



Effect of monocationic ionic liquids as electrolyte additives on the electrochemical and thermal properties of Li-ion batteries



T. Subburaj, Yong Nam Jo, Chang Woo Lee*

Department of Chemical Engineering, College of Engineering, Kyung Hee University, 1732 Deogyong-daero, Gihung, Yongin, Gyeonggi 446-701, Republic of Korea

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ABSTRACT

The conventional electrolyte system has been compared with the ionic liquid (IL) additive containing electrolyte system at room temperature as well as elevated temperature. In this work, two types of monocationic ILs such as 1-butyl-3-methylpyrrolidinium hexafluorophosphate (Pyr IL) and 1-ethyl-3-methylimidazolium hexafluorophosphate (IMI IL) are added as an additive at two different weight ratios in 1.15 M LiPF₆ (EC/EMC = 3/7 v/v) electrolyte solution, the structural, electrochemical and thermal characteristics of LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA)/carbon full-cell in different electrolyte formulations have been reconnoitered. X-ray diffraction (XRD) studies have proved that IL as an electrolyte additive does not alter the structural stability of cathode materials after cycling. Under room temperature, Pyr IL additives at 1 wt% and 3 wt% deliver better cycleability than others, with the retention ratios of 93.62% and 92.8%, respectively. At elevated temperature, only 1 wt% Pyr IL additive is giving stable capacity retention ratio of 80.74%. Ionic conductivity and self-extinguishing time (SET) values are increasing with respect to the amount of additive added to the electrolyte. Thermal studies reveal that 3 wt% Pyr IL is favorable regarding the safety of the battery as it shows shifting of peak to higher temperature of 272.10 °C. Among the IL additives evaluated in this study, addition of 1 wt% Pyr IL is the most desirable additive for achieving the best cycling performance as well as thermal behavior of Li-ion batteries.

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1. Introduction

The energy requirement of fast growing mobile society, prompts the researchers to focus more on the Li-ion batteries due to its high energy density and excellent cycle life than any other portable rechargeable battery. As the progress ascend from the small portable and static state devices to larger EV and PHEV applications, the requirement for safe rechargeable power sources continues to grow. The conventional electrolyte system shows two fold complications in integration of increasing energy density of batteries with respect to increasing safety of batteries. Under normal conditions, Li-ion batteries are probably safe. But under abnormal conditions, safety of Li-ion batteries is yet a practical obstacle for hybrid and electrical vehicle applications. So there has been an immense search to find out the suitable additives to enhance the safety concern of rechargeable Li-ion batteries. In general, the electrolyte for Li-ion batteries comprises mono-, binary-, or ternary-based carbonate solvent mixture dissolved with certain molar concentration of

lithium hexafluorophosphate (LiPF₆) salt. Though LiPF₆ has met properties for commercial Li-ion batteries, there are few significant drawbacks pertaining to thermal stability, unwanted reaction with carbonate solvents especially at higher temperature, moisture sensitivity and environmental toxicity. Various research studies have been going on to progress either in new electrolyte system or in modifying the conventional electrolyte system by addition of suitable additives [1]. Criteria for electrolyte additives are; supporting the formation of SEI layer on anode surface, lessening irreversible capacity and gas formation, improving thermal characteristics by masking unwanted reaction between Li⁺ species and electrolyte, safeguarding cathode from dissolution during de-intercalated state and from disintegration during over charged state, progressing in miscellaneous properties such as ionic conductivity, viscosity, wettability etc. Ionic liquids are organic molten salts which are liquid at ambient temperatures. Although Walden discovered ionic liquids at 1914 [2], their scientific relationship with energy storage devices has become more evident in last ten years. Undeniably ionic liquids are having lots of promising properties, which create them enviable for various applications. And moreover ionic liquids are having noteworthy properties like non-flammability, low vapor pressure, first-class thermal and chemical stability,

* Corresponding author. Tel.: +82 31 201 3825; fax: +82 31 204 8114.
E-mail address: cwlee@khu.ac.kr (C.W. Lee).

acceptable ionic conductivity and relatively wide electrochemical potential window [3–6]. So they do not explosively ignite as most other common organic solvent do. The enhancement of conductivity by IL additives is up to 25% and much more than that of LiPF₆ based conventional electrolyte systems, which can be used to improve the power performance of Li-ion batteries [7]. Normally ILs are consisting of organic ions which would subject to unlimited structural variations, this implies that the choice of cation and anion will have imperative role in their physicochemical properties [8–10].

Many studies have been reported that pyrrolidinium-imide salts possess high conductivity and wide potential window at ambient temperature [11,12]. Also, it has been reported that imidazolium IL containing mobile Li⁺ species has increment in viscosity and decrement in conductivity due to interactions between Li cations and anions of ionic liquid, however, it does not give a significant effect because it still provide enough conductivity applicable for Li-ion batteries [13]. So to avoid this controversy we have chosen the hexafluorinated cations to group with ILs. However there have been no reports regarding use of hexafluorinated monocationic ionic liquids as an electrolyte additive in full cell studies of Li-ion batteries. As imidazolium and pyrrolidinium based ILs are having a sensibly wide potential window with stability and good conductivity, it is gaining more consideration for Li-ion battery applications [10,14–18]. Our research investigates hexafluorinated monocationic ionic liquids as an additive in modified electrolyte system for improving the electrochemical and thermal behavior of Li-ion batteries.

2. Experimental

2.1. Preparation of modified electrolytes using ILs

The chemical structure of studied ILs, 1-ethyl-3-methylimidazolium hexafluorophosphate (IMI IL) and 1-butyl-3-methylpyrrolidinium hexafluorophosphate (Pyr IL) are shown in Fig. 1. The ionic liquids are having below 30 ppm of water content, according to the producer's (Chem. Tech Research Incorporation, Korea) norm. Those ionic liquids are dried in vacuum oven under 60 °C for 8 h and then added as an additive in conventional electrolyte (1.15 M LiPF₆ in EC/EMC = 3/7 (v/v)) inside of glove box filled with argon. We have prepared 1 wt% and 3 wt% of IMI IL additive-added electrolyte by adding them in a proportionate amount in the given conventional electrolyte. As well as we prepared 1 wt% and 3 wt% of Pyr IL additive-added electrolyte by the same procedure. The conventional electrolyte is also containing 1 wt% of VC and 1 wt% of PS as other additives.

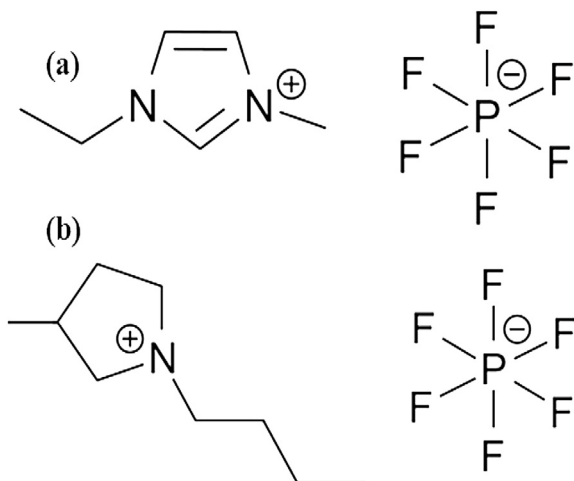


Fig. 1. Chemical structure of ILs: (a) IMI IL; (b) Pyr IL.

2.2. Electrode preparation and cell assembly

To prepare the cathode electrode, 90 wt% of the LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA) cathode active material from Ecopro Corporation, 5 wt% of Super P black as a conductive agent, 5 wt% polyvinylidene fluoride (PVDF) as a binder and *N*-methyl-2-pyrrolidone (NMP) as a solvent are mixed to form slurry. After 15 min of grinding with mortar to form homogeneous slurry, the viscous slurry is coated on aluminum foil and then dried in oven at 100 °C for 5 h. The dried coating electrode was pressed under a 7 ton cm⁻² loads and then it was punched out with size of 14 mm in diameter, which is going to be used as the positive electrode. The punched cathode was additionally dried at 120 °C for 5 h in vacuum oven. The thickness of the cathode film was about 44 μm. To prepare anode electrode, 90 wt% of super-P carbon powder, 10 wt% of PVDF and NMP are mixed to form slurry. After 15 min of grinding with mortar to form homogeneous slurry, the viscous slurry is coated on copper foil and then dried in oven at 120 °C for 5 h. The dried coating electrode was pressed under a 7 ton cm⁻² loads and then it was punched out with size of 16 mm in diameter, which is going to be used as the negative electrode. The punched cathode was additionally dried at 120 °C for 5 h in vacuum oven. The thickness of the cathode film was about 42 μm.

The 2032 coin-type cells (20 mm in diameter and 32 mm in thickness) were assembled in a glove box under high purity argon atmosphere (>1 mg/L of O₂ and H₂O). The cell consisted of a prepared cathode, carbon anode as a reference electrode as well as counter, micro porous membrane (Celgard 3501) as a separator, non-aqueous conventional electrolyte (1.15 M LiPF₆ in EC/EMC = 3/7 (v/v)) and IL additives composed modified electrolytes as an electrolytes.

2.3. X-ray diffraction

X-ray diffraction analysis was conducted to reveal the crystalline structure of the material of interest by using X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, 45 kV, 50.0 mA). XRD data are observed at $2\theta = 10^\circ - 90^\circ$ with a step size of 0.02° .

2.4. Electrochemical measurements

The 2032 coin cells were assembled by sandwiching the separator between NCA cathode and carbon anode along with the conventional electrolyte and IL additives composed modified electrolytes in a glove box filled with argon. The prepared full cells were typically cycled between 2.7 V and 4.3 V at room temperature as well as elevated temperature (55 °C) using BT2000 Arbin cycler. Conductivity measurements of the electrolyte solutions with or without IL addition were measured using a Mettler Toledo conductivity meter.

2.5. Thermal analysis

For DSC sampling, after 200 cycles in a fully charged state, cells are transferred to glove box under high purity argon atmosphere. The cells were disassembled and then the delithiated cathodes were removed from the coin cells. Approximately 1.5–2.5 mg of the active materials of interest is taken and placed in aluminum DSC cells and hermetically sealed by crimping. The carbon anode and separator are discarded and all DSC calculations are based on the overall weight of the sample. The DSC scans were carried out via differential scanning calorimetry (Model: DSC Q1000) at a heating rate of 10 °C/min from 50 °C to 350 °C. Exothermic and endothermic reactions as a function of the temperature are plotted as positive and negative heat flow, respectively. All the thermograms

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