

Construction of E-pH diagram and experimental study on wet synthesis of FePO_4 as the precursor of cathode materials

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Abstract. The preparation of FePO_4 as a precursor by co-precipitation method is widely used. Due to the lack of the guidance of thermodynamic theory, The prepared FePO_4 often contains impurity phase, which leads to unsatisfactory performance of LiFeO_4 . The E-pH diagram of Fe-P- H_2O system at the temperature of 25°C were drawn through the basic E-pH principle with a number of thermodynamic data. According to the E-pH Diagram, the pH value is approximately 2.5, and the FePO_4 with less impurity can be prepared by adding proper oxidant. Base on the above mentioned condition, a simple verification experiment was carried out. The results showed that the prepared iron FePO_4 had fewer impurities, which provided a theoretical basis for preparing high-performance LiFeO_4 .

Keywords: LiFeO_4 cathode material, LiFeO_4 , E-pH diagram.

1 Introduction

LiFeO_4 with a large number of advantages, such as a relatively higher theoretical capacity of 170mAh/g, low cost of raw materials, high thermal stability at high temperature and environmental friendliness, has been widely investigated since it was firstly reported as a battery cathode material by Goodenough[1-7]. FePO_4 is an important precursor for the preparation of LiFeO_4 . The better precursor can reduce the impurity phase of the LiFeO_4 , in order to save the raw material and reduce the production cost. Many preparation methods have been used to fabricate FePO_4 , such as sol-gel method, carbothermal reduction method, mechanical milling method and co-precipitation and so on[7-13]. It is generally recognized that using FePO_4 as a precursor to synthesize LiFeO_4 is greatly helpful to uniformity of LiFeO_4 when a co-precipitation method is employed and the electrochemical properties of LiFeO_4 are closely associated with the characteristics of FePO_4 . The E-pH diagram of Fe-P- H_2O system at the temperature of 25°C and the activity of 1.0 were drawn based on the E-pH principle with a number of thermodynamic data[14-15]. The possibility of synthesizing

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FePO₄ in aqueous solution has been analyzed from thermodynamic point of view, and the precursor of FePO₄ was synthesized in aqueous solution in a confirmatory experiment.

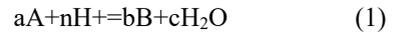
2 Thermodynamic analysis

2.1 E-pH diagram

The equilibrium in aqueous solution system is closely related to various parameters, such as reaction temperature, concentration of leaching agent, pH value of solution, redox potential and so on. Among these factors, the redox potential and pH value of the solution have a significant effect on the leaching rate of metals, thus the E-pH diagram is usually drawn with the parameters of E and pH to study the equilibrium conditions of the system.

There are three kinds of reactions in aqueous solution[16-17]:

(1) Hydrogen ion takes part in the reaction but without redox process:



According to Gibbs free energy equation:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln[a_B^b / (a_A^a \cdot a_{H^+}^n)] = \Delta_r G^\ominus + RT \ln(a_B^b / a_A^a) + 2.303nRT pH$$

In equilibrium with $\Delta_r G=0$, pH value is as follow:

$$pH = -\frac{\Delta_r G^\ominus}{2.303nRT} - \frac{1}{n} \lg(a_B^b / a_A^a) \quad (2)$$

When a_A and a_B are 1.0, the pH is defined as pH[⊖]. The value of pH[⊖] is $-\Delta_r G^\ominus / (2.303nRT)$ and pH value is as follow:

$$pH = pH^\ominus - \frac{1}{n} \lg(a_B^b / a_A^a) \quad (3)$$

(2) It exists redox process but without hydrogen ion :



$$E = -\frac{\Delta_r G}{zF} = -\frac{\Delta_r G^\ominus}{zF} - \frac{RT}{zF} \ln(a_B^b / a_A^a)$$

When a_A and a_B are 1.0, the E is defined as E[⊖]. $E^\ominus = -\frac{\Delta_r G^\ominus}{zF}$ and E value is as follow:

$$E = E^\ominus - \frac{RT}{zF} \ln(a_B^b / a_A^a) = E^\ominus - \frac{0.0591}{z} \ln(a_B^b / a_A^a) \quad (5)$$

(3) It exists redox process with hydrogen ion :



$$E = -\frac{\Delta_r G}{zF} = -\frac{\Delta_r G^\ominus}{zF} - \frac{RT}{zF} \ln(a_B^b / a_A^a) - 2.303n \frac{RT}{zF} pH$$

$$E = E^\ominus - \frac{0.0591}{z} \ln(a_B^b / a_A^a) - \frac{0.0591n}{z} pH \quad (7)$$

2.2 The E-pH diagram of Fe-P-H₂O

Based on the above three kinds of reaction calculation methods and the reactions existing in the Fe-P-H₂O system, the E and pH expressions of the equilibrium of the system under the conditions of 298.15 K, O₂ and H₂ with partial pressures of 101325Pa are obtained as shown in table 1[18-20]. According to the relationship between E and pH in Table 1, the corresponding E-pH diagram is drawn as shown in Figure1.

Table 1. Chemical reaction and the equilibrium equations in the system.

Chemical reaction equations	Equilibrium equations
$O_2+4H^++4e=2H_2O$	$E=1.229-0.0591pH$
$2H^++2e=H_2$	$E=-0.0591pH$
$Fe^{3+}+e=Fe^{2+}$	$E=0.769-0.0591lg a(Fe^{2+})+0.0591lg a(Fe^{3+})$
$Fe^{3+}+H_3PO_4+2H_2O=FePO_4\cdot 2H_2O+3H^+$	$pH=-1.083-\frac{1}{2}lg a(Fe^{3+})-\frac{1}{2}lg a(H_3PO_4)$
$FePO_4\cdot 2H_2O+3H^++e=Fe^{2+}+H_3PO_4+2H_2O$	$E=0.577-0.0591lg a(Fe^{2+})-0.0591lg a(Fe^{3+})-0.$
$Fe(OH)_4^-+H^+=Fe(OH)_3+H_2O$	$E=13.317+0.0591pH+lg a(Fe(OH)_4^-)$
$Fe(OH)_4^-+2H^++e=Fe(OH)_2+2H_2O$	$E=1.263-0.118pH+0.0591lg a(Fe(OH)_4^-)$
$Fe(OH)_3+H^++e=Fe(OH)_2+H_2O$	$E=0.476-0.0591pH$
$H_2PO_4^-+H^+=H_3PO_4$	$E=2.146+lg a(H_2PO_4^-)$
$3FePO_4\cdot 2H_2O+2H_2O+2H^++3e=Fe_3(PO_4)_2\cdot 8H_2O$	$E=0.333-0.039pH-0.020lg a(H_2PO_4^-)$
$+H_2PO_4^-$	
$3FePO_4\cdot 2H_2O+2H_2O+H^++3e=Fe_3(PO_4)_2\cdot 8H_2O+$	$E=0.191-0.020pH-0.020lg a(HPO_4^{2-})$
HPO_4^{2-}	
$Fe_3(PO_4)_2\cdot 8H_2O=3Fe(OH)_2+2HPO_4^{2-}$	$E=9.137+0.5lg a(HPO_4^{2-})$
$+2H_2O+4H^+$	
$3Fe(OH)_3+2HPO_4^{2-}$	$E=1.197-0.138pH+0.039lg a(HPO_4^{2-})$
$+7H^++3e=Fe_3(PO_4)_2\cdot 8H_2O+H_2O$	
$3Fe^{2+}+2H_2PO_4^-+8H_2O=Fe_3(PO_4)_2\cdot 8H_2O+4H^+$	$E=2.417-0.75lg(Fe^{2+})-0.5lg a(H_2PO_4^-)$
$3FePO_4\cdot 2H_2O+2H_2O+3e=Fe_3(PO_4)_2\cdot 8H_2O+PO_4^{3-}$	$E=-0.048-lg a(PO_4^{3-})$

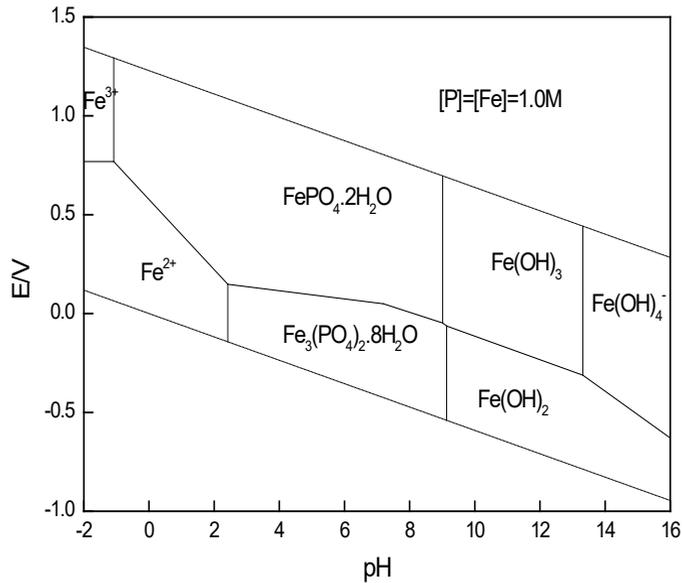


Fig. 1. E-pH diagram of Fe-P-H₂O system.

It can be seen from Fig.1 that $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ will exist stably under the condition of pH 2.4~9.1 and lower redox potential. With the increase of redox potential, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ will gradually change into $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ with a larger range of pH -1.1~9.0. At a higher pH value, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ will become $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$. While at a lower pH value, it will exist in the form of Fe^{3+} or Fe^{2+} . Therefore, in order to save the amount of alkali and oxidant, this point is generally selected in practice adding a small amount of oxidant.

3 Experiment and discussions

3.1 Experimental method

A certain concentration of phosphoric acid, ferrous sulfate and hydrogen peroxide were accurately added to a flat-bottom flask with three holes. A stirring paddle was inserted into the middle hole of the flask for stirring, a pH meter into one side for measuring pH and the rest hole for sampling. At set time, 1mL supernatant was taken from the reactor and the contents of P and Fe were determined by ICP after proper dilution, meanwhile, 1mL fresh sulfuric acid solution was added immediately. The reaction temperature and agitation are controlled by a water bath, and the pH value is adjusted by adding a certain amount of sodium hydroxide after a moment.

3.2 Composite and physical phrase analysis

The main equipment are: constant temperature magnetic stirring water bath with the model JJ5179HW-1(Jintan medical instrument factory, Jiangsu Province) ; electronic balance with the model Quintix-1cn (Seidolis Group, Germany) ; Ph meter with the model phs-3c precision; ICP analyzer with the model ICP-2000(Jiangsu Skyray Instrument Co., Ltd.).

3.3 Verdict experiment and discussions

0.1mol FeSO₄, 0.1mol H₃PO₄ and deionized water are taken into a flask with 100ml solution. Then 0.06mol H₂O₂ are added to oxidize ferrous ion. The temperature is set at 40°C. NaOH is added to adjust the pH value with 2.4. Then the temperature is increased to 80°C. the process is kept about 2 hours and then the solution is separated. The solid is dried about 4 hours with the temperature 105°C. The dried solid is tested with Fe/P ratio and phrase analysis. According to the XRF result shown Table 2, the Fe/P ratio is 0.99:1 and the XRD result is shown in Figure 2. As shown in Figure2, the peaks are consistent with those of FePO₄·2H₂O.

Table 2. Contents of the elements Fe, P and O.

	Fe	P	O
wt.%	33.56	18.75	47.69

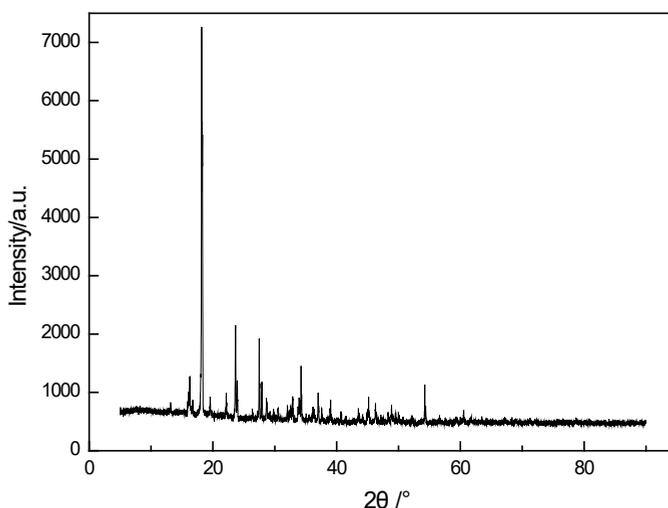


Fig. 2. XRD of FePO₄·2H₂O.

4 Conclusion

1) Through the thermodynamic analysis, it is proved theoretically that FePO₄ can be synthesized by wet co-precipitation method. The suitable condition of pH approximately 2.4 with adding proper amount of oxidant.

2) The experimental results show that the crystal form is perfect with less impurities and the ratio of Fe and P is suitable when pH is controlled at 2.4 adding hydrogen peroxide.

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