A DFT study on energy storage applications and phase transition analysis of Prussian blue analogues (PBAs)

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Prussian blue (PB) with formula $Fe^{III}_4[Fe^{II}(CN)_6]_3$ was firstly produced as a cheap dark blue pigment in 18th century. Numerous Prussian blue analogues (PBAs) can be synthesized through the substitution of Fe with other transition metals (TMs) or the insertion of alkali metals (AMs) or alkali-earth metals. PBAs are of interest as a promising cathode candidate in beyond-Li batteries owing to low cost and outstanding electrochemistry properties. Tunable TMs and AMs provide complex structural flexibility and electrochemistry properties. Vacancies in PBAs are considered as double-edged sword of electrochemistry properties which are deserving of exploration. The investigation of structural transformations and reaction mechanisms during the dis-/charge process can be performed by Density Functional Theory (DFT) simulations, and thus providing a feasible proposal for material design.

In this context, we aim to investigate the structure evolution along with AM concentrations and migration pathway and barriers of AMs. All calculations are running by CRYSTAL17 with PBE0 global hybrid functional. In structure evolution, we found an unreported 2D-distortion when the AMs are in small size and low concentration. AMs with small size are more likely to fill the square window between two sub-cubes. 2D-distortion is only available at low AMs concentration, as this structure will be broken when the N in the cyano ligand is subjected to an electrostatic interaction from more than one AMs. The migration pathway and energy barriers of AMs (Na and K in $A_xMnFe(CN)_6$) along the <100> direction are calculated and compared as well. There are two energy barriers during migration, at the centre and at the window of sub-cubes. Based on present work, we plan to carry out the simulation of PBAs with vacancies to explore the intercalation energies and mobility of AMs with the effect of vacancies and coordinated water. Meanwhile the stability of PBAs with different arrangement of vacancies will be studied as well.