



# A mixture of triethylphosphate and ethylene carbonate as a safe additive for ionic liquid-based electrolytes of lithium ion batteries

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## ABSTRACT

A binary mixture of triethylphosphate (TEP) and ethylene carbonate (EC) has been examined as a new non-flammable additive for ionic liquid-based electrolytes for lithium-ion batteries. The optimized electrolyte composition consists of  $0.6 \text{ mol dm}^{-3}$  (=M) LiTFSI in PP13TFSI mixed with TEP and EC in volume ratio of 80:10:10, where TFSI and PP13 denote bis(trifluoromethanesulfonyl)imide and *N*-methyl-*N*-propylpiperidinium, respectively. The ionic conductivity of PP13TFSI dissolving 0.4 M LiTFSI was improved from  $8.2 \times 10^{-4} \text{ S cm}^{-1}$  to  $3.5 \times 10^{-3} \text{ S cm}^{-1}$  (at  $20^\circ\text{C}$ ) with the addition of TEP and EC. The electrochemical behavior of 0.4 M LiTFSI/PP13TFSI with and without TEP and EC was studied by cyclic voltammetry, which showed no deteriorating effect by the addition of TEP and EC on the electrochemical window of PP13TFSI. The flammability of the electrolyte was tested by a direct flame test. The proposed ionic liquid-based electrolyte revealed significant improvements in the electrochemical charge–discharge characteristics for both graphite negative and  $\text{LiMn}_2\text{O}_4$  positive electrodes.

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## 1. Introduction

Considerable attention has been drawn to room temperature ionic liquids (RTILs) as “green” alternative solvents to traditional organic solvents used in lithium-ion batteries (LIBs) [1–6]. They have substantial potential as solvents due to their unique properties, such as non-flammable, non-volatile, thermally stable, wide liquidus range and relatively wide electrochemical window [7–10]. These properties make RTILs as attractive candidates for the electrolyte of a safer LIB. The RTILs generally consist of organic cations like alkylimidazolium, alkylpyridinium, alkylpyrrolidinium, alkylpyrazolium, quaternary ammonium, etc. [11–15], and large size of inorganic or organic anions, such as tetrafluoroborate ( $\text{BF}_4^-$ ), hexafluorophosphate ( $\text{PF}_6^-$ ), trifluoromethanesulfonate ( $\text{Tf}^-$ ), and bis(trifluoromethanesulfonyl)imide (TFSI $^-$ ). Thus, the physical and chemical properties of RTIL can be tuned by a combination of cation and anion.

Alkylimidazolium based ionic liquids have been widely studied due to their low viscosity and high ionic conductivity. But the most of them are suffered from poor cathodic stability and cannot be used for graphite/lithium metal anode [16]. Among RTILs, imide salts of quaternary alkylammonium and alkylpyridinium are of particular interest due to their wide electrochemical window and cathodic stability [17,18]. These ionic liquids showed excellent properties

in a Li/LiCoO<sub>2</sub> cell system. However, they are highly viscous and have low ionic conductivity. The electrolytes having high ionic conductivity are desirable for high power-density applications such as electric vehicles (EVs) and hybrid electric vehicles (HEVs). Some efforts have been made to improve the performance of ionic liquid-based electrolytes by addition of organic solvents like ethylene carbonate (EC), dimethylcarbonate (DMC), ethylmethyl carbonate (EMC), vinylencarbonate (VC), etc. [19–22]. The addition of flammable organic solvents, however, affects the flammability and thermal properties of the resulting electrolytes. From the viewpoint of the safety of LIBs, there needs to look for non-flammable additive for ionic liquid-based electrolytes to realize a safe battery system. Alkylphosphates have been used as fire retardant co-solvents in organic solution electrolytes [23–25]. The addition of alkylphosphates effectively suppresses the flammability of the organic electrolytes. In the previous work, we reported that trimethylphosphate (TMP) and triethylphosphate (TEP) can be used as the fire retardant components in novel non-flammable organic electrolyte systems [26,27].

In the present paper, a binary mixture of TEP and EC has been proposed as a non-flammable additive for electrolytes based on an ionic liquid, *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI). TEP has low viscosity, low melting point, high boiling point, non-flammability and relatively high dielectric constant. These properties are useful to improve the ionic conductivity, viscosity, thermal stability and operational temperature range of the PP13TFSI-based electrolyte. On the other hand, EC component would contribute to

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form good interface between a graphite-based negative electrode and liquid electrolyte. The effects of addition of EC and TEP on the ionic conductivity, electrochemical stability, interfacial properties and thermal stability of PP13TFSI dissolving lithium salt (LiTFSI/PP13TFSI) have been investigated.

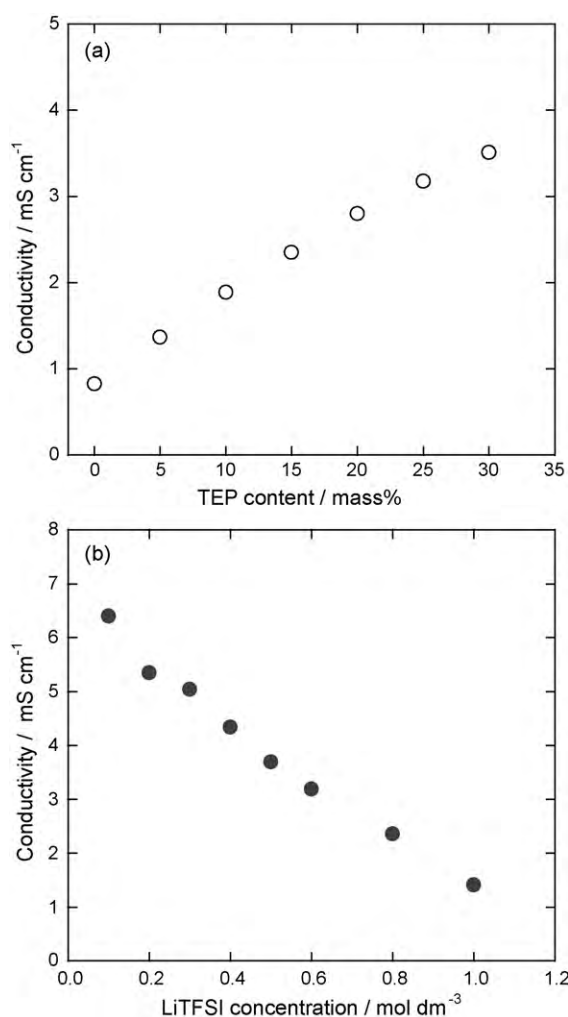
## 2. Experimental

PP13TFSI (Kanto Reagent), LiTFSI (Aldrich), EC (Kishida Chemical; Battery grade) and TEP (Wako Chemical) were used as received due to their high purity and low water contamination. The liquid electrolyte was prepared by dissolving 0.4 M LiTFSI in PP13TFSI. The mixed electrolytes were prepared by adding appropriate amount of LiTFSI in PP13TFSI, EC and TEP under an Ar atmosphere. A direct flame test was carried out to examine the flammability of the binary mixture of TEP and EC, and the electrolyte containing PP13TFSI, TEP and EC. A piece of glass filter paper impregnated with the test solution was set at 30 mm above the flame of Bunsen burner. The ignition time after flame setting and the self-extinguish time after removing the burner flame were measured as indices of the nonflammability.

The ionic conductivity of the electrolytes was measured by an ac impedance method in a frequency range from 100 kHz to 1 Hz using a frequency response analyzer controlled by a personal computer. The interfacial properties were examined by means of a symmetric cell, Li/electrolyte/Li, using Li foil disks (14 mm diameter) as the active electrode material. The electrochemical stability of the electrolyte was measured at a glassy carbon (GC: GC-30, Tokai Carbon) or a synthetic graphite (TIMREX KS6, TIMCAL) electrode by cyclic voltammetry (CV) using a three-electrode cell with Li foil counter and reference electrodes. The potential scan rates in these experiments were  $1 \text{ mV s}^{-1}$  for GC and  $0.1 \text{ mV s}^{-1}$  for the graphite electrode.

Charge–discharge cycling tests were conducted using a CR2036 coin-type two-electrode cell with the graphite or  $\text{LiMn}_2\text{O}_4$  (Toda Kogyo) working electrode and a Li foil counter electrode. A sheet of glass microfiber filter paper (Whatman, Grade GF/A, pore size  $1.6 \mu\text{m}$ ) was used as the separator. The negative electrode was prepared from a slurry containing 96 mass% active material (KS6) with 4 mass% poly(vinylidene fluoride) (PVdF) binder and 1-methylpyrrolidine-2-on (NMP) solvent. The size of the negative electrode was 13 mm in diameter and the average active material loading was  $1.7 \text{ mg cm}^{-2}$ . Charge–discharge curves were measured in the voltage range of 0.01–2.0 V. In this paper, the term “charge” for the test cell using graphite working electrode denotes the cathodic reduction of the graphite working electrode and the term “discharge” is used for the anodic oxidation of the lithiated graphite electrode. The cell was first charged at  $C/3$  current rate to 0.01 V and then charged at constant voltage of 0.01 V for 3 h. The discharge was carried out under a constant current rate of  $1C$  or  $C/5$ .

With respect to the examination in the positive electrode side, the working electrode was prepared by coating slurry containing 80 mass% of the active material  $\text{LiMn}_2\text{O}_4$ , 10 mass% of acetylene black as a conductive reagent, and 10 mass% of PVdF binder in NMP solvent. The working electrode having 13 mm in diameter and the active mass loading of  $2.3 \text{ mg cm}^{-2}$  was punched from the electrode sheet. The counter electrode was a Li foil disk with 15 mm in diameter. The cell was charged to the cut-off voltage of 4.6 V at  $C/2$  rate and then discharged to 3.5 V at  $1C$  or  $3C$  current rate, where we employed rather high cut-off voltage for charging because of the two-electrode cell using Li metal counter electrode. These electrochemical measurements were carried out at room temperature ( $23 \pm 2^\circ\text{C}$ ) under a dry Ar atmosphere.



**Fig. 1.** Ionic conductivity of (a) 0.4 M LiTFSI/PP13TFSI+TEP as a function of TEP content and (b) LiTFSI/PP13TFSI+TEP+EC (80:10:10) as a function of LiTFSI concentration.

## 3. Results and discussion

Fig. 1a shows the variation in the ionic conductivity of 0.4 M LiTFSI/PP13TFSI with the addition of 0–30 mass% of TEP at  $20^\circ\text{C}$ . The addition of 30 mass% TEP led to increase in the conductivity of 0.4 M LiTFSI/PP13TFSI from  $8.2 \times 10^{-4} \text{ S cm}^{-1}$  to  $3.5 \times 10^{-3} \text{ S cm}^{-1}$ . The conductivity variation of LiTFSI/PP13TFSI+TEP+EC (80:10:10) with the content of LiTFSI is given in Fig. 1b. With the increase in the LiTFSI concentration in the ternary mixture of PP13TFSI, TEP and EC, the ionic conductivity of the solution electrolyte decreases. This may be due to an increase in the viscosity of the electrolyte with addition of the Li salt, which decreases the mobility of whole ions in the system. The major ionic species for charge transportation will be the ionic liquid cation and anion, while the mobility of  $\text{Li}^+$  is also influenced by the viscosity of the electrolyte system. Some important properties of PP13TFSI, TEP and EC are given in Table 1. The base

**Table 1**  
Selected physico-chemical properties of the solvents.

	Viscosity ( $\eta$ ), mPa s	Melting point, $^\circ\text{C}$	Dielectric constant ( $\epsilon_r$ )	Density ( $\rho$ ), $10^3 \text{ kg m}^{-3}$
PP13TFSI	151	12	–	1.43
EC	1.9 <sup>a</sup>	38	91.2 <sup>a</sup>	1.32
TEP	1.6	–56	13.1	1.07

<sup>a</sup> At  $40^\circ\text{C}$ .

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