

# MECHANISM OF OXYGEN RELEASE FROM LI-RICH CATHODE MATERIAL FOR LITHIUM ION BATTERIES

Takashi Nakamura, IMRAM, Tohoku University  
 takashi.nakamura.e3@tohoku.ac.jp  
 Hongze Gao, Tohoku University  
 Kento Ohta, Tohoku University  
 Yuta Kimura, Tohoku University  
 Yusuke Tamenori, JASRI  
 Koji Amezawa, Tohoku University

Key Words: Oxygen release; Oxygen nonstoichiometry; Lithium ion batteries; Li-rich cathodes

For further wide spread of high energy density batteries, one of the most important technological challenges is preventing thermal runaway. For that, a key phenomenon is the oxygen release from cathode active materials, because released oxygen may react with the organic solvent and generate heat. Therefore, it is important to understand the mechanism of oxygen release to ensure safe battery operation. While the reaction of charged cathode material and organic solvent was investigated well [1], the mechanism of oxygen release from cathode material is not understood so far [2]. In this study, oxygen release behavior of Li-rich cathode material  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  was investigated, and the mechanism of oxygen release was discussed based on defect chemistry and thermodynamics.

$\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  was synthesized by a solid state reaction method from  $\text{Li}(\text{OH})\cdot\text{H}_2\text{O}$  and the Ni-Mn mixed carbonate precursor which was prepared by co-precipitation method. The mixed powder was sintered at 1173 K for 10 h and grounded in a mortar thoroughly. Oxygen nonstoichiometry of  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  was evaluated by a thermogravimetry and a coulometric titration. The absolute value of the oxygen content was determined by an iodometric titration. The crystal structure and electronic structure of the pristine and the oxygen extracted samples were investigated by XRD and soft X-ray absorption spectroscopy at BL27SU SPring-8, Japan. Figure 1 shows the relation between the oxygen content (O/M) and the equilibrium  $\text{PO}_2$  of  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  at 873 K. We successfully observed the oxygen release phenomena from Li-rich cathode material,  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$ . In this figure, O/M is the molar ratio of oxygen and cations. Therefore,  $\text{O}/\text{M} = 1.0$  means the stoichiometric composition and  $\text{O}/\text{M} < 1$  means the oxygen deficient composition. Until  $\text{O}/\text{M} = \text{ca.}0.97$ , the equilibrium  $\text{PO}_2$  changes depending on O/M. This indicates that the oxygen vacancies are created in the oxygen sub-lattice of  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  while the original layered rock-salt structure was maintained. Namely, the oxygen deficient nonstoichiometry of  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  was observed in this region. On the contrary, when O/M is smaller than 0.97, the equilibrium  $\text{PO}_2$  is invariant regardless of O/M. This indicates  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  started to decompose at  $\text{O}/\text{M} = 0.97$ , and co-exist with the reduction decomposed phases. By XRD measurement,  $\text{MnNi}_6\text{O}_8$  was detected when O/M became smaller than 0.97. From these results, the oxygen release reaction can be expressed as follows.

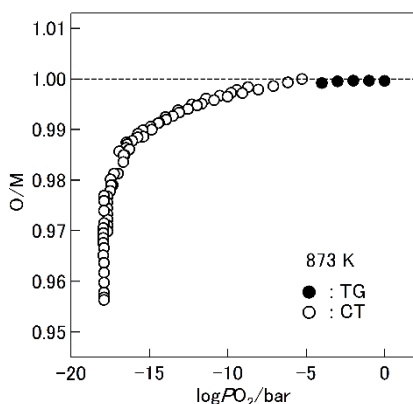
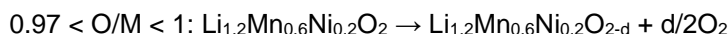
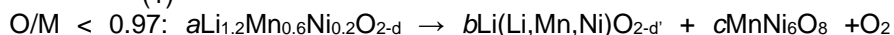


Figure 1. Oxygen release behavior from  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$  at 873 K



(1)



(2)

Detailed mechanism of the oxygen release was investigated by defect chemical and thermodynamic analyses. The crystal and electronic structural changes due to the oxygen release will be also discussed in the presentation.

## Acknowledgements

This work was supported by Grand-in-Aid for Scientific Research (c), Grant number JP18K05288

## References

- [1] A. W. Golubkow, *et al.*, RSC Adv., 2015, 5, 57171.
- [2] S. Kim, *et al.*, Energy Environ. Sci., 2017, 10, 2201.