

Short communication

Nonflammable gel electrolyte containing alkyl phosphate for rechargeable lithium batteries

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Abstract

A nonflammable polymeric gel electrolyte has been developed for rechargeable lithium battery systems. The gel film consists of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) swollen with lithium hexafluorophosphate (LiPF_6) solution in ternary solvent containing trimethyl phosphate (TMP). High ionic conductivity of 6.2 mS cm^{-1} at 20°C was obtained for the gel electrolyte consisting of $0.8 \text{ M LiPF}_6/\text{EC} + \text{DEC} + \text{TMP}$ (55:25:20) with PVdF-HFP, which is comparable to that of the liquid electrolyte containing the same electrolytic salt. Addition of a small amount of vinylene carbonate (VC) in the gel electrolyte improved the rechargeability of a graphite electrode. The rechargeable capacity of the graphite in the gel containing VC was ca. 300 mAh g^{-1} , which is almost the same as that in a conventional liquid electrolyte system. © 2006 Elsevier B.V. All rights reserved.

Keywords: Li-ion battery; Polymeric gel electrolyte; Nonflammability; Additive

1. Introduction

Polymeric gel electrolytes have widely been investigated for the use in advanced rechargeable lithium (Li)-ion batteries because they are expected to have both high room-temperature conductivity and advantages of solid polymer batteries [1–4]. A safety issue is one of the most important characteristics of solid polymer electrolytes toward conventional liquid ones, particularly for the scale-up and extended application of Li-ion batteries. In general, however, gel polymer electrolytes are not expected to improve the safety of cells because they contain significant amounts of volatile and flammable organic solvents, as in conventional liquid electrolytes.

To ensure the safety of the battery system, many kinds of nonflammable or fire-retardant solvents, such as fluorinated hydrocarbons, ionic liquids, or alkyl phosphates, have been proposed as either co-solvents or additives in conventional alkyl carbonate-based liquid electrolytes [5–20]. Among them, such organic phosphates as trimethyl phosphate (TMP), tributyl phosphate (TBP) and ethylene ethyl phosphate (EEP) are promising candidate components of nonflammable electrolytes [10,11,19].

Xu et al. reported that the fluorinated alkyl phosphate like tris(2,2,2-trifluoroethyl) phosphate (TTFP) is a promising co-solvent for nonflammable electrolytes of Li-ion batteries. They also found it being very effective in improving the thermal stability of LiPF_6 -based electrolytes [5,7,8,12,13,17]. These alkyl phosphates are also expected to be applied to gel polymer electrolyte systems due to their relatively low volatility and miscibility with conventional organic carbonate solvents. To our knowledge, however, little has so far been published about nonflammable gel polymer electrolyte based on alkyl phosphates for Li-ion batteries [21,22]. We have previously reported fundamental properties of the electrolyte solution containing TMP as a co-solvent of mixed alkyl carbonates, namely ethylene carbonate (EC) mixed with diethyl carbonate (DEC), and availability of them into a polymeric gel electrolyte system for Li-ion batteries [22].

In the present work, we have optimized the gel composition of the nonflammable or fire-retardant electrolyte. The electrochemical behavior of graphite as a negative electrode of the battery was investigated in the gel electrolyte containing $\text{LiPF}_6/\text{EC} + \text{DEC}$ mixed with TMP. The effects of an organic additive, vinylene carbonate (VC), on the electrochemistry of the nonflammable gel electrolyte was investigated from the viewpoint of the rechargeability of the graphite negative electrode.

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2. Experimental

The component solvents, EC (Kishida Chemical; Battery grade), DEC (Kishida Chemical; Battery grade), TMP (Wako Chemical) and VC (Aldrich) were used as received. The electrolytic salt, LiPF_6 (Tomiyama, Battery grade), and a host polymer, PVdF-HFP (ARKEMA, Kynar 2851) were also used as received, but kept in a glove box filled with dry Ar before use. The electrolytic solution was prepared by dissolving LiPF_6 in the ternary solvent system of EC, DEC and TMP, where the mixing ratio of EC and DEC was kept constant, 2:1 (v/v). The polymeric gel electrolyte was prepared by a thermal casting method. A proper amount of PVdF-HFP was once dissolved in a mixed ternary solvents (EC + DEC + TMP, typically 55:25:20 (v/v/v)) containing LiPF_6 . 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 110 °C for 13–30 min under a 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 host polymer in the resulting gel was about 5:1, which was slightly dependent on the curing condition.

Cyclic voltammetry (CV) was performed using a conventional three-electrode cell with a Pt wire or graphite (TIMREX KS6, TIMCAL) as the working electrode and Li foils as the counter and the reference electrodes. The graphite electrode was prepared from a slurry containing the active material with 4 wt.% of poly(vinylidene fluoride) binder and 1-methylpyrrolidine-2-on (NMP) solvent. The ionic conductivity of the gel electrolyte was measured by an ac impedance method in a frequency range from 100 kHz to 1 Hz using an impedance response analyzer controlled by a personal computer. The charge and discharge characteristics of the graphite electrode were investigated using a coin-shape two-electrode cell (2032-size) under constant-current charge and discharge conditions, typically with a current density of 0.1 mA cm^{-2} .

3. Results and discussion

TMP was miscible in most organic electrolyte solutions used in conventional Li-ion batteries without any phase separation by a given mixing ratio. We have previously examined a combustion test for electrolyte solutions containing TMP [22]. According to the experimental results, the minimum TMP content required to inhibit the flammability was 20 vol.% when it was mixed into EC + DEC (2:1 (v/v)) solvent before dissolving 1.0 M LiPF_6 . The addition of TMP to EC + DEC solvent also prevented the LiPF_6 salt from the thermal decomposition even when the solution was heated at 85 °C [22].

Fig. 1 shows the cyclic voltammograms for the graphite electrode in the liquid electrolyte systems containing 1.0 M LiPF_6 with different contents of TMP. In the case of the electrolyte solution without TMP (Fig. 1(a)), cathodic and anodic peaks were clearly observed in the potential region of 0.1–0.2 V versus Li/Li^+ , which is typically observed for the Li^+ insertion into and desorption from the graphite. In contrast, for electrolyte solutions containing TMP (Fig. 1(b) and (c)), such reversible peaks

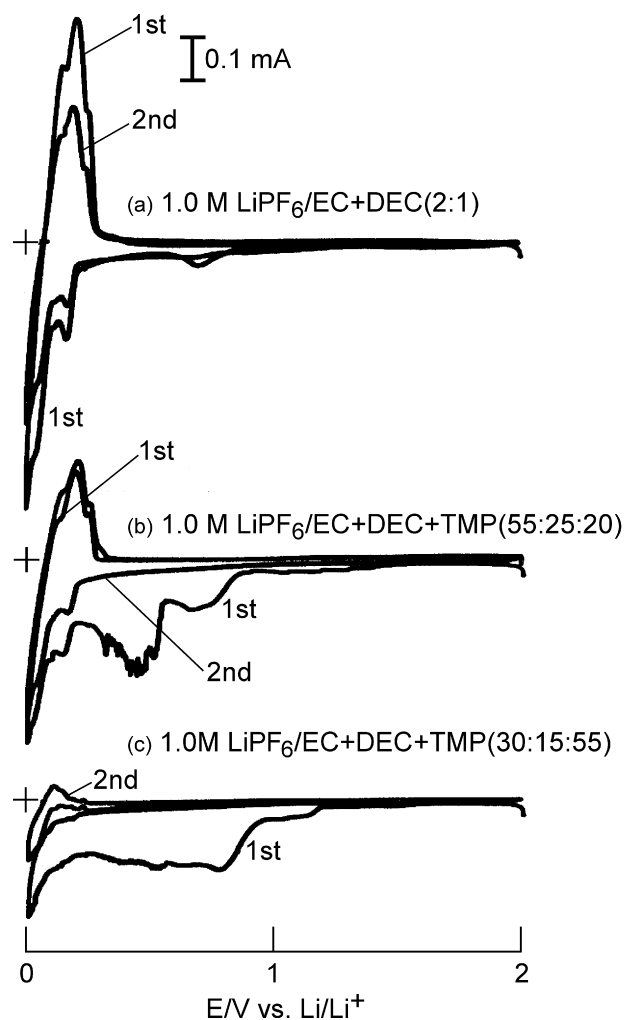


Fig. 1. Cyclic voltammograms for graphite electrode in 1.0 M LiPF_6 solution electrolytes. Working electrode: graphite (KS-6), reference and counter electrodes: Li foil, scan rate: 0.1 mV s^{-1} .

were suppressed markedly according to the content of TMP. In the latter cases, an additional cathodic current was observed at a wide potential range from 1.3 to 0 V. This irreversible current is considered to be attributed to the decomposition of the electrolyte component on the graphite. The decomposition product may be deposited on the graphite surface to form a passivation layer which suppresses the reversible Li^+ insertion and desorption. Therefore, it seems that the TMP content should be reduced to ensure the effective charge and discharge of graphite electrode.

Then nonflammable gel electrolytes consisting of 1.0 M $\text{LiPF}_6/\text{EC} + \text{DEC} + \text{TMP}$ (55:25:20 and 30:15:55) were prepared and their voltammetric responses were investigated. Fig. 2 shows the cyclic voltammograms for Pt working electrode toward the gel electrolytes. A series of reversible cathodic scan (-0.5 to 3.0 V versus Li/Li^+) was carried out for two cycles to observe the deposition and dissolution of Li on the Pt electrode. The current responses during a single anodic scan (3.0 – 6.0 V versus Li/Li^+) are also included in Fig. 2 to determine the anodic decomposition of the electrolytes. The irreversible cathodic current over the potential range of 0 – 2.5 V was high for the gel electrolytes, and the currents corresponding to reversible Li^+

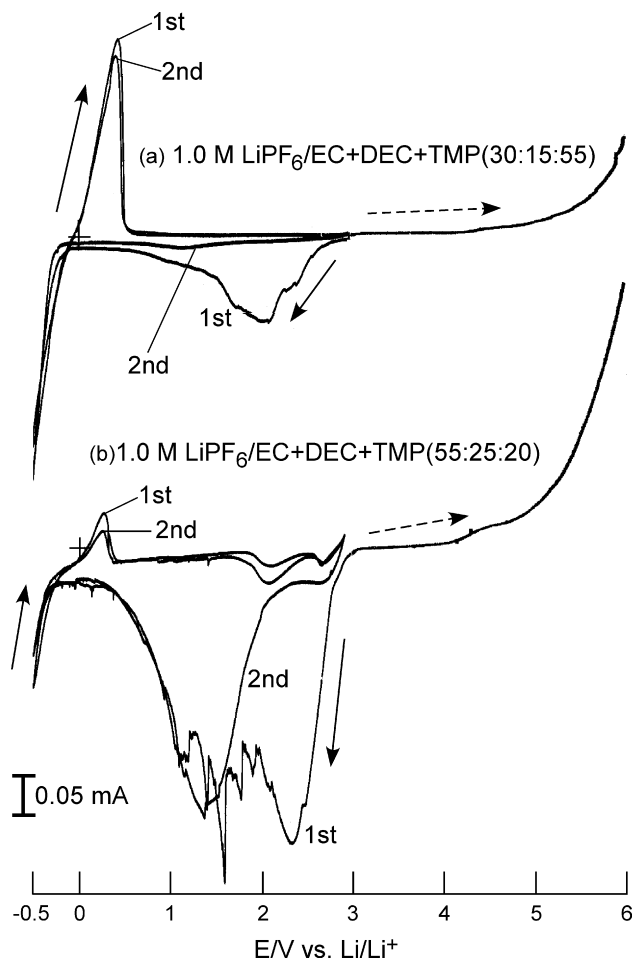


Fig. 2. Cyclic voltammograms for Pt electrode using gel electrolytes containing 1.0 M LiPF₆. Working electrode: Pt sheet, reference and counter electrodes: Li foil, scan rate: 5.0 mV s⁻¹.

deposition and dissolution were lowered with decreasing the TMP content in the gel. The gel electrolyte containing lower TMP content was anodically less stable. The reason of such instability of the gel electrolyte with lower TMP content is considered to be due to thermal decomposition of LiPF₆ during the gel preparation. When the TMP content was sufficiently high to prevent LiPF₆ from the thermal decomposition [22], the gel electrolyte showed good reversibility of Li deposition and dissolution (Fig. 2(a)).

From above experimental results, we have determined an optimum composition of the gel with respect to the contents of TMP and LiPF₆ salt. The gel electrolyte with optimized composition was obtained from the polymer solution with 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) by heating at 110 °C, 50 kPa for 13 min.

Fig. 3 shows the temperature dependence of the ionic conductivity for the gel electrolyte compared with that of the liquid electrolyte. As high ionic conductivity as 6.1 mS cm⁻¹ was obtained at 20 °C for the gel electrolyte composed of 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) (Fig. 3(c)), which is practically higher than that of 1.0 M LiPF₆/EC + DEC + TMP (55:25:20) gel, 3.6 mS cm⁻¹ at 20 °C (Fig. 3(d)). The ionic conductivity of the optimized gel composition was almost

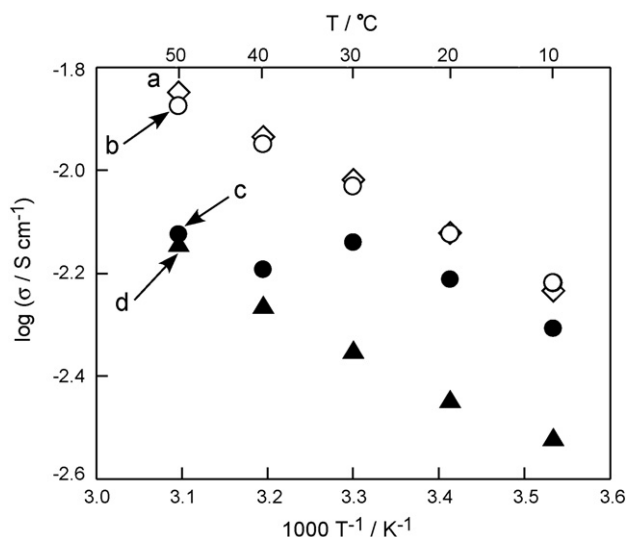


Fig. 3. Temperature dependence of the ionic conductivity for (a) 1.0 M LiPF₆/EC + DEC (2:1) solution, (b) 1.0 M LiPF₆/EC + DEC + TMP (55:25:20) solution, (c) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) gel, and (d) 1.0 M LiPF₆/EC + DEC + TMP (55:25:20) gel.

the same as those of liquid electrolyte systems, 1.0 M LiPF₆/EC + DEC + TMP (55:25:20) (Fig. 3(b)), and 1.0 M LiPF₆/EC + DEC (2:1) solution (Fig. 3(a)). However, the ionic conductivity of the gel with this composition decreased at above 40 °C, as shown in Fig. 3(c). This is probably due to deformation of the gel film during the conductivity measurement where some spring pressure is applied to the sample film to ensure the contact with the metal electrodes. When the gel is too soft to hold the liquid component in the polymer matrix, the gel film deforms with leaching out the liquid component, which would strongly influence the absolute value of the conductivity.

The constant-current charge and discharge characteristics of a Li/graphite half cell using the gel electrolyte were investigated. Fig. 4(A) shows the charge and discharge performances of the graphite electrode in the gel electrolyte of 0.8 M LiPF₆/EC + DEC + TMP (55:25:20). In this paper, we use the term “charge” for the Li⁺ insertion into the graphite and the term “discharge” for the desorption process, as in the conventional Li-ion battery. The discharge capacity of this cell was quite low at the first cycle, but increased with the repeated cycling. It achieved the value of about 200 mAh g⁻¹ after the 5th to the 10th cycles. However, the steady-state value was still ca. 2/3 of the theoretical capacity of the graphite. This low capacity of the graphite electrode in the gel electrolyte was probably due to the high impedance at the graphite surface where a thick surface film was formed by the decomposition of the electrolyte component. In order to suppress the surface reaction, an electrolyte additive was applied to this gel electrolyte system. Here we used VC as a typical additive for surface modification [23–26] and prepared a gel electrolyte containing a small amount of VC. The charge and discharge profiles of the cell using the gel electrolyte containing 2 wt.% of VC is shown in Fig. 4(B). The charge and discharge behavior was much improved and the discharge capacity of about 300 mAh g⁻¹ was obtained by adding VC. Thus,

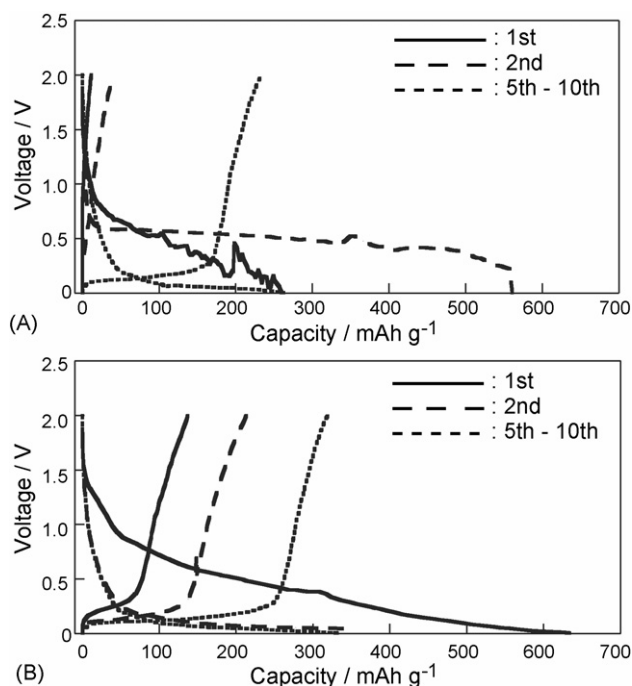


Fig. 4. Charge and discharge curves of graphite electrode in (A) 0.8 M $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{TMP}$ (55:25:20) gel electrolyte and (B) 0.8 M $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{TMP}$ (55:25:20)+VC (2 wt.%) gel electrolyte.

the addition of VC is effective for the graphite electrode in the present nonflammable gel electrolyte.

Variations in the discharge capacity of the graphite electrode in the gel electrolytes are shown in Fig. 5, compared with that obtained in the liquid electrolyte. For both gel electrolytes (shown as open and closed circles in Fig. 5), several cycles were initially required to achieve stable capacity. During such cycles the liquid component of the gel electrolytes may be introduced into the porous electrode structure and form good electrode/electrolyte interface. The gel electrolyte containing 2 wt.% VC showed almost the same capacity and cycling characteristics to those in the conventional organic electrolyte solution,

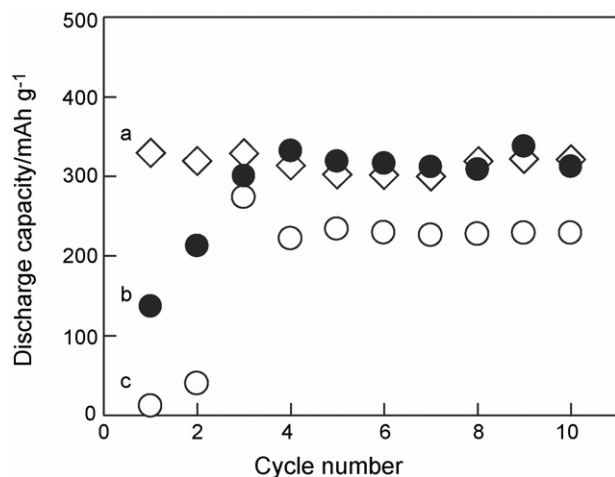


Fig. 5. Discharge capacity of graphite electrode in (a) 1.0 M $\text{LiPF}_6/\text{EC}+\text{DEC}$ (2:1) solution, (b) 0.8 M $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{TMP}$ (55:25:20)+VC (2 wt.%) gel, and (c) 0.8 M $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{TMP}$ (55:25:20) gel.

1.0 M $\text{LiPF}_6/\text{EC}+\text{DEC}$ (2:1), except for the first three cycles. This suggests that the stable SEI was formed by applying the gel electrolyte containing 2 wt.% VC. The reversible discharge capacity, ca. 330 mAh g^{-1} , in the gel electrolyte (Fig. 5(b)) will assure that the present gel electrolyte system is applicable for practical Li-ion battery as a safer electrolyte.

4. Conclusion

Nonflammable polymeric gel electrolyte was developed for Li-ion batteries using trimethyl phosphate (TMP) as a component solvent. LiPF_6 solutions containing TMP with mixed alkyl carbonates showed flame-retardant property. The gel electrolyte consisting of 0.8 M $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{TMP}$ (55:25:20) with PVdF-HFP as the host polymer showed sufficiently high ionic conductivity of 6.1 mS cm^{-1} at 20°C , which was comparable to that of the liquid electrolyte containing the same electrolyte component. The charge and discharge performances of the graphite electrode were improved by the addition of 2 wt.% vinylene carbonate (VC). Reversible discharge capacity of ca. 330 mAh g^{-1} was obtained for the graphite in the gel electrolyte containing TMP with VC.

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