



Suppressing the formation of Fe₂P: Thermodynamic study on the phase diagram and phase transformation for LiFePO₄ synthesis



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ABSTRACT

Impurity of iron phosphide (Fe₂P) may weaken the cycle performance of the LiFePO₄ battery cell, and it is mandatory to get rid of this impurity in actual production. In order to suppress the formation of Fe₂P, the phase transformation and thermodynamic analysis of Li₂CO₃-Fe₂O₃-NH₄H₂PO₄-C/CO system for LiFePO₄ synthesis were studied in this paper. The phase diagram for LiFePO₄ synthesis indicated that LiFePO₄ will be respectively decomposed to form FeP, Fe₂P, and Fe₃P at 718, 776, and 836 °C, corresponding with the insulating Li₃PO₄ being yielded. Considering the practical synthesis, the sintering temperature should be controlled below 776 °C to avoid the formation of Fe₂P impurity in theory. The thermodynamic analysis successfully explained why the sintering temperature for pure LiFePO₄ preparation currently controlled to be 650–750 °C. Besides the sintering temperature, adding excess of Li resource is an effective measure to avoid the formation of Fe₂P and other impurities.

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1. Introduction

Increasing demands for portable electronic devices, hybrid and plug-in electric vehicles, and storage of electricity from wind/solar energy promote the development of lower-cost and higher energy Li-ion batteries that are safe [1,2]. Herein, lithium transition metal orthophosphates LiMPO₄ (M = Mn, Fe, Co, and Ni) with olivine structure, especially LiFePO₄ proposed by Padhi et al., [3] have become a new class of cathodes and viable alternatives to the conventional cathode material of LiCoO₂ due to its low cost, nontoxic, high theoretical specific capacity and greater thermal stability [4,5]. Nevertheless, the current debates for the utilization of LiFePO₄ in large-size batteries are mainly focused on the perceived poor rate capability and low energy density because of its low electronic conductivity, low voltage platform (3.5Vvs. Li⁺/Li) and low tap density respectively.

For the improvement of the electronic conductivity of LiFePO₄, many works have been devoted and two main approaches have been reported to be effective: (i) coating with high conductivity materials like carbon [6–8] or Fe₂P [9–11]; (ii) doping with supervalent metal ion (Mg²⁺, Al³⁺, Zr⁴⁺, Nb⁵⁺ or W⁶⁺) [12,13].

However, for the doping ions method, it has been recognized that the increase of conductivity was not due to doping, instead, it was either due to second phase impurities such as iron phosphate(Fe₂P and/or FeP) [14], or simply due to carbon coating [15]. Additionally, recent researches have been proved that the dopant will block the channels, which is damageable to the electrochemical performance [16–18]. For the Fe₂P-coated method, although FeP or Fe₂P can enhance the conductivity of LiFePO₄/C, whereas above a critical concentration, it will block the one-dimensional Li⁺ pathways in LiFePO₄ and hinder Li⁺ movement in LiFePO₄ [19,20]. Even worse, Fe₂P will dissolve in the electrolyte after a long-term cycling, and the iron ions will migrate through the electrolyte from the LiFePO₄-positive electrode to the negative [21]. The net effect of this migration is a large decrease in capacity retention of the LiFePO₄ battery cell, corresponding with the calendar life being reduced sharply. Therefore, it is mandatory to get rid of this impurity in actual production [22].

So the promising method to improve the electronic conductivity of LiFePO₄ is still the carbon-coated method [23–26]. While the high sintering temperatures and/or a reductive environment (such as carbon, CO or H₂) always results in the formation of Fe₂P during the synthesis of carbon-coated LiFePO₄. Although many research works have been reported the formation temperature of Fe₂P, it varied with different synthetic methods and raw materials. Up to now, the exact temperature for Fe₂P formation or LiFePO₄

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decomposition has not been reported in literature. Therefore, ascertaining the formation temperature of Fe₂P and FeP in theory is of great significance for the preparation of pure carbon-coated LiFePO₄.

To achieve this goal, a key factor to optimize synthesis approaches for LiFePO₄ is a thorough understanding of the thermally stable phase under different temperatures. Herein, the thermodynamic predominance-area diagrams of LiFePO₄ synthesis system, especially the formation of Fe₂P and FeP at the high temperature stage, were systematically studied by using the Li₂CO₃–Fe₂O₃–NH₄H₂PO₄–C/CO system as the research object. From this thermodynamic analysis we can have a clear understanding of the predominance area of LiFePO₄, FeP, Fe₂P and Fe₃P. Moreover, the exact temperature of LiFePO₄ decomposition to form FeP, Fe₂P and Fe₃P was provided from the thermodynamic analysis results, which is beneficial for the preparation of pure LiFePO₄ powders.

2. Methodology

In this paper, the thermodynamic calculations of the assumed chemical reactions will be performed of the Li₂CO₃–Fe₂O₃–NH₄H₂PO₄–C/CO system. To this end, the first step was to inventory the various species which exist in the system, and that are reported in the literature, i.e. C, CO, CO₂, H₂O, NH₃, H₃PO₄, P₄O₁₀, NH₄H₂PO₄, Fe, FeO, Fe₂O₃, Fe₃O₄, Li₂CO₃, Li₃PO₄, Fe₃P, Fe₂P, FeP, FePO₄, Fe₃(PO₄)₂, and LiFePO₄. The accuracy of the calculations was restricted by the quality of the thermodynamic data available for the source reagents and reaction products, namely, the standard enthalpy of formation $\Delta_f H_{298}^\ominus$, standard Gibbs free energy of formation $\Delta_f G_{298}^\ominus$, standard entropy S_{298}^\ominus , and the standard molar heat capacity under constant pressure $C_{p,298}^\ominus$. Generally, the temperature function of the heat capacity can be written as:

$$C_{p,m}(T) = a + bT + cT^{-2}$$

In view of the above equation, the expressions for the temperature dependences of changes of the standard molar heat capacity $\Delta C_{p,m}(T)$, standard enthalpy of reaction $\Delta_r H_T^\ominus$, standard entropy of reaction $\Delta_r S_T^\ominus$, and the standard Gibbs energy of reaction $\Delta_r G_T^\ominus$, can be described as follow:

$$\Delta C_{p,m}(T) = \Delta a + \Delta bT + \Delta cT^{-2}$$

$$\begin{aligned} \Delta_r H_T^\ominus &= \Delta_r H_{298}^\ominus + \int_{298.15}^T \Delta C_p dT \\ &= \Delta_r H_{298}^\ominus + \Delta a(T - 298.15) + \Delta b(T^2 - 298.15^2) / 2 \\ &\quad - \Delta c(T^{-2} - 298.15^{-2}) \end{aligned}$$

$$\begin{aligned} \Delta_r S_T^\ominus &= \Delta_r S_{298.15}^\ominus + \int_{298.15}^T \frac{\Delta C_p}{T} dT \\ &= \Delta_r S_{298.15}^\ominus + \Delta a \ln(T/298.15) + \Delta b(T - 298.15) \\ &\quad - \Delta c(T^{-2} - 298.15^{-2}) / 2 \end{aligned}$$

$$\Delta_r G_T^\ominus = \Delta_r H_T^\ominus - T\Delta_r S_T^\ominus$$

where Δa , Δb , and Δc are the algebraic sums of the corresponding coefficients a , b , and c corresponding coefficients.

In this work, taking thermodynamic data from a sole source was

possible only for the well-known substances (CO, Fe₂O₃, Li₂CO₃, etc.) whose characteristics completely coincide in few reference books. But the thermodynamic information of the following compounds were most scarce: LiFePO₄ and Fe₃(PO₄)₂. Herein, the thermodynamic properties of those substances were calculated by using a method of evaluating the thermodynamic parameters of phosphate compounds as the sum of oxide units at high and low temperatures, recently developed by A. La Iglesia [27]. This method can calculate the values of $\Delta_f G_{298}^\ominus$ and $\Delta_f H_{298}^\ominus$ for mineral phosphates with a high accuracy, by using the sets of constituent h_i and g_i values for each basic oxide units.

For the standard enthalpy of formation $\Delta_f H_{298}^\ominus$ of LiFePO₄ and Fe₃(PO₄)₂. Both of them were estimated by using the above method basing on the units: $h(\text{Li}_2\text{O}) = -817.3 \text{ kJ mol}^{-1}$, $h(\text{P}_2\text{O}_5) = -1726.84 \text{ kJ mol}^{-1}$ and $h(\text{FeO}) = -319.16 \text{ kJ mol}^{-1}$, respectively, and the value for each of them can be calculated as follow:

$$\begin{aligned} \Delta_f H_{298}^\ominus(\text{LiFePO}_4) &= 0.5h(\text{Li}_2\text{O}) + h(\text{FeO}) + 0.5h(\text{P}_2\text{O}_5) \\ &= -1591.02 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_f H_{298}^\ominus(\text{Fe}_3(\text{PO}_4)_2) &= 3h(\text{FeO}) + h(\text{P}_2\text{O}_5) \\ &= -2684.32 \text{ kJ mol}^{-1} \end{aligned}$$

Nevertheless, the value of S_{298}^\ominus and C_p for Fe₃(PO₄)₂ was still absent and no literature have been reported. So, a Two-Parameter Model reported by P.M. Guo [28,29] was used to estimate the standard entropy and heat capacity of complex oxide, and the calculated value of S_{298}^\ominus and $C_{p,298}^\ominus$ was 280.17 J mol⁻¹K⁻¹ and 240.088 J mol⁻¹K⁻¹, respectively.

Table 1 presented the standard thermodynamic values which were taken from various sources with a necessary indication of the references. According to the inventory listed in Table 1, 34 equilibriums were assumed and listed in Table 2. To clarify, the thermodynamic calculations of the assumed chemical reactions will be performed in a practically important temperature range for LiFePO₄ synthesis. It was evident that any of Eqs (1)–(34) can proceed under these conditions in principle.

3. Calculation results

Typically, LiFePO₄ can be synthesized via solid-state reaction, mechanochemical activation, sol-gel route, hydrothermal reaction, or co-precipitation methods, and the initial-obtained LiFePO₄ powders need a high temperature treatment at about 650–750 °C under a highly reducing condition to form a well-crystallized LiFePO₄/C composites. Generally, this high temperature treatment process can be called as carbothermal reduction process.

In this study, LiFePO₄ was synthesized via a carbothermal reduction method by using Fe₂O₃ as the iron source. Actually the carbothermal reduction (CTR) was used extensively to reduce metal oxides to metals in steel metallurgy, and the carbon oxidation during CTR can take place via two different reactions, namely, Boudouard reactions (35,36). For the CO₂ reaction, which is more thermodynamically favorable at the lower temperatures, has minimal volume change and hence negligible entropy change. And when the temperature is over 700 °C, the formation of CO becomes more thermodynamically favorable than the CO₂ reaction.



For the reduction of Fe₂O₃, one of the premises is to insure that

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