

## Phase instability of layered $\text{Li}_x\text{CoO}_2$ at $x \sim 0.5$ composition

Akiho Nakamura,<sup>1</sup> Hideki Oki,<sup>2,3</sup> Naoya Shibata,<sup>1,4</sup> and Yuichi Ikuhara<sup>1,5</sup>

<sup>1</sup>Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan

<sup>2</sup>Toyota Motor Co Ltd, Battery Mat Div, Shizuoka 4101193, Japan

<sup>3</sup>Graduate School of Frontier Sciences, The University of Tokyo, Tokyo 1130033, Japan

<sup>4</sup>PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan

<sup>5</sup>Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

**Introduction:**  $\text{Li}_x\text{CoO}_2$  is categorized into layered rock-salt structure, and widely utilized as a basic cathode material of lithium ion battery (LIB). Although the theoretical energy density is relatively high (274 mAh/g), the effective capacity is limited to its half value ( $\sim 130$  mAh/g) due to severe electrode degradation in delithiated state beyond  $x \sim 0.5$ . Importantly, this composition range also contains phase transition from hexagonal to monoclinic lattice, therefore its relation to the irreversible capacity fade will be critical for controlling battery performance and stability. In this study, we analyzed the local structural evolutions of  $\text{Li}_{0.5}\text{CoO}_2$  in an atomic scale, mainly focus on the transient state from starting layered structure.

**Experimental section:** Pristine  $\text{LiCoO}_2$  powder was fabricated by solid state reaction, and successively delithiated by electrochemical treatment. Li-metal was set as a counter electrode, and whole battery system was equilibrated under constant applied voltage at  $\text{Li}_{0.5}\text{CoO}_2$  composition. In-situ TEM experiment was performed in variable temperature, using double tilt  $\text{LN}_2$  cooling holder (model 636, Gatan Inc.) installed into JEOL-2010HC microscope. Atomic resolution HAADF-STEM imaging was conducted after in-situ experiments, using JEOL-ARM200F equipped with  $\text{C}_s$ -corrector in the illumination system (CEOS GmbH).

**Results and Discussion:** The diffraction pattern of delithiated  $\text{Li}_x\text{CoO}_2$  particle, taken at ambient temperature, is shown in figure 1. It represents characteristic spots attributed to  $P2/m$  symmetry [1], indicating that the monoclinic phase near  $x=0.5$  was successfully obtained. Moreover, such transition from  $R\bar{3}m$  hexagonal lattice suggests that Li ordering would be maintained even at room temperature, as reported previously [2]. Here, we cannot find other phase transitions down to 100K (lower limit of  $\text{LN}_2$  cooling system), although some anomalies in magnetic susceptibility have been observed around 150K [3].

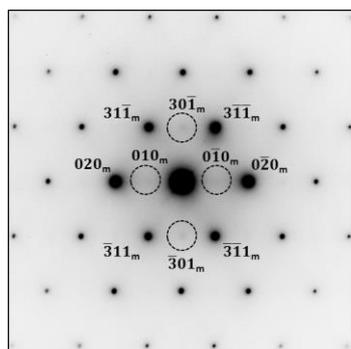
In the past in-situ electrochemical experiment [2], Reimer *et al* stated that such ordered structure will be broken over 340K ( $\sim 70^\circ\text{C}$ ) by thermal vibrations of Li ions, and translated into Li-disordered  $\text{C}2/m$  monoclinic phase. To verify the phase stability as a function of working temperature, we tried to reproduce the temperature-driven Li-order breaking using the heating mode of in-situ TEM holder. Interestingly, however, the diffraction spots due to  $P2/m$  symmetry were not disappeared even at  $100^\circ\text{C}$ . Moreover, atomic resolution HAADF-STEM images of thermally treated sample clearly show the weak bright contrasts at the Li column positions (figure 2). Such weak contrast is a direct evidence of antisite Co ions, *partially* filled the neighbor Li sites.

It should be mentioned that these antisite Co ions form an ordered array as indicated in figure 2, the pattern of which is close to the projected spinel structure along  $[110]_{\text{cubic}}$ . In addition, this periodicity corresponds to that of Li-vacancy ordering in  $\text{Li}_{0.5}\text{CoO}_2$ . Thus,

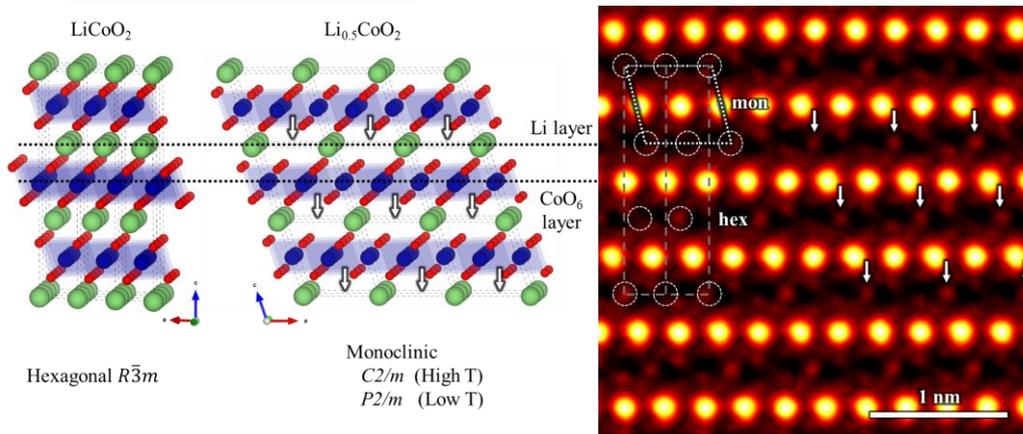
it can be expected that Co ions will not be randomly displaced, but selectively migrate into 1D Li-vacancy lines within the Li-ordered  $\text{Li}_{0.5}\text{CoO}_2$  structure, as schematically shown in figure 2. These Co ions are much heavier than diffusive Li ions and their ordering can be hardly disturbed, suppressing the thermal breaking of  $P2/m$  symmetry.

The observed structure would be a transient state from Li-ordered  $\text{Li}_{0.5}\text{CoO}_2$  to stable  $\text{LiCo}_2\text{O}_4$  spinel, promoted by thermally activated diffusions of unstable Co ions. The origin of such ordered Co antisite lattice is still unclear, but one possibility is the change of antisite formation energy under chain-like Li / Li-vacancy distribution. The deep understandings for such defect formation behavior will be necessary for overcoming the  $x=0.5$  criteria in  $\text{Li}_x\text{CoO}_2$  cathode material.

**Acknowledgements:** The authors gratefully acknowledge the financial support by a Grant-in-Aid for Scientific Research on Innovative Areas “Nano Informatics” ( Grant No. 25106003 ) from Japan Society for the Promotion of Science ( JSPS ), and Funding Program for World-Leading Innovative R&D on Science and Technology ( FIRST program ).



**Figure 1**  
Diffraction pattern of  $\text{Li}_{0.5}\text{CoO}_2$  taken at ambient temperature, along  $[103]$  direction in monoclinic setting (corresponds to  $[001]$  in hexagonal setting).



**Figure 2**  
HAADF-STEM image of thermally treated  $\text{Li}_{0.5}\text{CoO}_2$  particle, showing weak and periodic bright contrast at Li atomic columns indicated by white arrows. The schematic views of  $\text{LiCoO}_2$  and  $\text{Li}_{0.5}\text{CoO}_2$  structures are represented in the left figures.

## References

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