

Analysis of the FePO₄ to LiFePO₄ phase transition

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Abstract The electrochemical phase transformation of carbon coated nanophase (60–70 nm) FePO₄ to LiFePO₄ was investigated by use of the Avrami–Johnson–Mehl–Eroofev equation. The analysis at three temperatures showed an Avrami exponent equal to one. Based upon reinterpretation and in agreement with recent microstructural evidence, a two-dimensional growth mechanism for the phase transformation is proposed in which the new phase grows in a direction perpendicular to the direction of lithium ion transport. Furthermore, the relatively low value of the activation energy for the phase transformation of 13 kJ/mol suggests that the phase transition is controlled by lithium ion diffusion along the phase boundary.

Keywords Lithium iron phosphate · Kinetics · Phase transition · Avrami equation

Introduction

LiFePO₄ has been under intense study as a next generation positive electrode material. Its high safety, low cost, and cycle life all suggest that it may have potential application in hybrid electric vehicles, and it has been recently commercialized in power tool applications. During charge and discharge of the LiFePO₄ system, two phases are present, LiFePO₄ and FePO₄. This differs from LiCoO₂, which forms a Li_{1-x}CoO₂ solid solution during charge and

discharge. Thus, the process of discharge and charge in the LiFePO₄ system differs from conventional lithium ion battery positive electrode materials. It is therefore of great interest to understand the mechanism of the FePO₄–LiFePO₄ phase transformation to design an improved LiFePO₄ positive electrode material.

Pahdi et al. [1] suggested a model of this two phase system based on a “shrinking core”, which was mathematically modeled by Srinivasan and Newman [2]. The “shrinking core” model assumes a three-dimensional growth mechanism. To shed light on the mechanism, we have reported a study of the kinetics of this phase transition [3]. Based upon this analysis, a linear, one-dimensional growth mechanism with a phase boundary rate determining step was proposed [3] based upon the Avrami–Johnson–Mehl–Eroofev analysis of the phase transition [4–11]. However, further, in-depth study has led us to reexamine our conclusion. This paper refines our previously proposed model. We believe that the revised model is a better description of the transformation and it is in excellent agreement with electron microscopy imaging of the FePO₄/LiFePO₄ phase boundary reported by Chen et al. [12].

Results and discussion

A kinetic study, using the Avrami–Johnson–Mehl–Eroofev analysis of the electrochemical FePO₄ to LiFePO₄ phase transformation, was reported in Allen et al. [3]. The analysis is based on the Avrami equation

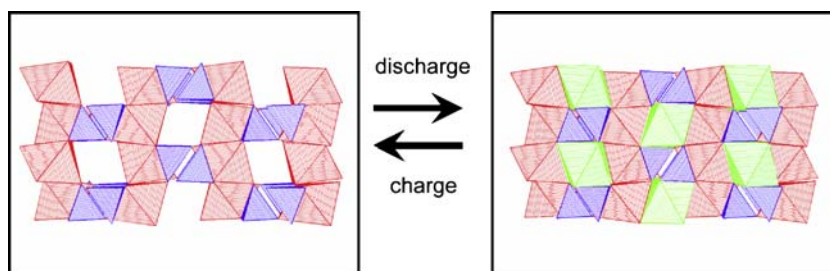
$$f = 1 - \exp(-kt)^n \quad (1)$$

where f is the volume fraction of LiFePO₄, k is a rate constant parameter, and the exponent, n , is a constant whose value is dependent upon the geometry of the

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Fig. 1 Structure of FePO_4 (left) and LiFePO_4 (right) viewed down the b -axis (Pnma space group). The b -axis is the direction of lithium transport in both phases



transformation. The dimensionality (1-D, 2-D, or 3-D) of the transformation is related to the value of the Avrami exponent. Higher dimensionality leads to a higher value of the exponent. Therefore, determination of the Avrami exponent can aid one to determine which geometric model of the phase transformation is the best fit: one-, two- or three-dimensional growth [9]. From this model, a plot of the $\log [\log(1/1 - f)]$ against the \log time will give a straight line of slope n and intercept $n \log k - \log e$ [7]. Such a plot was reported by Allen et al. [3]. The slope of the line was found to approximately one at the three temperatures. The value of $n=1$ allows us to rule out the possibility of a three-dimensional shrinking core growth mechanism. The value of $n=1$ suggests either a one-dimensional growth mechanism with a phase boundary control of the rate determining step or a two-dimensional growth mechanism with a diffusion controlled rate limiting step as described below.

In Allen et al. [3], we proposed a model based upon the assumption that one-dimensional lithium ion diffusion will lead to a one-dimensional growth mechanism. As one can see from inspection of Fig. 1, it is clear that lithium ion diffusion should be one-dimensional. LiFePO_4 adopts an orthorhombic olivine structure based upon PO_4 tetrahedra, corner-sharing FeO_6 octahedra, and edge-sharing LiO_6 octahedra in which the oxygen atoms form a distorted hexagonal close-packed framework. The edge-sharing LiO_6 octahedra form chains along the b -axis (space group Pnma), the [010] direction and thus by inspection of the structure one expects that lithium ion transport should occur predominantly along this axis. Theoretical predictions based on first principle calculations [13] and atomistic modeling [14] support this hypothesis. Thus, a model involving one-dimensional growth in the direction of the lithium ion transport was proposed [3].

However, one-dimensional lithium ion diffusion does not rule out a two-dimensional growth mechanism. The distinction between one- and two-dimensional growth is subtle. The growth *direction* is one-dimensional but because the phase boundary is a plane in the Avrami nomenclature, this is considered to be a two-dimensional growth mechanism. Therefore, this reanalysis, which is in agreement with the microstructural evidence [12], leads us to conclude that the phase growth is two-dimensional, as

defined by the Avrami model, in a direction perpendicular to the direction of lithium ion diffusion.

Furthermore, the revised model proposing two-dimensional growth affects our determination of the rate-determining step. As reported by Allen et al. [3], the rate-determining step can be found by using a detailed description of the Avrami exponent, n , as a function of the nucleation (a), dimensionality (b), and growth (c) parameters [15–17]:

$$n = a + bc \quad (2)$$

where a , the nucleation index, reflects the time dependence of the number of nuclei per unit volume of untransformed material ($a=0$ for nucleation rate 0, $a=1$ for constant nucleation, $a>1$ for increasing nucleation rate, and $0 < a < 1$

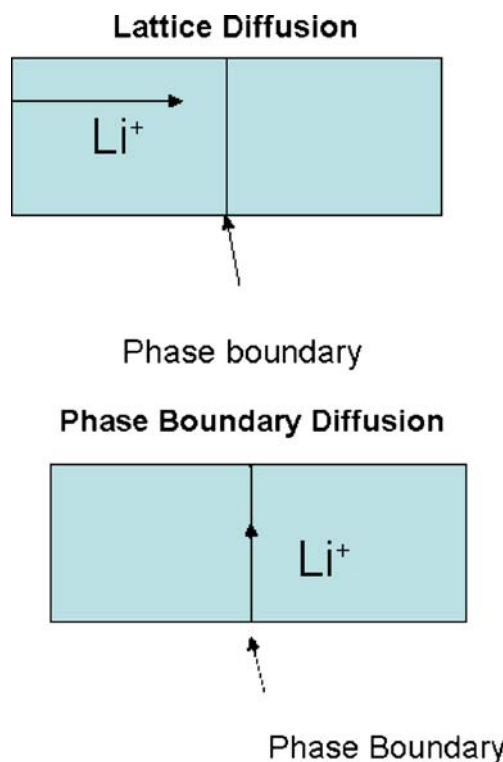


Fig. 2 A lattice diffusion model of lithium ion diffusion during the electrochemically driven phase transformation of FePO_4 to LiFePO_4 (top) and a phase boundary mechanism of lithium ion diffusion (below)

for decreasing nucleation rate), b is the dimensionality of the growth ($b=1, 2, 3$ for 1-D, 2-D, 3-D growth, respectively), and c is a growth index dependent on the rate-determining step of the transformation ($c=1$ for phase boundary control, $c=1/2$ for diffusion controlled growth). Using $a=0$ based upon our interpretation of the phase nucleation to be instantaneous as previously noted [3] and if we assume, as in our earlier model [3] that $b=1$ based on the structural argument that we have presented, then the only possible values of a and c leading to $n=1$ are 0 and 1, respectively. Therefore, this analysis suggested that the rate-determining step is the rearrangement of the bonds at the reaction interface (phase boundary control). However, if we choose a two-dimensional growth mechanism as per our revised model, then $b=2$ and, in this case, $a=0$ and $c=1/2$. Thus, the rate-determining step is diffusion and is not phase boundary control as previously [3] reported.

For this case, we use the activation energy to determine the diffusion mechanism. An Arrhenius plot of the electrochemical lithiation of FePO_4 to form LiFePO_4 was reported in Allen et al. [3]. The activation energy of the process calculated from the Arrhenius relationship was found to be 13 kJ/mol. Because we propose that the rate-determining step is lithium diffusion, we can use this value to determine the pathway for lithium diffusion during the phase transformation. Diffusion generally occurs by two possible mechanisms, lattice or phase boundary. Figure 2 illustrates the two possible lithium ion diffusion pathways. A comparison of the activation energy for the process compared to the activation energy for lattice and phase boundary diffusion of lithium in $\text{LiFePO}_4/\text{FePO}_4$ can be used to identify the Li ion diffusion mechanism. Takahashi et al. [18] found an activation energy of 39 kJ/mol for lattice lithium ion diffusion within LiFePO_4 . The fact that we obtained a much lower value for the activation energy of the FePO_4 to LiFePO_4 phase transformation suggests that lithium ion diffusion within our nanophase system occurs by phase boundary diffusion. This interpretation is in agreement with Chen et al. [12] who suggested that “rather than diffusing through the $[\text{LiFePO}_4/\text{FePO}_4]$ crystals, Li is extracted or inserted only at the phase boundary”. Furthermore, the value of the activation energy is about a third that of the bulk diffusion activation energy, which is consistent with what is known about the relative activation energy of bulk vs phase boundary paths [19]. In conclusion, the obtained activation energy, which is about one third that of the bulk diffusion (for a macrosized sample) is consistent with the model of Chen et al. [12] of a phase boundary lithium diffusion pathway.

Conclusions

The kinetics of the electrochemical conversion of carbon-coated nanophase (60–70 nm) FePO_4 to LiFePO_4 were followed and analyzed with the Avrami–Johnson–Mehl–Eroofev equation. Determination of the Avrami exponent suggests either a one-dimensional growth mechanism with the rate-determining step being controlled at the boundary or a two-dimensional growth mechanism with diffusion being the rate-determining step. The two-dimensional model was chosen based on microscopy evidence. An activation energy of 13 kJ/mol for the phase transformation was determined. A comparison of the activation energy with that of lithium ion lattice and phase boundary diffusion suggests that lithium ion diffusion occurs along the phase boundary. In summary, the electrochemical phase transformation of FePO_4 to LiFePO_4 occurs by a 2-D growth reaction controlled by lithium ion boundary diffusion.

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