

Thermodynamics analysis of LiFePO_4 precipitation from $\text{Li-Fe(II)-P-H}_2\text{O}$ system at 298 K

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Abstract: Thermodynamics of the precipitation from $\text{Li-Fe(II)-P-H}_2\text{O}$ system at 298 K was investigated. The results demonstrate that LiFePO_4 can be formed at room temperature under pH value of 0–11.3, and the impurities Li_3PO_4 and Fe(OH)_2 will be yielded at pH value above 11.3 and 12.9, respectively. The optimum pH value for LiFePO_4 precipitation is 8–10.5. Considering the low rate of phase transformation kinetics, metastable $\text{Li-Fe(II)-P-H}_2\text{O}$ system was also studied. The results indicate that equimolar ratio of co-precipitation precursor $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and Li_3PO_4 cannot be obtained at the initial molar ratio 1:1:1 and 1:1:3 of Li:Fe:P . In contrast, equimolar ratio of the co-precipitation precursor can be yielded by adjusting the pH value to 7–9.2, matching the molar ratio 3:1:1 of Li:Fe:P , meaning that Li^+ -excess is one of the essential conditions for LiFePO_4 preparation by co-precipitation method.

Key words: lithium iron phosphate; lithium ion batteries; $\text{Li-Fe(II)-P-H}_2\text{O}$ system; thermodynamics; co-precipitation

1 Introduction

Since lithium iron phosphate, LiFePO_4 , was first reported as a positive electrode for rechargeable lithium ion batteries in 1997 by PADHI et al [1], it has been actively investigated and considered one of the most promising cathode materials for lithium ion batteries due to its low cost, nontoxic, high lithium intercalation voltage, high theoretical specific capacity and great thermal stability [2,3]. Conventionally, LiFePO_4 powders are prepared by solid-state synthesis with their repeated grinding and a long period of high temperature operations. However, this approach has some conspicuous disadvantages such as large particle size, broad particle size distribution, and impurities. In contrast, wet chemical preparation routes, such as hydrothermal, solvothermal, sol-gel, emulsion-drying and co-precipitation methods, have an indisputable advantage over solid-state reactions in achieving better homogeneity and mixing the starting compounds on molecular level. Especially, precipitation and/or hydrothermal approach, as a commercially feasible process, has attracted much attention recently. For instance, PARK et al [4,5] and YANG et al [6] synthesized the single phase of LiFePO_4 successfully via

co-precipitation method. YANG et al [7] and CHEN and WHITTINGHAM [8] synthesized LiFePO_4 directly in a hydrothermal reaction, and no impurities were detected. Additionally, similar studies repeatedly demonstrated that the precipitation and hydrothermal methods are promising synthesis methods for LiFePO_4 [9–12].

Nevertheless, precipitation and hydrothermal methods suffer from the impurities formation, such as Li_3PO_4 , $\text{Fe}_8(\text{PO}_4)_2$, Fe_2O_3 , $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ [4,10], which have predominant influence on the electrochemical performances. And the experimental conditions for LiFePO_4 preparation via wet chemical routes in the present researches were almost obtained on experience, and the conditions varied with different processes and/or experimental devices which are of a certain extent randomness and blindness. So, if the conditions, under which pure LiFePO_4 can be obtained in solution medium, could be predicted, it will guide us to later researches and practical production.

In this work, the thermodynamics of the precipitation from $\text{Li-Fe-P-H}_2\text{O}$ system is studied, aiming to understand the precipitation characteristics. Meanwhile, the predominance-area and optimum conditions for the formation of LiFePO_4 will be predicted theoretically.

2 Data treatment and calculation model

In this work, the precipitation processes are based on the LiOH–FeSO₄–H₂PO₄–H₂O system, in which 19 ionic species are assumed to exist in the solution to a significant extent: H⁺, OH[−], PO₄^{3−}, HPO₄^{2−}, H₂PO₄[−], H₃PO₄(aq), SO₄^{2−}, HSO₄[−], H₂SO₄(aq), Li⁺, LiOH, LiHPO₄[−], Fe²⁺, Fe(OH)⁺, Fe(OH)₂(aq), Fe(OH)₃[−], Fe(OH)₄^{2−}, FeHPO₄(aq), FeH₂PO₄⁺, and 5 species as insoluble compounds were assumed to exist: Li₃PO₄(s), Fe(OH)₂(s), Fe₃(PO₄)₂·8H₂O(s), FeHPO₄(s), LiFePO₄(s). These inventory leads to 19 equilibriums listed in Table 1, each of them gives rise to an independent equilibrium equation from the mass action law.

Table 1 Thermodynamic equilibrium equations of precipitation system at 298 K

No.	Equilibrium reaction	lg <i>K</i>	Ref.
1	H ₂ O = H ⁺ + OH [−]	−14	[13]
2	H ₃ PO ₄ (aq) = H ₂ PO ₄ [−] + H ⁺	−2.14	[13]
3	H ₂ PO ₄ [−] = HPO ₄ ^{2−} + H ⁺	−7.19	[13]
4	HPO ₄ ^{2−} = PO ₄ ^{3−} + H ⁺	−12.32	[13]
5	H ₂ SO ₄ (aq) = HSO ₄ [−] + H ⁺	3	[13]
6	HSO ₄ [−] = SO ₄ ^{2−} + H ⁺	−1.99	[13]
7	HPO ₄ ^{2−} + Li ⁺ = LiHPO ₄ [−]	−0.72	[13]
8	Li ⁺ + OH [−] = LiOH(aq)	0.36	[13]
9	Fe ²⁺ + OH [−] = Fe(OH) ⁺	−5.56	[13]
10	Fe ²⁺ + 2OH [−] = Fe(OH) ₂ (aq)	−9.77	[13]
11	Fe ²⁺ + 3OH [−] = Fe(OH) ₃ [−]	−9.67	[13]
12	Fe ²⁺ + 4OH [−] = Fe(OH) ₄ ^{2−}	−8.58	[13]
13	Fe ²⁺ + HPO ₄ ^{2−} = FeHPO ₄ (aq)	−3.6	[14]
14	Fe ²⁺ + H ₂ PO ₄ [−] = FeH ₂ PO ₄ ⁺	−2.7	[14]
15	Li ₃ PO ₄ (s) = 3 Li ⁺ + PO ₄ ^{3−}	−10.63	[13]
16	Fe(OH) ₂ (s) = Fe ²⁺ + 2OH [−]	−16.31	[13]
17	Fe ₃ (PO ₄) ₂ ·8H ₂ O(s) = 3Fe ²⁺ + 2PO ₄ ^{3−} + 8 H ₂ O	−36	[15]
18	FeHPO ₄ (s) = Fe ²⁺ + HPO ₄ ^{2−}	−5.89	−
19	LiFePO ₄ (s) = Li ⁺ + Fe ²⁺ + PO ₄ ^{3−}	−24.6	−

The equilibrium reactions (20) and (21) are related to FeHPO₄(s) and LiFePO₄(s) which have no solubility product available in literatures. However, the *K*_{sp} can be evaluated by the following equation:

$$\Delta_r G_m^\ominus = -RT \ln K \quad (20)$$

where $\Delta_r G_m^\ominus$ is the standard Gibbs free energy of the reaction, *R* is the gas constant (8.314 J K/mol), and *T* is temperature in Kelvin.

The Gibbs free energy value of FeHPO₄(s) can be estimated by the method in Ref. [16], with the result of

−1201.77 kJ/mol. And the Gibbs free energy value of LiFePO₄(s), which was calculated in our previous work [17], is −1517.7 kJ/mol. Using Eq. (22), the *K*_{sp} values, which are 10^{−5.89} and 10^{−24.6} for FeHPO₄(s) and LiFePO₄(s), respectively, are calculated.

At the same time, the charge balance and 4 mass balance equations are given as follows:

$$\begin{aligned} [H^+] + [Li^+] + 2[Fe^{2+}] + [Fe(OH)^+] + [FeH_2PO_4^+] \\ = [OH^-] + 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + \\ 2[SO_4^{2-}] + [HSO_4^-] + [LiHPO_4^-] + [Fe(OH)_3^-] + \\ 2[Fe(OH)_4^{2-}] \end{aligned} \quad (21)$$

$$[Li]_T = [Li^+] + [LiOH] + [LiHPO_4^-] \quad (22)$$

$$\begin{aligned} [Fe(II)]_T = [Fe^{2+}] + [Fe(OH)^+] + [Fe(OH)_2(aq)] + \\ [Fe(OH)_3^-] + [Fe(OH)_4^{2-}] + [FeHPO_4(aq)] + \\ [FeH_2PO_4^+] \end{aligned} \quad (23)$$

$$[P]_T = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4(aq)] + [LiHPO_4^-] \quad (24)$$

$$[S]_T = [SO_4^{2-}] + [HSO_4^-] + [H_2SO_4(aq)] \quad (25)$$

where [M] is the equilibrium concentration for each species; [Li]_T, [Fe(II)]_T, [P]_T and [S]_T are designated as the total concentration of Li, Fe, phosphate and sulphate in equilibrium conditions; while [Li]ⁱ_T, [Fe(II)]ⁱ_T, [P]ⁱ_T and [S]ⁱ_T are defined as the initial total concentrations of Li, Fe, phosphate and sulphate before the precipitation of solid phases.

The calculation process based on the Newton–Raphson iteration method was carried out by using Microsoft Excel.

3 Results and discussion

3.1 Li–Fe(II)–P–H₂O system

Figure 1 shows the molar ratio of solid species diagram and solubility diagram of the Li–Fe(II)–P–H₂O system. Three predominance-areas exist at the given pH value. At 0 ≤ pH ≤ 11.3, LiFePO₄(s) appears to be the stable single phase, and its solubility decreases basically with increasing pH value. At 11.3 ≤ pH ≤ 12.9, a two-phase domain of LiFePO₄(s) + Li₃PO₄(s) is observed, showing that no pure LiFePO₄ can be formed. Furthermore, another two-phase domain, where Fe(OH)₂(s) and Li₃PO₄(s) coexist (1:1 in molar ratio), is found in the pH value range of 12.9 to 14. Note that no coexistent region of Fe₃(PO₄)₂·8H₂O(s) + Li₃PO₄(s) appears, indicating that Fe₃(PO₄)₂·8H₂O(s) and Li₃PO₄(s) exist in a metastable state and can react with each other, accompanied by the formation of LiFePO₄. The results are consistent with the previous studies that Fe₃(PO₄)₂·8H₂O(s) and Li₃PO₄(s) must be an intermediate in the formation of LiFePO₄ [18–20].

Therefore, it is clear from the above discussion that the pH value is one of the key factors affecting LiFePO₄

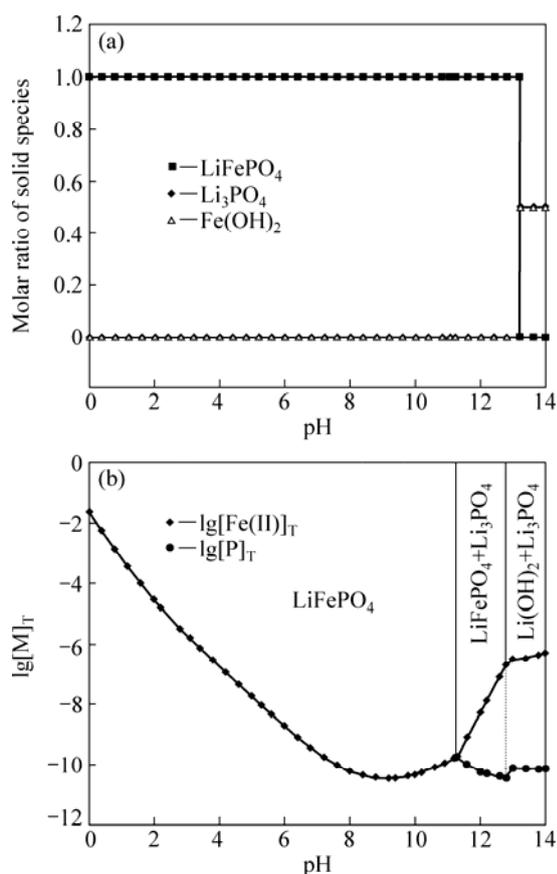


Fig. 1 Molar ratio of solid species diagram (a) and solubility diagram (b) of Li-Fe(II)-P-H₂O system ($[\text{Fe}(\text{II})]_r = [\text{P}]_r = 0.1$ mol/L, $[\text{Li}]_r = 1$ mol/L)

precipitation in solution medium. For example, LIU et al [21] reported that LiFePO_4 just was prepared by hydrothermal method at $\text{pH} = 6.3\text{--}9.04$, but not at $\text{pH} = 5.4$ and 11.04 . Coincidentally, LEE and TEJA [19] showed that pure LiFePO_4 was synthesized at $\text{pH} = 6.5$ and 9.22 ; LiFePO_4 , iron oxide and Li_3PO_4 coexisted at $\text{pH} = 10.62$; and a mixture of iron oxide (Fe_3O_4) and lithium phosphate (Li_3PO_4) was obtained at $\text{pH} = 14.32$. Note that LiFePO_4 cannot be prepared at strong acid pH condition in the above practical experiments, which seems to be in conflict with the thermodynamic computation in this work. This can be reconciled by recognizing the similar principle of the hydroxyapatite precipitation that phosphate appears mainly in the form of H_3PO_4 and/or H_2PO_4^- in strong acid aqueous medium, causing too low reaction probability of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ crystallization to nucleate [22], whereas it was the same for LiFePO_4 . Using the method in Ref. [22], the reaction probability of LiFePO_4 crystallization was calculated and is shown in Fig. 2. The results show that the reaction probability increases dramatically with increasing pH value.

PARK et al [5] and YANG et al [6] reported that only green color co-precipitated powders ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and Li_3PO_4) were obtained via co-precipitation method at

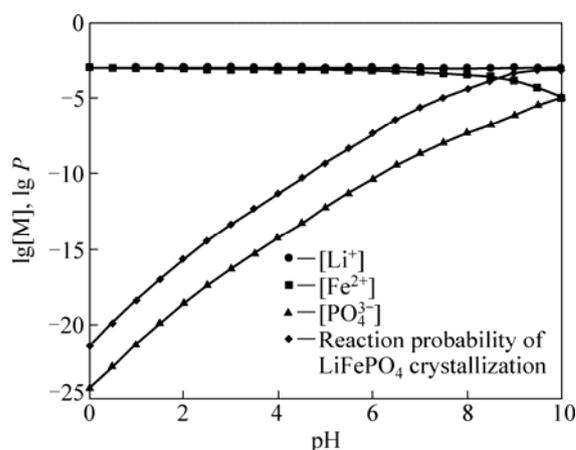


Fig. 2 Growth unit concentration and probability (P) of LiFePO_4 crystallization

$60\text{ }^\circ\text{C}$. Moreover, LEE and TEJA [19] found that large irregular $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ particles were synthesized at room temperature, and both LiFePO_4 and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ particles were obtained at $120\text{ }^\circ\text{C}$, whereas at $300\text{ }^\circ\text{C}$ and higher temperatures, only LiFePO_4 was yielded, indicating that temperature also played an important role in the formation of LiFePO_4 . This was because the processes of LiFePO_4 precipitation were controlled by phase-transformation kinetics, so it was favorable for the intermediate products converting to LiFePO_4 phase at high temperature, and some research inferred that there was a critical temperature [23].

The nucleation rate of LiFePO_4 was affected by many factors, such as kinetic coefficient, temperature, supersaturation, interfacial free energy. It was possible to obtain LiFePO_4 at low temperature and broad pH range via special treatment, e.g. adding nucleator and surfactant, precipitation at high supersaturated solution.

3.2 Metastable Li-Fe(II)-P-H₂O system

According to the above investigation on precipitation from Li-Fe(II)-P-H₂O system and practical experiments, we know that in the actual precipitation process of LiFePO_4 , it is easy to form the transition phases, e.g. $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and Li_3PO_4 , at the initial stage. In order to obtain pure LiFePO_4 , precipitation parameters should be controlled precisely and strictly, such as pH value, temperature. $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and Li_3PO_4 can be yielded at low temperature, meanwhile, it provides us with another idea for preparing LiFePO_4 . In fact, many works had been done to synthesize LiFePO_4 by co-precipitation method [4–6]. In the process, obtaining equimolar ratio of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$ and $\text{Li}_3\text{PO}_4(\text{s})$ was the basic prerequisite for preparing pure LiFePO_4 . Based on this situation, it is necessary for us to have an investigation on the metastable Li-Fe(II)-P-H₂O system, in which we

assume that the LiFePO_4 does not exist.

Figure 3(a) shows the solubility diagram of the metastable $\text{Li-Fe(II)-P-H}_2\text{O}$ system in the initial concentration of 0.1 mol/L $[\text{Li}]^i$, $[\text{Fe(II)}]^i$, and $[\text{P}]^i$. Four predominance areas can be found. At $3 \leq \text{pH} \leq 6.6$, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$ appears to be the stable single phase. A two-phase domain of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s}) + \text{Li}_3\text{PO}_4(\text{s})$ is defined in pH value range of 6.6 to 10.45, in which its solubility decreases as the pH value increases. At $\text{pH} \geq 10.45$, another two-phase domain, where $\text{Li}_3\text{PO}_4(\text{s})$ and $\text{Fe}(\text{OH})_2(\text{s})$ coexist, is found. However, the molar ratio of solid species from Fig. 3(b) suggests that it is impossible to obtain equimolar ratio of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$ and $\text{Li}_3\text{PO}_4(\text{s})$ in the whole range of pH value theoretically, and the calculation result is consistent with the experimental results [24].

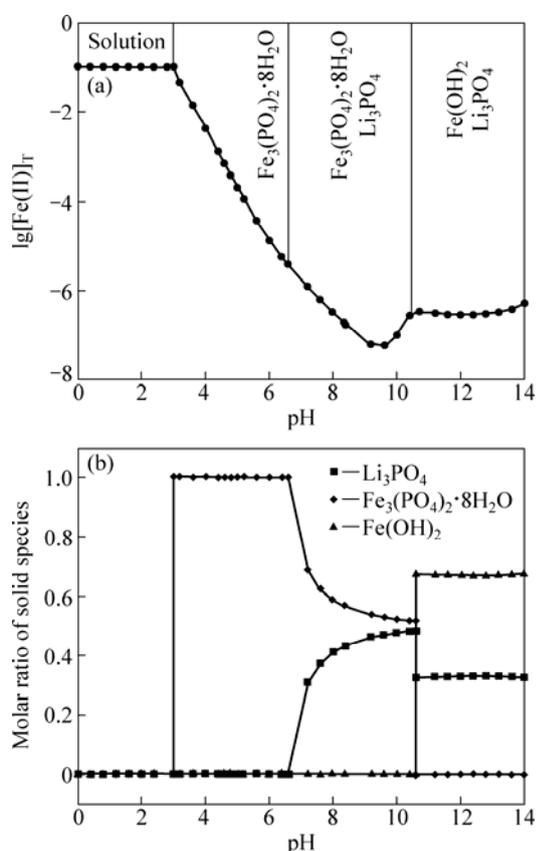


Fig. 3 Solubility (a) and molar ratio (b) of solid species of metastable $\text{Li-Fe(II)-P-H}_2\text{O}$ system ($[\text{Fe(II)}]^i = [\text{P}]^i = [\text{Li}]^i = 0.1 \text{ mol/L}$)

In order to obtain equimolar ratio of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$ and $\text{Li}_3\text{PO}_4(\text{s})$, we reckoned that the results will be improved under phosphate or Li^+ -excess conditions, and the molar ratio of solid species diagrams with the molar ratio 1:1:3 and 3:1:1 of Li:Fe:P are shown in Figs. 4(a) and (b), respectively. Figure 4(a) suggests that it is also hard to obtain equimolar ratio of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$ and $\text{Li}_3\text{PO}_4(\text{s})$, indicating the effect of

phosphate-excess is not obvious. In contrast, equimolar ratio of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s})$ and $\text{Li}_3\text{PO}_4(\text{s})$ can be obtained by adjusting the pH value to 7–9.2 with the molar ratio 3:1:1 of Li:Fe:P . This result is consistent with the experimental pH value in Refs. [25–27]. And the optimal conditions for $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}(\text{s}) + \text{Li}_3\text{PO}_4(\text{s})$ co-existing precursor are in the neutral or slightly basic/acid solution medium.

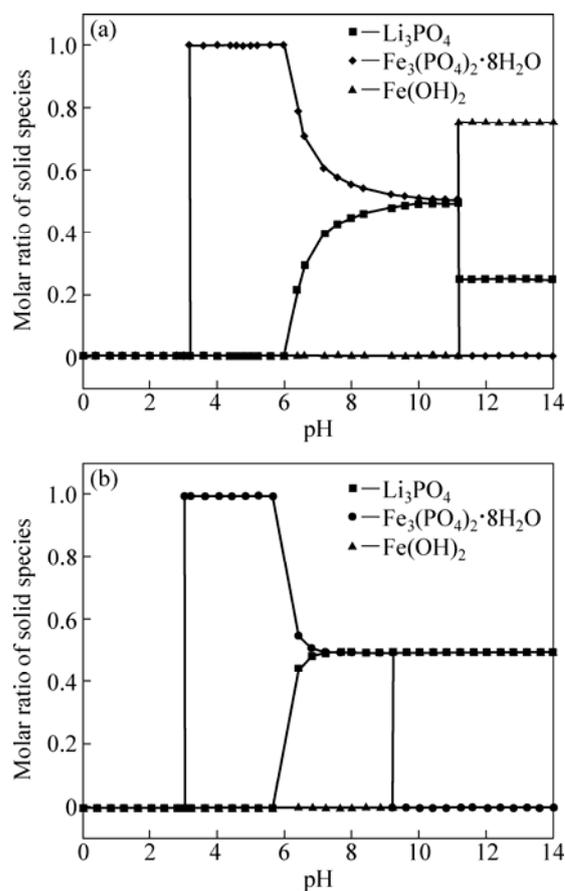


Fig. 4 Molar ratio of solid species of metastable $\text{Li-Fe(II)-P-H}_2\text{O}$ system with P^- - or Li^+ -excess: (a) $[\text{Fe(II)}]^i = [\text{Li}]^i = 0.1 \text{ mol/L}$, $[\text{P}]^i = 0.3 \text{ mol/L}$; (b) $[\text{Fe(II)}]^i = [\text{P}]^i = 0.1 \text{ mol/L}$, $[\text{Li}]^i = 0.3 \text{ mol/L}$

4 Conclusions

Thermodynamic analysis shows that LiFePO_4 can be obtained at 298 K and $\text{pH} = 0-11.3$, with its optimum precipitation $\text{pH} = 8-10.5$. So it is possible to obtain pure LiFePO_4 through wet chemical preparation routes. However, because of the low phase transformation kinetic rate, it is hard to obtain LiFePO_4 at low temperature. In this case, the metastable $\text{Li-Fe(II)-P-H}_2\text{O}$ precipitation system was also studied and the results indicate that Li^+ -excess is essential to obtain equimolar ratio of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and Li_3PO_4 for LiFePO_4 , and the optimal conditions are in the neutral or slightly basic/acid solution medium.

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室温下 $\text{Li-Fe(II)-P-H}_2\text{O}$ 体系共沉淀制备 LiFePO_4 的热力学分析

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摘要: 对 $\text{Li-Fe(II)-P-H}_2\text{O}$ 体系共沉淀制备 LiFePO_4 进行热力学研究。在常温条件下, 当 pH 值为 0~11.3 时可生成 LiFePO_4 ; 而当 pH 值大于 11.3 和 12.9 时, 会依次生成 Li_3PO_4 和 Fe(OH)_2 。 LiFePO_4 共沉淀的最佳 pH 值为 8~10.5。考虑到低温条件下共沉淀前躯体向 LiFePO_4 相转变的动力学速度较慢, 对亚稳态 $\text{Li-Fe(II)-P-H}_2\text{O}$ 体系进行研究。结果表明, 当共沉淀体系的初始 Li 与 Fe 与 P 摩尔比为 1:1:1 或 1:1:3 时, 不能得到等摩尔量的 $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ 和 Li_3PO_4 沉淀; 而当摩尔比为 3:1:1、溶液 pH 值为 7~9.2 时, 能够制备出符合化学计量比的前躯体。这表明采用共沉淀法制备 LiFePO_4 的一个重要条件是溶液中要存在过量的 Li^+ 。

关键词: 磷酸铁锂; 锂离子电池; $\text{Li-Fe(II)-P-H}_2\text{O}$ 系; 热力学; 共沉淀

(Edited by YUAN Sai-qian)