Tuning Electrochemical Potential of LiCoO2 with Cation Substitution: Firstprinciples Predictions and Electronic Origin

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

Publisher: Springer

doi:10.1007/s11581-013-0970-6

Link: http://link.springer.com/article/10.1007/s11581-013-0970-6

Abstract: With a goal to improve the performance of $LiCoO_2$ as a cathode material in Li-ion batteries, we simulate substitution of various elements (X = Be, Mg, Al, Ga, Si and Ti) for Co using first-principles density functional theory and predict changes in its electrochemical potential. While the electrochemical potential of $LiCoO_2$ is enhanced with substitution of Be, Mg, Al and Ga for Co, an opposite effect is predicted of Si and Ti substitution. We determine the electronic origin of these changes in electrochemical potential using (a) Bader method of topological analysis of charge density, (b) partial density of electronic states to estimate oxidation states of metal and oxygen, and charge re-distribution upon lithiation. We find that the distribution of electronic charge donated by Li is influenced by the nature of the X–O bond. A larger electron transfer to O (in XO_6 octahedron) upon lithiation leads to stronger Li intercalation and thereby higher electrochemical voltage. Our findings provide a platform for a rational design of cathode materials in Li batteries with enhanced voltage.