Nano-level characterization of the $LiFePO_4/FePO_4$ interface by scanning transmission electron microscopy

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$LiFePO_4$ is one of the most intensively studied cathode materials for lithium ion batteries. Recently, many experimental and theoretical studies have focused on the intermediate phase in partially delithiated $LiFePO_4$ with the aim of improving its electrochemical performance. In this work, we report results of nano-scale structural analyses of the intermediate phase at interfaces between $LiFePO_4$ and $FePO_4$ phases in partially delithiated $LiFePO_4$ crystals using scanning transmission electron microscopy (STEM) techniques [1].

A commercially available $LiFePO_4$ single crystal was used for all experiments [2]. Chemical delithiation was performed in an acetonitrile solvent using NO_2BF_4 as the oxidant. The morphology of the intermediate phase was analyzed by STEM and electron energy loss (EEL) spectroscopy techniques.

After partial chemical delithiation, a number of microcracks formed in response to the large difference in lattice volume between $LiFePO_4$ and $FePO_4$ (Fig. 1a). Li concentration maps using EEL spectra revealed the location and morphology of the intermediate phase at the interface between the end-member phases. The electron diffraction pattern (Fig. 1b) obtained from the circled area spanning the boundary region in Fig. 1a indicates that part of it consists of a monoclinic phase of approximate composition $Li_{2/3}FePO_4$ (Fig. 1c). The monoclinic phase has a lattice volume midway between those of the end-member phases. Formation of the intermediate phase thus plays an important role in ameliorating the large lattice strain between $LiFePO_4$ and $FePO_4$ phases.

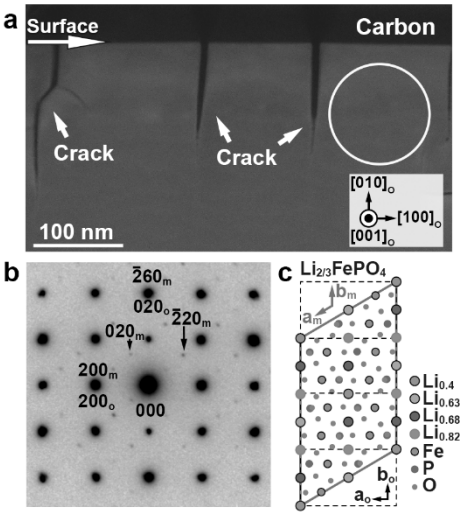

Fig. 1. (a) ADF STEM image of a (010) surface after delithiation. (b) Electron diffraction pattern obtained from the circled region in a. (c) Crystal model of $Li_{2/3}FePO_4$ [3]. Subscripts "o" and "m" refer to orthorhombic and monoclinic structures, respectively.

References:
[1] S. Kobayashi et al., Microscopy 66 (2017) 254-260.
[2] S. Kobayashi et al., Nano Lett. 16 (2016) 5409−5414.
[3] S. Nishimura et al., Angew. Chem. Int. Ed. 54 (2015) 8939-8942.

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