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Electrolytes Containing Ionic Liquids for Improved Safety of Lithium-ion Batteries

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ABSTRACT

Ionic liquids are of interest for application in electrolytes of lithium-ion batteries, because of their non-flammability, thermal stability, and non-volatility. Electrolytes containing ionic liquids have therefore been used to improve the safety of lithium-ion cells. Both the liquid electrolyte and the gelled electrolyte, which was composed of 1-ethyl-3-methyl-imidazolium tetrafluoroborate and LiBF_4 , were shown to have good thermal and electrochemical stability and to be applicable for use in lithium-ion cells with $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ as the negative electrode active material. Electrolytes containing a mixture of organic solvents and *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide were also found to exhibit good discharge performance for use in lithium-ion cells and non-flammability for use as an electrolyte. Furthermore, it was found that graphite was able to perform in the electrolyte containing the ionic liquid.

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Keywords : Lithium-ion Cell, Ionic Liquid, Non-flammable Electrolyte

1. Introduction

Lithium-ion batteries have contributed greatly to the practical use of various electrical instruments. Especially, large-sized lithium-ion batteries have been actively developed for use in advanced vehicles, such as electric vehicles (EVs) and hybrid electric vehicles (HEVs). Presently, the use of flammable organic solvents as electrolytes in small-sized lithium-ion cells cannot be avoided; therefore, studies to improve the safety of large-sized lithium-ion cells have become increasingly significant.

Ionic liquids have attracted growing interest for application in electrochemical devices because of their non-flammability and negligible vapor pressure. Various practical applications of ionic liquids have been suggested since the discovery of stable compounds, such as 1-ethyl-3-methyl-imidazolium tetrafluoroborate (EMI-BF_4).¹ Since the combination of ionic liquids with free anions instead of aluminum chloride (AlCl_3) was reported by Bonhôte et al.,² applications for use in solar cells,^{3,4} fuel cells,⁵ double-layer capacitors,⁶ and various batteries⁷ were attempted. Meanwhile, attempts to use an ionic liquid- AlCl_3 complex in lithium batteries were also reported. The possibility of using a LiCl-EMICl-AlCl_3 electrolyte for the $\text{Li-Al/LiCl-EMICl-AlCl}_3/\text{V}_2\text{O}_5$ system cell⁸ and the electrochemical performance of the $\text{Li-Al/LiCl-EMICl-AlCl}_3/\text{LiCoO}_2$ system cell⁹ were reported. The electrochemical characteristics of carbon electrodes using ionic liquids have also been studied.^{10,11} These results showed that ionic liquids were capable of functioning as “non-flammable solvents” for electrolytes without the necessity for any conventional organic solvents. Especially, among the various series of ionic liquids, combinations of cyclic aliphatic or asymmetric quaternary ammonium cations and imide anions, such as *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide (PP13-TFSI), are able to perform the role of the electrolyte solvent in Li/LiCoO_2 system cells as effectively as conventional organic solvents.¹² Both oxidation and reduction potentials are determined by the electrochemical stability of the cation of the ionic liquid. Cyclic aliphatic or asymmetric quaternary ammonium

cations, such as the PP13 cation, are more stable than aromatic cations, such as the EMI cation. The electrochemical stability of the ionic liquid was found to be sufficient for lithium cells; however, there were some limitations in terms of application in cells with high-power requirements, such as HEVs, because of the higher viscosity and lower ionic conductivity of the electrolyte than those of conventional organic electrolytes.^{13,14} Furthermore, some researchers also reported mixtures of the electrolyte with organic solvents and ionic liquids.^{15,16} Ionic liquids may also be applicable as flame-retardant additives for improving the safety of lithium-ion cells containing flammable organic solvents, because they are non-flammable and non-volatile.

In this comprehensive paper, the results obtained for the electrochemical performance of lithium-ion cells and thermal stability of the electrolytes with (1) mixtures of neat ionic liquids and lithium salts¹⁷ and (2) ternary mixtures of ionic liquids, lithium salts, and organic solvents¹⁸ are discussed. In the first section, EMI-BF_4 was selected as the ionic liquid because of its low viscosity and low melting point. On the other hand, PP13-TFSI was selected as the ionic liquid in the second section because of its electrochemical stability.

2. Experimental

2.1 Application of electrolytes using mixtures of neat ionic liquids and lithium salts

The binary mixture, LiBF_4 and EMI-BF_4 , i.e., LiEMIBF_4 , was prepared by mixing EMI-BF_4 and LiBF_4 . The salt concentration of LiBF_4 was fixed at 1 mol dm^{-3} in the EMI-BF_4 . In addition, the gelled electrolyte, GLEMIBF_4 , was prepared by adding 15 mass% poly(ethylene glycol)diacrylate monomer ($M_w = \text{ca. } 600$) to LiEMIBF_4 , after which the monomer was polymerized. For the reference, the conventional liquid electrolyte, $1 \text{ mol dm}^{-3} \text{ LiBF}_4$ in a mixture of γ -butyrolactone (GBL) and ethylenecarbonate (EC) with a 60:40 volume ratio of $\text{LiBF}_4\text{-GBL/EC}$, was prepared. Thermogravimetry (TG) and differential thermal measurements

(DTA) were performed for confirmation of the thermal stability of the electrolytes. The measurements were made in the temperature range from 30 to 500°C under an argon gas flow with a scanning rate of 10°C min⁻¹. An open platinum pan was used to record the measurements. The small-sized demonstration cells were composed of Li[Li_{1/3}Ti_{5/3}]O₄ and LiCoO₂ as the negative and positive electrode active materials, respectively. LiBF₄-GBL/EC, LiEMIBF₄, or GLiEMIBF₄ were used as the electrolyte. The discharge capacities of the demonstration cells were investigated at rates of 0.1, 0.2, 0.4, and 1.0 C mA at 25°C. The charge rate was fixed at 0.1 C mA. The charging and discharging processes of the demonstration cells were repeated with a constant current rate of 0.2 C mA at 25°C. The operating voltage ranged from 1.2 to 2.6 V.

2.2 Application of electrolytes with ionic liquids, lithium salts, and organic solvents

PP13-TFSI was used as the ionic liquid. The mixed electrolyte was prepared by adding a certain amount of PP13-TFSI to the organic solvent mixture, which was composed of EC:dimethylcarbonate (DMC):ethylmethylcarbonate (EMC) = 1:1:1 (in volume ratio), and then 1 mol dm⁻³ of LiPF₆ was dissolved in this solvent-ionic liquid mixture. The safety of the electrolyte was confirmed by examining its flammability as below. A glass filter, impregnated with the electrolyte, was held in close proximity to the flame of an alcohol lamp for 10 seconds. When the electrolyte continued burning after removal of the flame, this test was considered to indicate that ignition was possible. Each electrolyte was tested three times. If the ignition occurred every time, the electrolyte was decided to be a flammable electrolyte based on this test. The pouch-type lithium-ion demonstration cells were constructed using the mixed electrolytes containing 0, 25, and 50 mass% PP13-TFSI. Graphite and LiCoO₂ was used as the negative and positive electrode active materials, respectively. Discharge performances of the demonstration cells at various current were investigated at current rates of 0.2, 1.0, and 2.0 C mA at 25°C. The charge and discharge cycling performances were also investigated by repeating the performance 50 times for each charging and discharging current rate of 1.0 C mA at 25°C. The limiting voltages of the charging and discharging cycles were 4.2 and 3.0 V.

3. Results and Discussion

3.1 Application of the electrolytes with mixtures of the neat ionic liquids and lithium salts

The TG and DTA curves for the five electrolyte samples are shown in Fig. 1. The DTA curve of neat EMI-BF₄ showed two

Figure 1. TG and DTA curves plotted versus temperature for the five electrolyte samples. (Reproduced by permission of The Electrochemical Society.¹⁷)

broad exothermic peaks on heating, and weight loss started at ca. 300°C and became apparent at ca. 350°C in the TG curve. As shown in the TG curve of LiEMIBF₄, the clear decomposition of LiEMIBF₄ started at ca. 350°C and two decomposition steps were observed, which indicated a change in the decomposition mechanisms by adding LiBF₄. The slightly lower decomposition temperature of LiEMIBF₄ compared to neat EMI-BF₄ and the two-step decomposition indicate the changes in ionic interactions between EMI⁺ and BF₄⁻ by addition of LiBF₄. It was suggested that ionic clusters among Li⁺, EMI⁺, and BF₄⁻ existed in LiEMIBF₄. On the other hand, the TG and DTA curves of GLiEMIBF₄ indicate a decomposition reaction without a clear DTA exothermic peak, and the weight loss was observed between 350 and 480°C. The decomposition behavior of GLiEMIBF₄ resembles that of EMIBF₄ rather than LiEMIBF₄, and GLiEMIBF₄ has higher thermal stability than both EMIBF₄ and LiEMIBF₄. The TG-DTA results also suggest the existence of interaction between the polymer chain and Li⁺. Thus, most of the lithium ions interact with the polymer chain in GLiEMIBF₄ and LiBF₄ apparently did not reduce the extent to which high-temperature decomposition occurred.

EMIBF₄ has a wide potential window; however, the lithium metal and carbon materials are not suitable active materials for the negative electrode due to its reductive instability below 1.1 V. The reduction limit is determined by the decomposition of EMI⁺.^{6,19} The specific capabilities of the Li[Li_{1/3}Ti_{5/3}]O₄/LiCoO₂ system cells are plotted versus the discharge rate in Fig. 2. The discharge capacity was found to decrease with an increase in the discharge current in the LiEMIBF₄ cell, and to a larger extent in the GLiEMIBF₄ cell. This result might be related to the low ionic conductivity and the polarization of LiEMIBF₄ and GLiEMIBF₄ by high concentrations of EMI⁺ and BF₄⁻, and slow Li⁺ transportation.

The cyclic performances of these cells at a rate of 0.2 C mA are shown in Fig. 3. Good cyclability of the LiEMIBF₄ and GLiEMIBF₄ cells, similar to that of the conventional LiBF₄-GBL/EC cell was obtained, where the rated capacity was different in each cell. Capacity retention of 94.4% in terms of the initial capacity was achieved in the LiEMIBF₄ cell after 50 cycles. The discharge capacity of the GLiEMIBF₄ cell decreased gradually to 73.1% of the initial value after 50 cycles. This result showed that the initial experiments achieved a reasonable performance of 50 cycles for the electrolytes containing the non-chlorinated ionic liquid.

Figure 2. Specific capacity of the demonstration cells. Electrolytes were LiBF₄-GBL/EC, LiEMIBF₄, and GLiEMIBF₄. The charge current was fixed at 0.1 C mA, and various discharge currents were used. The cut-off limit voltages were 2.6 and 1.2 V for charge and discharge, respectively. (Reproduced by permission of The Electrochemical Society.¹⁷)

Figure 3. Cycle life performance of the demonstration cells. The charge-discharge process was performed at 0.2 C mA constant current. The cut-off limit voltages were 2.6 and 1.2 V for the charge and discharge, respectively. (Reproduced by permission of The Electrochemical Society.¹⁷⁾)

Table 1. Result of flammability test of mixed electrolyte containing PP13-TFSI and organic solvents. Each sample was tested three times. Flammability is expressed as (times of ignition)/(trial number). (Reproduced by permission of Elsevier.¹⁸⁾)

Content of PP13-TFSI (mass%)	Occurrence of ignition
0	3/3
25	3/3
30	2/3
40	0/3
50	0/3
100	0/3

3.2 Application of the electrolytes with ionic liquids, lithium salts, and organic solvents

Table 1 lists the result of the flammability test for the mixed electrolyte containing PP13-TFSI and the organic solvents. The conventional electrolyte (0 mass% PP13-TFSI) ignited and continued burning for 10 seconds every time, because organic solvents easily retain their flammability at ambient temperature. The addition of PP13-TFSI to the mixed electrolyte reduces the content of the organic solvents. The mixed electrolyte continues to be flammable at 25 mass% PP13-TFSI; however, electrolytes containing 30 mass% PP13-TFSI retained their flammability in the all repeated experiments. Eventually, non-flammability of the mixed electrolyte with 40 mass% PP13-TFSI appears, even when it also contains flammable organic solvents. This result can be explained as follows. The partial pressure of flammable gas (i.e., the vapor of the organic solvents) around the test flame is reduced by the addition of ionic liquid.

Figure 4 shows the discharge performance of the graphite /LiCoO₂ system lithium-ion demonstration cells with the electrolyte consisting of a mixture of PP13-TFSI and organic solvents. At 0.2 and 1.0 C mA discharge, almost no capacity fading was observed for the cell with the electrolyte containing 50 mass% PP13-TFSI. However, at 2.0 C mA, the discharge capacity decreased. The reason for this capacity decrease at higher current is that the viscosity of the electrolyte containing PP13-TFSI is higher than the conventional electrolyte. In this case, the ionic conductivity and mobility of ions in the electrolyte also mainly depend upon the bulk viscosity.

Figure 4. Discharge performance of the lithium-ion demonstration cells with mixed electrolyte containing PP13-TFSI and organic solvents at 25°C. The concentration of PP13-TFSI is 0 (◇), 25 (□), and 50 (△) mass%. Charging condition is 1.0 C mA to 4.2 V followed by constant voltage; Discharging condition is 0.2, 1.0, and 2.0 C mA to 3.0 V. (Reproduced by permission of Elsevier.¹⁸⁾)

Figure 5. Cycle life performance of the lithium-ion demonstration cells with mixed electrolyte containing PP13-TFSI and organic solvents at 25°C. The concentration of PP13-TFSI is 0 (◇), and 50 (△) mass%. Charging condition is 1.0 C mA to 4.2 V followed by constant voltage; discharging condition is 1.0 C mA to 3.0 V. (Reproduced by permission of Elsevier.¹⁸⁾)

Therefore, the supply of lithium ions from the bulk electrolyte to the surface of LiCoO₂ was considered insufficient under severe conditions. As already reported, a large capacity fading was observed even at 1.0 C mA for discharge on the cell with neat PP13-TFSI.^{12,14} However, it is clear that the cell containing the mixed electrolyte is able to exhibit a large capacity even at 1.0 C mA in this study. This result suggested that it would be possible to use lithium-ion cells containing mixtures of PP13-TFSI and organic solvents as electrolytes in high-power applications by optimization of the cell design.

Figure 5 shows the cycle life performance of the demonstration cells with and without PP13-TFSI in the electrolyte. As a result, both cells maintained a ratio higher than 90% of the initial discharge capacity after 50 cycles. This means that the solid electrolyte interface (SEI) of the negative electrode would be capable of continuously preventing any side reaction during cycle charging and discharging even if the electrolyte were to contain PP13-TFSI. That is, even if the mixed electrolyte were to contain PP13-TFSI, the surface of the graphite could easily be covered by a good SEI before beginning the first lithium insertion reaction, because of the coexistence of the organic solvent, such as EC. Furthermore, the SEI should be the factor to prevent any side reaction, such as reduction

or co-insertion into the graphite layer of the PP13 cation. Therefore, cells containing a mixed electrolyte and a carbon negative electrode showed good cycle life performance. As a result, the electrolyte containing 50 mass% PP13-TFSI was found to show both good discharge performance of the lithium-ion cell with a carbon negative electrode and non-flammability of the electrolyte.

4. Conclusion

This paper presents an investigation of non-flammable electrolytes containing ionic liquids for improving the safety of lithium-ion cells. The liquid electrolyte, LiEMIBF₄, which was composed of EMI-BF₄ and LiBF₄, and the gelled electrolyte, GLiEMIBF₄, were shown to have both thermal and electrochemical stability and to be applicable to lithium-ion cells of which the negative electrode active material was Li[Li_{1/3}Ti_{5/3}]O₄. The demonstration cells with LiEMIBF₄ and GLiEMIBF₄ showed good performance up to 50 charge-discharge cycles. This result indicated that ionic liquids could be successfully applied as electrolytes in lithium-ion cells, provided that the active materials of the positive and negative electrodes are selected appropriately. The mixed electrolyte consisting of flammable organic solvents and the non-flammable ionic liquid, PP13-TFSI, was shown to be non-flammable, and was also found to exhibit good discharge performance in the lithium-ion cell. Furthermore, graphite was found capable of performing in the electrolyte containing 50 mass% PP13-TFSI. These results suggested that EMI-BF₄, PP13-TFSI, and probably other ionic liquids can be applied as non-flammable solvents and/or flame-retardant additives for electrolytes towards the realization of advanced safe lithium-ion batteries. Actually, many researchers are participating in the research and development of various ionic liquids for lithium-ion batteries. The development of novel ionic liquids with superior stability to EMI-BF₄ and lower viscosity than PP13-TFSI would lead to the realization of safe lithium-ion batteries. It is expected that safe lithium-ion batteries based on ionic liquids will be realized in the near future.

Acknowledgment

The second section of this work forms part of collaborative research with National Institute of Advanced Industrial Science and Technology (AIST), and supported by New Energy and Industrial Technology Development Organization (NEDO), Japan.

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