

Improved Thermal Stability of LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Cathodes in the EC-based Electrolyte with Phosphazene-type Additives

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Introduction

Recently, lots of interests have been focused on the modification of the traditional electrolytes based on aprotic solvents and lithium salts by adding functional additives to improve the cycleability, safety performance, and etc. for Li-ion batteries.¹ The thermal stability is a very important concern for the safety performance of commercially available batteries especially for large-scale applications. In this presentation, the effect of adding phosphazene derivative containing fluorine as a flame-retardant additive is characterized by electrochemical and thermal analyses.

Experimental

The electrochemical and thermal performance of LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes were evaluated using electrolytes based on 1M LiPF_6 in EC/DMC (1:2 in volume), and the effect of adding phosphazene derivatives was investigated by fabricating half cells of CR2032-type. After charging to the designed voltage, the cells were disassembled and DSC experiments were carried out.

Results and discussions

An additive hexamethoxycyclotriphosphazene was first investigated by Lee et al to improve the thermal performance of cathodes for Li-ion batteries. Here, a new cyclotriphosphazene derivative containing fluorine was investigated. The cyclic voltammetric measurements indicated that the new phosphazene additive is very stable in the EC-based electrolyte and no oxidation peak was observed before 5.0V (versus Li metal). In addition, no detrimental effect on the cycling performance was observed after the new additive was added.

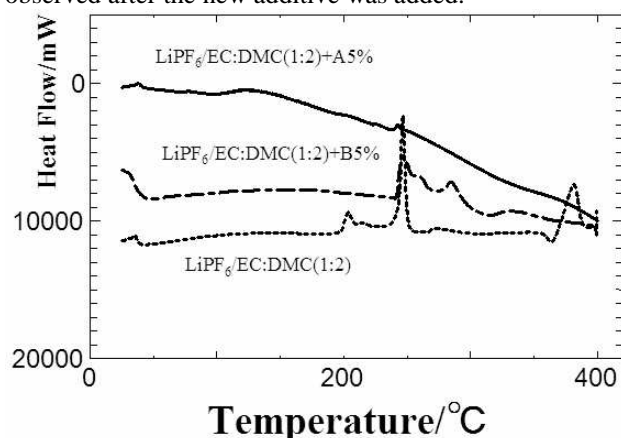


Figure 1. The DSC curves for the charged LiCoO_2 electrodes at 4.3V (vs. Li) containing electrolytes. A, cyclotriphosphazene containing fluorine; B, hexamethoxycyclotriphosphazene

The DSC measurements for the charged LiCoO_2 cathodes containing electrolytes with or without phosphazene additive are shown in Figure 1 for comparison. After hexamethoxycyclotriphosphazene was added, the exothermal peak at about 250°C was decreased, and it would be reduced to be much smaller if the new phosphazene derivative was added. Figure 2 shows the calculated exothermal quantity for the charged LiCoO_2 as a function of time at 700°C , and the heat emission is suppressed significantly with phosphazene additive. Based on kinetic and thermodynamic investigations, it is proposed that the decomposition of LiCoO_2 in the charged state was not suppressed by the adding of phosphazenes. And it is believed that the phosphazenes may obstruct the reaction of decomposed products of charged LiCoO_2 with aprotic solvents, and then the exothermal process was controlled.

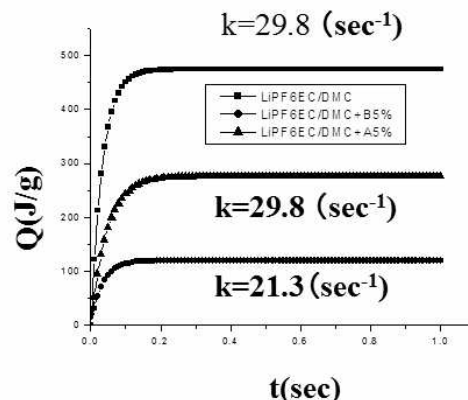


Figure 2. The calculated thermal quantity for the LiCoO_2 cathodes at 4.3 V containing electrolytes.

References

1. C. Wang, H. Nakamura, H. Komatsu, M. Yoshio, and H. Yoshitake, *J. Power Sources*, 74, 142 (1998)
2. C. W. Lee, R. Venkatachalapathy, J. Prakash, *Electrochemical Solid-state Lett.*, 3, 63 (2000).