

Performance and thermal stability of LiCoO_2 cathode modified with ionic liquid

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Abstract

A unique approach for improving the thermal stability of LiCoO_2 cathode is presented, which is based on the treatment of LiCoO_2 with ionic liquid (BDMIPF₆, butyldimethylimidazolium-hexafluorophosphate), instead of traditional electrolyte modification. The electrolyte modification by the BDMIPF₆ addition deteriorates the C-rate performances especially at high charge/discharge rates, with slightly improving the exothermic reaction between delithiated (charged) LiCoO_2 and electrolytes. On the other hand, the BDMIPF₆-modified cathode noticeably improves the thermal stability as well as little changes the C-rate performances. This is believed mainly due to the preferential location of BDMIPF₆ in the LiCoO_2 cathode rather than in the carbon anode, which might make it possible that the BDMIPF₆ could effectively contribute to the suppression of exothermic reaction of delithiated LiCoO_2 with electrolytes, with little affecting the electrolyte and the carbon anode. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

With pursuing larger capacity and higher performance of rechargeable lithium ion secondary batteries, their safety issue has been accompanied as a major concern. Volatile and flammable liquid electrolytes have been considered as a main cause for serious safety problems in lithium ion batteries. Among many efforts to improve the safety of lithium ion batteries, employing ionic liquids (i.e., room temperature molten salts) is recommended as one of the promising candidates [1–9]. Non-flammability and negligible vapor pressure of ionic liquid are expected to improve violent properties of liquid electrolytes. Many battery applications of ionic liquids have been focused on the modification of liquid electrolytes. However, the ionic liquid-added electrolytes have caused several side effects when combined with carbon anode. Especially, the poorer C-rate performance is observed as a big obstacle for practical uses. These problems are believed to be mainly due to the ionic liquid's high reactivity

with carbon anode [1,2]. Various attempts to improve the poor C-rate performances have been carried out, which includes synthesizing more stable ionic liquids toward carbon anode [5,6], adding some additives for good SEI layer formation [7,8] and changing the electrolyte injection procedure [9].

Meanwhile, it has been known that the main cause of thermal accidents in the lithium ion batteries employing the LiCoO_2 cathode is related with a vigorous exothermic reaction between delithiated (charged) LiCoO_2 and liquid electrolytes [10–13]. Therefore, it has been believed that the suppression of exothermic reaction is a key factor to control the overall thermal stability of lithium ion batteries.

In this study, in order to improve the thermal stability of LiCoO_2 cathode, a unique approach based on the treatment of LiCoO_2 with BDMIPF₆ is presented, instead of the traditional electrolyte modification. It is expected that through this new process, the BDMIPF₆ could locate preferentially in the LiCoO_2 cathode rather than in the carbon anode, with little affecting the electrolyte and the anode. This new approach (BDMIPF₆-modified cathode) is compared with the traditional one (BDMIPF₆-added electrolyte) in terms of the

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C-rate performance and the exothermic heat between delithiated LiCoO₂ and electrolytes.

2. Experimental

The ionic liquid-modified cathode was prepared by applying 3 wt% of BDMIPF₆ (C-Tri, Korea) cautiously to the cathode slurry mixture consisting of LiCoO₂ active materials, carbon black and PVdF binder. The existence of BDMIPF₆ in the LiCoO₂ cathode was confirmed with the H MAS NMR characteristic peaks (Fig. 1). The BDMIPF₆-modified cathode was assembled with a carbon anode, a polyolefin separator and a 1 M LiPF₆-based electrolyte by using lithium ion polymer battery technology of LG Chem [14]. For comparison, the 10 wt% of BDMIPF₆-added electrolyte was injected into the cells consisting of a pristine LiCoO₂ cathode and a carbon anode. All the reagents were handled in a glove box under argon atmosphere. Capacity and C-rate performance of the cells were examined with changing a discharge rate from 0.2C (152 mA) to 2C (1520 mA) at a constant charge rate of 0.5C (380 mA). For the DSC measurements, the cells were charged to 4.2 V at a charge rate of 0.2C. The cells were then disassembled in a dry room to remove the delithiated LiCoO₂ cathode containing the liquid electrolyte. Approximately, 10 mg of the delithiated LiCoO₂ cathode was cut and hermetically sealed into an aluminum sample pan. The DSC measurements were carried out under nitrogen atmosphere with a heating rate of 5 K min⁻¹.

3. Results and discussion

As a first step, the effect of BDMIPF₆-added electrolyte on the performance of lithium ion batteries is examined (Fig. 2). Compared to the pristine electrolyte, the BDMIPF₆-added

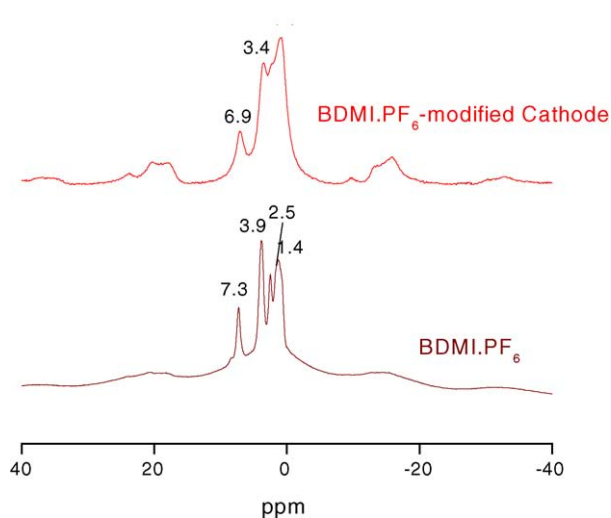


Fig. 1. H MAS NMR characteristic peaks of BDMIPF₆-modified LiCoO₂ cathode.

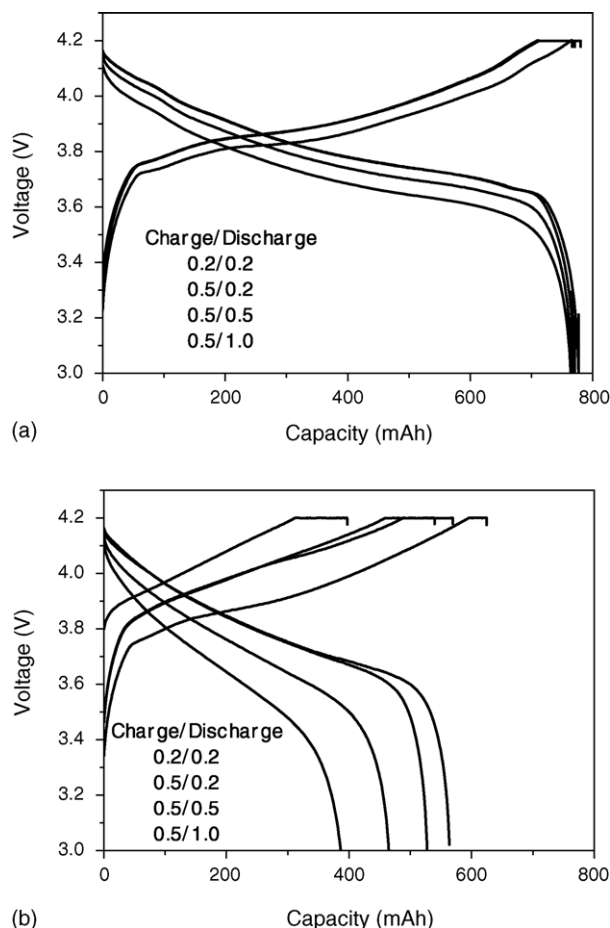


Fig. 2. Charge/discharge profiles of (a) pristine electrolyte (LiPF₆-based electrolyte) and (b) BDMIPF₆-added electrolyte. Charge/discharge rates are 0.2C/0.2C, 0.5C/0.2C, 0.5C/0.5C and 0.5C/1C, respectively.

electrolyte shows a lower initial capacity, and its capacity becomes significantly deteriorated with increasing the charge/discharge rate. It has been previously reported that the ionic liquid-added electrolytes have brought about poor C-rate performances when combined with carbon anode. This is believed mainly due to the poor SEI formation caused by the ionic liquid's reactivity with carbon anode such as co-intercalation and its higher reduction potential than the carbon [7–9].

The thermal stability of LiCoO₂ cathode with the BDMIPF₆-added electrolyte is compared to the pristine electrolyte (Fig. 3a and b). It is found that the pristine electrolyte generates a high exothermic heat ($\Delta H = 587 \text{ J g}^{-1}$) and shows well-classified exothermic peaks, where the first peak is attributed to the surface reaction of the delithiated LiCoO₂ with the electrolyte, the second peak to the decomposition of layered LiCoO₂ structure and the third peak to the reaction of electrolyte with oxygen generated from the decomposition of the layered LiCoO₂ structure. The details have been discussed in the literatures [10,11]. Fig. 3 also shows that the BDMIPF₆-added electrolyte is not so effective to

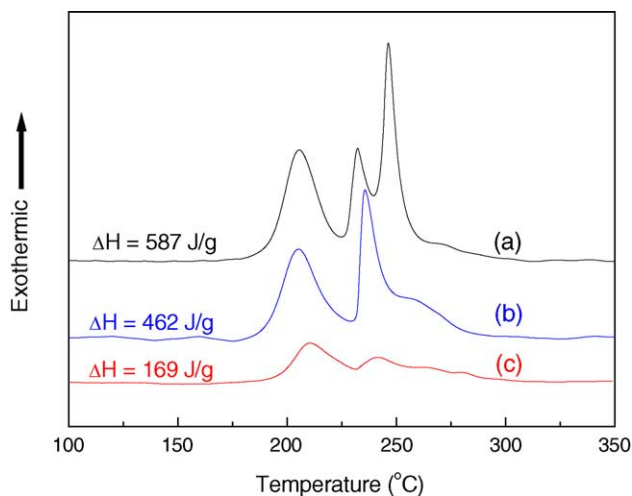


Fig. 3. DSC thermograms of exothermic reaction between delithiated LiCoO_2 cathode and electrolyte for (a) pristine electrolyte, (b) BDMIPF_6 -added electrolyte and (c) BDMIPF_6 -modified cathode.

sufficiently decrease the exothermic heat with the delithiated LiCoO_2 ($\Delta H = 462 \text{ J g}^{-1}$).

Prior to investigating electrochemical and thermal properties of the BDMIPF_6 -modified cathode, the existence of the BDMIPF_6 in the modified cathode has been checked using the H MAS NMR. The NMR spectra have confirmed that the characteristic peaks of BDMIPF_6 are found in the modified cathode (Fig. 1).

It is of interest to note that the C -rate performance of BDMIPF_6 -modified cathode is comparable to that of the unmodified one, while the BDMIPF_6 -added electrolyte shows quite a poor C -rate performance (Fig. 4). This possibly reflects that the ionic liquid's reactivity with carbon anode may be suppressed, which could indicate that the SEI layer on the carbon anode might be formed properly and also the transport of the lithium ion in the electrolyte would be little influenced by BDMI^+ cation.

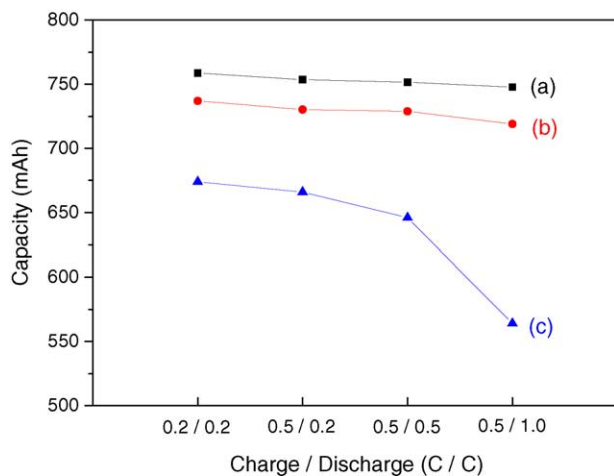


Fig. 4. C -rate performances of (a) pristine electrolyte, (b) BDMIPF_6 -modified cathode and (c) BDMIPF_6 -added electrolyte.

Most importantly, the BDMIPF_6 -modified cathode improves the thermal stability, with little affecting the C -rate performance. The DSC measurement indicates a smaller exothermic heat with the ΔH decreasing from 587 J g^{-1} (pristine) to 169 J g^{-1} for the BDMIPF_6 -modified cathode (Fig. 3a and c). The noticeable enhancement of BDMIPF_6 -modified cathode may be attributed to the preferential localization of BDMIPF_6 to LiCoO_2 cathode. It has been known that the exothermic reaction depends on the concentration of the reactants such as the delithiated LiCoO_2 and the electrolytes [10–13]. It is possibly assumed that the BDMIPF_6 localized in the LiCoO_2 cathode may decrease the local concentration of electrolytes around the delithiated LiCoO_2 , which could contribute to the suppression of exothermic reaction. Though the exact mechanism on the localization of the BDMIPF_6 to the LiCoO_2 cathode is not yet elucidated, some possible speculations could be drawn, which includes the interaction of BDMIPF_6 with PVdF binder and the surface coverage of LiCoO_2 with bulky cation (BDMI^+).

This is, to the best of our knowledge, the first report that has improved the thermal stability with slightly influencing the electrochemical performances in the ionic liquid-applied lithium ion batteries. Future work will be focused on the practical safety tests such as hotbox and overcharge of the modified cells, which will be correlated with the DSC results. Also, fundamental work on the ion transport mechanism of the electrolyte in the presence of the ionic liquid should be followed.

4. Conclusion

The new approach based on the treatment of LiCoO_2 with BDMIPF_6 has been presented in order to improve the thermal stability of LiCoO_2 . The traditional electrolyte modification by the BDMIPF_6 addition deteriorates the C -rate performances especially at high charge/discharge rates, with slightly improving the exothermic reaction between delithiated LiCoO_2 and electrolytes. This is believed mainly due to the ionic liquid's reactivity with carbon anode. On the other hand, the direct LiCoO_2 modification with BDMIPF_6 has improved the thermal stability as well as little changed the C -rate performance. This may be attributed to the preferential localization of BDMIPF_6 to LiCoO_2 cathode rather than carbon anode, which could effectively suppress the vigorous exothermic reaction between delithiated LiCoO_2 and electrolytes with little affecting the electrolyte and the carbon anode.

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