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A review of recent research on nonequilibrium solid solution behavior in Li_XFePO_4

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ABSTRACT

Li_XFePO_4 ($0 < X < 1$) is one of the most well-studied cathode battery materials and is notable for its large miscibility gap. Although its phase-separating behaviors under equilibrium conditions have been well documented, recent research has shown that phase separation is suppressed at elevated rates of lithium insertion and removal. Specifically, Li_XFePO_4 exhibits a nonequilibrium solid solution behavior at elevated cycling rates. This article reviews recent research on nonequilibrium solid solution in Li_XFePO_4; these insights have been largely enabled by *operando* characterization techniques. Such studies have not only unambiguously confirmed the existence of this solid solution, but also show how surface reaction and diffusion kinetics ultimately affect phase separation and other spatially nonuniform lithiation and delithiation behavior.

1. Introduction

Together with the layered oxides based on $LiCoO_2$ and the spinel $LiMn_2O_4$, olivine $LiFePO_4$ is one of the cathode materials used in commercial Li-ion batteries [1,2]. Of the three classes of cathodes, $LiFePO_4$ was the most recent to have been discovered; its reversible intercalation properties were first demonstrated in the group of J. B. Goodenough [3]. $LiFePO_4$'s potential as a safer cathode that utilizes non-toxic, earth-abundant materials was immediately recognized. While its specific capacity at 170 mAh g^{-1} is comparable to the usable capacity of the layered oxides and spinels, $LiFePO_4$'s voltage and volumetric mass density (3.4 V and 3.6 g cm^{-3}) are significantly lower than that of the layered oxides and spinels (~4 V and 4.3-5.1 g cm^{-3} respectively).

One defining characteristic of Li_XFePO_4 ($0 < X < 1$) is its wide miscibility gap. While Li_XCoO_2 and $Li_XMn_2O_4$ exhibit small miscibility gaps [4,5], Li_XFePO_4's miscibility gap encompasses nearly the entire lithium composition range of the material, from X~0.11 to X~0.95 [6]. If lithiation in Li_XFePO_4 progresses via phase boundary motion, it would be expected that the slow movement of these phase boundaries limits lithium intercalation [3]. Furthermore, elastic stresses from the phase boundaries induce cracking, fracture, and limit the cycle life [7]. These intuitions are at odds with Li_XFePO_4's observed fast charge rate, as short as 9 s [8], and remarkable cycle life, up to tens of thousands of cycles [9]. This apparent contradiction motivated research to determine whether Li_XFePO_4 in fact undergoes phase separation during cycling, or if phase separation is suppressed and replaced by a nonequilibrium solid solution pathway.

In 2010, Tang, Carter, and Chiang presented a comprehensive review of fundamental research on Li_XFePO_4 [2]. At the time, however, there was no evidence of a nonequilibrium solid solution. In 2011, Malik, Zhou, and Ceder [10] and Bai, Cogswell, and Bazant [11] used Monte Carlo cluster expansion and continuum phase-field modeling, respectively, to show that a solid solution is likely to arise under certain conditions. The nonequilibrium solid solution, however, will relax into phase-separated domains under equilibrium, which explains why solid solution behaviors have not been previously observed experimentally using ex situ measurements. A review paper by Malik, Aziz, and Ceder in 2013 suggested that experimental observations of solid solutions, especially within single particles, were beyond the *operando* characterization capabilities available at the time [12].

Since then, many researchers have used a variety of *operando* techniques to unambiguously demonstrate the existence of this nonequilibrium solid solution behaviors. Additional research has aimed to understand the mechanisms which stabilize this solid solution, especially focusing on its relationship to the surface reaction kinetics. This review summarizes the research on solid solution behavior in Li_XFePO_4.

2. Thermodynamics and lithium transport properties in Li_XFePO_4

The thermodynamics and lithium transport of Li_XFePO_4 have been subject to extensive experimental and theoretical investigation and

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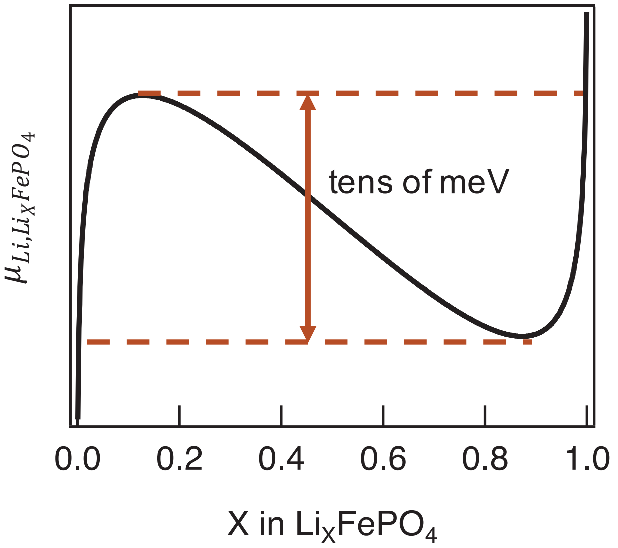

Fig. 1. A regular solution model of the chemical potential of lithium in Li_XFePO_4 as a function of the lithium concentration X. The non-monotonic chemical potential profile gives rise to phase separation. The difference in chemical potential between the spinodal points is estimated to be on the order of tens of meV [10,13].

previously reviewed [2,12]. This section summarizes two important characteristics towards understanding nonequilibrium solid solution behaviors. Firstly, standard Li_XFePO_4 phase-separates with a miscibility gap around 90% of the range of lithium concentrations. Under certain circumstances, however, Li_XFePO_4 contains no miscibility gap, and those circumstances are documented in Section 3. The Gibbs energy of a solid solution with a given lithium content inside the miscibility gap is higher than that of a combination of the phase-separated Li-rich and Li-poor domains. The difference in energy is calculated through Monte Carlo cluster expansion to be about 10 meV/formula unit [10]; a regular solution fitting yields a difference of about 20 meV/formula unit [13]. Interfacial energy and coherency strain both increase the energy of the phase-separated state and reduce the energy penalty of solid solution formation relative to phase separation. Because the solid solution has higher Gibbs energy, phase separation, either within or between particles [14–16], is observed under equilibrium conditions.

The chemical potential is the differential change in the Gibbs energy upon adding another lithium, given that the lithium is removed from a reference electrode material with a constant and known change in Gibbs energy per mole of lithium. Fig. 1 provides a regular solution model of the chemical potential of Li_XFePO_4. In this model, the non-monotonic change in the chemical potential with lithium concentration is the signature of phase separation; the spinodal region between the local maximum at X~0.15 and the local minimum at X~0.85 is particularly unstable, and any particles with those lithium concentrations will phase-separate at equilibrium. Phase boundaries parallel to the (100) and (001) planes, or a linear combination of the two, such as the (101) plane, are believed to be more energetically favorable as a result of elastic strain [13], although smaller particles may prefer a phase boundary parallel to the (010) plane [17].

The second important characteristic is that lithium diffuses quickly along the [010] crystallographic direction [18,19], and many orders of magnitude slower in the other directions, making Li_XFePO_4 a one-dimensional lithium conductor in the bulk. $Fe_{Li}^{\cdot}$ anti-site defects significantly reduce the diffusivity of along the [010] direction by blocking the one-dimensional conduction channels [20]. At the same time, the anti-site defects increase the diffusivity along the [100] and [001] directions, making lithium transport less anisotropic [21]. These effects yield two categories of Li_XFePO_4. Particles with blocked channels have long [010] diffusion lengths (typically > 1 μm) and a high fraction of anti-site defects (> 1%), while particles with unblocked channels have shorter [010] diffusion lengths (typically < 200 nm) and a low fraction of anti-site defects (< 0.5%). Malik et al. calculated the fraction of blocked channels as a function of the particle size and anti-site defect concentrations [20]. Smaller particles with unblocked channels cycle faster [22]. However, while particles smaller than 50 nm usually have few blocked channels, they may suffer from higher self-discharge because of high surface energies [23], sluggish reaction rates from higher-dimensional structural defects [24], and reduced open-circuit voltage [25].

3. Diffusion limited Li_XFePO_4 and thermodynamically-stable Li_XFePO_4

Most fundamental research of Li_XFePO_4 utilizes phase-separating particles with a large miscibility gap and relatively few blocked channels. These particles have [010] dimensions that are shorter than ~200 nm to minimize the number of blocked channels. Furthermore, the particles are large enough (typically > 50 nm) to minimize the effect of nanosizing on the miscibility gap; experiments are generally conducted at room temperature. The majority of this article reviews research utilizing particles that meet these criteria. However, some studies of Li_XFePO_4 operate outside these conditions, which lead to different observations; these studies will be briefly summarized in this section.

3.1. *Diffusion-limited Li_XFePO_4 in large particles*

When the anti-site defect concentration is high and/or the lithium diffusion distance in the [010] direction is long, the one-dimensional conduction channels become blocked [20], so the (de)intercalation of lithium in such Li_XFePO_4 particles is often diffusion limited. Particles larger than 1 μm in the [010] direction will likely have all its channels blocked by anti-site defects [20].

Operando X-ray microscopy has been used to study particles in this diffusion-limited regime [26–29]. Results show that lithiation begins at the electrolyte/particle or current collector/particle interface and progresses into the bulk of the particle. X-ray imaging of a cross-sectioned solid-state Li_XFePO_4 battery with a relatively high anti-site defect concentration showed that the new phase grows like a filament [26]. Wang et al. used two-dimensional projection imaging [27] and three-dimensional tomography [28] to study ~20 μm particles. The three-dimensional images showed that delithiation largely proceeds from the outside of the particle inwards to the center, although there is initially some anisotropy in the delithiation patterns. Such an experiment was conducted at a very slow rate of C/50, where C/n signifies the rate for which the electrode finishes (de)lithiation in n hours. Hong et al. used microrod particles that contain a high 3.5% anti-site defect concentration [29]. Such particles show poor lithium diffusion along all three directions; however, even with anti-site defects, lithium diffusion is faster in the [010] direction. As a result, lithium insertion in that direction is surface-reaction limited while lithium insertion in the other directions is bulk diffusion limited. None of these results have shown a significant solid solution character, likely because the lithium diffusion front controls the lithium distribution in these particles.

3.2. *Elimination of the miscibility gap in small particles*

While particles larger than ~200 nm in the [010] direction often have different bulk transport behavior due to the blocked channels, particles smaller than ~50 nm in any direction often have different bulk thermodynamics due to the increased effects of interfacial energy [30] and coherency strain [31]. The miscibility gap is eliminated altogether in very small particles. Experimental X-ray diffraction has shown an increase in the solubility for smaller particles [32,33]. Gibot et al. further showed that ~40 nm, non-carbon-coated particles (de)lithiate