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Electronic Properties of LiFePO₄ and Li doped LiFePO₄

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The potential use of different iron phosphates as cathode materials in lithium-ion batteries has recently been investigated.¹ One of the promising candidates is LiFePO₄. This compound has several advantages in comparison to the state-of-the-art cathode material in commercial rechargeable lithium batteries. Firstly, it has a high theoretical capacity (170 mAh/g). Secondly, it occurs as mineral *triphylite* in nature and is inexpensive, thermally stable, non-toxic and non-hygroscopic. However, its low electronic conductivity ($\sim 10^{-9}$ S/cm) results in low power capability. There has been intense worldwide research activity to find methods to increase the electronic conductivity of LiFePO₄, including supervalent ion doping,² introducing non-carbonaceous network conduction³ and carbon coating, and the optimization of the carbon coating on LiFePO₄ particle surfaces.⁴

Recently, the Li doped LiFePO₄ (Li_{1+x}Fe_{1-x}PO₄) synthesized at ARL has yield electronic conductivity increase up to 10⁶.⁵ We studied electronic structure of LiFePO₄ and Li doped LiFePO₄ by synchrotron based soft X-ray emission (XES) and X-ray absorption (XAS) spectroscopies. XAS probes the unoccupied partial density of states, while XES the occupied partial density of states. By combining XAS and XES measurements, we obtained information on band gap and orbital character of both LiFePO₄ and Li doped LiFePO₄. The occupied and unoccupied oxygen partial density of states (DOS) of LiFePO₄ and 5% Li doped LiFePO₄ are presented in Fig.1. Our experimental results clearly indicate that LiFePO₄ has wide band gap (~ 4 eV). This value is much larger than what is predicted by DFT calculation. For 5% Li doped LiFePO₄, a new doping state was created closer to the Fermi level, imparting p-type conductivity, consistent with thermopower measurement. Such observation substantiates the suggestion that high electronic conductivity in Li_{1.05}Fe_{0.95}PO₄ is due to available number of charge carriers in the material. Furthermore, Hall effect measurement on Li doped sample confirmed presence of free charge carriers, which are responsible for the observed electronic conductivity increase in Li doped LiFePO₄. There is no evidence that Fe³⁺ valence is created by doping with excessive Li⁺ in Li_{1.05}Fe_{0.95}PO₄, as shown by Fe-edge XAS. (Fig.2) Instead, charge-carrier holes reside primarily in unoccupied O 2p states, which compensate for the charge deficiency from Li⁺ substitution for Fe²⁺. The increased conductivity in Li_{1.05}Fe_{0.95}PO₄ is attributed to the new charge carriers (doped holes) and the strong electron correlation between O 2p and Fe 3d states.

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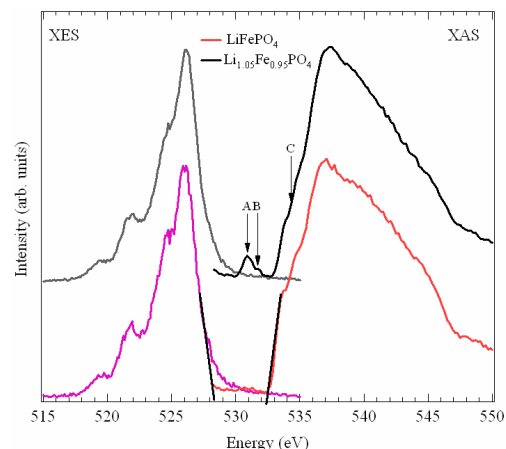


Fig.1 Occupied and unoccupied DOS of LiFePO₄ and 5% Li doped LiFePO₄ as measured by XAS and XES.

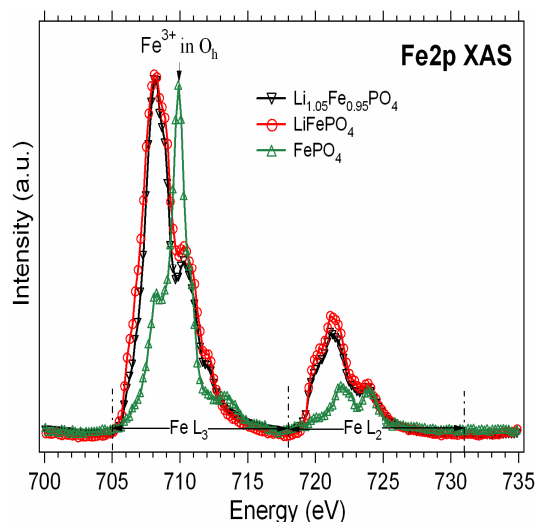


Figure 2. Fe 2p X-ray absorption spectra of FePO₄, LiFePO₄ and Li_{1.05}Fe_{0.95}PO₄.