

Systematic comparison of LiMPO_4 ($M = \text{Mn, Fe, Co, and Ni}$) crystal surfaces

Craig A. J. Fisher^a, Akihide Kuwabara^a, Shunsuke Kobayashi^a, Yumi H. Ikuhara^a,
Yoshio Ukyo^b, Yuichi Ikuhara^{a,c}

^a Nanostructures Research Laboratory, Japan Fine Ceramics Center,
Atsuta, Nagoya 456-8587, Japan

^b Office of Society-Academia Collaboration for Innovation, Kyoto University,
Uji, Kyoto 611-0011, Japan

^c Institute of Engineering Innovation, The University of Tokyo,
Bunkyo, Tokyo 113-8656, Japan

E-mail: c_fisher@jfcc.or.jp

Charge-discharge rates and cycle lifetimes of Li-ion batteries depend critically on the structures and properties of particle surfaces in the cathode material. Optimal design of advanced cathode materials thus requires detailed knowledge of the electrochemically active surfaces, and atomistic simulation provides a powerful means of examining such phenomena systematically [1]. Here we report results of first-principles calculations of several low-index surfaces of lithium-ion battery cathode materials LiMPO_4 ($M = \text{Mn, Fe, Co, Ni}$), and compare the structures with sub-angstrom-resolution scanning transmission electron microscopy (STEM) images.

The structures and stabilities of planar surfaces exhibited similar trends for all the transition metals examined. In particular, comparison of (010) surfaces revealed that there is only a small deformation to the framework structure after complete delithiation, confirming the suitability of this surface for repeated rapid charging/discharging. Displacements of Fe and P atoms neighboring Li vacancies from calculations of the (010) surface also allowed the presence of Li atoms at surfaces of a single crystal of LiFePO_4 to be located using annular bright field (ABF) STEM (Fig. 1). Calculations of electronic and defect properties of different surfaces also provide insights into how the cathodic properties can be tailored by preparing nano-sized particles in which specific surface orientations dominate.

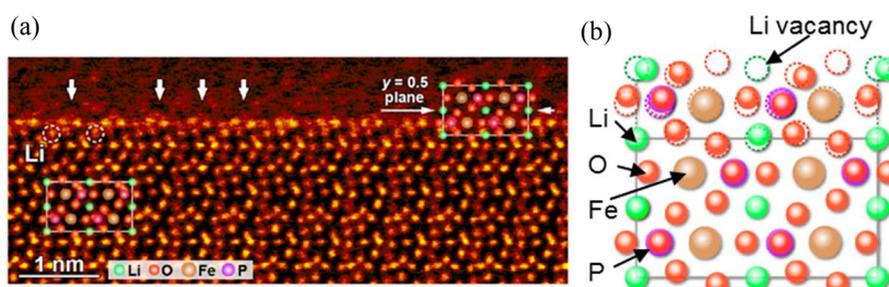


Fig. 1. (a) ABF STEM image of the (010) surface of LiFePO_4 , and (b) the predicted structure from first-principles calculations. Comparison of cation displacements in the observed and calculated structures allowed positions of Li atoms, indicated by white arrows in (a), in the outermost surface layer to be deduced [2].

References:

- [1] M. S. Islam and C. A. J. Fisher, Chem. Soc. Rev. 43 (2014) 185-204.
- [2] S. Kobayashi, C. A. J. Fisher, T. Kato, Y. Ukyo, T. Hirayama and Y. Ikuhara, Nano Lett. 16 (2016) 5409–5414.

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