Thermal Stability And Electrochemical Properties Of Electrodes In Ionic Liquid Electrolyte For Lithium Batteries

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Introduction

Ionic liquids have been studied as attractive candidates for a safer electrolyte in rechargeable lithium batteries. The authors have previously investigated that quaternary ammonium-based ionic liquids containing a cyano group mixed with 1-ethyl-3-mehyl imidazolium(EMI)-based ionic liquid provided reversible charge-discharge behavior in lithium metal[1].

In the present study, the thermal stability related to a previous study [2] and the charge-discharge properties of such ionic liquids with electrodes are estimated.

Experimental

N-cyanometyle-N-ethyl-N-N-dimethyl ammonium (CEMA) iodide was synthesized via the procedure reported by Bhatachrjee et al. [3]. EMI chloride was purchased from Aldrich. Each ionic liquid was prepared by mixing corresponding cation source and lithium bis(trifluoromethane sulfone) imide (LiTFSI;Fluka) in water, and by further purifying and drying. The purity of the products was verified by elemental analysis and ^{1}H-NMR. CEMATFSI and EMITFSI were mixed at 3:7 in weight, and LiTFSI (Fluka) was dissolved to 0.2 M to prepare the ionic liquid electrolyte.

$Li_{0.46}CoO_2$ was prepared by the extraction of lithium from $LiCoO_2$ with H_2SO_4 [2]. The thermal stability of the ionic liquid with $Li_{0.46}CoO_2$ was monitored using differential scanning calorimetry (DSC) (Thermo plus 8110, Rigaku). Electrolyte and $Li_{0.46}CoO_2$ were mixed at 1:1 in weight, packed in a stainless steel pan, and the pan was crimp-sealed in a glove box filled with argon to be subejected to DSC measurement. DSC experiments were carried out at a heating range of 5°C/min. $LiCoO_2$ with 5 wt% of acetylene black and 5 wt% of poly (vinylidene difluoride) was coated on aluminum foil for positive electrode. Both positive and negative (lithium foil from Honjo Metal Co.) electrodes were cut in 1.5 cm diameter and assembled into a R2032 coin cell with the ionic liquid electrolyte. A constant charge-discharge current density of between 3.0 and 4.2 V vs.Li/Li$^+$ was applied to the cell.

Result and discussion

Fig.1 shows the constant charge-discharge curves of $LiCoO_2$ in the ionic liquid electrolyte. $LiCoO_2$ exhibited a reversible capacity of 105 mAhg^{-1} at 0.02 mAcm^{-2}. However, the discharge capacity decreased to 10 mAhg^{-1} when the current density was increased to 0.1mAcm^{-2}.

The conductivity of the ionic liquid electrolyte is about 7 mScm^{-1}. In this case, the transport number of Li$^+$ in the ionic liquid electrolyte may be insufficient for a high charge-discharge rate.

Fig.2 shows the DSC profiles of the electrolyte (1M LiPF$_6$ /EC+DMC) and the ionic liquid electrolyte with $Li_{0.46}CoO_2$.The exothermic peak of the EC+DMC electrolyte was observed around 200°C, 220°C, and 250°C. In case of the ionic liquid, the former two peaks were markedly depressed. Moreover, the total amount of exothermic heat between 180°C and 300°C was decreased to 289 J/g in the latter case and from 1008 J/g in the former case. The ionic liquid electrolyte was found to exhibit improved thermal stability with the coexistence of Li_xCoO_2.

References

[1]M.Egashira, M.Nagakawa, I.Watanabe, S.Okada and J Yamaki, extend abstract of IMLB-12 Meeting, L1-0355, Nara 2004.
[2]Y.Baba, S.Okada and J.Yamaki, Solid State Ionics, 148, 311 (2002).
[3]S.S.Bhattacharjee, H.Ila and H.Junjappa, Syntesis, 4, 301 (1982).

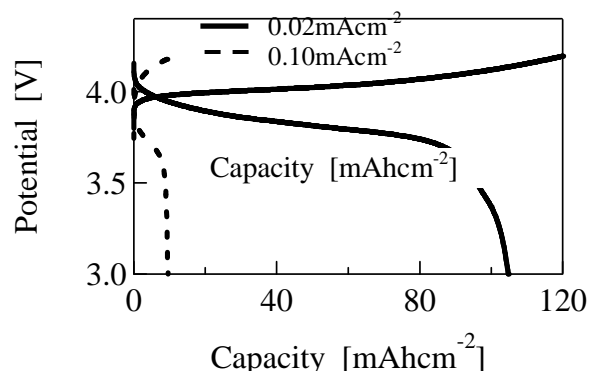Fig.1 Charge-Discharge profiles of $LiCoO_2$ electrode in 0.2 M /LiTFSI CEMATFSI:EMITFSI=3:7. Current density is 0.1 or 0.02 mAcm^{-2}.
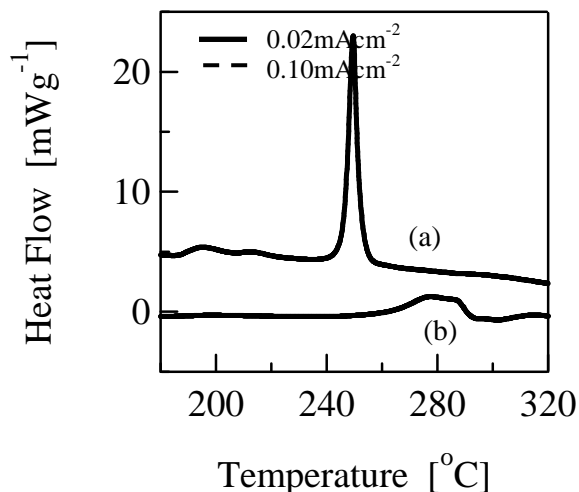

Fig.2 DSC profiles of ionic liquid of 1M LiPF$_6$ /EC+ DMC (1:1 in vol %) (a) and CEMATFSI:EMITFSI =3:7 (b) with $Li_{0.46}CoO_2$