Thermal Stability of Li$_4$CoO$_2$ Cathode in Li-ion cells

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Introduction

Safety improvements to large Li-ion batteries are indispensable for their practical application. It is generally considered that the "thermal runaway" of Li cells occurs if their heat output exceeds their thermal diffusion.

The thermal stability or the thermal behavior of Li-ion cells has been investigated energetically by DSC or Accelerating Rate Calorimetry (ARC) in order to reduce their heat output.

Figure 1 shows DSC profiles of chemically delithiated Li$_4$CoO$_2$ and 1M PC electrolytes with various Li salts (1 M) [1]. Each sample for DSC measurement was packed in a stainless steel case, which was then crimp-sealed in a glove box filled with argon gas. Oxygen loss from Li$_4$CoO$_2$ occurs at temperatures above 230 °C [2]. Therefore, it is considered that the exothermic heat starting from 190 °C is a surface reaction of Li$_4$CoO$_2$ with an electrolyte, and the reaction from 230 °C is caused mainly by the evolved oxygen from Li$_{4-x}$CoO$_2$ [2-4]. The inhibition effect of the surface reaction was large when LiBF$_4$, LiPF$_6$, and LiClO$_4$ were used. The sample in PC showed the largest heat-output at the region of the surface reaction. In the present study, we investigated the surface state of Li$_{4-x}$CoO$_2$ in order to determine the existence of a protection film on the surface.

Experimental and Results

LiCoO$_2$ was prepared by firing a mixture of Li$_2$CO$_3$ and Co$_2$O$_3$ at 850 °C for 24 h following firing at 500 °C for 5 h in air. Chemical delithiation of LiCoO$_2$ was carried out by stirring a suspension of 5 g of LiCoO$_2$ in 250 ml of 0.5M H$_2$SO$_4$ from 1 to 24 h [2]. The product was filtered and washed several times with acetone, and dried at 80 °C in a vacuum. The Li content of Li$_{4-x}$CoO$_2$ was analyzed by atomic absorption spectroscopy (HTACHII, Z-5000). 1 M Li[N(CF$_3$SO$_2$)$_2$]$_2$ and 1 M LiPF$_6$ solution in PC were used. Chemically delithiated Li$_{4-x}$CoO$_2$ was stirred in the solutions or PC at 20 °C for 24 hr. The treated Li$_{4-x}$CoO$_2$ was washed several times with PC, and dried at room temperature in a vacuum.

Figure 2 shows the FT-IR spectra (FT/IR-680 Plus, JASCO. The transmission mode using pelletized samples with KBr powder) obtained from the treated and non-treated Li$_{4-x}$CoO$_2$. The FT-IR spectra of Li$_{4-x}$CoO$_2$ without treatment and treated with PC showed almost the same profile, which indicates no film formation by PC. However, the spectra of Li$_{4-x}$CoO$_2$ treated in Li[N(CF$_3$SO$_2$)$_2$]/PC and LiPF$_6$/PC were different from that of non-treated Li$_{4-x}$CoO$_2$. Based on this result, we can conclude that a protection film on Li$_{4-x}$CoO$_2$ inhibited the surface reaction.

Fig. 2. FT-IR spectra obtained from the treated and non-treated Li$_{4-x}$CoO$_2$; a) In LiPF$_6$/PC, b) In Li[N(CF$_3$SO$_2$)$_2$]/PC, c) In PC, d) Without treatment.

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References