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Effect of Quaternary Phosphonium Salts in Organic Electrolyte for Lithium Secondary Batteries

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Additive behaviors of several bis (trifluoromethylsulfonyl) amide-based phosphonium salts in an organic electrolyte used for lithium secondary batteries are reported. Electrolytic properties of a lithium hexafluorophosphate-based organic electrolyte mixed with the phosphonium salts were examined. It was found that the mixed electrolytes containing the phosphonium salts showed lower conductivities and higher viscosities than the organic electrolyte. However, in the case of the mixed phosphonium electrolytes based on asymmetrical cations, the charge-discharge cyclabilities of the lithium battery cells were superior to that of the cell containing the organic electrolyte. Furthermore, the thermal stability of LiCoO₂ cathodes charged in the mixed phosphonium electrolytes was considerably improved. These results suggest that the phosphonium salts are regarded as effective electrolyte additives for lithium secondary batteries.

Key Words : Quaternary Phosphonium Salts, Lithium Secondary Battery, Electrolyte Additives, Thermal Stability

1 Introduction

Lithium secondary batteries are high-performance energy storage devices that have been employed as key components for portable electronic devices, electric vehicles, large-scale power systems, etc. In recent years, the practical use of electrolyte additives for lithium secondary batteries have been intensively studied from the viewpoint of improvement of cell properties such as charge-discharge capacity and cyclability, durability, overcharge safety, and so forth.¹⁻³⁾ Many chemical compounds have been investigated as electrolyte additives on the basis of improvement of the charge-discharge performance. For instance, electrolyte additives based on quaternary ammonium salts to afford the high cycling efficiency have been proposed.^{4,5)} Hirai et al. reported that several quaternary ammonium compounds containing a long alkyl chain exhibited improving effects on the cycling properties of the lithium battery cells.⁴⁾ A quaternary ammonium salt based on a perfluorinated anion (tetraethylammonium perfluorooctanesulfonate) was also examined as a performance electrolyte additive for the improvement of cycling efficiency.⁵⁾ In both reports, it was demonstrated that the quaternary ammonium compounds significantly act as surfactants to give uniform films of lithium on the anode surface, suppressing the formation of needle-like lithium dendrites.

On the other hand, quaternary salts based on phosphonium cations have been regarded as the potential substitutes for the corresponding ammonium salts since it is well known that quaternary phosphonium compounds offer chemical and thermal stabilities as practical advantages.⁶⁻⁸⁾ From this point of view, quaternary phosphonium salts are of considerable interest for the battery electrolyte application. We have designed a new class of

quaternary phosphonium compounds consisted of triethylphosphine (C₂H₅)₃P (TEP)- and tributylphosphine (C₄H₉)₃P (TBP)-based cations together with a bis (trifluoromethylsulfonyl) amide N(SO₂CF₃)₂ (TFSA) anion,^{9,10)} and have explored their lithium battery application.¹¹⁻¹³⁾ Tributylmethylphosphonium TFSA (C₄H₉)₃CH₃P-N(SO₂CF₃)₂ (P₄₄₄₁-TFSA) is one of the typical TFSA-based phosphonium compounds possessing favorable electrochemical stability for the use of lithium battery electrolytes.¹⁰⁾ Our preliminary investigation revealed that P₄₄₄₁-TFSA significantly improved the cycling performance of the lithium battery cell when added into a

Fig. 1 Structural illustration of ionic components of quaternary phosphonium salts investigated in this work.

conventional organic electrolyte;¹⁴⁾ however, only P_{4441} -TFSA has been tested. Therefore, extensive researches on the additive effects of the quaternary phosphonium compounds should be required.

In this paper, we report the additive effects of several quaternary phosphonium salts on the charge-discharge property of the lithium battery cells. In order to discuss the dependence of cation structures, three phosphonium cations are selected in this work: triethylpentylphosphonium (P_{2225}^+), tributylmethylphosphonium (P_{4441}^+)¹⁴⁾ and tetrabutylphosphonium (P_{4444}^+) cations (Fig. 1). Additionally, thermal stability of the cathode materials charged in the mixed electrolytes containing the phosphonium salts is also investigated.

2 Experimental

2.1 Preparation of mixed electrolytes

The synthesis and purification of quaternary phosphonium salts were performed according to the methods described in our previously published paper.^{9,10)} The mixed electrolytes containing the phosphonium salts were prepared by the same procedures reported previously.¹⁴⁾ One of the precursor phosphonium halides, triethylpentylphosphonium bromide ($(C_2H_5)_3C_5H_{11}P-Br$), was synthesized by the nucleophilic addition of TEP (Nippon Chemical Industrial Co., Ltd., 20 % toluene solution, trade name Hishicolin P-2) to 1-bromopentane (Tokyo Chemical Industry Co., Ltd.) at 80 °C under nitrogen atmosphere. Tributylmethylphosphonium chloride ($(C_4H_9)_3CH_3P-Cl$) and tetrabutylphosphonium chloride ($(C_4H_9)_4P-Cl$) were supplied by Nippon Chemical Industrial Co., Ltd. (trade name Hishicolin® PX-4MC and Hishicolin® PX-4C, respectively). The aqueous ion exchange reaction of the precursor phosphonium halides with Li-TFSA (Kanto Chemical Co., Inc.) at ambient temperature gave crude phosphonium TFSA salts (P_{2225} -TFSA, P_{4441} -TFSA and P_{4444} -TFSA). The resulting salts were extracted by dichloromethane and were purified by washing with pure water several times until no residual halide anion was detected with the use of $AgNO_3$. P_{2225} -TFSA and P_{4441} -TFSA were viscous liquids at room temperature (so-called room-temperature molten salts or room-temperature ionic liquids) whereas P_{4444} -TFSA was a crystalline solid (melting point: 83 °C).^{9,10)} The residual content of halide anions (<50 ppm) in each salt was checked by an ion chromatography. The lithium hexafluorophosphate ($LiPF_6$, 1.0 M)-ethylene carbonate (EC)-ethyl methyl carbonate (EMC) (1:2, v/v) electrolyte¹⁵⁾ was used as a conventional organic electrolyte (Ube Industries, Ltd.). The preparation of mixed electrolytes consisting of the phosphonium salts and the $LiPF_6$ -EC-EMC electrolyte was made in an argon atmosphere glove box ($[H_2O]<1$ ppm, $[O_2]<1$ ppm).

2.2 Measurements of transport property

The conductivity of each electrolyte was measured by using an ac impedance analyzer (Ivium Technologies, CompactStat) and a two Pt electrode conductivity cell (cell constant: 1.27 cm^{-1}). The viscosity of each electrolyte was determined by using a vibration-type viscometer (CBC Materials Co. Ltd., VM-10A Laboratory Viscom-

eter calibrated with the Brookfield Viscosity Standard). All measurements were performed under dry condition of argon flow at 25 °C.

2.3 Lithium battery tests

The lithium secondary batteries used for the charge-discharge tests were fabricated using conventional two-electrode cells (CR2032). The fabrication of the lithium battery cells was carried out in an argon-atmosphere glove box ($[H_2O]<1$ ppm, $[O_2]<1$ ppm). A paste mixture containing $LiCoO_2$ (Nippon Chemical Industrial Co., Ltd., trade name Cellseed® C-5), conductive carbon black (Timcal, Super P®) and poly(vinylidene fluoride) (PVDF, Kureha Co., W#1300) was prepared with a weight ratio of 95:2.5:2.5. *N*-methylpyrrolidone (BASF Japan, Ltd.) was used as a dispersant for the paste mixture. The preparation of the cathode sheets (area: 1 cm^2) was carried out by spreading the paste mixture onto an Al current collector (battery use, 99.5 %, Hosen Co., Ltd.). The content of the active material in the cathode sheet was *ca.* 7.2 $mg\ cm^{-2}$. Li foils (area: 1 cm^2 , thickness: 0.5 mm, Honjo Metal Co., Ltd.) were used as anodes. The polyethylene sheets (45 μm thick, Celgard Inc.) were employed as separators. The charge-discharge tests of the cells were conducted by using a charge-discharge system (Hokuto Denko Co., Ltd, HJR-110mSM6) at 4.2–3.4 V of cut-off voltage with 0.2–0.5 C current rates at 25 °C. The cells were charged and discharged by a constant current/constant voltage (CCCV) and constant current (CC) modes, respectively.

2.4 Thermal stability measurements of cathode

All of the $LiCoO_2$ cathode sheets for this measurement were basically prepared by the same procedure as described above. Each $LiCoO_2$ cathode sheet was charged using a CR2032 coin-type cell (anode: Li metal) containing each mixed electrolyte at 4.3 V of voltage with 0.5 C current rates (5 h). The $LiCoO_2$ thus charged were removed from the cells and then were rinsed with a battery-grade dimethyl carbonate in an argon-atmosphere glove box ($[H_2O]<1$ ppm, $[O_2]<1$ ppm). The thermograms of dried $LiCoO_2$ samples were recorded by using a differential scanning calorimeter (Seiko Instruments Inc., DSC6200) with a heating rate of 2 °C min^{-1} under nitrogen atmosphere.

3 Results and Discussion

3.1 Transport property of mixed electrolytes

In our preliminary study, an additive effect of P_{4441} -TFSA into the $LiPF_6$ -EC-EMC electrolyte was remarkably observed at a volume ratio of 1:1,¹⁴⁾ so that the mixed electrolytes investigated in this work were prepared with the 1:1 volume ratio. Table 1 summarizes the transport property data (conductivity and viscosity) of various electrolytes at 25 °C. When each phosphonium salt was added into the $LiPF_6$ -EC-EMC electrolyte, the viscosity was increased and the conductivity was correspondingly decreased. In the three phosphonium salts, P_{2225} -TFSA significantly gave the lowest viscosity and highest conductivity to its mixed electrolyte. However, there is a slight difference in the transport property between mixed P_{4441} -TFSA and P_{4444} -TFSA electrolytes,

Table 1 Conductivity and viscosity of various electrolytes at 25 °C.

Electrolyte	σ^a /mS cm ⁻¹	η^b /mPa s
LiPF ₆ -EC-EMC (no additive) ^c	9.1 ¹⁴⁾	<10 ¹⁴⁾
Mixed P ₂₂₂₅ -TFSA electrolyte ^{d, e}	5.1	13
Mixed P ₄₄₄₁ -TFSA electrolyte ^{d, f}	3.6 ¹⁴⁾	16 ¹⁴⁾
Mixed P ₄₄₄₄ -TFSA electrolyte ^{d, g}	3.5	14
P ₂₂₂₅ -TFSA (neat)	1.7 ⁹⁾	88 ⁹⁾
P ₄₄₄₁ -TFSA (neat)	0.42 ¹⁰⁾	207 ¹⁰⁾

^a Conductivity at 25 °C.^b Viscosity at 25 °C.^c 1.0 M LiPF₆/EC + EMC (1:2, v/v).^d Phosphonium salts/LiPF₆-EC-EMC (1:1, v/v).^e LiPF₆ : P₂₂₂₅-TFSA = 1.0 : 2.8 (mol/mol)^f LiPF₆ : P₄₄₄₁-TFSA = 1.0 : 2.6 (mol/mol)^g LiPF₆ : P₄₄₄₄-TFSA = 1.0 : 2.3 (mol/mol)

which seems to be due to their similar cation structures. Hence, it is thought that the transport property of the mixed electrolytes would be influenced by the cation sizes of added salts when the volume ratio of mixing is constant. The P₂₂₂₅ cation is smaller than P₄₄₄₁ and P₄₄₄₄ cations, which might be also supported by the comparison of their molar concentrations (P₂₂₂₅-TFSA: 2.81 mol dm⁻³, P₄₄₄₁-TFSA: 2.57 mol dm⁻³, at 25 °C), so that the mixed P₂₂₂₅-TFSA electrolyte exhibited relatively high transport property when compared to other mixed electrolytes.

3.2 Charge-discharge property of lithium battery cells

Figure 2 represents the charge-discharge curves of lithium battery cells containing the mixed phosphonium electrolytes in comparison with that containing the LiPF₆-EC-EMC electrolyte with no additives. The discharge capacity and coulombic efficiency as a function of cycle number are also plotted in Fig. 3. All of the lithium battery cells containing the mixed phosphonium electrolytes exhibited typical charge-discharge behaviors. As shown in Fig. 2 (a), the cell containing the mixed P₂₂₂₅-TFSA electrolyte indicated sufficiently high discharge capacities (*e.g.* 160 mAh g⁻¹ at the first cycle) with a high capacity retention ratio (95 % after 20 cycles). The coulombic efficiencies after the third cycle also approached 100 % (*ca.* 98–99 %). It is noted that this cycling performance is superior to that of the cell containing the highly conductive LiPF₆-EC-EMC electrolyte without adding P₂₂₂₅-TFSA (Fig. 2 (d)), which reveals that P₂₂₂₅-TFSA acts as an electrolyte additive for the improvement of cycling efficiency. However, in the case of the mixed P₄₄₄₁-TFSA electrolyte (Fig. 2 (b)), further favorable charge-discharge performance with relatively high capacity retention ratio (97 % after 20 cycles) was observed despite the fact that the transport property of the mixed P₄₄₄₁-TFSA electrolyte is lower than that of the mixed P₂₂₂₅-TFSA electrolyte (Table 1). On the other hand, as shown in Fig. 2 (c), it is obvious that the cell containing the mixed P₄₄₄₄-TFSA electrolyte exhibited relatively low charge-discharge performance when com-

pared to that containing the LiPF₆-EC-EMC electrolyte without adding P₄₄₄₄-TFSA (Fig. 2 (d)).

The results given in Figs. 2 and 3 significantly suggest that both P₂₂₂₅-TFSA and P₄₄₄₁-TFSA were regarded as effective additives to improve the charge-discharge cyclability whereas P₄₄₄₄-TFSA reduced the cycling performance. Especially, in these phosphonium salts, P₄₄₄₁-TFSA showed the most remarkable improving effect. It should be noted that additive behavior thus observed did not correspond to the transport property of the mixed electrolytes. However, the improving effect clearly depends on the structures of the phosphonium cations because both P₄₄₄₁ and P₂₂₂₅ cations are relatively asymmetrical when compared to the symmetrical P₄₄₄₄ cation. Therefore, the salts having asymmetrical phosphonium cations seem to play an important role in the vicinity of the electrode surface.

As a considerable possibility, this effect might be attributed to the uniform formation of lithium on the anode surface, suppressing the unfavorable formation of needle-like lithium dendrites to accumulate dead lithium area on the surface. Such a suppression of lithium dendrite formation by the phosphonium salts has also been suggested by Kohl and coworkers who examined the voltammetric behavior of tributylhexylphosphonium TFSA.¹⁶⁾ In our preliminary investigation by using a cyclic voltammetry technique, it has been found that the mixed P₄₄₄₁-TFSA electrolyte gave a remarkable voltammetric response in deposition/dissolution processes of metallic lithium,¹⁴⁾ which seems to assist the above discussion of the effect on the anode surface. Additionally, it is well known that the formation of needle-like lithium dendrites on the anode surface can give short circuits, rendering the cells unsafe owing to the risk of fire and explosion. From this point of view, the additive performance of the phosphonium salts to suppress the lithium dendrite formation is thought to be of much practical significance for the safety performance as well as the charge-discharge cycling property of lithium secondary batteries.

Another possible effect seems to be on the LiCoO₂

Fig. 2 The charge-discharge curves of Li/electrolytes/LiCoO₂ cells at 0.5 C (CCCV mode, 5 h, 0.56 mA cm⁻²) of charge current rate and at 0.2 C (CC mode, 0.22 mA cm⁻²) of discharge current rate; the charge-discharge curves of the cells containing (a) the mixed P₂₂₂₅-TFSA electrolyte, (b) the mixed P₄₄₁-TFSA electrolyte, (c) the mixed P₄₄₄-TFSA electrolyte and (d) the LiPF₆-EC-EMC electrolyte (no additives). The data shown in (b) and (d) were taken from the reference.¹⁴⁾

Fig. 3 Dependence of cycle number on (a) the discharge capacity and (b) the coulombic efficiency for the cells containing various electrolytes.

cathode surface. It is well known that charge-discharge processes often involve the formation of a conductive passivation film, the so-called solid electrolyte interface (or solid electrolyte interphase) (SEI) film, to prevent further decomposition of the electrolytes. The specific effect of the phosphonium salts on the cell performance also might be attributed to the formation of a SEI-like film on the cathode surface; however, unfortunately at present we are unable to obtain clear information concerning the cathode surface. Further investigation of the SEI formation associated with the phosphonium salts should be required and will be conducted.

3.3 Thermal stability of cathode

Our additional attempt was made directly toward the effect of the phosphonium salts on the LiCoO₂ cathode. Since it is well known that the phosphonium compounds possess high thermal stability,^{6,7)} we were motivated to investigate the thermal decomposition behavior of the cathode in the mixed phosphonium electrolytes. Figure 4 depicts the DSC thermograms of LiCoO₂ cathodes charged in various electrolytes. As shown by dotted line in Fig. 4, the LiCoO₂ cathode charged in the LiPF₆-EC-EMC electrolyte with no additives was thermally decomposed, exhibiting one large exothermic peak around 198 °C and two relatively small peaks at 204 and 240 °C. It is worthwhile to note that, in the case of LiCoO₂ cathodes charged in the mixed electrolyte containing the phosphonium salts (P₂₂₂₅-TFSA and P₄₄₁-TFSA, solid and dashed lines, respectively), the peak around 198 °C significantly vanished whereas the peak around 240 °C grew larger. This means that the thermal decomposition

Fig. 4 DSC thermograms of LiCoO₂ charged in mixed P₂₂₂₅-TFSA electrolyte (solid line), mixed P₄₄₄₁-TFSA electrolyte (dashed line) and LiPF₆-EC-EMC electrolyte (dotted line).

points of LiCoO₂ cathodes were shifted to relatively high temperature regions, indicating the thermal stabilization of LiCoO₂ by the phosphonium salts. Although the detailed mechanism remains still unclear at present, such a thermal stabilization effect by the phosphonium salts should contribute to the safety performance of lithium battery cells.

4 Conclusions

We have shown the electrolyte additive properties of three phosphonium salts (P₂₂₂₅-TFSA, P₄₄₄₁-TFSA and P₄₄₄₄-TFSA) on the charge-discharge property of lithium battery cells and the thermal stability of LiCoO₂ cathode. The mixed electrolytes containing the phosphonium salts showed lower conductivities and higher viscosities than the LiPF₆-EC-EMC electrolyte with no additives. Nevertheless, it was found that the charge-discharge cyclabilities of the cells containing the mixed phosphonium electrolytes based on asymmetrical cations (P₂₂₂₅⁺ and P₄₄₄₁⁺) were superior to that of the LiPF₆-EC-EMC electrolyte. Especially, the mixed P₄₄₄₁-TFSA electrolyte gave relatively high cycling efficiency. Furthermore, the LiCoO₂ cathodes charged in the mixed P₂₂₂₅-TFSA and

P₄₄₄₁-TFSA electrolytes were more thermally stable than that charged in the LiPF₆-EC-EMC electrolyte. These results allow us to suggest that both P₂₂₂₅-TFSA and P₄₄₄₁-TFSA can be used as effective electrolyte additives to improve both the charge-discharge cycling performance of lithium battery cells and the thermal stability of LiCoO₂ cathode. Additional and continuing investigations for lithium battery applications using quaternary phosphonium compounds are in progress and will be reported.

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