



Microscopic mechanism of path-dependence on charge–discharge history in lithium iron phosphate cathode analysis using scanning transmission electron microscopy and electron energy-loss spectroscopy spectral imaging



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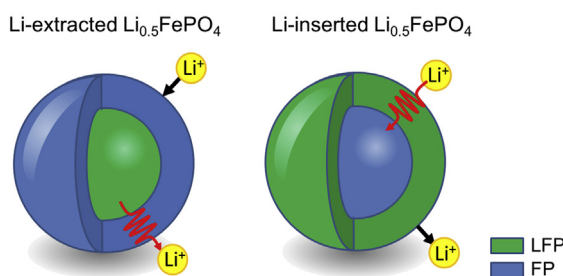
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HIGHLIGHTS

- LiFePO₄ and FePO₄ almost always form core/shell structures in the SOC50% electrodes.
- The size dependence of the core volume ratio was explained by a simple static model.
- The path-dependence of the electrodes was broadly reproduced by the model.
- The interphase boundaries in the particles exhibited weak anisotropy.

GRAPHICAL ABSTRACT



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ABSTRACT

We revisited the “path-dependence” problem, *i.e.*, the differing polarization observed in LiFePO₄ cathode charge/discharge curves depending on the electrochemical treatment history of the material. The phase distributions of the active material particles with different charge/discharge histories in the LiFePO₄ cathode were investigated through spectral imaging (SI) using scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS). The STEM-EELS-SI experiments revealed that LiFePO₄ (LFP) and FePO₄ (FP) almost always coexist in the individual primary particles of Li_{0.5}FePO₄ (50% state of charge (SOC)) electrodes, forming core/shell structures. This is unlike the conventional domino-cascade model, in that LFP-inside/FP-outside is observed in the lithium-extracted Li_{0.5}FePO₄ particles, whereas FP-inside/LFP-outside is seen in the lithium-inserted Li_{0.5}FePO₄ particles. We examined the particle-size dependence of the core/total volume ratio of each Li_{0.5}FePO₄ particle, and the essential features of the path-dependent charge/discharge curves were semi-quantitatively reproduced by a simple static model that considered the ionic conductivity of the shell phase.

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1. Introduction

Of the wide variety of commercially viable positive-electrode active materials used in lithium ion secondary batteries, LiFePO₄

is one of the substances considered suitable for use in automobiles. This is because it has several advantages over the other candidates, such as superior thermal stability, relatively low cost, and excellent high-rate charge/discharge characteristics. Since the pioneering work of Padhi, Nanjundaswamy, and Goodenough [1], a large number of studies have been conducted on the electrochemical and crystallographic properties of LiFePO_4 , thereby improving its rate performance and clarifying the lithium insertion/extraction mechanism. Key improvements, e.g., for use in high-rate applications, have been achieved by reducing the particle size to the nano-scale and coating the particles with carbon in order to overcome the inherent low electronic and ionic conductivities of the bulk material [2,3]. The charge/discharge reactions in this material undergo a two-phase reaction [1], exhibiting a very flat region in the charge/discharge voltage curve with solid-solution states at both ends over narrow concentration ranges (Li_xFePO_4 : $x \leq \sim 0.05$, $x \geq \sim 0.9$) [4]. In this sense, the lithium-rich Li_xFePO_4 ($x \geq \sim 0.9$ at $T < 400$ K) and lithium-poor Li_yFePO_4 ($y \leq \sim 0.05$) phases are thermodynamically balanced with each other in the flat two-phase juxtaposition regime: $\text{Li}_x\text{FePO}_4 \leftrightarrow \text{Li}_y\text{FePO}_4 + (x - y) \text{Li}^+ + (x - y) \text{e}^-$ [4]. Hereafter, we refer to the lithium-rich Li_xFePO_4 and lithium-poor Li_yFePO_4 phases as LFP and FP, respectively, for the sake of convenience.

In 2006, Srinivasan and Newman reported the path-dependence of the LiFePO_4 electrode [5], where the high-rate electrochemical behavior of the electrode at a particular state of charge (SOC: roughly corresponding to x in $\text{Li}_{1-x}\text{FePO}_4$) depends on the path by which the electrode reached that SOC. They qualitatively explained the path-dependence by assuming a shrinking-core model that was first proposed by Padhi et al. [1]. Upon discharge, Li^+ and electrons are inserted into the material with a LFP shell covering a FP core, followed by Li^+ transport from the surface through the LFP to the phase-interface, resulting in core shrinking. Upon charging, on the other hand, the process described above is repeated with a LFP core covered by a FP shell, with the core again shrinking. An electrode brought to a 50% SOC from the fully-discharged state (0% SOC), for instance, will have a FP shell with a LFP core. If this electrode is charged further, lithium is then extracted from the core and the core shrinks. This results in an increasing distance through the FP that the Li^+ and electron must traverse in order to diffuse. On the other hand, an electrode brought to the same 50% SOC point from the fully-charged state (100% SOC) has a FP core with a LFP shell. If this electrode is also charged, a new FP shell region is formed over the existing LFP shell region. Under these conditions, the Li^+ and electron transport occurs through the outer FP region only, leading to a much smaller length over which the diffusion occurs. This difference in the diffusion length causes associated differences in the electrochemical behavior that results from these two paths [5]. However, studies using neutron diffraction analysis [6] and *ab initio* calculations [7,8] have suggested an anisotropic Li^+ diffusion path in LiFePO_4 that is preferentially along the [010] direction, with the flat LFP/FP interface aligned preferentially along the plane parallel to the b -axis. This orientation minimizes the mechanical strain energy [9] and, thus, the isotropic core-shell mechanism appears to be both energetically and kinetically unfavorable.

Delmas et al. reported a characterization of half-delithiated LFP nano-particles using high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) experiments, which indicated the coexistence of fully intercalated and fully delithiated individual particles. The result of this study indicates that the growth reaction is considerably faster than the nucleation [10]. These researchers also proposed an anisotropic model, in which the charge/discharge reaction in a single particle proceeds rapidly and two phases do not usually coexist within a single particle in the static state [10]. This 'domino-cascade model' has been supported

by studies using the phase-mapping method with nano-beam electron diffraction (NBED) [11,12]. This model, however, cannot explain the path-dependence of the charge/discharge curves, unless a macroscopic LFP/FP concentration gradient or an assembly of multiple particles exhibiting an apparent core-shell (inner/outer particles) characteristic is assumed. Synchrotron X-ray micro-diffraction studies have actually revealed that an electrode brought to 50% SOC from the fully discharged state at a rate of 18C exhibits an obvious lithium concentration gradient from the electrode surface to the current collector, while no such tendency was observed at a rate of 0.1C [13]. However, such a lithium concentration gradient at a very high charging rate is unlikely to be responsible for the path-dependence, because the path-dependence of LiFePO_4 has been observed even at a very low charging rate of C/25 [5]. Further, recent *in situ* XRD analyses [14,15] have revealed an intermediate transitional state between the LFP and FP in a single particle at a high rate of charge/discharge. Note that, under the domino-cascade model, the transition state was considered to relax either to the single LFP or FP stationary phase under open-circuit conditions, presumably due to Li^+ migration between particles.

Concerning the charge/discharge kinetics of the LiFePO_4 active material, additional interesting phenomena have been reported; one is a significant voltage hysteresis between the charge and discharge curves even at an extremely low rate (C/1000) [16], and the other is a memory effect, which manifests in a reduced working voltage and is observed in the discharge curves of batteries undergoing repeated shallow-depth discharge for a large number of cycles. Thus, the discharge voltage appears to memorize the discharge depth of the previous cycle [17]. These two phenomena can be well explained by a many-particle model [16,17], assuming that the reaction occurs on a particle-by-particle basis, so that the apparent voltage profile consists of the summation of each electrochemical potential of each individual particle incorporating time differences [18]. Unlike these hysteresis phenomena, however, the path-dependence cannot be explained based on the electrochemical potential shape of a single particle.

A mathematical model proposed by Safari and Delacourt [19] quantitatively describes the path-dependence and is consistent with the many-particle model. As mentioned above, the conductive coating around the LFP active material particles and the distribution of the conductive additives (carbon) in the electrode may give rise to a non-uniform current distribution. This is due to the ohmic drop as the electrons pass through the intra-particle or inter-particle resistance. In this sophisticated model, active material particles are divided into several groups of the same particle size, but with different electronic connectivities to the conductive matrix in the electrode. Safari and Delacourt [19] showed that the resistive-reactant feature of LFP can quantitatively account for the path dependence. This model appears to be successful, although no such microscopic evidence of particle groups with different contact resistances has yet been unambiguously obtained.

Again, it should be noted here that a number of conflicting reports on whether LFP and FP coexist in a single particle in the two-phase juxtaposition regime have been published. The two-phase mixture in a single particle has been observed using both electron energy loss spectroscopy (EELS) [20,21] and scanning transmission X-ray microscopy (STXM) [22], where the electrodes were chemically de/lithiated instead of being subjected to electrochemical processes. In contrast, *ex situ* NBED [11,12] studies of electrochemically de/lithiated electrodes and energy-filtered transmission electron microscopy (EFTEM) observation of electrochemically cycled samples [23] have shown that mixed phase particles are rare, which seems to support the domino-cascade model. However, the lattice relaxation associated with the phase change follows the fast de/lithiation observed in *in situ* XRD

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