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**論文の内容の要旨**

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. $LiNiO_2$. 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 $Li^+$ and $H^+$. 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 $LiNiO_2$ 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 $LiNiO_2$ 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 $LiNiO_2$ 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 $Li^+$ and $H^+$, 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 $Li^+/H^+$ exchange structure were consistent with the experiments. We found that the activation energy of $Li^+$ diffusion increases owing to the contraction of the Li-O interlayers through which the $Li^+$ 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 $LiNi_{1-x-y-z}Co_xMn_yAl_zO_2$ 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 $Li^+$ diffusion obtrained from Climbing Image Nudged Elastic Band (CI-NEB) calculation was found to change, depending on kinds of metal atoms locating near the $Li^+$ 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

**論文審査の結果の要旨**

脱炭素化社会の実現に資する純電気自動車が普及するには、優れたリチウムイオン二次電池(LIB)正極活物質の開発が鍵を握っており、その性能向上とコスト削減が最重要課題となっている。しかしながら、従来の実験主導研究開発だけでは、物性発現機序の電子論・原子論的解明やそれに基づく新規物質探索を進展させることは難しい。本論文は、従来の「実験駆動型研究アプローチ」に相補的なシミュレーションに基づく「計算駆動型研究アプローチ」を組み合わせた「統合型研究アプローチ」を提案・確立し、LIB 正極材料開発における２課題「1/大気中での劣化機序の解明」及び「2/金属元素置換に基づく材料設計指針の確立」に取り組み、以下の知見を得た：課題１では、$Li^+$と $H^+$のプロトン交換/拡散現象と推測されていたが、その実験的観測は困難であり、本研究は、第一原理遷移状態計算を用いた活性化エネルギー算定によりプロトン交換機構を解明した。特に、プロトン交換で固体内に侵入した水素が積層構造内の酸素と水素結合を形成し、$Li^+$拡散の活性化エネルギーを増加させることを見出した。課題２では、充放電容量に優れた正極材 $LiNiO_2$ 化合物系におけるレート特性（電流の瞬時取り出し）及びサイクル特性（充放電に伴う容量劣化）の改善を目的として、Ni 元素を他の金属に部分置換した元素置換化合物系の探索に取り組んだ。元素置換による電池特性改善の可能性は知られていたが、置換元素種、置換量、置換位置の組み合わせは膨大であり、その全てを網羅的に検証することは実験的には不可能である。本研究は、情報科学的技術を積極的に取り入れ、大量シミュレーションの並立実行を可能とする自動化計算システムを開発し、研究基盤を確立した。特にその核心部分として、シミュレーションによ

る直接検証困難なレート特性・サイクル特性について、シミュレーション可能な物性量と特性間の相関関係を見出し、計算科学の枠組み内で実験を経由せずに、元素置換による特性変化を検証する相関解析手法を開発した。当該システムを活用して置換化合物系に対するハイスループット第一原理計算を大型並列計算機上で実施し、電池特性を改善する置換元素種を見出した。これら研究成果の一部は既に、申請者を主著者とする査読付原著論文[T. Toma, R. Maezono, K. Hongo, ACS Appl. Energy Mater. 3, 4078 (2021/IF=6.024)]に発表されており、当該コミュニティにおいて一定の評価を獲得している。

以上、本論文は、リチウムイオン二次電池正極材料開発のための実験と計算を融合した統合型研究アプローチを提案し、大気中での劣化機序という当該分野の未解決問題を解決しただけではなく、新規正極材料探索における計算科学的研究展開の可能性を示した業績として学術的に貢献するところを認め、よって博士(情報科学)の学位論文として十分価値あるものと判断した。