

Mind the Band Gap:

Experimental determinations and theoretical calculations for LiFePO₄

Yin Zhang^{a, b, d}, J.A. Alarco^a, A.S. Best^b, G.A. Snook^c, P.C. Talbot^a and J.Y. Nerkar^a

^a Institute for Future Environments and Science and Engineering Faculty, Queensland University of Technology (QUT), Brisbane, QLD 4001 Australia

^b CSIRO Manufacturing, Private Bag 10, Clayton South, Victoria 3169, Australia

^c CSIRO Mineral Resources, Private Bag 10, Clayton South, Victoria 3169, Australia

^d CRRC Qingdao Sifang Rolling Stock Research Institute Co., Ltd., Qingdao 266031, China

E-mail: yin.zhang@hdr.qut.edu.au

In this research, the band gap of LiFePO₄ has been investigated experimentally and theoretically. Nano LiFePO₄ particles with low carbon content have been prepared for experimental band gap determination. Optical diffusion reflectance measurement was carried out between 175-2800. Unlike the results reported in previous studies^[1, 2], no obvious absorption edge was observed. The broad bump at ~5 eV vanished with the addition of carbon, indicating the absorption is charging related. A band gap of 6.34 eV was determined in the low electron energy loss spectrum (LEELS).

As the most popular functional within density functional theory (DFT) for the band structure calculation of LiFePO₄, GGA+U has been investigated. The effect of Hubbard U has been studied by applying different values of U. Although 6 eV of Hubbard U was applied, the estimated band gap (3.96 eV) was still much smaller than the experimental value. Furthermore, when U was above 4 eV, the occupied Fe-d states started to be pushed below and penetrated into the O-2p orbital. O-2p states even became the major states in valence band maximum (VBM) when Hubbard U was beyond 5 eV, which was not consistent with the LiFePO₄/FePO₄ phase transformation observed during charging and discharging. As one of the most efficient functionals for electronic structure calculations, sX-LDA was applied in this study. An estimated band gap of 6.19 eV was obtained which matched well with the experimental band gap. The hybrid states of Fe-3d-O-2p at VBM had a good agreement with recent study^[3].

In summary, a band gap of 6.34 eV for LiFePO₄ was determined by LEELS in this work. According to the experimental band gap, GGA+U was proved not suitable for electronic structure calculation of LiFePO₄ due to the underestimation of band gap and the questionable VBM. Accordingly, our results indicates sX-LDA is the most practical DFT functional for the electronic structure calculation on LiFePO₄.

The authors would like to acknowledge CSIRO for the studentship, and the involvement of CRRC and the Rail Manufacturing Cooperative Research Centre (funded jointly by participating rail organisations and the Australian Federal Government's Business Cooperative Research Centres Program). Computational resources and services used in this work were provided by the HPC and Research Support Group, Queensland University of Technology, Brisbane, Australia.

References:

- [1] F. Zhou, K. Kang, T. Maxisch, G. Ceder, and D. Morgan, *SSCom* 132 (2004) 181-186.
- [2] K. Zaghbi, A. Mauger, J.B. Goodenough, F. Gendron, and C. Julien, *Chemistry of materials* 19 (2007) 3740-3747.
- [3] S. Miao, M. Kocher, P. Rez, B. Fultz, R. Yazami, and C.C. Ahn, *The Journal of Physical Chemistry A* 111 (2007) 4242-4247.