First-Principles Study on Cathode Properties of Li-excess Rock-Salt Type $Li_{2+2x}Mn_{1-x}Ti_{1-x}O_4$

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Cation disordered rock-salt type Li_2MnTiO_4 has been attracted much attention as a cathode compound, because it has large theoretical capacity originated from two-electron reaction, high thermodynamical stability, and no rare metal. Electrochemical measurements and theoretical studies of this cathode compound respect to Li-metal anode have been performed, and it is clarified that battery reaction mechanism is composed of mainly two stages which are Mn- and O-redox reaction depending on different Li concentration in the cathode [1, 2]. However, its rechargeable capacity is limited by about one-electron reaction. Recently, Li-excess states of this compound have been experimentally investigated to enhance the rechargeable capacity, showing that their rechargeable capacities depend on Li-excess (x) and XANES measurements suggest that O-redox reaction region becomes increasing with increasing Li-excess (x). On the other hand, detailed battery reaction mechanism, which depends on Li-excess (x), as well as electronic structures in the cathode compounds and optimized Li-excess (x) in which the maximum rechargeable capacity can be obtained, are not clarified so far.

In this study, the first-principles calculations within the density functional theory (DFT) frameworks are performed for rock-salt type $Li_{2+2x}Mn_{1-x}Ti_{1-x}O_4$ with the different Li-excess and the different cation site patterns using supercell models, and the electronic structure changes associated with Li-ion insertions and dissociations are investigated. We use the HiLAPW [3] and the Quantum Espresso [4] codes, which utilizes the scalar-relativistic all-electron full-potential linearized augmented plane wave (FLAPW) method and the projected augmented wave (PAW) method, respectively. We analyze energy stabilities of $Li_{2+2x-y}Mn_{1-x}Ti_{1-x}O_4$ to theoretically predict discharge reaction formulae and calculated Li-vacancy formation energies, and also estimate theoretical voltages and the number of removable Li (NRL) as a function of Li concentration in the cathode. The calculated NRL suggests that the reversible capacities depend on Li-excess (x). The calculated electronic structures indicate that unoccupied O-2p states become increasing with increasing Li-excess (x) so that O-redox reaction becomes much remarkable with increasing Li-excess (x). These theoretical results support the experiments.

References:
[1] A. Kitajou, K. Tanaka, H. Miki, H. Koga, T. Okajima, and S. Okada, *Electrochem.* **84**, 597 (2016).
[2] M. Hamaguchi, H. Momida, and T. Oguchi, *J. Phys. Soc. Jpn.* accepted.
[3] First-principles calculation package: HiLAPW
(http://www.cmp.sanken.osakau.ac.jp/~oguchi/HiLAPW/index.html).
[4] First-principles calculation package: Quantum Espresso (P. Giannozzi *et al. J. Phys. Condens. Matter* **21**, 395502 (2009), and P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **29**, 465901 (2017))