博士論文公聴会の公示（物理学専攻）

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論文題目：First-Principles Investigations of Cation-Disordered Rock-Salt Type Oxides for Li-Ion Battery Cathodes (陽イオン不規則岩塩型構造を有するリチウムイオン電池用正極酸化物に対する第一原理的研究)

日時：2020 年 2 月 6 日 10: 30 ~ 12: 00
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論文要旨：

Li-ion battery is widely used for portable electric devices because of its high capacity, high voltage, and high energy-density compared to conventional rechargeable batteries such as a lead-acid battery. While the Li-ion battery is already successful as an energy storage system, improving its performance is essential to establish the sustainable society without dependence on fossil fuels and nuclear energy. The important characteristics above mentioned are predominantly determined by a cathode material, and transition-metal oxides such as $LiCoO_2$ with layered rock-salt type structure are typically used as cathodes. However, in $LiCoO_2$ cathode, structure changes with O_2-release take place during battery reactions, and the desorbed O_2-gas exothermically reacts with organic electrolyte. Therefore, its available capacity is limited by half of the theoretical capacity.

Recently, cation-disordered rock-salt type Li_2MTiO_4 (M = 3d-transition metals) has attracted much interest as a cathode material with high capacity originating from two-electron reaction. In this oxide, high structural stability at low Li-concentration is also expected because cation elements and Li vacancy are randomly distributed. However, experimental measured capacities have been limited by the theoretical capacities of one-electron reactions. Furthermore, several different reaction mechanisms have been proposed for each M, and systematic understanding of battery reactions has not been obtained. In the first part of this theses, comprehensive battery reactions were thoretically investigated, and effects of M on the reaction mechanisms were clarified. It was concluded that Li_2CrTiO_4 might be the best candidate among these calculations. In the second part of this theses, to improve the rechargeable capacities, their Li-excess phases $Li_{2+2x}Mn_{1-x}Ti_{1-x}O_4$ were theoretically studied. It was clarified that O-redox reactions play a significant role on the battery reactions, and optimized Li-excess phases were proposed in the viewpoints of capacity and structural stability against O_2-release.

I believe that the present studies, focusing on the effects of transition metals and Li excess on the battery characteristics, provide a new strategy for design and optimization of cathode materials.