

Origins of Electrochemical Performance of Olivine Phosphate as Cathodes in Li-batteries: Charge Transfer, Spin-state and Structural Distortion

Authors: Arghya Bhowmik, Tanmay Sarkar, Arun Kumar Varanasi, Umesh V. Waghmare and Mridula Dixit Bharadwaj

Publisher: AIP Publishing

Link: <http://scitation.aip.org/content/aip/journal/jrse/5/5/10.1063/1.4822258>

Abstract: We use first-principles density functional theory based calculations and topological analysis of the electronic charge density in lithiated and delithiated forms of olivine phosphates (LiMPO_4), an important class of cathode materials for Li-ion batteries, to determine the electronic mechanisms that govern their electrochemical potential and related properties. While electron charge transfer from Li to oxygen is known to be responsible for electrochemical properties of Li-transition metal oxides commonly used as cathodes in Li-ion batteries, the electrochemical performance of olivine phosphates involves two additional mechanisms: the spin state of transition metal (M) as stabilized by the Hund's rule and structural distortion. LiNiPO_4 exhibits the highest electrochemical potential among $M = \text{Mn, Fe, Co, and Ni}$, owing to the largest charge transfer to oxygen orbitals located at the Fermi energy. The lowest electrochemical potential of LiFePO_4 is associated with extra stability of the high-spin d^5 state in its delithiated form. While the electrochemical potential for $\text{LiMnPO}_4/\text{LiFePO}_4/\text{LiNiPO}_4$ or $\text{LiFePO}_4/\text{LiCoPO}_4/\text{LiNiPO}_4$ generally correlates with the charge transfer from Li to oxygen that of LiMnPO_4 and LiCoPO_4 shows anti-correlation. This is because the electrochemical potential of LiMnPO_4 is reduced by the energy lowering structural distortion of MnPO_4 . We confirm the local stability of the delithiated structures of the four phosphates through calculation of phonons, supporting the possibility of their fully charged state.