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Polymeric gel electrolyte containing alkyl phosphate for lithium-ion batteries

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Abstract

A nonflammable polymeric gel electrolyte film has been developed for rechargeable lithium battery systems. The gel film consists of poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) swollen with $LiPF_6$ solution of a ternary solvent containing nonflammable trimethyl phosphate (TMP). The addition of TMP to mixed ethylene carbonate plus diethyl carbonate (EC + DEC) solvent prevented the $LiPF_6$ salt from the thermal decomposition. The $LiPF_6$ solutions containing 20 vol% or higher content of TMP were fire-retardant. High ionic conductivity was obtained for both the liquid and the gel electrolyte systems containing 55 vol% of TMP in the liquid components: 7.1×10^{-3} S cm^{-1} for the liquid and 2.9×10^{-3} S cm^{-1} for the gel electrolytes at 20 °C. A wide potential window (-0.5 to 4.5 V versus Li/Li$^+$) and the redox activity of the electrode materials were established for the gel electrolyte containing TMP.
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1. Introduction

Lithium (Li)-ion batteries have so far been developed as advanced power sources for a variety of portable electronic devices such as cellular phones, laptop computers and camcorders. A larger size of the battery is now considered to fit power storage uses such as load-conditioning and electric vehicle (EV) systems. The safety and reliability of the battery become more important in such systems with higher energy capacity. Current Li-ion batteries employ flammable electrolyte solutions or gels based on organic solvents. Recently, much attention has been focused on the safety issue of Li-ion batteries. One of the promising methods to ensure the safety of the battery is use of nonflammable, or fire-retardant, solvent as either a co-solvent or an additive in the conventional alkyl carbonate-based electrolyte solution [1–16]. For instance, Arai reported on the nonflammable electrolyte containing alkyl–fluoroalkyl ether for Li-ion batteries [6,7]. We have also examined the utilization of ethylnonafluorobutyl ether (EFE)-based solution as a nonflammable elec-

trolyte [13]. The endothermic reactions of these fluoroalkyl ethers at elevated temperature suppress further explosive reactions of the organic electrolytes. However, the fluoroalkyl ethers have such disadvantages as low miscibility with polar solvents and high vapor pressure at elevated temperature. These properties are not fit to make a polymeric gel electrolyte.

Another choice to establish the safer electrolyte system is to use such a series of organic phosphates as trimethyl phosphate (TMP), tributyl phosphate (TBP) and ethylene ethyl phosphate (EEP), which are also promising solvents of nonflammable electrolytes [2,10,11]. Furthermore, Xu and coworkers reported that the fluorinated alkyl phosphate like tris(2,2,2-trifluoroethyl) phosphate (TTFP) is a promising candidate of the co-solvent for nonflammable electrolytes in Li-ion batteries and found to be very effective in improving the thermal stability of $LiPF_6$-based electrolytes [4,8,9,12–14]. These alkyl phosphates have high permittivity and low viscosity, and miscible with conventional organic carbonate solvents. Thus, we can make nonflammable, or fire-retardant, polymeric gel using mixed organic solvents containing alkyl phosphates [15,16]. To our knowledge, however, little has so far been published about nonflammable gel

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polymer electrolyte based on alkyl phosphates for Li-ion batteries.

In this work, we have tried to establish a polymeric gel electrolyte system containing trimethyl phosphate. At first, the solvent composition that reveals excellent thermal stability has been examined for the liquid electrolyte system containing TMP as a co-solvent of alkyl carbonates, namely ethylene carbonate (EC) mixed with diethyl carbonate (DEC). Next, we have prepared gel electrolytes using poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) which was swollen by $LiPF_6$ solution of the non-flammable ternary solvents (EC + DEC + TPM). The ionic conductance behavior and the electrochemical characteristics of both the solution and the gel system were investigated as a function of the solvent composition.

2. Experimental

The electrolytic solution was prepared by dissolving $LiPF_6$ in the ternary solvent system of EC, DEC and TMP, where the salt concentration and the mixing ratio of EC and DEC were kept constant, $1.0 \, mol \, dm^{-3}$ (M) of the salt concentration and 2:1 (v/v) of EC + DEC, respectively. The polymeric gel electrolyte was prepared by a thermal hardening method. A proper amount of PVdF-HFP as a host polymer was once dissolved in a mixed ternary solvents (EC + DEC + TMP, typically 30:15:55, v/v/v) containing $LiPF_6$ as an electrolytic salt. The resulting mixture was stirred for 1 h to form homogeneous solution and then developed on an Al pan. A transparent flexible film was obtained after heating the solution at 130 °C for 15–30 min under reduced pressure (typically at 50 kPa). These processes were carried out in a dry Ar atmosphere. The mass ratio of the solution component to the polymer was about 4:1 in the resulting gel.

The flame-retardant property of the electrolyte solution was briefly examined by a laboratory-made combustion test. The thermal deterioration of the electrolyte was estimated by an accelerated test. The test solution was sealed in a glass ample under a dry Ar atmosphere, and then the ample was heated at 85 °C for 250 h. Changes in the appearance, IR spectra and ionic conductance were used as the measure of the thermal deterioration of the solution. The IR data of the electrolytes were collected by an FT-IR spectrometer, and the ionic conductivity was measured at 10 kHz as a function of temperature. The electrochemical stability of the solution and the gel electrolytes were analyzed by cyclic voltammetry (CV), which was performed using a three-electrode cell with a Pt sheet working electrode and Li foils as the counter and the reference electrodes.

3. Results and discussion

Solubility tests proved that TMP is miscible in the most organic electrolyte solutions used in current Li-ion batter-
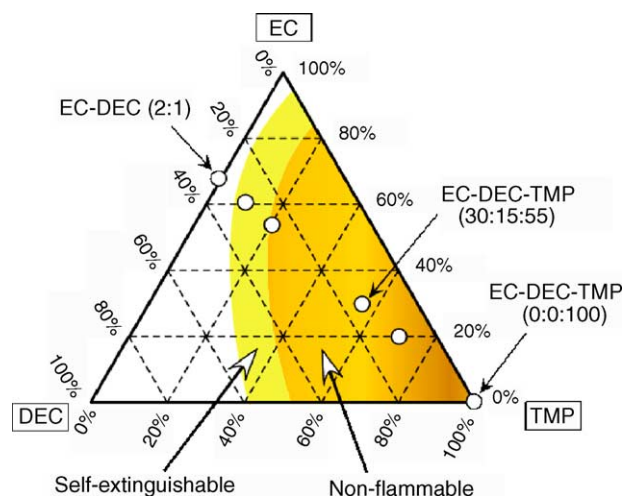

Fig. 1. A composition diagram for EC + DEC + TMP dissolving 1.0 M $LiPF_6$ at 25 °C.

ies without any phase separation. Fig. 1 shows a diagram of the ternary solvent system (EC–DEC–TMP) dissolving 1.0 M $LiPF_6$. According to the combustion test of the solution, the dark black (dark brown) region in the diagram was found to be nonflammable and the light black (light yellow) part was self-extinguishable. This result is consistent with those reported by Kasuya and co-workers [2,11] and Xu et al. [5] who present the TMP contents showing nonflammability for each binary system, EC + TMP, DEC + TMP or for ternary systems, EC + DEC + TMP and EC + EMC + TMP (EMC: ethyl methyl carbonate). The solution containing 10 vol% TMP in EC + DEC (2:1, v/v) was once ignited but immediately extinguished itself. The TMP content establishing the nonflammable ability of the solution was 20 vol% or higher.

The thermal stability of the electrolyte solution was examined by an accelerating heat test. The electrolyte solution containing different amount of TMP was heated at 85 °C for 250 h in a sealed glass ample. The solution containing no TMP, $LiPF_6$ (1.0 M)/EC + DEC (2:1), changed its color from colorless (transparent) to dark brown after the heat-treatment. The solutions containing 20 vol% or lower content of TMP also showed changes in color, but the degree of color change was rather low compared to the case without TMP. Higher TMP contents than 20 vol% did not cause any color change after the heat-treatment. These observations suggest that the TMP component suppressed the thermal decomposition of the $LiPF_6$ solution with mixed carbonate solvents [8].

The ionic conductivities of the 1.0 M $LiPF_6$ solutions measured at 25 °C before and after the heat-treatment are shown in Fig. 2 as a function of the TMP content in the solvent. The conductivity kept about 9 mS cm^{-1} or higher up to 70 vol% TMP before the heat-treatment, but the solution without the alkyl carbonates (1.0 M $LiPF_6$/TMP) showed rather low conductivity probably due to high viscosity of TMP itself. The solutions containing TMP less than 20 vol% showed significant decreases in the conductivity after the heat-treatment, while the solutions containing higher contents of TMP lead
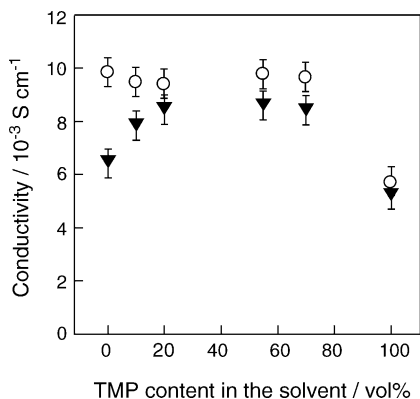
Fig. 2. Ionic conductivity of LiPF$_6$ (1.0 M) solutions in EC + DEC + TMP ternary solvents at 25 °C. EC/DEC ratio: 2/1 (v/v), (○) before heating and (▼) after heating (85 °C, 250 h).

to smaller changes in the conductivity, the results of which corresponded to the changes in the solution color after the heat-treatment. The thermal deterioration of the LiPF$_6$ solution with alkyl carbonate solvents is considered to be initiated by the thermal decomposition of PF$_6^-$ to PF$_5$ + F$^-$ under a trace amount of water in the system [8,13,17,18], which is followed by the oxidative decomposition of the solvent carbonate [18]. The addition of TMP probably suppresses the evolution of reactive PF$_5$ in the system although the detail of the suppression mechanism is not clear at this stage.

In Fig. 3 FT-IR spectra are given for the solutions with and without TMP after the heat-treatment. The absorption band
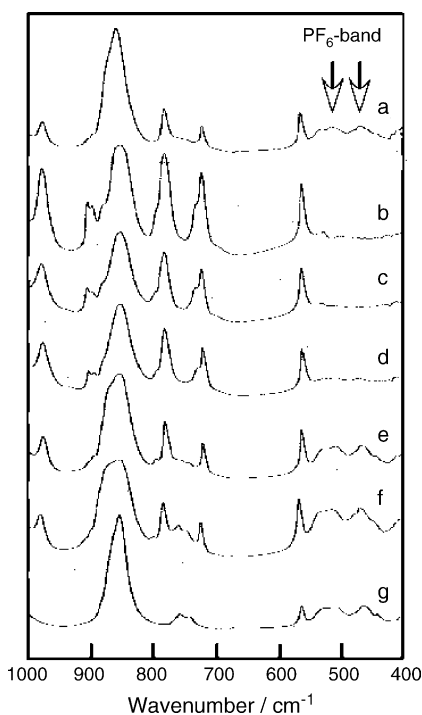

Fig. 3. IR spectra of LiPF$_6$ solutions in mixed EC + DEC + TMP before and after the heat-treatment (85 °C, 250 h). EC/DEC ratio: 2/1 (v/v), (a) before heating (EC + DEC), (b–g) after heating. TMP content (in vol%): 0 (a and b), 10 (c), 20 (d), 55 (e), 70 (f) and 100 (g).

characteristic to PF$_6^-$ is shown in the wavenumber range of 450–550 cm^{-1}. For the solutions containing higher contents (<55 vol%) of TMP, the PF$_6^-$ band remains even after the heat-treatment at 85 °C for 250 h, whereas the absorption is weakened for the solution containing lower (or no) amounts of TMP. Thus, the IR spectra after the heat-treatment also proved that the presence of TMP suppresses the thermal decomposition of the LiPF$_6$-based electrolytes.

The above-mentioned results suggest that the LiPF$_6$ solutions with the ternary solvent system of EC + DEC + TMP will be suitable as the liquid component of the polymeric gel electrolyte with good thermal properties. Similar trials have already been reported by other research groups. Morford et al. [15] and Akashi et al. [16], respectively, used poly(oxyethylene)-based polymers and polyacrylonitrile as the host polymer. We adopted, in the present work, PVdF-HFP as the host polymer because it shows high thermal stability by itself as well as can hold huge amount of liquid components without phase separation. The typical polymer/liquid mass ratio we used was 1:4 in the resulting gel film. As the solvent component tended to be evaporated in part during the film preparation, the gel composition was somewhat different from that in the starting polymer/liquid ratio. The polymeric gel film, PVDF-HFP/LiPF$_6$/EC + DEC + TMP, whose composition was 1:4 in polymer/liquid mass ratio and 30:15:55 in EC/DEC/TMP volume ratio, has sufficient mechanical strength for conducting the electrochemical measurements.

Fig. 4 shows the temperature dependence of the ionic conductivity of the gel film, compared with those of the liquid electrolytes, LiPF$_6$/EC + DEC and LiPF$_6$/EC + DEC + TMP. The plots for the liquid electrolytes followed an Arrhenius-type relation. The apparent activation energy for ionic conduction was calculated from the slope of the plots and was about 15 kJ mol^{-1}, which is typical for Li salt solutions with organic solvents. The ionic conductivity of the gel electrolyte also showed the Arrhenius-type relation although the conductivity itself is rather low compared with that of the component liquid electrolyte. The slight increase in the apparent
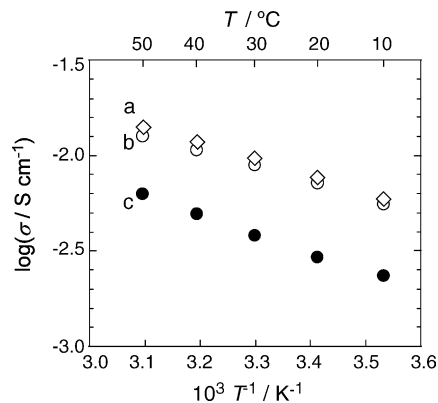

Fig. 4. Temperature dependence of the ionic conductivity, (a) LiPF$_6$ (1.0 M)/EC + DEC (67:33) (solution), (b) LiPF$_6$ (1.0 M)/EC + DEC + TMP (30:15:55) (solution) and (c) LiPF$_6$ (1.0 M)/EC + DEC + TMP (30:15:55) (gel).
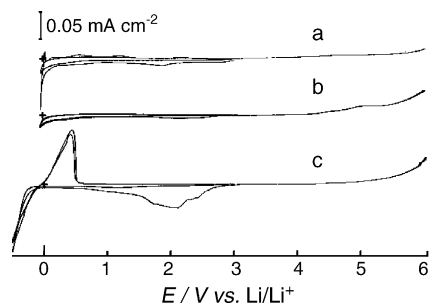
Fig. 5. Cyclic voltammograms for Pt in $LiPF_6$ solutions and in the gel electrolyte, at 25 °C. Scan rate: 5 mV s^{-1}, (a) $LiPF_6$ (1.0 M)/EC + DEC (67:33) (solution), (b) $LiPF_6$ (1.0 M)/EC + DEC + TMP (30:15:55) (solution) and (c) $LiPF_6$ (1.0 M)/EC + DEC + TMP (30:15:55) (gel).

activation energy (ca. 20 kJ mol^{-1}) for the gel electrolyte is probably due to decrease in the ionic mobility in the gel. The value of the conductivity, 2.9 mS cm^{-1} at 20 °C, however, will be acceptable for the practical battery system.

In Fig. 5 the cyclic voltammogram for Pt working electrode in the gel electrolyte is compared with those measured in the liquid electrolytes. A wide potential window (0–4.5 V versus Li/Li$^+$) was observed for both the solution and the gel electrolytes. A small and broad current peak was observed at anodic region (around 5 V versus Li/Li$^+$) in the solution and gel containing TMP. However, this anodic response will not become a subject of discussion because good battery performances have been reported for Li/CoO$_2$ and C/CoO$_2$ systems using liquid electrolytes containing TMP [2,3]. Almost the same current response was observed for the gel electrolyte containing TMP, except for the cathodic current response at around 2 V versus Li/Li$^+$ in the first potential scan. No visible current was observed in this potential region after the second scan and the Li deposition/dissolution reaction reversibly proceeded at around 0 V. Thus, we concluded that the process at around 2 V in the first scan would be related to some surface reaction caused by either gel components themselves or such contaminations as water and oxygen included during the film preparation process. The optimization of the gel composition is now under investigation using full cell with carbonaceous negative and lithiated transition-metal oxide positive electrodes, result of which will be reported in near future.

4. Conclusion

Nonflammable polymeric gel electrolyte film was developed for Li-ion batteries. The results obtained in this work are summarized as follows:

1. $LiPF_6$ solutions containing trimethyl phosphate with mixed alkyl carbonates showed flame retardant.
2. The addition of TMP suppressed the thermal decomposition of $LiPF_6$/EC + DEC.
3. High ionic conductivity was obtained for the gel electrolyte over wide temperature range: 2.9×10^{-3} S cm^{-1} at 20 °C.
4. Wide potential window (0–4.5 V versus Li/Li$^+$) and the electrochemical activity of Li deposition/dissolution were established for the gel electrolyte containing TMP.

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