

Atomic-Scale Studies of Surfaces and Crystal Morphologies of the Lithium Battery Cathode Material LiFePO_4

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Lithium iron orthophosphate (LiFePO_4) is isostructural with olivine and is a promising alternative cathode material for rechargeable lithium batteries on account of its low cost, lack of toxicity and good Li^+/Li potential (3.5 V) [1]. The low intrinsic ionic and electronic conductivities are typically overcome by synthesizing the material in the form of nanoparticles coated with thin carbon films. This simultaneously reduces the distance for Li^+ transport and increases the electronic contact between particles [2].

Given the importance of nanoparticles in achieving adequate performance, and the high surface-to-volume ratio this entails, further materials development will require knowledge of the surface structures and crystal morphology of LiFePO_4 at the atomic level. Computer simulation methods comprise a powerful means of obtaining such information, as the energies of impurity-free, ideal structures and the influence of defects on them can be studied reproducibly.

Interatomic pairwise and 3-body potentials that accurately model the bulk crystal structure of LiFePO_4 were used to examine intrinsic point and electronic defects in the system, as well as lithium ion diffusion mechanisms and dopant incorporation mechanisms [3]. This showed that the most common intrinsic defect involves exchange of ions between Li^+ (M1) and Fe^{2+} (M2) sites, i.e., “antisite” disorder across the two cation sublattices. Li^+ diffusion was also found to occur predominantly in the [010] direction.

Surfaces of LiFePO_4 were examined for all crystal orientations with Miller indices ≤ 2 . This involved cutting the crystal through certain planes to produce a block infinite in two dimensions but finite normal to the surface. For surface energies to converge, the crystal was cut in such a way as to preserve zero net dipole perpendicular to the surface plane. With reference to Tasker’s notation [4], Type III surfaces required reconstruction by moving a given number of ions from the upper layer to the bottom layer of the crystal block. The relaxed energies of the various surfaces were calculated using the two-region approach embodied in GULP [5].

The complexity of the olivine structure means that the surfaces are also complex, with

LiO_6 , FeO_6 and PO_4 groups at each interface forming relatively open and undulating topologies. The range of surface energies was narrow (0.71 to 1.19 Jm^{-2}), with (011), (201) and (010) the most stable faces. Attachment energies, which measure the energy released on attaching a new slice of material to the surface, showed greater variation, with the (010), (100) and (101) faces lowest in energy.

Wulff plots of the surface energies and attachment energies were used to predict the equilibrium and growth morphologies, respectively, of a LiFePO_4 nanoparticle (Figure 1). The growth morphology is more elongated and less isometric than its equilibrium counterpart.

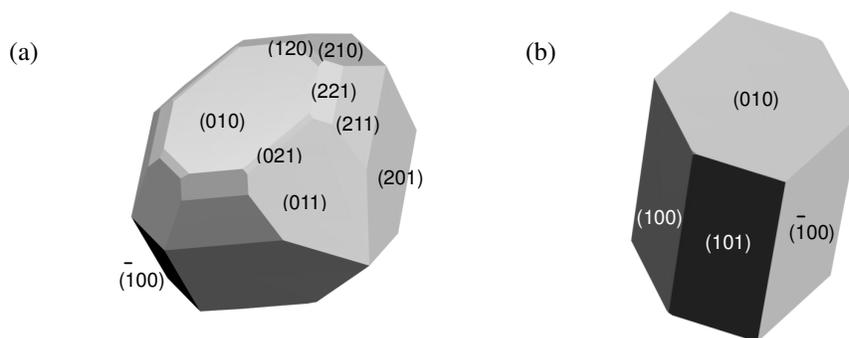


FIG. 1. (a) Equilibrium and (b) growth morphologies of LiFePO_4

Experimentally, hydrothermally synthesized LiFePO_4 has been observed to have platelet morphologies with the (010) surface dominating [6]. In this respect, the growth morphology is in better agreement than the equilibrium morphology. Since ion transport occurs principally down [010] channels [3], the morphology of the nanoparticles can be seen to have implications for the insertion/de-insertion of lithium in LiFePO_4 cathodes.

References

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