Charge–discharge and high temperature reaction of LiCoO$_2$ in ionic liquid electrolytes based on cyano-substituted quaternary ammonium cation

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Abstract

The charge–discharge performance of LiCoO$_2$ positive electrode was observed in a mixed electrolyte system consisting of two ionic liquids: cyano-substituted quaternary ammonium bis(trifluoromethane)sulfoneimide (TFSI) and a same-anion salt of 1-ethyl-3-methyl imidazolium (EMI). The positive electrode exhibited a discharge capacity rather close to the theoretical one when *N,N,N,N*-cyanoethyl trimethyl ammonium salt was applied. Differential scanning calorimetry (DSC) studies revealed that these electrolytes exhibited exotherm only around 260 °C, 50 °C higher than conventional carbonate-based electrolytes. This is the first attempt to reveal the thermal stability of ionic liquid electrolyte under a practical situation.
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1. Introduction

Safety has been recognized as one of the most important issues for advanced applications of lithium batteries [1–4]. In particular, electrolyte materials contribute to the unsafe situation of a battery cell not only by their flammable nature, but also by their reactivity toward charged positive and negative electrode materials at a high temperature [5–8]. In order to improve the safety of a lithium battery cell, electrolyte should have inflammability and lower reactivity toward charged, possibly even overcharged, electrode materials than conventional electrolyte. One example is methyl difluoroacetate (MFA)-based electrolyte that the authors previously reported about its surprisingly low reactivity toward both positive and negative electrode active materials lower than 300 °C as well as its flame-retardant nature [9–11].

Ionic liquids have been expected as promising electrolyte materials because of their high thermal stability and inflammability due to their almost-zero vapor pressure. Several attempts have been concentrated on the electrolyte properties of various ionic liquid-based electrolytes including practical test cell performance [12–17]. However, no reports have concerned about the reaction between such ionic liquid electrolytes and electrode materials at high temperature.

The authors previously proposed that some cyano-substituted quaternary ammonium ionic liquids provide an effective electrolyte system for lithium battery by mixing with 1-ethyl-3-methyl imidazolium (EMI) bis(trifluoromethane)sulfoneimide (TFSI) [18,19]. In our previous studies we only exhibited fundamental electrolyte properties for these electrolytes. In the present study, the compatibility of positive electrode LiCoO$_2$ in the mixed electrolytes of cyano-substituted quaternary ammonium ionic liquids with EMITFSI has been confirmed. In addition, the reactivity of these ionic liquid electrolytes with the coexistence of chemically delithiated LiCoO$_2$ was monitored using differential scanning calorimetry (DSC).

2. Experimental

Quaternary ammonium ionic liquids containing cyano group was synthesized and purified by the same procedure as

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reported previously [17]. The prepared salts are cyanomethyl trimethyl ammonium bis(trifluoromethane)sulfoneimide (CTM-ATFSI) and cyanoethyl trimethyl ammonium bis(trifluoromethane)sulfoneimide (CEMATFSI). Imidazolium ionic liquid, 1-ethyl-3-methyl imidazolium bis(trifluoromethane)sulfoneimide (EMITFSI), was prepared by an ion exchange reaction between EMICl (Aldrich) and LiTFSI (Fluka) in water. The lower phase was collected, washed with water, and dried in vacuum. Hereafter these ionic liquids were treated in Ar-filled glove box. CTMATFSI or CEMATFSI was mixed with EMITFSI by a prescribed ratio, and then $0.2 \, mol \, dm^{-3}$ of LiTFSI (Fluka) was dissolved in the mixed ionic liquid. A stainless-steel coin cell was assembled with a composite positive electrode containing 90 wt.% of $LiCoO_2$, 6 wt.% of acetylene black (Denki Kagaku Co., Japan), and 4 wt.% of polyvinylidene difluoride (PVdF; Kureha Co., Japan), lithium foil (Honjo Metal Co., Japan) negative electrode, and the LiTFSI/ionic liquid solution. The composite positive electrode film was coated on aluminum foil. $LiCoO_2$ used in the present study was prepared via solid-state process from Li_2CO_3 and Co_3O_4. A constant current charge–discharge test was performed using a charge–discharge cycler (BTS2004w, Nagano Electric Co., Japan) under current density of ca. $5.7 \, A \, cm^{-2}$ (ca. $C/200$ by the representation of C rate), cut off voltage of 4.2 V on charge and 3.0 V on discharge. During measurement coin-cells placed at ambient atmosphere without any temperature control.

DSC measurement was performed to monitor the thermal stability of ionic liquid electrolytes under the coexistence of delithiated Li_xCoO_2. In order to know intrinsic reactivity with ionic liquid electrolyte, Li_xCoO_2 was prepared via chemical process as reported previously [6,8]. In the case of the present study, the composition of delithiated sample was determined to be $Li_{0.46}CoO_2$. Ionic liquid electrolyte and the same weight of $Li_{0.46}CoO_2$ were placed in a sealed stainless-steel pan for DSC measurement using TG8110 calorimeter (Rigaku Electronic Co., Japan). DSC measurements were done from room temperature to 400 °C with heating rate of 5 K min^{-1}.

3. Results and discussion

Fig. 1 shows the charge–discharge curves of $LiCoO_2$ in (a) $0.2 \, mol \, dm^{-3}$ LiTFSI/CTMATFSI + EMITFSI and (b) $0.2 \, mol \, dm^{-3}$ LiTFSI/CEMATFSI + EMITFSI electrolytes with various contents of CTMATFSI or CEMATFSI. In both cases the electrolytes where EMITFSI was absent provided only ignorable capacity for $LiCoO_2$. In contrast, the electrolytes containing EMITFSI appeared to be available for the charge–discharge of $LiCoO_2$ positive electrode. Such a tendency relates to the order of the conductivity of these electrolytes. LiTFSI/CTMATFSI or CEMATFSI electrolytes suffer from as low conductivity as $10^{-4} \, S \, cm^{-1}$ at room temperature [17,18], which leads to high bulk resistance and a large *IR* contribution. When the LiTFSI/binary ionic liquid electrolytes were used, $LiCoO_2$ positive electrode showed significant discharge capacity. The conductivities of $0.2 \, mol \, dm^{-3}$ LiTFSI solutions of EMITFSI + CTMATFSI (9:1), (7:3), EMITFSI + CEMATFSI (9:1), and (7:3) are 6.4, 3.3, 7.3, and 3.8 mS cm^{-1}, respec-
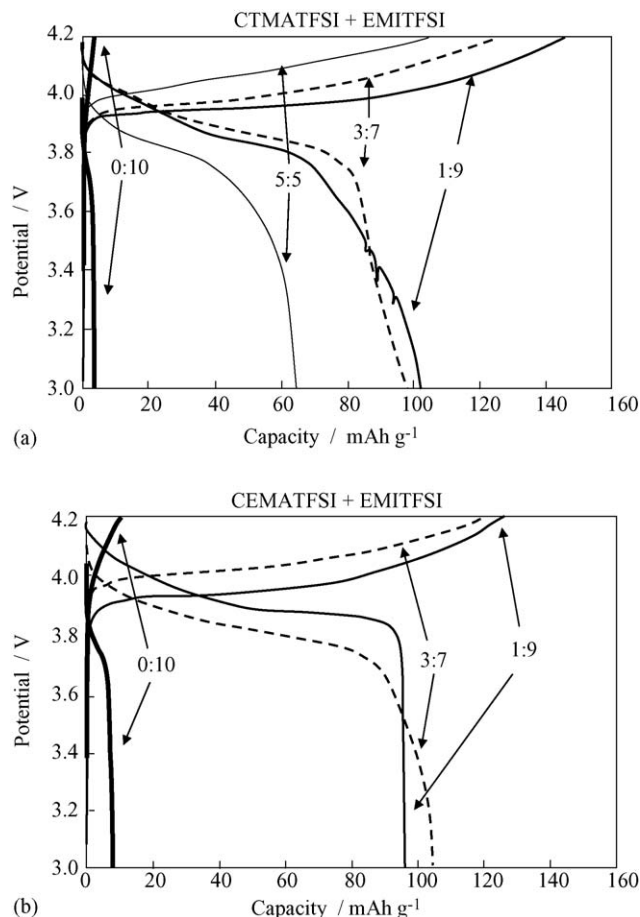

Fig. 1. Constant-current charge–discharge curves of $LiCoO_2$ in various ionic liquid electrolytes. (a) In $0.2 \, mol \, dm^{-3}$ LiTFSI/(EMITFSI + CTMATFSI) electrolyte with different ratio EMITFSI:CTMATFSI. (b) In $0.2 \, mol \, dm^{-3}$ LiTFSI/(EMITFSI + CEMATFSI) electrolyte with different ratio EMITFSI:CEMATFSI. Current density: $5.7 \, \mu A \, cm^{-2}$; cut-off voltage: 3.0–4.2 V.

tively. The application of binary ionic liquid surely improved the insertion/removal process of Li into/from LiCoO2 through the improvement of electrolyte conductivity.

While the solubility of LiTFSI in neat CTMATFSI and CEMATFSI is as low as ca. $0.5 \, mol \, dm^{-3}$, a larger amount of LiTFSI is soluble in the mixed solvent of EMITFSI with CTMATFSI or CEMATFSI. To confirm the effect of the concentration of Li$^+$, electrolyte solutions containing $1 \, mol \, dm^{-3}$ of LiTFSI were also prepared and the charge–discharge performance of $LiCoO_2$ was monitored in these electrolytes. Fig. 2 shows the charge–discharge profiles of $LiCoO_2$ in $1 \, mol \, dm^{-3}$ LiTFSI electrolytes with various ionic liquid compositions. Each electrolyte provided a similar charge–discharge behavior to that in conventional carbonate solvent electrolyte, except for their lower capacity, ca. 110 mA h g^{-1}, than those in the conventional electrolyte, ca. 126 mA h g^{-1} assuming $Li_{0.55}CoO_2$ for charged state. The charge–discharge curve was relatively smooth and stable in this case, while electrolyte became viscous by increasing the concentration of LiTFSI.

The discharge capacity and coulombic efficiency of $LiCoO_2$ electrode in some ionic liquid electrolytes are plotted in Fig. 3. The discharge capacity of $LiCoO_2$ seemed to depend on the con-
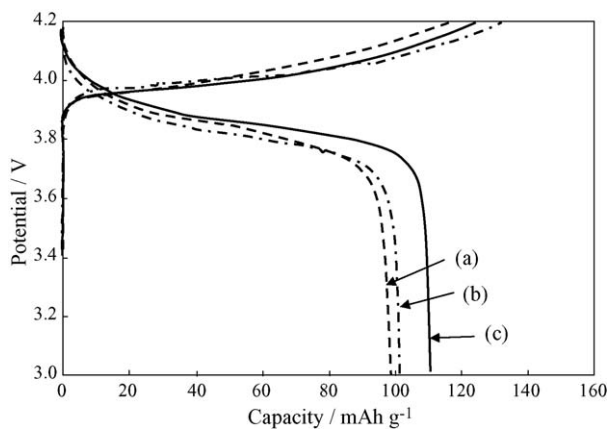
Fig. 2. Constant-current charge–discharge curves of LiCoO$_2$ in various ionic liquid electrolytes containing 1 mol dm^{-3} LiTFSI. (a) EMITFSI:CTMATFSI = 9:1, (b) EMITFSI:CTMATFSI = 7:3, (c) EMITFSI:CEMATFSI = 7:3. Current density: 5.7 μA cm^{-2}; cut-off voltage: 3.0–4.2 V.

centration of LiTFSI, in other words, the higher LiTFSI content brought the higher capacity, probably due to the increase of Li$^+$ transport number in electrolyte as reported by Hayamizu et al. for LiBF$_4$/EMIBF$_4$ system [20]. The discharge capacity was slightly lower than that to Li$_{0.45}$CoO$_2$, which shows ca. 4.2 V, even in 1 mol dm^{-3} LiTFSI solution, probably due to the slight shortage of the Li$^+$ transport number (Hayamizu et al. obtained 0.05 as a highest Li$^+$ transport number for lithium salt solution of ionic liquid). The coulombic efficiency for these cycles
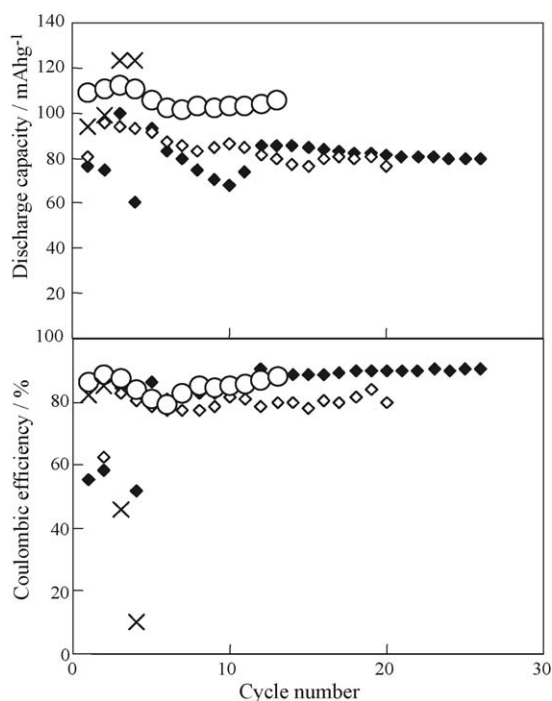
seemed to depend on the electrolyte component. When the electrolyte contained CEMATFSI, the charge–discharge cycles of LiCoO$_2$ provided coulombic efficiency in the range of 80–90%. These efficiency values are slightly lower than that in conventional organic solvent electrolytes using similar coin-cell setting. In contrast, 1 mol dm^{-3} LiTFSI/EMITFSI + CTMATFSI electrolyte lead to the drop in efficiency in initial four cycles. Such low efficiencies for CTMATFSI- and CEMATFSI-based electrolytes may be due to the relatively low electrochemical stability of EMITFSI, CTMATFSI and CEMATFSI. In particular, the low efficiency at third and fourth cycles in the electrolyte containing CTMATFSI is considered to be responsible to the decomposition of electrolyte on lithium counter electrode surface, because the values of discharge capacity for LiCoO$_2$ rather increased to ca. 120 mA h g^{-1}. CEMATFSI is assumed to provide a sufficient level of LiCoO$_2$ performance. The difference in cathodic stability between CTMATFSI and CEMATFSI may be addressed to that of the electron-withdrawing ability between ethyl and methyl substrate when the quaternary ammonium cation is reduced.

The thermal stability using DSC was measured for CEMATFSI + EMITFSI electrolyte systems. Fig. 4(a)–(c) illustrates the DSC profiles of chemically delithiated Li$_{0.46}$CoO$_2$ coexisted with various electrolytes. Under the coexistence of conventional organic solvent electrolyte, 1 mol dm^{-3} LiPF$_6$/EC + DMC, exothermic peaks are observed around 190, 210, and 250 °C. This profile is basically similar to the one reported previously [6,8]. In this case former two peaks are attributed to the oxidation of electrolyte by oxygen released from
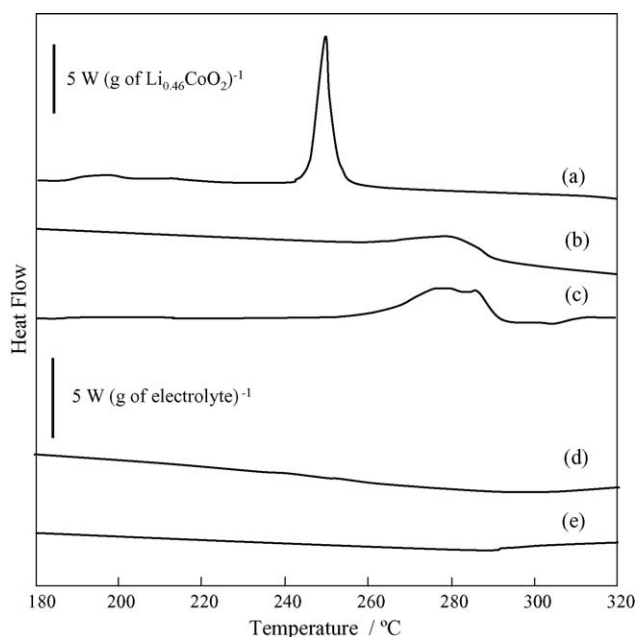

Fig. 3. Cycle performances of LiCoO$_2$ in various ionic liquid electrolytes. (a) Discharge capacities over cycles, (b) coulombic efficiencies over cycles. Electrolyte: (◇) 0.2 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (9:1); (◆) 0.2 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (7:3); (○) 1 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (9:1); (×) 1 mol dm^{-3} LiTFSI/(EMITFSI + CTMATFSI) (9:1).

Fig. 4. DSC profiles of electrolytes with or without Li$_{0.46}$CoO$_2$. (a) Li$_{0.46}$CoO$_2$ + 1 mol dm^{-3} LiPF$_6$/ethylene carbonate + dimethyl carbonate (1:1 by vol.), (b) Li$_{0.46}$CoO$_2$ + 0.2 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (9:1), (c) Li$_{0.46}$CoO$_2$ + 0.2 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (7:3). (a)–(c) Li$_{0.46}$CoO$_2$:electrolyte in a sample pan = 1:1 by weight. (d) 0.2 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (9:1), (e) 0.2 mol dm^{-3} LiTFSI/(EMITFSI + CEMATFSI) (7: 3).

the electrode active material, and the latter one is attributed to the self-decomposition of electrolyte. In contrast, $Li_{0.46}CoO_2$ coexisted with mixed electrolytes of EMITFSI and CEMATFSI showed no peaks at a lower temperature than $260\,^{\circ}C$. Furthermore, the heat amount of the exotherm in the measured temperature region is also suppressed in these electrolyte compared with conventional electrolyte. This result indicates that ionic liquid electrolytes are less reactive than carbonate solvents toward both the oxygen generated from $Li_{0.46}CoO_2$ and the electrode active material itself after the oxygen release. On the DSC profile of Li_xCoO_2 and carbonate solvent electrolyte, the reaction attributed to the peak at $250\,^{\circ}C$ is a point for discussion because the electrolyte performs the self-decomposition around the temperature. In the case of ionic liquid electrolyte, there seems no room for discussion on the exotherm around this temperature. Fig. 4(d) and (e) shows the DSC profile of ionic liquid electrolytes alone in the same temperature range. No peaks are observed in this temperature range without $Li_{0.46}CoO_2$. Such a difference in DSC profile reveals that the peak around $260\,^{\circ}C$ observed in Fig. 4(b)–(d) are attributed to a reaction where positive active electrode material are strongly concerned, preferably to the reaction between electrode material and ionic liquid electrolyte. More or less, it is suggested that ionic liquid electrolyte is less reactive toward charged $LiCoO_2$ than carbonate solvent electrolyte, and thus confirmed that this kind of electrolyte has a potential to improve the stability of lithium battery systems.

4. Conclusion

The electrolyte based on mixed ionic liquid of EMITFSI with a cyano-substituted quaternary ammonium salt, where lithium metal negative electrode exhibited good cycle stability, provided a reversible charge–discharge performance of $LiCoO_2$ positive electrode. The best discharge capacity and coulombic efficiency was observed when using electrolytes based on mixed ionic liquid of CEMATFSI with EMITFSI. Such ionic liquid electrolytes were found to be more stable than conventional organic solvent electrolyte at high temperature with the coexistence of delithiated $LiCoO_2$. The DSC profiles for mixed ionic liquid electrolyte and $Li_{0.46}CoO_2$ showed exothermic peak only above $260\,^{\circ}C$, attributed to the thermal reaction of electrolyte and an active material.

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