BEYOND THE INDUCTIVE EFFECT TO INCREASE THE WORKING VOLTAGE OF CATHODE MATERIALS FOR LI-ION BATTERIES

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In the field of Li-Ion batteries, searching for new electrode materials with high energy density is a permanent goal. This implies increasing the electrochemical potential of the cathode material vs. Li^+/Li^0 or the gravimetric / volumetric capacity of the material, both being difficult to improve concomitantly. The first report on the electrochemical activity of the olivine $LiFePO_4$ in 1997 [1,2] is a clear breakthrough in this direction. In addition to its high safety, low cost and low environmental impact, $LiFePO_4$ shows an electrochemical potential versus lithium at 3.45 Volt (with respect to 2.7 Volt in iron-oxide) and an impressive reversibility despite its poor electronic conductivity. Recently, the $LiFeSO_4F$ material has been reported as the highest potential Fe-based cathode material for Li-Ion batteries. Its working voltage vs. Li^+/Li^0 jumps from 3.6 V to 3.9 V when $LiFeSO_4F$ is synthesized in the fully ordered *tavorite* structure and in the fully disordered *triplite* structure, respectively. The present study aims at rationalizing the voltage increase from oxide to phosphates and fluorosulphates by means of DFT+U calculations combined with orbital interaction, electronic band structure and electrostatic analyses. In the fluorosulphate polymorphs, we demonstrate that the origin of the voltage increase lies in the difference in the anionic networks, and more specifically in the electrostatic repulsions arising from the configuration of the fluorine atoms around the transition metal (*trans*- vs. *cis*-configuration in *tavorite* vs. *triplite*). [3] Such a finding should help in the design of novel high potential materials with enhanced performances, using new concepts going beyond the inductive effect of Goodenough.[4]

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