First-principles Calculations Study on the Electrochemical Activity and Structural Stability of the Li_2MnO_3

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The layered Li_2MnO_3 is a key material to explain the high Li ion capacity in the layer-layer or layer-spinel composite materials, which are attracting much attention as promising Li-ion cathode materials. The material is intriguing as it shows electrochemical activity even though the oxidation state of Mn is already Mn^{4+}. Different studies point to oxygen release, conversion reactions and peroxide formation as possible oxidation mechanisms.

In this talk, we present an ab-initio cluster expansion model of the ionic interactions in Li_xMnO_3 ($0 \leq x \leq 2$) and predict the ground state as a function of the lithiation/delithiation and the corresponding voltage profiles. Furthermore, the oxygen stability during the lithiation/delithiation will be examined and discussed. By comparing our computational predictions with others' experimental observations, we derive the mechanisms of the lithiation and delithiation in the Li_2MnO_3. We also provide the evidence of the phase transformation to the spinel structure after the 1^{st} charge, which has been suggested as a cause of the voltage fade shown to occur during cycling at higher operating voltages.