

Analysis of the two-phase interface in LiFePO₄ cathode material

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It is well known that a flat plateau at 3.4 V appears in charging/discharging curve of olivine-type LiFePO₄ cathode[1]. The constant voltage indicates that the extraction/insertion proceeds under two-phase reaction in which the electrochemical potential of lithium ions keeps a constant value independent of the state of charge. Thus, in the two-phase reaction, it is considered that the lithium ions can be extracted from the interface between the endmembers, namely, LiFePO₄ and FePO₄.

The two-phase interface has been clearly observed on the surface of platelet nanoparticle by using transmission electron microscopy by several groups[2-4]. The typical interface has a finite thickness about 10 to 20 nm and locates parallel to *bc*-plane. Delmas et al. explained the mechanism of electrochemical charging by means of “domino cascade model” in which the lithium ions are continuously extracted from the cascade of the interface region[4]. However, the lithium distribution in the interface is not clearly understood.

The first-principles density functional theory (DFT) is a powerful tool to study such a small region from an atomic scale. In the present work, we theoretically investigated the interface region in LiFePO₄ compounds by using DFT. The crystal and the electronic structures are determined by using spin-polarized generalized gradient approximation with short-range Coulomb interactions (GGA+U). In this work, we employed selfconsistently obtained value of $U = 4.3$ eV which is sufficient to reproduce localized electronic structure. The wavefunction is expanded by planewaves with a kinetic-energy cutoff of 500 eV.

As shown in Fig. 1, the interface model is composed of three regions: fully lithiated (LiFePO₄), fully delithiated (FePO₄), and interface region. In this figure, the interface region is assumed to be parallel to *bc*-plane, and is sandwiched between the endmembers. It is considered that the lattice parameters in the interface gradually changes along *a*-axis. The total energy of the structure in the interface can be determined by giving the intermediate value of the lattice parameters to the unit cell at a microscopic area (broken line) in the interface. We calculated mixing energies of the endmembers to form partially delithiated structures at the microscopic area by considering possible configurations of lithium ions and localized electrons. The mixing energy[5] of the partially delithiated structure, F , is defined as

$$F = E(x) - [(1-x) E(x=1) + x E(x=0)],$$

where $E(x)$ is the total energy of Li_{*x*}FePO₄, and x is concentration of lithium ions. The positive value of F means that the two-phase separation is favored, and the negative value of F means that the solid-solution structure of Li_{*x*}FePO₄ is likely to appear.

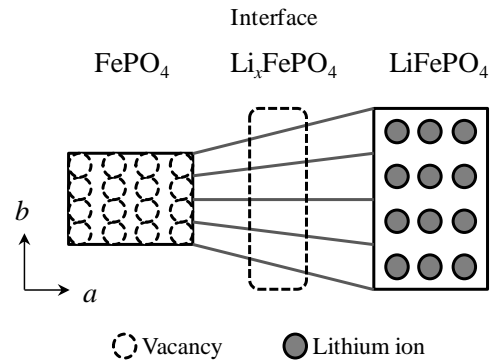


Figure 1. Schematic of interface parallel to *bc*-plane between two phases.

The mixing energy of the partially delithiated structure Li_{*x*}FePO₄, ($x=0, 0.25, 0.50, 0.75$, and 1) is shown in Fig. 2. The mixing energy is shown by a solid line for fully lithiated region, dotted line for fully delithiated one, and broken line for interface one. It is found that the curves of the mixing energy are different among the three regions. In the interface, the mixing energy shows negative value with lithium concentration of 0.5 and 0.75. It means that the solid-solution phase is spontaneously formed in the interface region parallel to *bc*-plane.

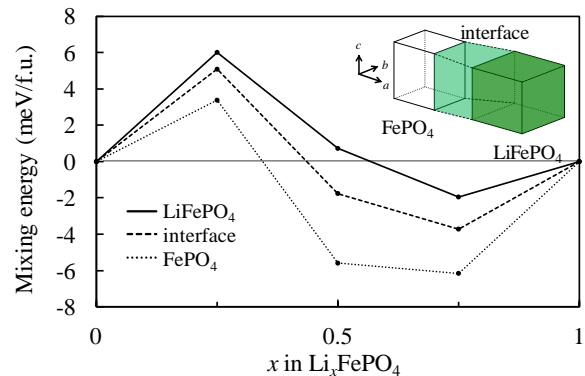


Figure 2. Mixing energy of partially delithiated structure in two-phase interface parallel to *bc*-plane. Solid, broken, and dotted lines indicate lithiated, interface, and delithiated regions, respectively. The inset shows calculated three regions.

References

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