Electronic Properties of $LiFePO_4$ and Li doped $LiFePO_4$

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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 $LiFePO_4$. 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 (~ 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 $LiFePO_4$, including supervalent ion doping,[2] introducing non-carbonaceous network conduction[3] and carbon coating, and the optimization of the carbon coating on $LiFePO_4$ particle surfaces.[4]

Recently, the Li doped $LiFePO_4$ ($Li_{1+x}Fe_{1-x}PO_4$) synthesized at ARL has yield electronic conductivity increase up to $10^{6.5}$. We studied electronic structure of $LiFePO_4$ and Li doped $LiFePO_4$ 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 $LiFePO_4$ and Li doped $LiFePO_4$. The occupied and unoccupied oxygen partial density of states (DOS) of $LiFePO_4$ and 5% Li doped $LiFePO_4$ are presented in Fig.1. Our experimental results clearly indicate that $LiFePO_4$ has wide band gap (~ 4 eV). This value is much larger than what is predicted by DFT calculation. For 5% Li doped $LiFePO_4$, 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 $Li_{1.05}Fe_{0.95}PO_4$ 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 $LiFePO_4$. There is no evidence that Fe^{3+} valence is created by doping with excessive Li^+ in $Li_{1.05}Fe_{0.95}PO_4$, 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 Fe^{2+}. The increased conductivity in $Li_{1.05}Fe_{0.95}PO_4$ is attributed to the new charge carriers (doped holes) and the strong electron correlation between O *2p* and Fe *3d* states.

References

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Acknowledgements

Financial support from the Chemical Sciences Division (GVZ and PNR) and the Material Sciences Division (JHG) of the Office of Basic Energy Sciences, U.S. Dept. of Energy, under contract No. DE-AC03-76SF00098 is gratefully acknowledged.

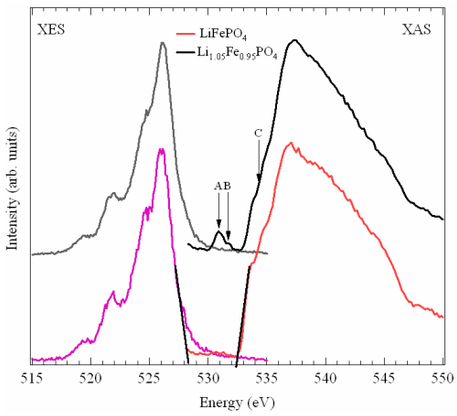

Fig.1 Occupied and unoccupied DOS of $LiFePO_4$ and 5% Li doped $LiFePO_4$ as measured by XAS and XES.

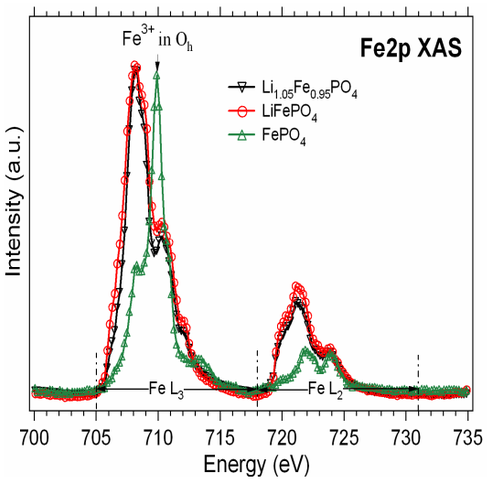

Figure 2. Fe 2p X-ray absorption spectra of $FePO_4$, $LiFePO_4$ and $Li_{1.05}Fe_{0.95}PO_4$.