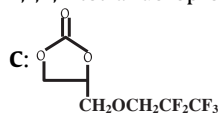
## 2. Experimental

### 2.1. Organo-fluorine compounds

The following fluoro-ethers and fluoro-carbonate (purity: 99.9%, H<sub>2</sub>O: <10 ppm), synthesized in Daikin Industries, Ltd., were used in the present study.

**A:** HCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H 3-(1,1,2,2-tetrafluoroethoxy)-1,1,2,2-tetrafluoropropane.

**B:** HCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CFCIH 3-(2-chloro-1,1,2-trifluoroethoxy)-1,1,2,2-tetrafluoropropane

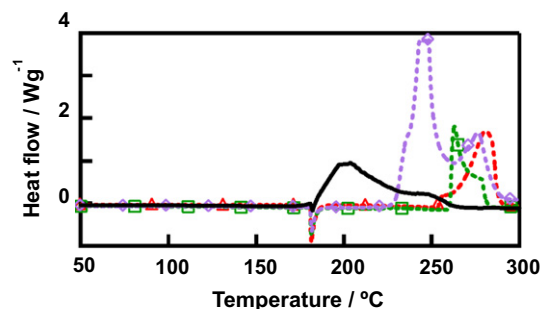


4-(2,2,3,3,3-pentafluoropropoxymethyl)-[1,3]dioxolan-2-one

Viscosities, dielectric constants, surface tensions and boiling points of **A** and **B** are 1.60 and 1.46 mPa s; 6.4 and 6.3; 20.2 and 21.6 mNm<sup>-1</sup>, and 92 and 107 °C, respectively.

### 2.2. Thermal stability by DSC measurements

Thermal stability of fluoro-ether or carbonate-mixed electrolyte solutions was examined by differential scanning calorimetry (DSC-60, Shimadzu). DSC measurement was carried out using a mixture of electrolyte solution with or without fluorine compound and lithiated or delithiated graphite (NG15 μm) between room temperature and 300 °C at a temperature increasing rate of 5 °C min<sup>-1</sup>. Fluorine compound-mixed electrolyte solutions used were 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC (**A** or **B**) (1:1:1.5 vol.), 1 molL<sup>-1</sup> LiPF<sub>6</sub>-EC/DMC/(**A**, **B** or **C**) (1:1:1 vol.) and 1 molL<sup>-1</sup> LiPF<sub>6</sub>-EC/EMC/PC/(**A** or **B**) (1:1:1.5 vol.). Thermal stability of only lithiated graphite without electrolyte solution, and reaction of metallic

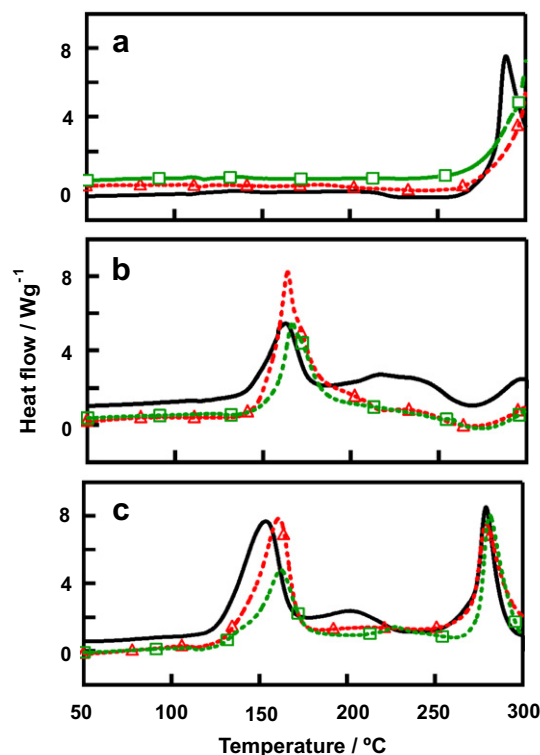


**Fig. 1.** DSC curves for mixtures of metallic Li and EC/DMC (1:1 vol.) or fluorine compound (**A**, **B** or **C**). —: EC/DMC, - - -Δ- - -: fluoro-ether **A**, - - -□- - -: fluoro-ether **B**, - - -◇- - -: fluoro-carbonate **C**.

Li with EC/DMC mixture (1:1 vol.) or fluorine compound **A**, **B** or **C** were also checked in the same manner. Fully lithiated and delithiated graphite samples were electrochemically prepared after 3 cycles. Li-intercalated graphite samples were Li<sub>0.91–0.99</sub>C<sub>6</sub> prepared in LiClO<sub>4</sub> solution (0.8–1.2 mg used for DSC) and Li<sub>0.88–0.98</sub>C<sub>6</sub> prepared in LiPF<sub>6</sub> solution (1.3–1.7 mg used for DSC). Electrolyte solution and metallic Li used for DSC measurements were 3 μL and 9.0–11.0 mg, respectively.

### 2.3. Electrochemical oxidation stability by oxidation current measurements

Oxidation currents were measured by linear sweep of potential at 0.1 mVs<sup>-1</sup> between 4 and 10 V vs Li/Li<sup>+</sup> for 0.90, 0.78 or 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC (1:1:1 vol.) and 0.90, 0.78 or 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC/(**A** or **B**) (1:1:1:0.33, 0.83 or 1.5 vol.,



**Fig. 2.** DSC curves for mixtures of 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC (1:1:1 vol.) or 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC/(**A** or **B**) (1:1:1.5 vol.) and delithiated graphite with SEI film (a), only lithiated graphite (Li<sub>0.91–0.99</sub>C<sub>6</sub>) (b), and 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC (1:1:1 vol.) or 0.67 molL<sup>-1</sup> LiClO<sub>4</sub>-EC/DEC/PC/(**A** or **B**) (1:1:1.5 vol.) and lithiated graphite (Li<sub>0.91–0.99</sub>C<sub>6</sub>) (c). —: EC/DEC/PC, - - -Δ- - -: EC/DEC/PC/**A**, - - -□- - -: EC/DEC/PC/**B**.

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