Effect of cation substitution on the electrochemical potential of LiCoBO$_3$: An ab initio study

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ABSTRACT

A first principle based study of the electrochemical properties of LiCoBO$_3$ has been carried out. The theoretical energy density of LiMBO$_3$ (M= Mn, Fe, Co) is comparable with the corresponding olivine phosphate. Low volume change during cycling gives it structural stability during full charging and discharging, hence making it a promising battery material. A 12.5% cation substitution with Mg, Mn, Ni, Cu and Zn was chosen to evaluate the electrochemical properties of the compounds. We have selected the substituent elements on the basis of: a) Goldschmidt's rule (ionic size difference between parent and substituent element within 15%), b) Coordination number of Co in LiCoBO$_3$ taken as 6 and c) oxidation state of Co in LiCoBO$_3$ as 2^+. For evaluation of various electrochemical properties of these materials, we carried out topological analysis of charge density by Bader method and partial density of states for O and substituents to study charge distribution phenomenon during lithiation. We observed significant correlation between Li charge transfer to oxygen and voltage across the systems studied. In this series, Zn substitution gives the highest and Mn substitution gives the lowest electrochemical potential. The high electrochemical potential of the Zn composition is on account of maximum charge transfer to O orbitals located at Fermi energy as the frontier orbital. This is due to the filled d orbitals of Zn in the lithiated material. However in the case of Mn, lower charge gets transferred to O due to the unfilled e$_g$ $\uparrow$ orbital of Mn sharing some charge. This imparts low electrochemical potential to the Mn substituted composition among all these materials. In this study, we explain the electrochemical performance of the select materials on the basis of Bader charge analysis, partial density of states and calculated oxidation states.