First principles study of reaction voltage of metal-fluoride cathodes in Li-ion rechargeable battery

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Binary metal compounds have been widely investigated for their potential applications in conversion reaction of Li-ion rechargeable batteries as they have high Li storage capacity compared to commercialized electrode materials of intercalation reaction. Metal fluorides, MF_2 (M=Fe, Ni, Cu) especially show a relatively higher reaction voltage among binary metal compounds and thus, can be considered as promising cathode materials for Li-ion rechargeable batteries. The deviation between conventionally obtained theoretical voltage and experimentally observed voltage is the key issue and is still not understood well, however. In this study, we combined first principles calculations and experiments to analyse the conversion reaction voltage for MF_2 (M=Fe, Ni, Cu) in Li-ion battery. We developed a new method to gain theoretical voltage of conversion reaction as a function of metal nanoparticle size. This methodology is different from conventional way of attaining voltage which adopts the Gibbs free energy of bulk metal. In order to calculate the reaction voltage, model systems of metal nanoparticles in different sizes are adopted with cuboctahedron and icosahedron morphologies. Based strictly on thermodynamics, the result points toward strongly size-dependent voltage. The property of voltage becomes similar to the voltage calculated from bulk metal, as the size of metal nanoparticle increases. The reaction voltage measured from PITT experiment supports the calculation results, indicating lower values compared to the voltage of bulk metal formation. It is remarkable that we proposed the excessive energy on the surface of a metal nanoparticle is an energy penalty, which leads the reaction voltage drop with respect to the voltage of bulk metal formation.