First Principles Study of Small Hole Polaron Formation in Doped Olivine $LiFe_{1-x}Co_xPO_4$: Effects of Li Deficiency

การศึกษาการเกิดโฮลโพลารอนขนาดเล็กในสารโอลิวีนที่ถูกเจือ ($LiFe_{1-x}Co_xPO_4$) โดยมีผลมาจากการดึงลิเธียมออกด้วยวิธีคำนวณแบบเฟิสต์พรินซิเพิล

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Understanding the localization of small polarons ($p+$) are important for improvement of electronic conductivity in cathode materials such as $LiFePO_4$ and $LiCoPO_4$ for Li-ion battery technology. In this study we calculate the formation energy (ΔF) due to Li vacancies in $LiFe_{1-x}Co_xPO_4$ by density functional theory with additional on-site Hubbard correction (DFT+U). We found that Li vacancies (V_{Li-}) can induce polaron formation preferentially at Fe rather than Co sites. Co also improves polaron binding to V_{Li-} to form a snall polaron complex (V_{Li-} - $p+$) and alters $Li_{1-y}FePO_4$ to the equilibrium phase ($\Delta F < 0$). Co doping can reduces the energy gap and increases the intercalation voltage. Overall, polaron localization plays key roles in electronic conductivity of $LiFe_{1-x}Co_xPO_4$ cathode materials.

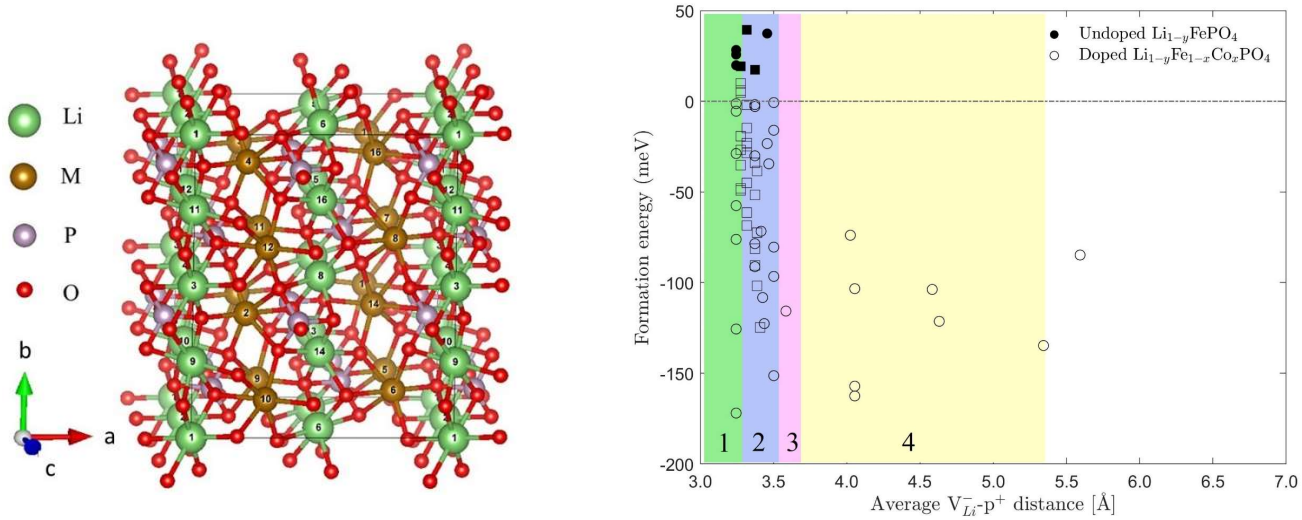

Figure : (Left) Olivine-type $LiMPO_4$ (M=Fe, Co) structure and (Right) formation energy (ΔF) of a snall polaron complex (V_{Li-} - $p+$) in an equilibrium position as a function of distance between V_{Li-} and $p+$ where the circle and square symbols denote $y \leq 0.50$ and $y > 0.50$ respectively. The shaded regions with the number represented for each nearest neighbor (NN). 1=1st NN, 2=2nd NN, 3=3rd NN and 4=4th NN.