

Electrochemical potentials of layered oxide and olivine phosphate with aluminum substitution: A first principles study

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Abstract: First-principles prediction of enhancement in the electrochemical potential of LiCoO_2 with aluminum substitution has been realized through earlier experiments. For safer and less expensive Li-ion batteries, it is desirable to have a similar enhancement for alternative cathode materials, LiFePO_4 and LiCoPO_4 . Here, we present first-principles density functional theory based analysis of the effects of aluminum substitution on electrochemical potential of LiCoO_2 , LiFePO_4 and LiCoPO_4 . While Al substitution for transition metal results in increase in electrochemical potential of LiCoO_2 , it leads to reduction in LiFePO_4 and LiCoPO_4 . Through comparative topological analysis of charge density of these materials, we identify a ratio of Bader charges that correlates with electrochemical potential and determine the chemical origin of these contrasting effects: while electronic charge from lithium is transferred largely to oxygen in LiCoO_2 , it gets shared by the oxygen and Co/Fe in olivine phosphates due to strong covalency between O and Co/Fe. Our work shows that covalency of transition metal–oxygen bond plays a key role in determining battery potential.