

# First-principles calculation and molecular dynamics simulations on reaction mechanism analysis of batteries used for the next generation automotive

## Project Representative

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## Abstract

Using first-principles calculation and first principles molecular dynamics (FPMDs), Mn behaviors of  $\text{Li}_{2-x}\text{MnO}_3$  ( $x = 0.5$  and  $1.0$ ) was investigated as an aim of elucidating the reaction mechanism of solid solution cathode materials ( $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ;  $M = \text{Co}$  and  $\text{Ni}$ , etc.) in the future. The simulation of X-ray absorption near edge structure (XANES) spectra predicted Mn in Mn-Li layer moved spinel like site of Li Layer. FPMDs calculations indicate the ratio of Mn moved to the Li layer increased with increasing Li deficiency. The ratio of Mn for  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_{1.5}\text{MnO}_3$ , and  $\text{Li}_{1.0}\text{MnO}_3$  are estimated 0, 13, and 44 %, respectively.

**Keywords:** first principles molecular dynamics, lithium-ion rechargeable battery,  $\text{Li}_2\text{MnO}_3$

## 1. Introduction

Development of high capacity Li-ion rechargeable batteries has been a key technology to accomplish the greener sustainable society. Solid solution systems ( $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$ ;  $M = \text{Co}$  and  $\text{Ni}$ , etc.) have high capacity with maintaining durability. Investigation of the instability of  $\text{Li}_2\text{MnO}_3$ , which is the mother material of solid solution systems, has been important to elucidate and improve the durability of solid solution systems. Simulation of Mn K-edge XANES spectra obtained from first-principles calculations predicts forming local spinel structure. Based on the prediction, FPMDs calculation is adopted to estimate the ratio of Mn which contributes to the forming local spinel structure. The calculation results indicate Li deficiency can be responsible for forming spinel like site which bring degradation of  $\text{Li}_2\text{MnO}_3$  positive cathode.

## 2. Results and discussion

XANES spectra simulations are carried out using WIEN2k [1]. VASP and VASP-MD were adopted for geometrical optimization and FPMDs calculation, respectively [2]. The FPMDs calculation was

carried out at 5 fs every one step under 3000 K. The first principles calculations reproduced the peak shifts of Mn K-edge at discharging (Figure 1 (a)) by assuming Mn has been remained at a local spinel site (Figure 1 (b)).

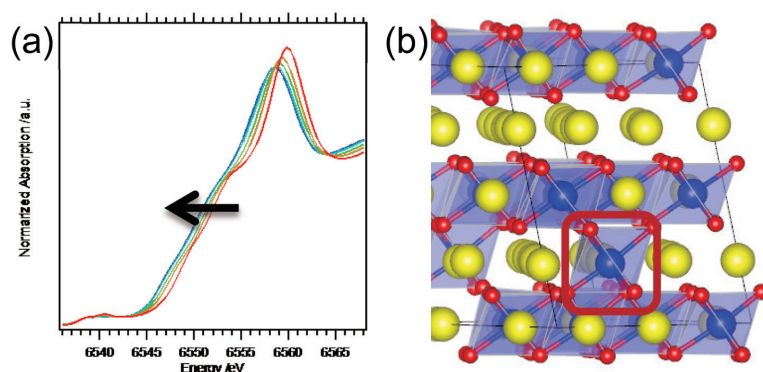


Figure 1. (a) Simulated Mn K-edge spectra originated from discharging process. (b) Mn at local spinel site. Each image drawn using VESTA[3]

As the simulation spectra supported the assumption Mn in Mn-Li layer can move Li layer, we estimate the ratio of Mn remaining in Li layer (Figure 2). To investigate the detail of Mn movement, the Mn states were classified in three ways (Figure 3).

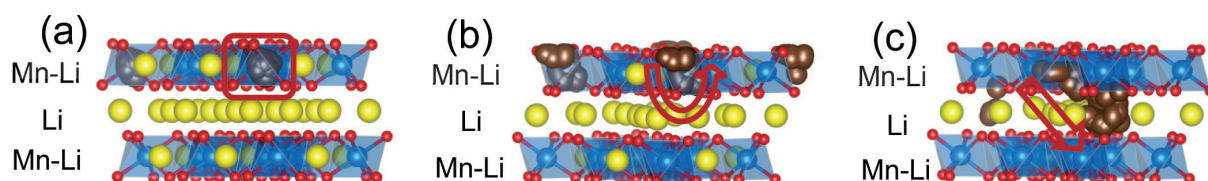


Figure 2. Illustrations of Mn ion movement. (a) Mn stays in Mn - Li layer. (b) Move to Li layer, but move back again Mn-Li layer. (c) Moved to Li layer. Each image drawn using VESTA[3]

Mn of  $\text{Li}_{2.0}\text{MnO}_3$  has remained in the Mn layer (Figure 3(a)). Otherwise, Mn in Mn-Li layer of Li deficiency state moved to Li layer (Figure 3(b) and (c)). The ratio of Mn staying at the local spinel site was increased with increasing Li deficiency. The ratio of Mn for  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_{1.5}\text{MnO}_3$ , and  $\text{Li}_{1.0}\text{MnO}_3$  are estimated 0, 13, and 44 %, respectively.

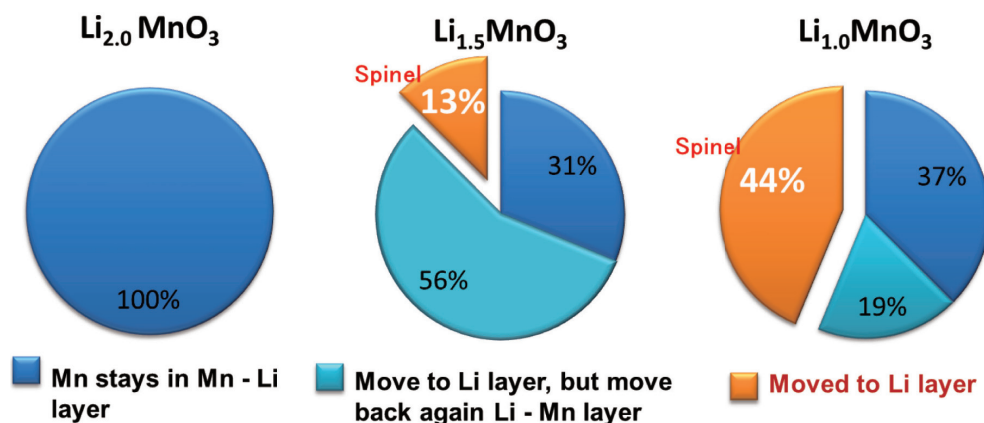


Figure 3. Relationship between Li deficiency and local spinel structure. (a)  $\text{Li}_{2.0}\text{MnO}_3$ . (b)  $\text{Li}_{1.5}\text{MnO}_3$ . (c)  $\text{Li}_{1.0}\text{MnO}_3$ .

## References

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