

Article title: Mechanism of Charge Transfer in Olivine-Type LiFeSiO_4 and $\text{LiFe}_{0.5}\text{M}_{0.5}\text{SiO}_4$ (M = Mg or Al) Cathode Materials: First-Principles Analysis

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Abstract:

Olivine silicates LiMSiO_4 (where M = Mn, Fe, Co, and Ni) are promising candidates for the next generation of cathode materials for use in lithium ion batteries (LIB). Among these compounds, LiFeSiO_4 is an attractive choice due to its low cost, environmental friendliness, high safety, and stability. In this work, we use first-principles density functional theory-based calculations to determine the structural and electrochemical properties of olivine-type LiFeSiO_4 and $\text{LiFe}_{0.5}\text{M}_{0.5}\text{SiO}_4$ (where M = Mg or Al). Because of the influence of stronger Si–O bonds in weakening Fe–O bonds via an inductive effect, we find that these compounds have a high lithium intercalation voltage (i.e., ~ 5 V) and undergo negligible changes in volume during lithiation and delithiation. Using the Bader scheme for topological partitioning of charge density and projected density of states (PDOS) in the electronic structure, we highlight the significant role of O-2p states and the relatively inert role of Fe-3d states in the charge transfer associated with delithiation. We show that 50% substitution of Fe with Al or Mg results in enhancement in the theoretical capacity of LiFeSiO_4 from 173 mAhg^{-1} to 191 mAhg^{-1} ($\sim 10\%$) and 193 mAhg^{-1} ($\sim 12\%$), respectively, while maintaining its intercalation voltage and structural stability during lithiation and delithiation.