



# Thermal and electrochemical properties of nonflammable electrolyte solutions containing fluorinated alkylphosphates for lithium-ion batteries



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## HIGHLIGHTS

- Electrolyte solutions containing fluorinated alkylphosphates were investigated.
- Ionic conductivity of LiPF<sub>6</sub> solution was improved by addition of alkylcarbonates.
- Solutions containing fluorinated alkylphosphates showed low exothermic heat.
- Proper solvent compositions were proposed as safer LIB electrolyte systems.

## ARTICLE INFO

### Article history:

Received 8 August 2016

Received in revised form

19 September 2016

Accepted 21 September 2016

Available online 29 September 2016

### Keywords:

Fluorinated alkylphosphates

Nonflammable electrolyte

Thermal safety

Fluoroethylene carbonate

Lithium-ion battery

## ABSTRACT

Nonflammable organic electrolyte solutions containing fluorinated alkylphosphates (FAP) have been examined as safer electrolytes for lithium-ion batteries (LIB). Although the ionic conductivity of LiPF<sub>6</sub> in neat tris(2,2,2-trifluoroethyl)phosphate (TFEP) solvent is very low, it increases upon the addition of alkyl carbonates such as ethylene carbonate (EC) and fluoroethylene carbonate (4-fluoro-2-oxo-1,3-dioxolane, FEC). A specific conductivity of 1 mS cm<sup>-1</sup> or higher was obtained at room temperature for the system containing proper amounts of the carbonates and 0.5 M (mol dm<sup>-3</sup>) LiPF<sub>6</sub>. A conventional mixed alkylcarbonate-based solution containing LiPF<sub>6</sub> showed a sign of considerable exothermic reactions on the differential scanning calorimetry (DSC) response below 300 °C. However, the LiPF<sub>6</sub>/TFEP solution showed no significant exothermic response up to 400 °C, even in the presence of charged LiCoO<sub>2</sub> (LCO) positive electrode. The addition of an alkylcarbonate to the LiPF<sub>6</sub>/TFEP solution produced an exothermic response as a result of the thermal decomposition of the carbonate over the charged LCO. However, the temperature at which the exothermic reaction starts was significantly higher in the system containing FEC than that containing EC. The thermal analysis results suggested that the LiPF<sub>6</sub>/FEC + TFEP combination could work as a safer electrolyte system in LIB under severe conditions.

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## 1. Introduction

Lithium-ion batteries (LIB) are currently used as common portable power sources in a wide range of application areas. However, higher specific energy (Wh kg<sup>-1</sup>) or energy density (Wh m<sup>-3</sup>) characteristics are highly required for LIB as compared to current battery systems. Apart from this energy performance,

safety and reliability issues become more important in large-size applications such as transportation (e.g., electric vehicles and aircrafts). Some serious issues concerning the safety of commercial LIB have been reported up to date [1]. With the aim to ensure safe operation, each cell component in the current system should be substituted with safer replacement. In this context, nonflammable electrolyte systems have so far been proposed by many research groups [2].

In general, organic compounds possessing fluorinated alkyl groups have been widely used as flame-retardant components. Fluorinated ethers and esters have been proposed and examined as

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flame-retardant additives or co-solvents in LIB electrolytes [2–7]. Among them, fluorinated alkylphosphates (FAP) and related compounds showed good compatibility with conventional LIB electrolytes [8–11]. Thus, they are considered the most promising organic components that have sufficient nonflammability characteristics to be used as additives or co-solvents of organic electrolyte solutions for LIB [12–17]. The effects of FAP addition to the conventional alkylcarbonate-based electrolyte solutions on battery performance were also reported [18].

Besides these flame-retardant properties, thermal stability of the electrolyte components is of practical importance from the viewpoint of the safety of the battery system. In this sense, thermal stability of the electrolyte systems in a practical cell is independently controlled by the reactivity of the electrolyte components with the active materials forming of the positive and negative electrodes, especially under highly charged states. Nevertheless, data on the thermal stability of the electrolyte system showing sufficient nonflammable behavior are scarce in the literature [4]. Herein, thermal stability was examined for electrolyte systems containing FAP as flame-retardant components. We aimed to find practical electrolyte system combining good battery performance and sufficient safety characteristics. Binary solvent electrolyte solutions composed of alkylcarbonates mixed with FAP having lithium salts dissolved were mainly examined as practical LIB electrolytes. In the present paper, we would focus our interests on the thermal behavior of electrolyte solutions that contain single FAP solvent or FAP-based mixed solvents, as the primary screening to find a safer electrolyte system for LIB.

## 2. Experimental

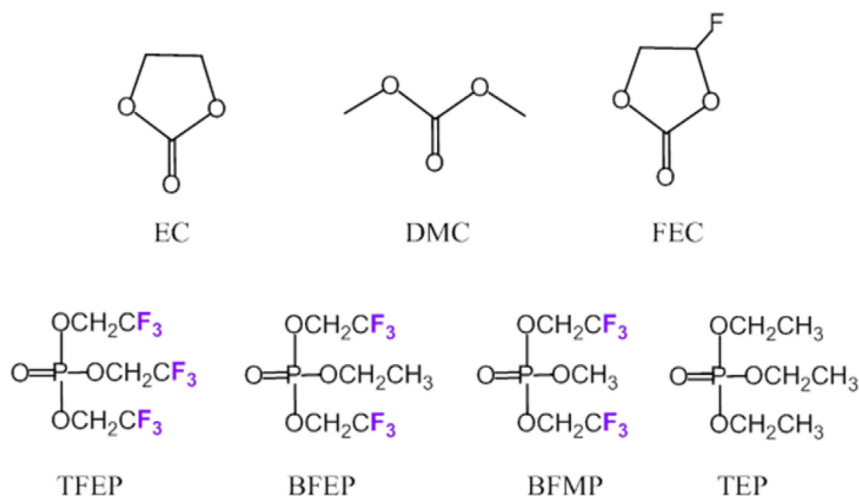
The organic solvents, ethylene carbonate (EC, battery grade, Kishida Chemical), dimethyl carbonate (DMC, battery grade, Kishida Chemical), and fluorinated ethylene carbonate (FEC, battery grade, Kishida Chemical), were used as received. Three kinds of FAP, tris(2,2,2-trifluoroethyl) phosphate (TFEP), bis(2,2,2-trifluoroethyl)-ethyl phosphate (BFEP), and bis(2,2,2-trifluoroethyl)-methyl phosphate (BFMP), were examined as flame-retardant solvents. These FAP were synthesized and purified by TOSOH F-TEC. Commercially available triethylphosphate (TEP, reagent grade, Wako Chemicals) was also used as a flame-retardant component for comparison [19,20]. The chemical formulas and selected physico-chemical properties of these solvent components

are listed in Scheme 1 and Table 1, respectively. We would emphasize here that all FAP (TFEP, BFEP and BFMP) have no flashpoint.

Each FAP was used alone (i.e., neat solvent) or mixed with alkyl carbonate, maintaining the carbonate to the lithium salt molar ratio kept constant. Residual water in the solvent was removed with molecular sieves (5A 1/16, Wako Chemicals, pretreated at 300 °C under vacuum) when the concentration was higher than 50 ppm. The electrolytic salt ( $\text{LiPF}_6$ , battery grade, Kishida Chemical) was dissolved in neat or mixed solvent systems at constant concentration (i.e.,  $0.5 \text{ mol dm}^{-3} = \text{M}$ ), unless otherwise noted.

The ionic conductivity of the electrolyte solution was measured by an AC impedance method in the frequency range from 1 MHz to 10 Hz using an impedance response analyzer (SI-1260, Solartron) coupled with an electrochemical interface (SI-1287, Solartron). A cell equipped with two parallel platinum sheet electrodes was used for the measurements. The cell constant was determined using aqueous KCl solutions (0.01, 0.1 and 1.0 M). The cell was set in a thermostatically controlled container and the conductivity was measured in the temperature range from  $-20 \text{ }^\circ\text{C}$  to  $60 \text{ }^\circ\text{C}$  (253 K–333 K).

The electrochemical window of the electrolyte solution was determined by linear sweep voltammetry (LSV, HZ-5000, Hokuto Denko) using a three-electrode beaker cell equipped with Pt working, lithium-sheet counter, and lithium-tip reference electrodes. The potential of the Pt working electrode was scanned from an open-circuit (rest) potential toward positive values at a scan rate of  $5 \text{ mV s}^{-1}$ . The compatibility of the electrolyte solution with the LIB electrodes was briefly examined by cyclic voltammetry (CV, HZ-5000, Hokuto Denko) using a conventional three-electrode cell at a scan rate of  $0.2 \text{ mV s}^{-1}$ . The working electrodes examined were synthetic graphite (TIMREX KS6, TIMCAL) and  $\text{LiCoO}_2$  (LCO, CELL-SEED C-5H, Nippon Chemical Industrial Co.) serving as the negative and positive electrodes, respectively. The negative electrode was prepared from a slurry of graphite powder with poly(vinylidene difluoride) (PVdF) as a binder (mass ratio of 85:15) dispersed in *N*-methylpyrrolidone (NMP). The obtained slurry was coated onto a Cu foil (20  $\mu\text{m}$  thickness) current collector, dried at  $70 \text{ }^\circ\text{C}$  in air, and finally vacuum-dried at  $120 \text{ }^\circ\text{C}$ . The obtained graphite electrode was finally roll-pressed to ensure the adhesion. The LCO electrode was prepared by a similar wet process, although the slurry was composed of a mixture of LCO, a conductive support (acetylene black, Denka Black, Denki Kagaku Kogyo) and the PVdF



**Scheme 1.** Chemical formulas for the solvents under study.

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