Olivine-type LiMPO₄ (M = Fe, Mn, Co, Ni) has been investigated as promising cathode materials due to their excellent electrochemical performance, thermal stability. Although LiFePO₄ has practical reversible capacity (about 160mAh/g) closed to the theoretical value (170mAh/g), it has lower energy density because of relatively low Fe²⁺/Fe³⁺ redox reaction potential. LiMnPO₄ material generates high energy density due to its high chemical potential (4.1 V), but undergoes poor lithium ion diffusion kinetics due to low electric, ionic conductivity, and large anisotropic distortion of Mn³⁺ during cycle. It also has been reported that the capacity of LiMnPO₄ is not achieved without Fe coexisting in the Mn octahedral site. In the olivine-type, LiFeMnPO₄ mixed system is considered as one of the promising materials due to benefit of energy density and their favored operation voltage. The Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺ redox reactions are operated at 3.4V and 4.1V plateau in the LiFeMnPO₄ system. However, many researches show the capacity fading by increasing the Mn content in the binary LiFeMnPO₄ system. To remedy this problem, improvement of Mn redox reaction and understanding of structural and electrochemical properties are necessary to improve the material performance.

To achieve the high capacity and rate performance in olivine system, various strategies were developed such as decrease of particle size, carbon coating on surface, doping of supervlent metal ion, and non-stoichiometry. Ceder et al. reported the strategies of non-stoichiometric synthesis shows the significant improvement on electrochemical performance of LFP resulted from the formation of glass formers with high Li conductivity on the surface. In this study, we successfully controlled the anti-site defects in LFMP system by the non-stoichiometric process. For getting the insight of correlation between the structural defect and electrochemical performance, neutron and synchrotron X-ray techniques were used. Furthermore, the Cr-doped LFMP was investigated to understand the doping effect improving the electrochemical performance.