Ab initio study of doping effects on $LiMnO_2$ and Li_2MnO_3 in OLO cathode for Li ion batteries

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The over-lithiated-oxides (OLOs) are a composite of layered structures of Li_2MnO_3 and $LiMO_2$ (M=Mn,Fe,Co, Ni), and shown to have much higher storage capacity than traditional layered oxides as Li ion battery cathode, due to the presence of Li_2MnO_3 phase. However, experimental results indicate Li_2MnO_3 is not stable after the 1st charge-discharge cycle and would partly transform into layered $LiMnO_2$, which would form a practically used phase as a mixture of both Li_2MnO_3 and $LiMnO_2$. During the subsequent charging cycles, OLO capacity is known to reduce gradually in connection with Mn spinel phase formation. To improve the OLO cathode material performance, it is desirable to suppress such spinel phase formation. On the other hand, serious conductivity problems of both layered oxide phases are observed leading to low kinetic performance of the OLO cathodes. To address the stability of layered oxides, and the electric and ionic conductivities, we have examined the doping effects on the layered oxides using the *ab initio* density-functional theory (DFT) simulations. A detailed OLO materials phase stability is examined as a function of two chemical potentials, μ(Li) and μ(O). From the DFT simulations, we can identify the effects of different doping elements on the ionic diffusion in each phase and also the basic mechanisms of electronic conductivity. These DFT findings are providing conceptual guidance in the experimental search for the effective dopants which would satisfy multiple cathode materials requirement of thermodynamic stability, optimized voltage, and improve kinetics based on ionic and electronic conductivities.

This work was supported by Samsung GRO project.