

Thermal Stability of Li_xCoO_2 Cathode in Li-ion cells

N. Katayama, I. Watanabe*, and J. Yamaki*
 Interdisciplinary Graduate School of Engineering
 Sciences, Kyushu University
 *Institute for Materials Chemistry and Engineering,
 Kyushu University
 Kasuga Koen 6-1, Kasuga 816-8580, Japan

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 $\text{Li}_{0.49}\text{CoO}_2$ and 1M PC electrolytes with various Li salts (1 □l)[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 $\text{Li}_{0.49}\text{CoO}_2$ occurs at temperatures above 230 °C [2]. Therefore, it is considered that the exothermic heat starting from 190 °C is a surface reaction of $\text{Li}_{0.49}\text{CoO}_2$ with an electrolyte, and the reaction from 230 °C is caused mainly by the evolved oxygen from $\text{Li}_{0.49}\text{CoO}_2$ [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 $\text{Li}_{0.49}\text{CoO}_2$ in order to determine the existence of a protection film on the surface.

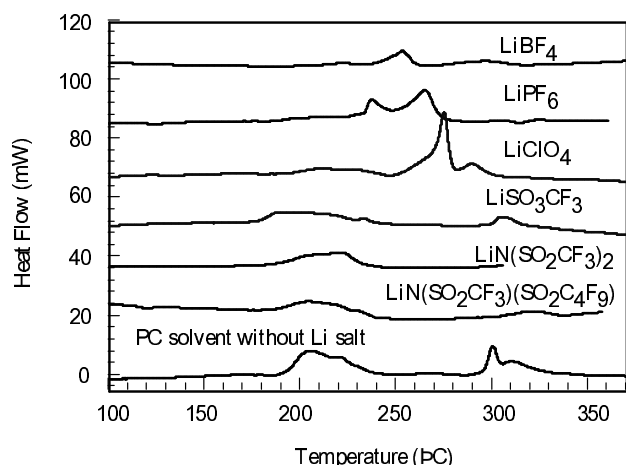


Fig. 1. DSC profiles of chemically delithiated $\text{Li}_{0.49}\text{CoO}_2$ and 1 M Li salt PC electrolyte (Scan rate: 5 °C / min., Rigaku Thermo plus TG8110, Rigaku, Japan) [3].

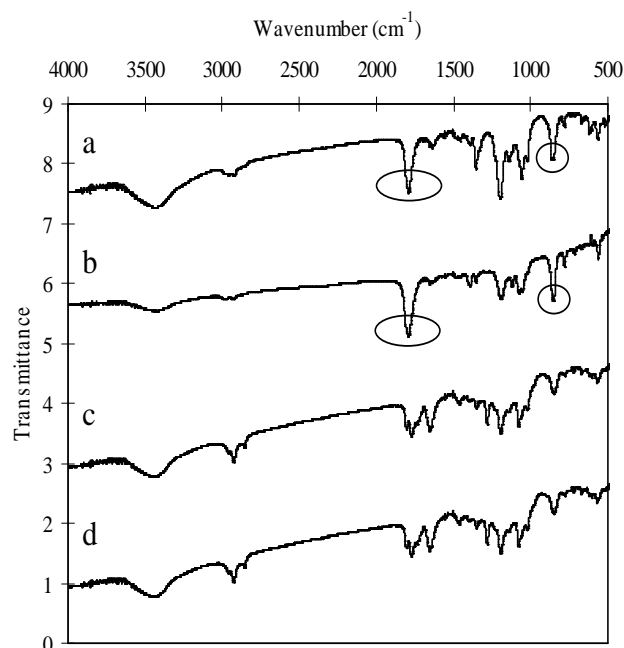
Experimental and Results

LiCoO_2 was prepared by firing a mixture of Li_2CO_3 and Co_3O_4 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_2SO_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_xCoO_2 was analyzed by atomic absorption spectroscopy (HITACHI, Z-5000). 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 M LiPF_6 solution in PC were used. Chemically delithiated $\text{Li}_{0.7}\text{CoO}_2$ was started in the

solutions or PC at 20 °C for 24 hr. The treated $\text{Li}_{0.7}\text{CoO}_2$ 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 palletized samples with KBr powder) obtained from the treated and non-treated $\text{Li}_{0.7}\text{CoO}_2$. The FT-IR spectra of $\text{Li}_{0.7}\text{CoO}_2$ without treatment and treated with PC showed almost the same profile, which indicates no film formation by PC. However, the spectra of $\text{Li}_{0.7}\text{CoO}_2$ treated in $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{PC}$ and LiPF_6/PC were different from that of non-treated $\text{Li}_{0.7}\text{CoO}_2$. Based on this result, we can conclude that a protection film on $\text{Li}_{0.7}\text{CoO}_2$ inhibited the surface reaction.

Fig. 2. FT-IR spectra obtained from the treated and non-treated $\text{Li}_{0.7}\text{CoO}_2$. a) In LiPF_6/PC , b) In $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{PC}$, c) In PC, d) Without treatment.



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