



## Full paper

# Different thermal degradation mechanisms: Role of aluminum in Ni-rich layered cathode materials<sup>☆</sup>

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## ABSTRACT

Despite increasing demands for higher energy density cathode materials, they can be bigger threats unless thermal stability is guaranteed. Herein, the thermal stability of  $\text{Li}_x\text{Ni}_{0.835}\text{Co}_{0.15}\text{Al}_{0.015}\text{O}_2$  (NCA83) and  $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA80) is compared by using *in-situ* transmission electron microscopy. Analysis demonstrates that NCA83 and NCA80 degrade thermally by distinct mechanisms. Al prevents the transition to  $\text{CoO}_2$ -type O1 phase by suppressing O-slab gliding by residual Li. At 67% SOC, in the sub-surface area, thermal degradation of NCA80 is mainly due to reduction of Ni, whereas thermal degradation of NCA83 is a result of concurrent reduction of Ni and Co. The difference indicates that NCA83 has both earlier transition to the rock-salt structure and poorer thermal stability than NCA80. This study presents a protocol to properly evaluate new high energy density cathode materials, and provides important insights into the thermal degradation mechanism of Ni-based layered oxides.

## 1. Introduction

Lithium ion batteries (LIBs) are primary power sources for portable electronic devices, and are being adapted for use in electric vehicles [1–3]. Increase in energy density of LIBs is a primary research goal to extend the usage time of a cellular phone or the range of an electric vehicle on a single charge. However, mechanical impact or sudden heat can cause a LIB to explode, and increasing the energy density increases the severity of this reaction [4,5]. An electric vehicle uses a LIB pack that weighs a few hundred kilograms, and that can explode violently if chain reactions of unstable components are triggered. Therefore, developing electrode materials with high energy density balanced by appropriate stability and also methods to properly evaluate their stability are of critical importance.

Ni-based layered oxides ( $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$ , M = Co, Mn, and Al) have

been regarded as promising cathode materials for EV applications due to high energy density and relatively high stability [6]. To increase energy density, the simplest way is to charge or discharge the cathode materials to deeper state of charge (SOC) as long as the thermal stability can be maintained. However, the thermal stabilities of Ni-based layered oxides highly depend on their SOC [7–10]. Therefore, practical upper limits of SOC to guarantee safe operation have been determined for various applications of LIBs.

Modification of composition is a common approach to increase the energy density of Ni-based layered oxides. Especially, Ni content  $x$  has a strong influence on the electrochemical capacity [11–13]. However, at high  $x$ , undesirable phase transformation can occur, particularly at a high SOC or elevated temperatures [7,8,14,15]. This instability may be caused by formation of unstable  $\text{Ni}^{4+}$  ions in the delithiated state, because they have a strong tendency to reduce to the  $\text{Ni}^{2+}$  state,

<sup>☆</sup> Different thermal degradation mechanisms of  $\text{LiNi}_{0.8+x}\text{Co}_{0.15}\text{Al}_{0.05-x}\text{O}_2$  ( $x = 0, 0.035$ ) particles were investigated using *in-situ* TEM techniques. At 67% SOC, NCA83 shows a strong particle-to-particle variations on thermal stability, and the most thermally vulnerable particle degrades rapidly by the formation of fully-delithiated O1 ( $\text{CoO}_2$ ) regions due to lack of non-redox element, Al.

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