

Thermal Decomposition Process of $\text{Li}_{1-y}\text{CoO}_2$

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Introduction

Owing to its rigid layered structure, LiCoO_2 has been widely used as one of the 4V cathode materials for the lithium-ion rechargeable batteries. However, as the application of lithium-ion batteries spread, higher feature became to be demanded for LiCoO_2 . Especially, its thermal stability is of major interest, because safety and performance under higher temperatures are related to this feature. It has been reported that $\text{Li}_{1-y}\text{NiO}_2$ decompose through a spinel structure stage [1,2]. With an objective to make clear the thermal decomposition process of $\text{Li}_{1-y}\text{CoO}_2$, we have investigated structural changes and weight loss during temperature elevation.

Experimental

LiCoO_2 was synthesized by a solid-state reaction. A mixture of Li_2CO_3 and Co_3O_4 was heated at 900°C in air and characterized by XRD. To analyze the delithiated state, 60% of the lithium was extracted electrochemically from LiCoO_2 by charging in a coin-type cell with Li-metal anode and 1M $\text{LiPF}_6\text{-EC/DMC}$ electrolyte. The weight loss during temperature elevation was measured by Thermal Gravimetric Analysis(TGA), and the phases formed by thermal decomposition were identified by High Temperature XRD.

Results and Discussion

The results of TGA measurements of $\text{Li}_{0.4}\text{CoO}_2$ is shown in Fig.1. Large weight loss caused by decomposition and oxygen release was observed at above 250°C . XRD patterns of $\text{Li}_{0.4}\text{CoO}_2$ as a function of heating temperature is shown in Fig.2. Layered rocksalt structure transformed to cubic spinel structure at above 200°C . This transformation resulted from migration of some Co into Li layer in order to compensate for Li vacancy generated by charging. Slight (220) peak was observed in the XRD pattern between 200°C and 300°C , which indicates that Co prefers 16d and 16c sites to 8a site of spinel phase in that temperature. The excess oxygen thus caused was released and weight decreased. At higher temperatures above 300°C , Co gradually moved to the 8a site in addition to the 16d and 16c sites, which corresponds to growth of (220) or (224) peaks. It suggests the formation of Co_3O_4 -like spinel phase as the products of thermal decomposition. More details concerning the decomposition process and the effect of substitution of Co with other cations will be presented.

References

1. H.Arai, S.Okada, Y.Sakurai and J.Yamaki, Solid State Ionics, 109,295(1998).
2. A.Manthiram and S.Choi, 198th The Electrochem. Soc. Meeting, Arizona, Abs.No.72, 1999.

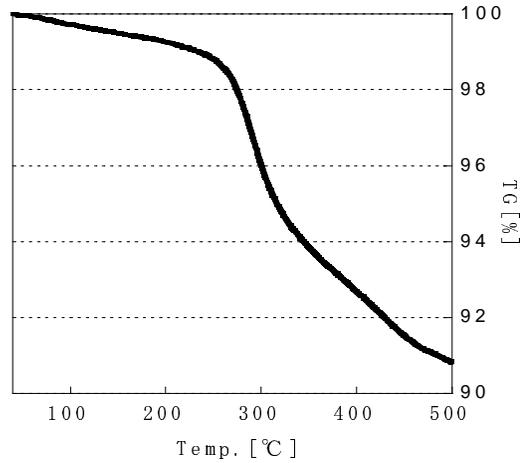


Fig.1 TG profile of $\text{Li}_{0.4}\text{CoO}_2$

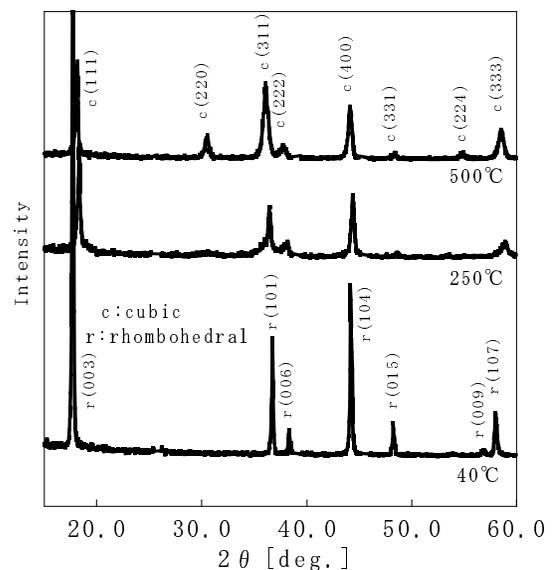


Fig.2 High-Temp. XRD patterns of $\text{Li}_{0.4}\text{CoO}_2$