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Electrode Properties in Mixed Imidazolium Ionic Liquid Electrolyte

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The compatibility of the mixed electrolyte of two ionic liquids based on 1,3-substituted imidazolium cations with lithium manganese oxide LiMnO₂, lithium iron phoshate LiFePO₄, and a hard carbon has been confirmed. For LiMnO₂ and LiFePO₄, the mixed imidazolium ionic liquid electrolyte provides slightly higher plateau in discharge curves, while the initial capacity is slightly lower, when compared with piperidinium ionic liquid. In case of LiMnO₂, the capacity in the mixed ionic liquid is recovered by subsequent cycling. The thermal stabilities of charged positive electrodes with the mixed ionic liquid, as well as with the piperidinium one, from accelerating rate calorimetry are far over those in conventional carbonate electrolyte. A hard carbon electrode is compatible with the mixed ionic liquid electrolyte.

Key Words: Lithium Ion Battery, Ionic Liquid, Thermal Stability

1 Introduction

Focusing on the safety aspect of lithium ion batteries, the searching of advanced materials for electrodes and electrolyte have intensively been investigated. In particular, the replacement of flammable alkyl-carbonate solvents into non-flammable and thermally-stable material has been considered to be effective to suppress the probability of accidental mode caused by the thermal runaway of battery cell. In these years, ionic liquids have been attracted as novel candidates of electrolyte component because of their low volatility, wide electrochemical window, high ionic conductivity, and variety of selection of cation and anion to have desired characteristics. A number of attempts have been made to prepare ionic liquid for this purpose, and to apply ionic liquids to test cell systems consisting of various positive and negative electrodes. Among them, 1-ethyl-3-methyl imidazolium (EMI) bis(fluorosulfonyl)imide (FSI) appears to be an excellent candidate because this material exhibits not only good electrolyte properties such as high ionic conductivity and low viscosity, but good compatibility with graphite negative electrode as well as various positive electrodes. However, some researchers have worried about the small impact of this ionic liquid for the improvement of thermal stability of battery cell. Recently the expected application field of lithium ion batteries has been wider and wider, and thus it may be better to propose more and more ionic liquid candidates having various characteristics.

The authors have investigated the properties of a series of ionic liquids having 1-cyanomethyl-3-methyl imidazolium (CmMI) cation and bis(trifluoromethanesulfon)ylimide (TFSI) anion on the focus of utilizing in lithium batteries. By mixing CmMITFSI with LiTFSI and EMITFSI at appropriate ratio, the mixed ionic liquid electrolyte with the moderate conductivity and the film-forming property on lithium metal electrode that enable the reversible dissolution-plating of lithium. In the present study, the compatibility of the mixed ionic liquid electrolyte based on CmMITFSI and EMITFSI with some positive electrodes and carbonaceous negative electrodes have been confirmed. For the positive electrodes combined with this electrolyte, spinel-type lithium manganese oxide LiMnO₂ and olivine-type lithium iron phosphate LiFePO₄ were selected on the focus of utilizing large-scale battery cells. The thermal behavior of the positive electrodes with coexistence of this electrolyte has also been estimated here.

2 Experimental

An active material of positive electrode, LiMnO₂ (Toda Kogyo Co., Japan) or LiFePO₄ (provided by Hohns Co., Japan) was mixed with acetylene black and poly(vinylidene difluoride) (PVdF; Kureha Chemical Co., Japan) binder as the gravimetric ratio of active material: AB : PVdF was 8 : 1 : 1 in 2-methylpirrolidinone (NMP) solvent. The resulting slurry was spread onto an aluminum foil, dried under vacuum, and then composite electrode sheet was obtained. An artificial graphite (TIMCAL, KS-6) or a hard carbon (Kureha Chemical Co., Japan, Carbotron P) were used as negative electrodes. An active material and PVdF (6 wt%) were mixed in NMP solvent and electrode sheet was prepared on a copper foil. To assemble in a coin cell, these electrode sheets were cut into a disk with 15 mm in diameter. The loading amount of active material in a coin cell was ca. 1.7 mg both for positive and negative electrodes.

EMITFSI and CmMITFSI were kindly provided by Nippon Gosei Kagaku Co., Japan. N-methyl-N-propylpiperidinium bis(trifluoromethanesulfon)ylimide (PP13TFSI; Kanto Chemical Co., Japan) was used for comparison. The ionic liquid electrolytes with the molar ratio of EMITFSI : CmMITFSI : LiTFSI and PP13TFSI : LiTFSI became 6 : 2 : 2 and 8 : 2, respectively was pre-
pared. The former and the latter electrolytes are denoted later as EMI : CmMI and PP13, respectively. Some properties, such as the room temperature conductivity and viscosity, of EMI : CmMI electrolyte were already presented previously.25

A 2032 stainless-steel coin cell was assembled with test electrode above, lithium metal counter electrode, electrolyte and separator (Celgard 2500 for positive electrodes and Whatmann glass filter for negative electrodes). The LiTFSI/ionic liquid electrolytes described above, and the electrolyte solution of 0.8 mol dm$^{-3}$ LiPF$_6$ in the mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) with the volumetric ratio of 2 : 1 (later denoted as EC : DEC) were used here. Charge-discharge tests of the two-electrode cells under constant-current conditions were conducted with a cycle test apparatus (BTS2004, Nagano Co., Japan). The cut-off voltages were from 3.5 V to 4.6 V for LiMn$_2$O$_4$, from 2.5 V to 3.8 V for LiFePO$_4$, and from 2.0 V to −0.01 V for carbon electrodes. The applied current density was 0.02 mA cm$^{-2}$ (ca. 1/10 O). These measurements were conducted at room temperature.

The thermal stability of positive electrodes at charged state with coexistence of electrolyte was estimated by accelerated rate calorimetry (ARC), using a special calorimeter (RADEX, Systag Co., Switzerland). A positive electrode sheet after charged at cut-off voltage as acquired from the cell was placed in a glass vessel with 0.3 cm$^{-3}$ of electrolyte. The vessel was sealed in a stainless-steel autoclave, and put into the chamber. The temperature of the vessel was initially set at 80 °C, increased stepwise by 10 K and hold at 30 minutes. Once the self-heating started, the vessel was hold in adiabatic atmosphere and the temperature increase was monitored.

3 Results and Discussion

Figure 1 shows the typical (at initial state) charge-discharge profiles of (a) LiMn$_2$O$_4$ and (b) LiFePO$_4$ positive electrodes in the EC : DEC organic solvent electrolyte and the ionic liquid electrolytes. It is clear that the intercalation process of both LiMn$_2$O$_4$ and LiFePO$_4$ occurs in the both ionic liquid electrolytes. The discharge capacities and the charge-discharge efficiencies for LiMn$_2$O$_4$ in EC : DEC, EMI : CmMI, and PP13 electrolytes are 105, 85, 87 mAh g$^{-1}$ and 94, 94, 95 %, respectively. For LiFePO$_4$, the discharge capacities and the charge-discharge efficiencies in EC : DEC, EMI : CmMI, and PP13 electrolytes are 146, 113, 134 mAh g$^{-1}$ and 98, 100, 90 %, respectively. Both positive electrodes exhibit nominal capacity values in the EC : DEC organic solvent electrolyte. The discharge capacities of these positive electrodes in the ionic liquid electrolytes are lower than those in the EC : DEC. However, the precise behavior is different by the electrolyte EMI : CmMI and PP13. In the PP13, both electrodes exhibit typical profiles with large overpotential. In the EMI : CmMI, the discharge curve of both electrodes exhibit plateau at higher voltage than in the PP13, while the capacity of LiMn$_2$O$_4$ is similar and that of LiFePO$_4$ is lower. Such low capacities in the EMI : CmMI electrolyte may be due to the low wettability of CmMTFSI having polar moiety toward carbon conductive agent.

The discharge capacities and the charge-discharge efficiencies in the EMI : CmMI electrolyte are plotted over cycles in Fig. 2. In the EMI : CmMI both LiMn$_2$O$_4$ and LiFePO$_4$ exhibit good cycle performances with capacity retention during initial 30 cycles. In particular, the discharge capacity of LiMn$_2$O$_4$ increase steeply up to 100 mAh g$^{-1}$ during initial several cycles, comprising that the penetration of electrolyte into porous composite electrode is improved. In the case of LiFePO$_4$ such significant increase of capacity would not be observable, probably due to the coating of the surface by carbon. The charge-discharge efficiencies of both electrodes are close to 100 %, indicating no significant side reaction occurs.

The behavior of temperature of (a) electrolyte themselves, (b) LiMn$_2$O$_4$ and (c) LiFePO$_4$ with coexistence of various electrolytes is summarized in Fig. 3. The switching temperature from the stepwise increase to the rather series increase of temperature can be assumed as the initial temperature of the self-heating for a certain sample. The self-heating temperatures for EC : DEC, EMI :
Fig. 2 Cycle behavior of discharge capacities and charge-discharge efficiencies of positive electrodes in the EMI-CmMI ionic liquid electrolyte. Electrode: (a) LiMn$_2$O$_4$ (b) LiFePO$_4$. Current density: 0.02 mA cm$^{-2}$. Cut-off voltage: (a) 3.5 – 4.6 V, (b) 2.5 – 3.8 V.

CmMI and PP13 are ca. 160°C, 300°C, and 250°C, respectively. When EC : DEC electrolyte is coexisted with charged LiMn$_2$O$_4$ or LiFePO$_4$, the self-heating is ca. 170°C or ca. 120°C, basically similar to the case of electrolyte itself. Both ionic liquid electrodes appear to contribute to improve the self-heating temperature up to around 250°C regardless of the positive electrode. Under the coexistence of charged positive electrodes, the self-heating temperature in the EMI : CmMI electrolyte becomes slightly lower than that in the PP13, probably due to the reaction with electrodes around 250°C. The rate of temperature increase under adiabatic atmosphere is considered to suggest roughly the rate of the self-heating. The temperature increase rates in this region in the ionic liquid electrolytes appear to be suppressed compared with that in the EC : DEC electrolyte, while the difference of heat capacity among these electrolytes should be taken into consideration for more precise discussion. In addition, the experimental condition is to be investigated further because the results in Fig. 3 show rather minor influence of positive electrode than expected.

Fig. 3 ARC temperature profiles of various electrolytes with coexistence of charged positive electrode. Electrode: (a) none (b) LiMn$_2$O$_4$ (c) LiFePO$_4$. Status of positive electrode: after constant-current charge to (b) 4.6 V and (c) 3.8 V. Heating step: 10 K/30 min. Sample: 0.3 cm$^{-3}$ electrolyte with ca. 0.01 g electrode.

The compatibility of graphite and hard carbon electrodes in the EMI: CmMI electrolyte is to be estimated by the charge-discharge profiles of these electrodes shown in Fig. 4. KS-6 graphite electrode exhibits a large irreversible capacity at initial charging (lithium intercalation...
Fig. 4  Charge-discharge profiles of the Li/carbonaceous negative electrode cells in the EMI : CmMI ionic liquid electrolyte. Electrode: (a) KS-6 graphite  (b) Carbotron P. Current density: 0.02 mA cm$^{-2}$. Cut-off voltage: -0.01 – 20 V.

electrode under a certain condition. In the case of the hard carbon electrode, the decomposition product of the electrolyte may act effectively as a protective film. In this stage the difference of the electrolyte decomposition product on a graphite electrode from the one on a hard carbon is still unclear. One possibility comprised from the similar results reported by Ui et al. is that the lithium intercalation process into the graphite in this ionic liquid electrolyte is inhibited even with the coexistence of intrinsically effective protective film.

The above results clearly indicate the potential of the mixed ionic liquid electrolyte EMITFSI-CmMITFSI-LiTFSI for lithium ion batteries, while a number of points for improvement, such as high-rate capability (because the above performances of positive and negative electrodes were observed at current density as low as 1/10 C), electrolyte penetration into porous electrode, and irreversible capacity of carbon electrode at initial charging, still remains. The thermal stability of charged positive electrodes with this electrolyte is an expecting aspect for the improvement of battery cell safety. Further modification of this kind of electrolyte, e.g., the optimization of composition, the application of additives, the selection and design of appropriate electrodes, may provide a useful candidate for advanced cell candidate.

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References


