



Short communication

Alkylphosphate-based nonflammable gel electrolyte for LiMn_2O_4 positive electrode in lithium-ion battery

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ABSTRACT

Polymeric gel containing alkylphosphate has been examined as nonflammable gel electrolyte for LiMn_2O_4 positive electrode of lithium-ion battery (LIB). The gel was composed of a polymer matrix of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and a liquid component consisting of ternary solvent of trimethyl phosphate (TMP) mixed with ethylene carbonate (EC) and diethyl carbonate (DEC) that dissolves lithium salt (LiPF_6 or LiBF_4). The gel composition of 0.8 M (mol dm^{-3}) LiX ($X = \text{PF}_6$ and BF_4) dissolved in EC + DEC + TMP (55:25:20) with PVdF-HFP showed excellent nonflammable characteristics and high ionic conductivity of ca. 3.1 mS cm^{-1} at room temperature (20°C). The charge–discharge cycling test of LiMn_2O_4 positive electrode gave good reversibility with high capacitance in the gel electrolyte. With respect to the electrolyte salt, LiBF_4 was better than LiPF_6 due to its thermal stability during the gel preparation.

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1. Introduction

Lithium-ion batteries (LIBs) have 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 LIB is now considered to fit power storage uses such as load-conditioning and electric vehicle (EV) systems due to their merits in high energy density, high power and long cycle life. Much attention has recently been focused on the safety issue of LIB as the increases in the battery size and application area.

To ensure the safety of Li-ion battery system from the material levels, many kinds of nonflammable or fire-retardant electrolyte systems have been proposed [1–20]. Typical trials are utilization of solid polymer complexes and ionic liquids as the electrolytes in LIBs [1,3–7]. The use of such nonflammable or fire-retardant compounds as fluorinated hydrocarbons and alkyl phosphates have also been examined as an additive or co-solvent of the conventional alkyl carbonate-based electrolytes [2,8–20]. Among them, alkyl phosphate compounds, trimethyl phosphate, tributyl phosphate (TBP) and ethylene ethyl phosphate (EEP) are promising candidates that have high compatibility in nonflammable properties and battery performances [13,14,19]. Xu et al. reported that fluorinated alkyl phosphate, tris(2,2,2-trifluoroethyl) phosphate (TTFP), is an excellent co-solvent for nonflammable electrolytes of LIBs. They

also found it being very effective in the improvement of the thermal stability of LiPF_6 -based electrolytes [8,10,11,15,18]. These alkyl phosphate compounds are also expected to be applied to gel polymer electrolyte systems due to their relatively low volatility and good miscibility with conventional alkyl carbonate solvents. However, publications have so far been limited about nonflammable gel polymer electrolytes based on alkyl phosphates for LIBs [21]. 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 LIBs [22]. Optimization of the gel composition and the electrochemical behavior of graphite as a negative electrode in the gel electrolyte have also been reported. We have concluded that the nonflammable gel electrolyte containing $\text{LiPF}_6/\text{EC} + \text{DEC}$ mixed with TMP and a proper amount of vinylene carbonate (VC) as an additive was applicable to LIB system [23].

In the present paper, we demonstrate the compatibility of the nonflammable gel electrolyte containing TMP as a nonflammable component to LiMn_2O_4 positive electrode. Preliminary discussion is made on the electrochemical behavior of LiMn_2O_4 in the gel electrolyte containing LiX ($X = \text{PF}_6, \text{BF}_4$)/EC + DEC mixed with TMP.

2. Experimental

Organic solvents in the gel components, EC (Kishida Chemical; Battery grade), DEC (Kishida Chemical; Battery grade), and TMP (Wako Chemical), were used as received. The electrolytic salts, LiPF_6

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Table 1
Combustion test of polymeric gel electrolyte.

Composition of liquid phase in the gel electrolyte	After warming the gel electrolyte at a flame
0.8 M LiPF ₆ /EC + DEC (2:1)	○
0.8 M LiPF ₆ /EC + DEC + TMP (55:25:20)	×
0.8 M LiBF ₄ /EC + DEC (2:1)	○
0.8 M LiBF ₄ /EC + DEC + TMP (55:25:20)	×

×: nonflammable, ○: combustible.

and LiBF₄ (Tomiyama, Battery grade), and the 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 first prepared by dissolving the Li salt (LiX) in a ternary solvent system of EC+DEC+TMP, where the mixing ratio of EC and DEC was kept constant, about 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 the LiX solution of mixed ternary solvents (EC + DEC + TMP, 55:25:20, v/v/v). The resulting mixture was stirred for 1 h to form homogeneous solution, and then developed on an aluminum pan. A transparent flexible film was obtained after heating the solution at 110 °C for 13 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. That is, the solution component in the gel electrolyte was ca. 83 mass%. A simple combustion test was performed by heating the gel electrolyte film with flame of Bunsen burner.

Powdered LiMn₂O₄ (Toda Kogyo Co.) was used as the active material of positive electrode. The test electrode was prepared from a slurry made of 1-methylpyrrolidine-2-on (NMP) containing 80 mass% of the active material, 10 mass% of acetylene black as a conducting support and 10 mass% of poly(vinylidene fluoride) as a binder.

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 LiMn₂O₄ electrode were investigated using a laboratory made three-electrode cell under constant-current charge and discharge conditions, typically with a current density of 0.05 mA cm⁻², which is equivalent to about C/10 rate.

3. Results and discussion

TMP is miscible with the most organic solvents that are used in conventional LIBs, without any phase separation over wide mixing ratios. We have previously reported that the minimum TMP content that inhibits the flammability of the binary system of EC + DEC (2:1, v/v) was 20 vol.% before dissolving 1.0 M LiPF₆ [22]. Thus, in this paper, we have chosen the solvent composition of EC + DEC + TMP (55:25:20, v/v/v) that dissolves 0.8 M LiX (X = PF₆ or BF₄) as the plasticizing component of the polymeric gel electrolyte based on PVdF-HFP. Nonflammability of the gel electrolyte was briefly examined by heating the gel electrolyte film directly on the burner flame. Polymeric gel electrolytes without TMP burned with flame continuously regardless of the dissolved Li salts, even after keeping away from the flame. By contrast, polymeric gel electrolyte films containing TMP were not combustible on the burner flame. The results of the simple combustion test are summarized in Table 1. It was experimentally confirmed that the present polymeric gel electrolytes containing TMP are nonflammable.

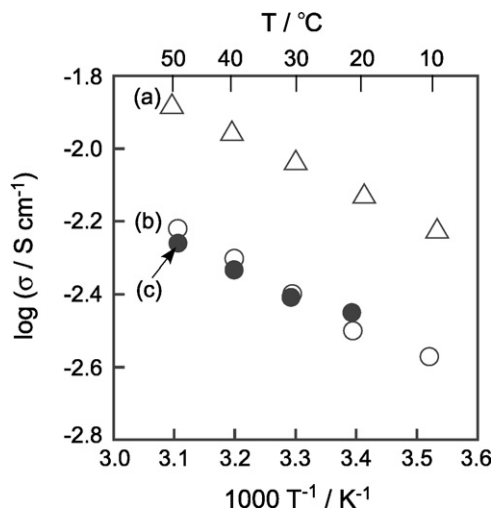


Fig. 1. Temperature dependence of the ionic conductivity for (a) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) solution, (b) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) gel, and (c) 0.8 M LiBF₄/EC + DEC + TMP (55:25:20) gel.

Fig. 1 shows the temperature dependence of the ionic conductivity for the nonflammable gel electrolytes, where data obtained for liquid electrolyte solution with the same solvent composition are also given for comparison. The ionic conductivity of the gel electrolytes was generally lower than that of the mother liquid electrolytes with the same solvent and salt compositions. However, practically high values of 3 mS cm⁻¹ were observed for the gel electrolytes composed of 0.8 M LiX (X = PF₆, BF₄)/EC + DEC + TMP (55:25:20) at 20 °C, as shown for the plots (b) and (c) in Fig. 1. These conductivity values will be enough for gel electrolyte film to be used in a practical LiB.

Constant-current charge–discharge cycling was carried out for LiMn₂O₄ positive electrode in the gel electrolyte using a three-electrode cell with Li-metal reference and counter electrodes. Fig. 2(A) shows the charge and discharge curves of LiMn₂O₄ electrode in liquid electrolyte containing TMP, 0.8 M LiPF₆/EC + DEC + TMP (55:25:20), as a control experiment. The voltage profile in each cycle presented typical one for LiMn₂O₄ electrode with spinel structure, except for the first charge in which some irreversible processes are included. The delivered discharge capacity of ca. 100 mA h g⁻¹ was almost ideal for this material. Fig. 2(B) gives the charge and discharge curves for LiMn₂O₄ in the gel electrolyte containing 0.8 M LiPF₆/EC + DEC + TMP (55:25:20). The capacity of the first discharge was about 90 mA h g⁻¹. However, the potential plateaus corresponding to the desorption/insertion processes of Li⁺ were not clearly observed, and discharge capacity was remarkably decreased with the repeated cycles. The charge and discharge performance of LiMn₂O₄ electrode in the gel containing LiBF₄ as the electrolytic salt is shown in Fig. 2(C). The discharge capacity of the first cycle was rather low compared with that obtained in the gel containing LiPF₆. However, the potential plateau was observed for each of charging and discharging process. Also the decrease in the discharge capacity with the cycle was much lower than in the gel using LiPF₆. These results clearly demonstrate that LiBF₄ salt is better than LiPF₆ in the present gel system. As a control data, the charge and discharge profiles of LiMn₂O₄ in the gel without TMP are also given in Fig. 2(D). The charge–discharge cycling behavior was almost the same as in the electrolytes containing TMP component. Consequently, it was proved that the cathodic behavior of LiMn₂O₄ was not so influenced by the addition of TMP in the gel.

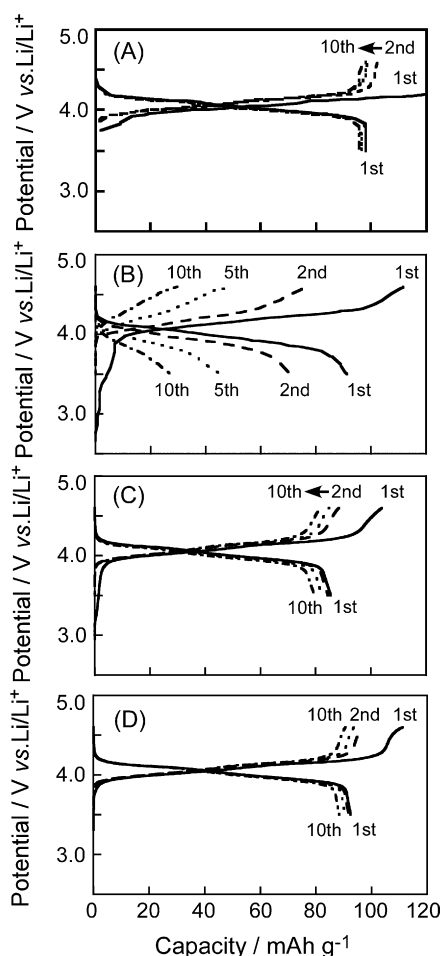


Fig. 2. Charge and discharge curves of Li/LiMn₂O₄ cells in liquid electrolyte: (A) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) and polymeric gel electrolytes containing (B) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20), (C) 0.8 M LiBF₄/EC + DEC + TMP (55:25:20), and (D) 0.8 M LiBF₄/EC + DEC (2:1). Current density: 0.05 mA cm⁻².

Variations in the discharge capacity of LiMn₂O₄ electrode in the gel electrolytes containing ternary solvent of EC + DEC + TMP are shown in Fig. 3, compared with that obtained in the liquid electrolyte containing the same solvent composition. About 100% utilization of the active material LiMn₂O₄ was obtained in the liquid electrolyte dissolving LiPF₆. However, the capacity loss with the cycle was significant in the gel containing LiPF₆ salt. The specific discharge capacity, hence the utilization of the active material LiMn₂O₄, in the gel containing LiBF₄ salt was slightly lower than that in LiPF₆-based gel at the first cycle, but the cycleability in the former electrolyte (LiBF₄) was much better than the latter (LiPF₆). The poor cycleability of the Li/LiMn₂O₄ cell using LiPF₆-based gel electrolyte was attributed to thermal decomposition of LiPF₆ during the heating process in gel preparation. Water impurity in the raw materials of the gel components would cause the liberation of acid HF through the decomposition of LiPF₆, as shown in scheme (1) [24]:



As this thermal reaction is somewhat depressed by co-existence of TMP, compared with the case without TMP [22], such bulk properties as the ionic conductivity of the gel would not be much influenced, as shown in Fig. 1. However, the resulting small amount of HF species in the gel electrolyte can significantly influence

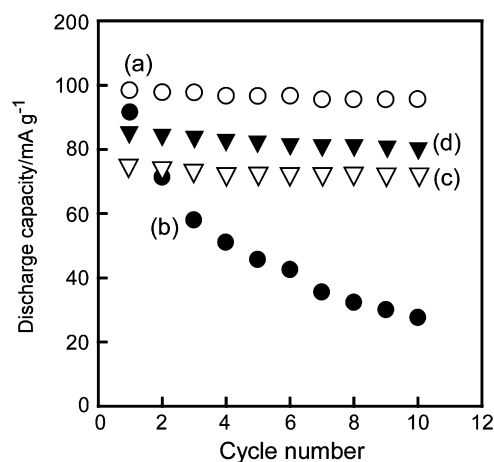


Fig. 3. Cycle performance under constant-current charge and discharge for Li/LiMn₂O₄ cells with (a) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) liquid, (b) 0.8 M LiPF₆/EC + DEC + TMP (55:25:20) gel, (c) 0.8 M LiBF₄/EC + DEC + TMP (55:25:20) liquid, and (d) 0.8 M LiBF₄/EC + DEC + TMP (55:25:20) gel. Current density: 0.05 mA cm⁻².

the surface chemistry of LiMn₂O₄ and lead to degradation of its cycleability. Thus, the thermal stability of LiBF₄ would be main advantage in the present gel electrolyte system containing TMP.

4. Conclusion

The compatibility of the nonflammable polymeric gel electrolyte containing trimethyl phosphate (TMP) as a component solvent was investigated with LiMn₂O₄ positive electrode. The gel electrolyte consisting of 0.8 M LiX (X = PF₆ or BF₄)/EC + DEC + TMP (55:25:20) with PVdF-HFP as the host polymer showed high ionic conductivity of 3.1 mS cm⁻¹ at 20 °C, which was applicable to the electrolyte of practical LIB. Although the discharge capacity of the first cycle of LiMn₂O₄ electrode using LiBF₄-based gel electrolyte was as low as ca. 84 mA h g⁻¹, the decrease of the discharge capacity with the repeated cycles was much lower than that in the gel using LiPF₆. Thus, the present polymeric gel electrolyte consisting of EC + DEC + TMP (55:25:20) dissolving 0.8 M LiBF₄ is suitable for LiMn₂O₄ positive electrode of LIBs with improved safety.

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