

Title	第一原理計算を用いた高容量リチウムイオン二次電池正極材の材料設計
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# Abstract

To realize a decarbonized society, research and development of pure electric vehicles (EV) is being promoted internationally. However, the popularization of EV has been sluggish due to issues of energy density and cost in the lithium-ion batteries (LIBs). One of the solutions to achieving high energy density and low cost in LIBs is the use of Ni-rich cathode active materials, e.g.  $\text{LiNiO}_2$ . While Ni-rich cathode materials have excellent charge/discharge specific capacity, they have problems that cannot be overlooked in terms of battery characteristics such as rate characteristics, cycle characteristics, and weather resistance. Therefore, a practical application of Ni-rich cathode materials to LIBs requires us to improve their battery characteristics of “high specific capacity/low cost” and “rate characteristics/cycle characteristics/weather resistance” simultaneously.

In this study, we aim to establish an “integrated research approach” that combines an experimentally driven approach with a computationally driven approach as a way to accelerate the research and development of new Ni-rich cathode materials. Among the various issues in the development of Ni-rich cathode materials, this research will focus on the following two issues:

(1) Elucidation of the mechanism of degradation in the atmosphere: It is assumed that the degradation phenomenon is caused by a proton exchange/diffusion between  $\text{Li}^+$  and  $\text{H}^+$ . However, it is difficult to observe the phenomenon experimentally, and computational science is expected to clarify the phenomenon. From the viewpoint of predictive reliability, the first-principles transition state calculation is one of the most promising approaches within the state-of-the-art simulation techniques for the quantitative description of diffusion phenomena. In this study, we will perform large-scale parallel calculations based on the first-principles transition state calculations to quantitatively evaluate the proton exchange mechanism in  $\text{LiNiO}_2$  and elucidate the degradation mechanism in the air.

(2) Establishment of clear guidelines on material design based on atomic substitution: It has been reported that various battery properties can be improved by replacing Ni atoms in  $\text{LiNiO}_2$  with other metal atoms. Since the number of combinations of substituent species, substitution amounts, and substitution positions is enormous, it is impossible to find the best combination in an exhaustive way by experiment alone. In this study, we use high-throughput first-principles calculations to identify the stable structures of substituted compounds realized with various substitution species and amounts; electronic properties are computed for the most stable cases by first-principles. Correlation analysis of the obtained structural/electronic properties with various battery properties will be conducted to establish guidelines on how to improve the battery properties by atomic substitution.

The results for the above two issues can be summarized as follows:

(1) In  $\text{LiNiO}_2$  exposed to the air, we experimentally observed “a small amount of shrinkage of the  $c$ -axis lattice parameter” and “a decrease in the rate characteristics due to an increase in the activation energy of Li diffusion”. These findings can be attributed to the proton exchange between  $\text{Li}^+$  and  $\text{H}^+$ , which was suggested by our quantitative chemical analysis of H in the solid by the Karl Fischer titration. Our first-principles results for the lattice parameter and the activation energy of Li diffusion of the  $\text{Li}^+/\text{H}^+$  exchange structure were consistent with the experiments. We found that the activation energy of  $\text{Li}^+$  diffusion increases owing to the contraction of the Li-O interlayers through which the  $\text{Li}^+$  ions diffuse. This contraction is caused by the hydrogen bonding between the H and O atoms.

(2) To computationally design the Ni-rich materials achieving both high specific capacity and good rate/cycle characteristics, the performances of  $\text{LiNi}_{1-x-y-z}\text{Co}_x\text{Mn}_y\text{Al}_z\text{O}_2$  were verified and discussed. We have, for the first time, proposed a method for predicting the equilibrium redox potential from the density of states, which is important when considering the charge-discharge specific capacity. Note that the former is a quantity that cannot be directly evaluated by computation, while the latter is easily computed. The barrier energy of  $\text{Li}^+$  diffusion obtained from Climbing Image Nudged Elastic Band (CI-NEB) calculation was found to change, depending on kinds of metal atoms locating near the  $\text{Li}^+$  diffusion path. In particular, it was found that the diffusion path near the Co atom(s) has excellent rate characteristics due to its low barrier energy.

In future research, we will expand our search space to a wider chemical space including various combinations of substitution elements. Novel Ni-rich cathode active materials with the excellent overall performance are expected to be explored in such a wider chemical space.

**Keywords:** Lithium-ion battery, Cathode material, First-principles simulations, Transition state theory, Electrochemical properties