Kinetic Study of the Electrochemical $FePO_4$ to $LiFePO_4$ Phase Transition

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The electrochemical phase transformation of carbon-coated nanophase (60−70 nm) $FePO_4$ to $LiFePO_4$ has been investigated by use of the Avrami−Johnson−Mehl−Eroofev equation. The analysis shows an Avrami exponent equal to 1, which is indicative of one-dimensional growth. The analysis does not support the conventional shrinking core model for the electrochemical conversion of $FePO_4$ to $LiFePO_4$. Analysis of the Avrami exponent reveals that the phase transformation is not controlled by diffusion but by a phase boundary reaction. Measurements at different temperatures allowed for an estimate of the activation energy, which was found to be about 13 kJ/mol for the electrochemical $FePO_4$ to $LiFePO_4$ transformation.

Introduction

A lithium ion battery is assembled in a discharged state and becomes activated after a charging step removes lithium from the positive electrode (generally, a lithiated transition metal oxide) and concurrently inserts lithium into the negative electrode (generally, graphite). The first commercially successful positive electrode was $LiCoO_2$; however, concerns about the cost of cobalt and the potential safety hazards associated with overcharging of $LiCoO_2$ has led to a search for alternative materials containing less expensive materials that are more stable under abusive conditions. $LiFePO_4$, whose electrochemical activity was first reported by Pahdi et al.,[1] has emerged as a viable positive electrode based on these criteria. A modified version of $LiFePO_4$ has been commercialized recently by the A123 company.[2] During charge and discharge of the $LiFePO_4$ system, two phases are present, $LiFePO_4$ and $FePO_4$. This two-phase nature is manifested in a very flat voltage plateau which is consistent with the chemical potential of lithium being constant during the plateau. This differs from $LiCoO_2$, which forms a $Li_{1-x}CoO_2$ solid solution during charge and discharge, and it therefore demonstrates sloping charge and discharge curves. Thus, the process of discharge and charge is completely different in the $LiFePO_4$ system compared to conventional lithium ion battery positive electrode materials. It is therefore of great interest to understand the mechanism of the $FePO_4$−$LiFePO_4$ phase transformation to design an improved $LiFePO_4$ 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[3] and others.[4] The “shrinking core” model assumes a three-dimensional growth mechanism. However, recent experimental evidence has led to a re-examination of this model and evidence via electron microscopy[5] and high-resolution electron energy loss spectroscopy[6] points to a one-dimensional growth mechanism. From a structural viewpoint, intuitively one expects that lithium ion diffusion should be one-dimensional. $LiFePO_4$ adopts an orthorhombic olivine structure, space group *Pnma*, 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, 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[7] and atomistic modeling[8] support this hypothesis. In agreement with this, Srinivasan and Newman[3] pointed out that arguments can be made that lithium diffusion will be preferred along a certain crystallographic direction and therefore the shrinking core model may not be an accurate description of the phase transformation. However, owing to lack of mechanistic information at the time of their study, the charging/discharging mechanism was modeled using the “shrinking core” idea.

To shed light on the mechanism, in this paper we study the kinetics of this phase transition. We measured the overall rate of transformation of $FePO_4$ to $LiFePO_4$ and analyzed the data using the Avrami−Johnson−Mehl−Eroofev equation,

$$f = 1 - \exp(-kt)^n \tag{1}$$

where f is the volume fraction of $LiFePO_4$, k is a rate constant parameter, and n is an exponent whose value is dependent

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upon the geometry of the transformation.[9−14] In particular, the comparison of the experimental Avrami exponent value to theoretical predictions can be used to determine the geometry of the transformation mechanism. The Avrami exponent increases with the dimensionality of growth. An Avrami exponent value of 1−2 is indicative of one-dimensional growth, 2−3 of two-dimensional growth, and 3−4 of three-dimensional growth. Thus, a shrinking core model of phase transformation would have an Avrami exponent of between 3 and 4 and a model based on a linear growth would have an Avrami exponent of about 1−2.[14]

Experimental Section

Nanophase carbon-coated $LiFePO_4$ was obtained from NEI Corporation (Nanomyte BE-20). The reported surface area is 25−30 m^2/g.[15] The average particle size can be estimated based on this surface area, assuming a spherical particle, using the equation[16]

$$d = 6/\rho S_{BET} \qquad (2)$$

where d is the particle size, ρ is the density of $LiFePO_4$ (3.6 g/mL)[17] and S_{BET} is the BET surface area. From the application of the equation, a particle size of 60−70 nm was calculated.

For electrochemical testing, a composite electrode was fabricated by a slurry coating method. With use of *N*-methylpyrrolidone (NMP) as solvent, a slurry of 78 wt % $LiFePO_4$, 10 wt % polyvinylidene fluoride, and 12 wt % super-P carbon was prepared and coated onto an aluminum foil substrate. The electrode film was cut into small discs with an area of 0.97 cm^2 and dried at 80 °C in air before use. In a dry room (dew point < -80 °C), Li/$LiFePO_4$ button cells were assembled using a microporous polypropylene membrane as the separator and a 1.5 M $LiPF_6$ solution in a 3:7 (wt) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) electrolyte. Electrochemical testing was performed using a Maccor Series 4000 tester. A Tenney Environmental Oven was used to provide constant temperature. At room temperature, the cells were charged to 4.2 V at $c/10$ and then held at 4.2 V until the current dropped to less than $c/20$, where c = cell discharge capacity, reported to be 150 mA·h/g.[15] The cells were then equilibrated at the chosen temperature (22, 10, or 0 °C) for a minimum of 4 h and then discharged at a constant voltage of 3.0 V. The fraction of $FePO_4$ lithiated to form $LiFePO_4$ during the constant 3.0 V step was measured by recording current as a function of time. This will be explained in detail in the Results and Discussion section.

Results and Discussion

To obtain insight into the phase transformation of $FePO_4$ to $LiFePO_4$ during the discharge of a lithium ion battery based on the $LiFePO_4$ positive electrode material, the kinetics of the electrochemical phase transition from $FePO_4$ (charged state) to $LiFePO_4$ (discharged state) were followed. This will help us to understand how to improve the rate capability, in other words, the power of the battery. This is critically important for use in high-power applications such as hybrid electric vehicles (HEV). The application of the Avrami−Johnson−Mehl−Erofeev equation allows determination of the transformation mechanism geometry, the rate constant parameter, and the activation energy of the transformation. To apply this equation, one must measure the volume fraction of the product phase as a function of time. Measurement at different temperatures will allow a determination of the activation energy through use of Arrhenius-type plots. This method of analysis has been commonly applied to polymorphic phase transitions by changing the temperature so that the starting phase is no longer thermodynamically favored and then measuring the volume fraction of the thermodynamically stable product as a function of time through X-ray diffraction. For example, the transformation kinetics of $\beta \rightarrow \gamma$ Li_2ZnSiO_4 were analyzed with the Avrami method.[18] It has also been commonly used to describe phase transformations in metal and alloy systems.[13] In our study, we perturb the system not by change of temperature but by change of the voltage to a potential where the Fe(III)-containing $FePO_4$ is thermodynamically unstable with respect to the Fe(II)-containing $LiFePO_4$. As this was done electrochemically, we can conveniently measure the rate of transformation by measuring the current flow between the electrodes as a function of time. That is, the amount of $FePO_4$ converted to $LiFePO_4$ was determined by measuring the current as a function of time with the assumption that all electrons measured correspond to the conversion of $FePO_4$ to $LiFePO_4$ according to the equation

$$FePO_4 + e^- + Li^+ \rightarrow LiFePO_4 \qquad (3)$$

In practice, we started by assembling $LiFePO_4$/Li coin cells and because, in this study, we wanted to understand the kinetics of the discharge process, the $LiFePO_4$/Li coin cells were first charged to convert the $LiFePO_4$ to $FePO_4$, the charged state of the functioning battery. We then set out to determine how quickly the $FePO_4$ could be lithiated under electrochemically reducing conditions. The voltage of lithium insertion is about 3.5 V, so a constant voltage of 3 V was applied. At this voltage, the Fe(III) in $FePO_4$ will be reduced to Fe(II) and lithium will be inserted to form $LiFePO_4$.

The results of the electrochemical phase transformation are shown in Figure 1. The shapes of the curves indicate a cellular transformation, a type of transformation in which all of the parent phase is consumed by the transformation product.[13] In accordance with a cellular transformation, a rapid conversion of $FePO_4$ was observed during the initial portion of the lithiation followed by a slowdown of the reaction rate as the $LiFePO_4$ "cells" impinge upon adjacent "cells". This phenomenon can be described by the Avrami−Johnson−Mehl−Eroofev equation. In simple terms, as the product phase grows over time and the volume fraction of product becomes larger than the reactant, the reaction rate

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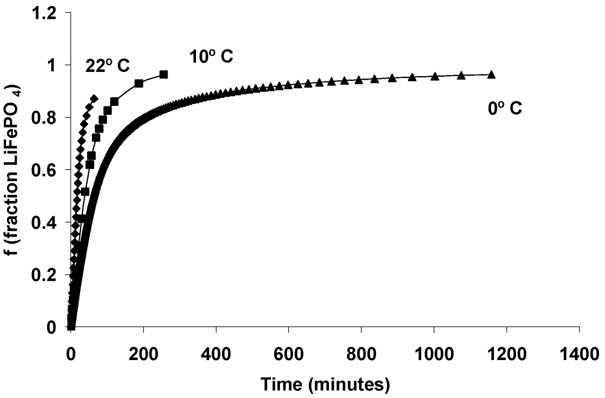

Figure 1. Fraction of $LiFePO_4$, formed from electrochemical lithiation of $FePO_4$, against time at three temperatures.

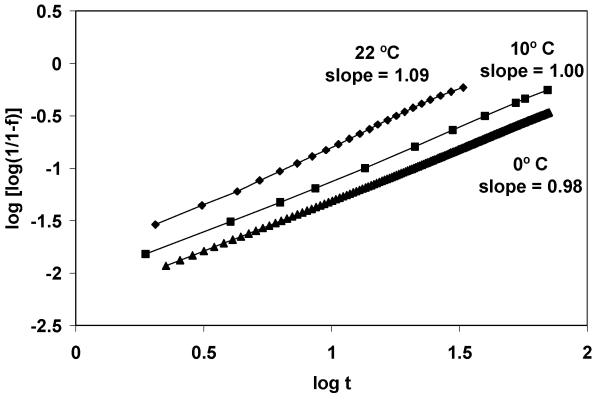

Figure 2. Determination of the Avrami exponent, *n*, and Avrami rate constant parameter, *k*. The slope of the line is equal to the Avrami exponent. The intercept is equal to $n \log k - \log e$ and allows the determination of rate constant parameter, *k*.

Table 1. Kinetic Data for the Electrochemical $FePO_4 \rightarrow LiFePO_4$ Phase Transformation

temperature (°C)	slope (*n*)	*k* (min^{-1})
22	1.09	0.036
10	1.00	0.021
0	0.98	0.014

of the transformation slows down because there is less room to grow without bumping into the transformed phase. This simple concept can be modeled based on the dimensionality of the transformation. The volumetric function of the growth mechanism directly affects the transformation rate and the dimensionality of the transformation is reflected in the value of the Avrami exponent. Higher dimensionality leads to a higher value of the exponent. Therefore, determination of the Avrami exponent allows one to then determine which geometric model of the phase transformation is the best fit: one-, two-, or three-dimensional growth.[14] From this model, a plot of $\log[\log(1/1 - f)]$ against log time will give a straight line of slope *n* and intercept $n \log k - \log e$.[18] Such a plot is shown as Figure 2 for the electrochemical $FePO_4$ to $LiFePO_4$ transformation. The slope of the line is approximately 1 at the three temperatures. The value of $n = 1$ is indicative of a one-dimensional growth mechanism[14] and supports the conclusions from electron microscopy[5] and high-resolution electron energy loss spectroscopy[6] that suggest a one-dimensional growth mechanism instead of a "shrinking core" where three-dimensional growth and $n = \sim 3-4$ should be exhibited. The likelihood that lithium ion diffuses most favorably along the chains of edge-sharing LiO_6 octahedra, found along the *b*-axis, suggests that the phase boundary will be constrained to a plane parallel to the *b*-axis and the phase growth will therefore be one-dimensional and the Avrami constant will reflect this dimensionality. This conclusion should be applicable to the $FePO_4-LiFePO_4$ transformation irrespective of particle size and coating since it is based on the crystal structures of the two phases, $FePO_4$ and $LiFePO_4$.

The Avrami exponent, in addition to giving information regarding the dimensionality of the growth, can also yield insight into the rate-determining step (phase boundary control or diffusion control). To do this, we express the Avrami exponent, *n*, as function of the nucleation (*a*), dimensionality (*b*), and growth (*c*) parameters,[19-21]

$$n = a + bc \tag{4}$$

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 rates, and $0 < a < 1$ for decreasing nucleation rates), *b* is the dimensionality of the growth ($b = 1, 2, 3$ for 1D, 2D, 3D 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). If we then assume 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 suggests that the rate-determining step must be the rearrangement of the bonds at the reaction interface (phase boundary control) and not the diffusion of lithium. Table 1 summarizes the information obtained from the Avrami analysis depicted in Figure 2. Furthermore, the temperature dependence of the $FePO_4$ lithiation is clearly illustrated in Figure 1. The reaction slows considerably at 10 and 0 °C relative to 22 °C.

From the measurement of the rate of transformation at the three different temperatures, *T*, it is possible to estimate an activation energy for the process using an Arrhenius plot of log *k* against $1/T$.[5] The Arrhenius plot of the electrochemical lithiation of $FePO_4$ to form $LiFePO_4$ was plotted in Figure 3 using the values of the Avrami rate constant, *k*, obtained from the analysis of Figure 2. The straight line shown in Figure 3 is a linear best fit of the data points. The activation energy, E_a, of the process was calculated from the well-known Arrhenius relationship:

$$\text{slope} = -E_a/R \tag{5}$$

From this analysis, a value of about 13 kJ/mol was obtained. This is a small activation energy for a solid−solid transformation. For example, the activation energy of the $\beta \rightarrow \gamma$ Li_2ZnSiO_4 phase transformation was found to be about 147 kJ/mol.[18] The low activation energy obtained in this study is not surprising in light of the fact that the rate-determining

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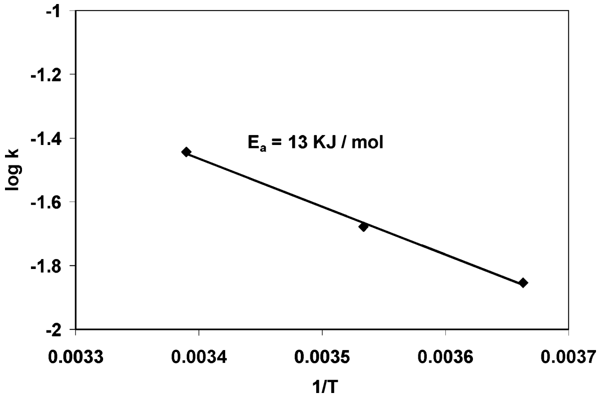

Figure 3. Activation energy was obtained from this Arrhenius plot of the electrochemical lithiation of $FePO_4$ to form $LiFePO_4$ using the values of the Avrami rate constant parameter obtained from Figure 2. Trend line is a linear best fit of the data points. The slope of the line was used to obtain the activation energy for this process.

step (phase boundary control, from analysis of the Avrami exponent) is a topotactic rearrangement—the $FePO_4$ framework is maintained throughout the reaction and the phase transformation simply involves a volume increase (6.81%)[22] as lithium enters the $FePO_4$ framework. Further, this also implies that lithium ion diffusion must occur by an even lower energy pathway. Takahashi et al.[23] found an activation energy of 39 kJ/mol for lattice lithium ion diffusion within $LiFePO_4$. The fact that we obtained a lower value for the activation energy of the $FePO_4$ to $LiFePO_4$ phase transformation suggests that lithium ion diffusion during phase transformation proceeds along a lower energy pathway. One possibility is that there may be enhanced lithium ion mobility at the phase boundary as suggested by Chen et al.[5] Chen et al. speculated that local bond stretching and bending in the phase boundary region, which results from the lattice mismatch between $FePO_4$ and $LiFePO_4$, may significantly enhance Li ion mobility. They suggest that "rather than diffusing through the [$LiFePO_4$/$FePO_4$] crystals, Li is extracted or inserted only at the phase boundary." 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.[5] of a phase boundary lithium diffusion pathway.

As a cautionary note, the kinetic parameter, *k*, and the resultant activation energy may be altered by use of different particle sized material and other processing parameters, so the number obtained has to be viewed from a comparison viewpoint unlike the Avrami exponent *n* which at least for small particle size samples should not change from sample to sample. Although the shrinking core model clearly does not apply to nanocrystalline samples, it is possible in the case of multidomained, micrometer-sized particles that although locally the transformation mechanism will be one-dimensional, the overall transformation will resemble a shrinking core. In this case, the activation energy would be higher, reflecting the need for lithium to diffuse through the bulk, a higher energy pathway, and if diffusion control becomes rate-determining, the Avrami exponent will also change. However, since it is highly likely that the $LiFePO_4$ that will be used in practical applications such as HEV will be nanophase, the results of this study are highly relevant.

We also note that when we consider extremely low temperatures, the rate-determining step may change as there is a well-known drop in cell performance of state-of-the-art lithium ion cells at very low temperatures.[24] This temperature-dependent drop in performance has been attributed to slow ion transport in the bulk electrolyte, the increased resistance of surface films at the electrode/electrolyte interfaces, the resistance associated with the charge-transfer processes at electrode interfaces, and the retarded diffusion coefficients of lithium ion in the electrodes.[24] The drop in performance begins at temperatures below −20 °C, while above this threshold temperature at least 80% of the rated capacity is deliverable.[25,26] Thus, within the temperature range of this study (from 22 to 0 °C), the temperature dependence of these cell components will not be important with respect to the rate performance of the cell. Future kinetic studies to explore this can be done using different electrolytes.

A further study can also vary the potential used for the constant voltage lithiation of $FePO_4$ to determine if any differences in activation energy are seen as one moves further away or closer to the equilibrium voltage of intercalation. Thus, one could construct a time−voltage−transformation diagram analogous to a time−temperature−transformation (TTT) diagram.[12] It is known that there is a rate dependence caused by the difference in the temperature of the kinetic study relative to the equilibrium transition temperature and it will be interesting to determine if a similar relationship is observed for voltage.

Conclusion

The kinetics of the electrochemical conversion of carbon-coated nanophase (60−70 nm) $FePO_4$ to $LiFePO_4$ was followed and analyzed with the Avrami−Johnson−Mehl−Eroofev equation. Determination of the Avrami exponent supports a linear, one-dimensional growth mechanism instead of a three-dimensional shrinking core model. Analysis of the Avrami exponent suggests a phase boundary controlled mechanism. The kinetic parameter, *k*, was also evaluated from the Avrami equation and its measurement as a function of temperature enabled us to calculate an activation energy for this process. The nanoscale material exhibited an activation energy of around 13 kJ/mol.

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