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Formation Mechanism and Growth Habit of Olivine-$LiFePO_4$ Materials by Hydrothermal Synthesis

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The formation mechanism and growth habit of olivine-$LiFePO_4$ material by hydrothermal synthesis are investigated by calculating the stability energy of the crystal growth unit on the basis of anion coordination polyhedron model and molecular simulation. The binding energy of a growth unit and the dehydration reactions among growth units are calculated to reveal the crystal nucleation process. The crystal growth habit is predicted by evaluating stability energies of growth units on the {200}, {101}, {210}, {011}, {020} and {002} faces. The effects of pH on nucleation, morphology and crystal habit of olivine-$LiFePO_4$ crystalline under hydrothermal condition, are explained relevantly according to its effect on the formation of various growth units. The understanding on olivine-$LiFePO_4$ formation and crystal growth in hydrothermal process is of great significance for controllable synthesis of high performance $LiFePO_4$ cathode materials.

Keywords: Hydrothermal crystal growth; Phosphates; Nucleation; Computer simulation; Crystal morphology

1. INTRODUCTION

Olivine $LiFePO_4$ [1] is considered to be one of the most promising cathode material for Li-ion batteries, due to its advantages including intrinsic thermal safety, low cost, environmental friendliness and excellent cycling stability. $LiFePO_4$ has proved itself an advanced electrochemical energy storage and conversion system for mobile power, especially electric vehicles (EVs). Now the important challenge is to realize mass production with high stability and consistency in structure and crystallinity by using low cost preparation technology.

The studies [2-4] show that the electrochemical performance of $LiFePO_4$ crystal depends on crystallinity, purity, crystal habit, crystal morphology, crystal size, particle size distribution and etc., particularly the exposure degree of the advantageous face for the aeolotropic crystal. However, a controllable crystal orientation cannot be achieved by the traditional solid-phase method, thereby restricting the performance improvement of $LiFePO_4$ electrode.

Hydrothermal synthesis receives particular interest due to mild operating temperature, low cost, high crystallization, morphology control, and the potential for large-scale production. Particularly, it is also considerably convenient to control the advantageous crystal-face growth and crystal size by tuning experiment parameters such as temperature, pressure, concentration, and additive [2]. These factors are closely related to the formation mechanism of controlled hydrothermal crystallization.

It's well-known fact that the $LiFePO_4$ crystal formation in hydrothermal experiences, "dissolution-nucleation-crystallization".[3-4] In previous studies, including precursor, precursor concentration, temperature, pH, stirring rate, organic reagents and etc., on the morphology and crystal size have been explored extensively. [5-10]

However, the relationships between these external factors and the internal causes in terms of the formation process and growth habit have not been well understood. Here, a complete understanding of $LiFePO_4$ crystal growth mechanisms and morphology evolution in hydrothermal process is proposed based on growth unit model. The results are essential for controllable synthesis of high performance $LiFePO_4$ cathode material.

2. FORMATION OF GROWTH UNIT

According to the crystal unit model [11-19], cations exist in the form of anion coordination polyhedron. The structure of the growth units in the aqueous solution is theoretically and practically found to be the same to that in the bulk crystals. Consequently, the formation of crystal nucleuses are formed by ordered assembling of growth units through dehydration reaction. In olvine-$LiFePO_4$, which belongs to space group Pnma, every orthorhombic unit cell contains four formula units. Every FeO_6 octahedra is surrounded by five PO_4 tetrahedrons (four corner-sharing and one edge-sharing), while lithium ions occupy the large open channels running parallel to the *b*-axis.[20]

The geometry conformation of ligand was simulated by PM3 semi-empirical algorithms. Furthermore, the total energy and binding energy of the geometric optimized conformation were calculated using the quantum chemistry ab initio method with 3-21G basis set, basis set superposition error (BSSE) correction and zero point energy (ZPE) correction.

The binding energy of growth units can be defined as the difference of total energy and isolated atomic energy. The binding energies and molecular structure of the possible complex compounds are listed in Table 1.

As shown in Table 1, with the increase of pH, the possible complex compound change from $[Fe(OH)]^+$ to $[Fe(OH)_6]^{4-}$ and $[H_2PO_4]^-$ to $[PO_4]^{3-}$, according to their binding energies. The results show that $[Fe(OH)_6]^{4-}$ and $[H_2PO_4]^-$ are the most stable growth units in the aqueous solution, on account of the structure base of combination between FeO_6 octahedra and PO_4 tetrahedron in $LiFePO_4$ crystal. In addition, the binding energy of $[Fe(OH)]^+$ is positive, and it indicates that $[Fe(OH)]^+$ hardly exists in the aqueous solution.

Table 2. Molecular formula and the total energies of $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ (x=0-6) complex compounds

Molecular Formula	Total Energy ($kcal \cdot mol^{-1}$)
$[Fe(H_2O)_6]^{2+}$	-56890.2
$[Fe(OH)(H_2O)_5]^{+}$	-56778.6
$[Fe(OH)_2(H_2O)_4]$	-56555.5
$[Fe(OH)_3(H_2O)_3]^{-}$	-56225.9
$[Fe(OH)_4(H_2O)_2]^{2-}$	-55783.9
$[Fe(OH)_5(H_2O)]^{3-}$	-55204.8
$[Fe(OH)_6]^{4-}$	-54873.8

3. THE EFFECT OF pH ON GROWTH UNIT

The pH of the precursor solution has been confirmed to play an important role on the particle morphology, crystal orientation and electrochemical activity of the $LiFePO_4$ particles prepared by hydrothermal.[21] As reported [21] when pH of the precursor solution changing from 2.5 to 9.5, the product undergoes the morphology evolution from needle-like, plate-like, massive aggregated particles and disorderly aggregate. The plate-like $LiFePO_4$ crystals can be obtained when the pH value falls into the range of 5<pH<6.5. The plate-like crystal with preferably exposure facet along ac-plane exhibits superior electrochemical performance.

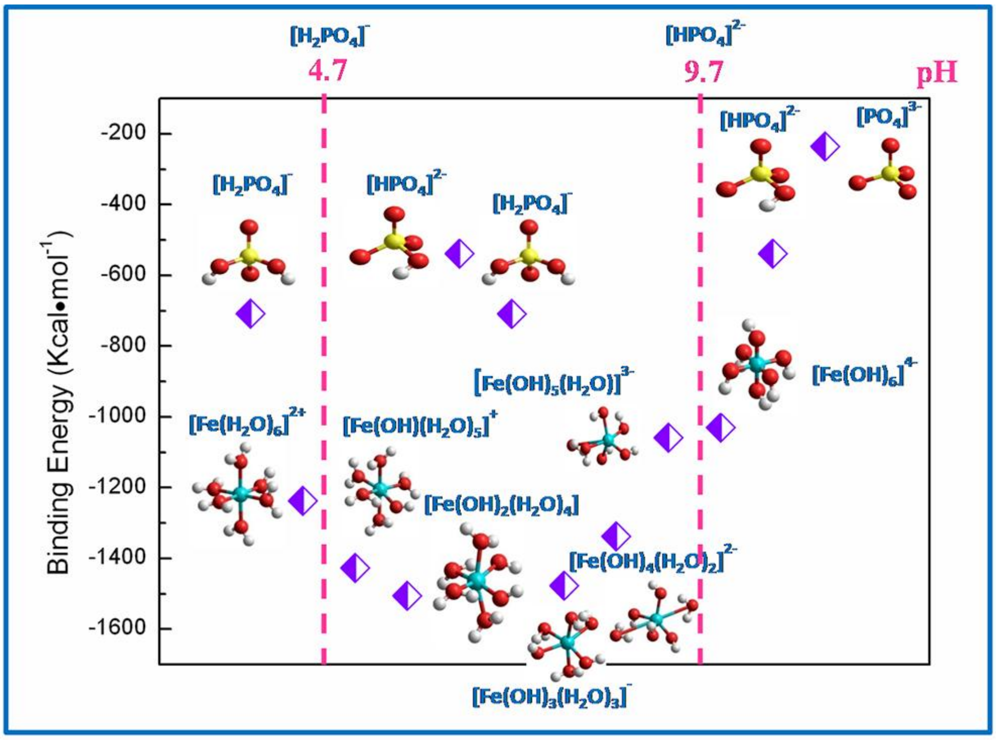


Figure 1. The binding energy of the geometric optimized $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ (x=0-6) and $[H_yPO_4]^{y-3}$ (y=0-2) complex compounds. Fe^{2+}: cyan; O^{2-}: red; H^{+}: white; P^{5+}: yellow.

Above morphology variation is determined by the relative growth rate of various faces, which is mainly related to the interface characteristic and the combination manners of anionic coordination polyhedra onto various crystal facets. The growth units may exist in the form of different structure under different conditions.

Generally, the stable growth unit obtained from an acidic aqueous solution (pH<4) is $[Fe(H_2O)_6]^{2+}$. On the other hand, $[Fe(OH)_6]^{4-}$ complex compound exists at pH higher than 7.2. When the pH in the range of 4 to 6.5, $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ (x=1-5) exists as stable complex compound. Figure 1 shows the binding energy of the geometric optimized $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ compound by molecular simulation.

Fe^{2+} ions are hydrated in aqueous solution. With the center ionic polarization effect, the joint effects of the exclusion of center ion and the attraction of solvent molecules or ions, hydrated ion will easily ionize a proton and form a dual-ligand complex compound, such as $[Fe(OH)(H_2O)_5]^+$. From the binding energy image of Figure 1, we can see that the complex compound molecule become stable from $[Fe(H_2O)_6]^{2+}$ to $[Fe(OH)_2(H_2O)_4]$. But the binding energy of the complex compound gradually increases from $[Fe(OH)_2(H_2O)_4]$ to $[Fe(OH)_6]^{4-}$. $[Fe(OH)_2(H_2O)_4]$ compound, which is formed in weak acidic solution, is the most stable. The ionization equation of the hydrated Fe^{2+} ion is shown as follows.

$$[Fe(H_2O)_6]^{2+} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} [Fe(OH)_x(H_2O)_{6-x}]^{2-x} + xH^+, (0 \le x \le 6) \qquad (1)$$

As seen from the deprotonation process, the pH value will be reduced. The result is consistent with literature [12] and our observation. In our experiment, the pH value of the filtrate after hydrothermal are around 4.5, while it is 6.5 of the precursor solution when $LiOH \cdot H_2O$, $FeSO_4 \cdot 7H_2O$ and H_3PO_4 are in a mole ratio of 3:1:1.

Similarly, the pH value has an important effect on the form of PO_4^{3-} in aqueous solution. The stable state in an acidic aqueous solution (pH=4.7) is $[H_2PO_4]^-$. On the other hand, $[HPO_4]^{2-}$ exists at pH=9.7. In weak acidic solutions of 4.5<pH<6.5, $[H_2PO_4]^-$ and $[HPO_4]^{2-}$ exist jointly as stable complex compound.

Table 2 shows the total energies of $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ (x=0-6) complex compounds and we can see that the complex compound molecule gradually reduced in the negative from $[Fe(H_2O)_6]^{2+}$ to $[Fe(OH)_6]^{4-}$.

The calculation result indicates that in order to reduce the total energy, the larger dimension growth unit will be formed certainly by dehydration reaction between $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ and $[H_2PO_4]^-$ or $[HPO_4]^{2-}$ complex compounds in form of Fe-O-Fe or Fe-O-P binding.

As the pH essentially affects the structure of stable growth units, as well as the nucleation rate and crystal growth rate subsequently, it is reasonable to control the crystal orientation and size by tuning the pH of precursor solution.

4. THE FORMATION OF THE LARGER DIMENSION GROWTH UNIT AND NUCLEATION

On the basis of growth unit model of anion coordination polyhedron, the structure of the solution units are found as the anion coordination polyhedral which are as the same as those in the crystals. Furthermore, according to the Pauling's fourth rule, in a crystal containing different cations, those of high valency and small coordination number tend not to share polyhedron elements with one another. In a $LiFePO_4$ crystal containing two kinds of coordination polyhedral, $[FeO_6]$ octahedra and $[PO_4]$ tetrahedron, P^{5+} cation of high valency and small coordination number tend to be separated by $[FeO_6]$ octahedra instead of sharing polyhedron elements with each other. Growth units, $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ and $[H_2PO_4]^-$ or $[HPO_4]^{2-}$ complex compounds, can have different ways to connect in weak acidic solutions in form of Fe-O-Fe or Fe-O-P binding. When the growth units are connected by sharing corner, edge or face, the binding energies of the complex compounds will be different. The results are shown in Figure 2.

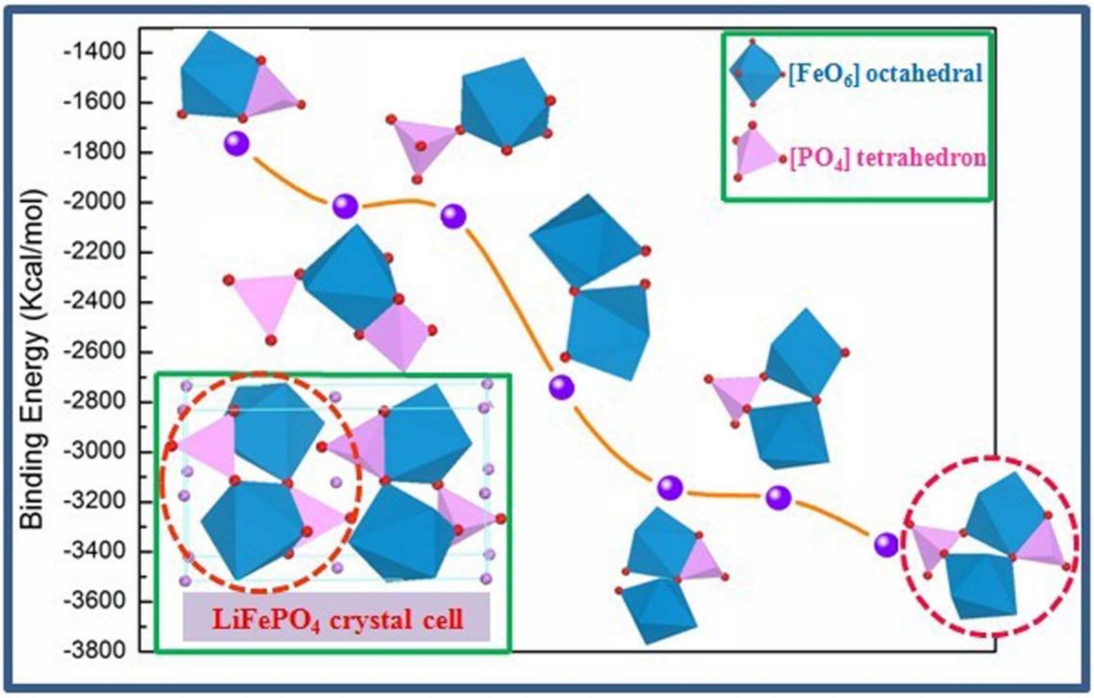


Figure 2. The binding energy of the larger dimension growth unit connected by $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ and $[H_2PO_4]^-$ or $[HPO_4]^{2-}$ complex compounds in form of coordination polyhedral, $[FeO_6]$ octahedra and $[PO_4]$ tetrahedron. Li^+: violet; O^{2-}: red.

With the increase of hydrothermal temperature, precipitation precursors formed at normal pressure and room temperature gradually dissolve and cations exist in the form of growth units. The $LiFePO_4$ crystal nucleus then separated out when the more stable big dimension structure unit was large enough to overcome dissociation by dehydration and proton reaction between $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ and $[H_2PO_4]^-$ or $[HPO_4]^{2-}$ complex compounds. As shown in figure 2, the binding energy of a large dimension growth unit containing four formula units, two FeO_6 octahedra and two PO_4 tetrahedron (two PO_4 tetrahedron separated by two corner-sharing FeO_6 octahedra, which corner-sharing and one edge-sharing with FeO_6 octahedra, respectively) is the lowest among all types of structures. Then this growth unit is theoretically the most stable and practically found as the anion coordination polyhedral. Besides, possess the same structure to $LiFePO_4$ crystal cell unit, as seen in the inset in figure 2. So it should be the most possible growth unit during $LiFePO_4$ crystal nucleation and growth, according to the growth unit model of anion coordination polyhedron.

5. THE GROWTH HABIT OF $LiFePO_4$ CRYSTAL UNDER HYDROTHERMAL CONDITION

Under different hydrothermal conditions, the crystal morphology is kaleidoscopic. The growth habit of the crystal is determined by the relative growth rate of various faces, which is mainly related to not only the surface characteristic of various crystal faces but also the combination energy of growth units with different faces. The combination of the growth units on the crystal surface can be regarded as the reaction of the anion coordination polyhedral with the structure units on the interface. The structure and dimensions of growth units are under different conditions, which are depended on the supersaturation of the solution, pH, etc.

According to the Pauling's third rule for ionic crystal, the crystal faces, which the vertexes of growth units point to, grow faster and they appear poorly or even disappear. On the other hand, the crystal faces, which the faces of anionic coordination polyhedron back to, grow slower and are exposed preferably. The faces, where the edges point to, grow at the middle rate and appear frequently. But on the contrary, the combination of octahedra is by sharing edge is most stable while by sharing corner is most un-stable, as far as the incorporation of growth units of transition metal compound are concerned.

The incorporation manner and dimension of growth units on various crystal faces are in fact complicated on account of two kinds of coordination polyhedral, such as FeO_6 octahedra and PO_4 tetrahedron, are involved.

But no matter how the new structure and form, in the prediction of growth habit of the crystal follows the basic principles: Firstly, the greater the stabilization energy for combination of growth units, the faster the growth rate of the crystal face. Secondly, the unit structure of the crystal-liquid interface boundary layer is supposed to be in keeping with those in the crystal face. Finally, the evolution of the crystal habit is that the favorable growth units interconnect essentially to the larger-scale macroscopic crystal.

The stabilization energy of growth units can be expressed as the following classical relation:

$$U = U_c + U_p \qquad (2)$$

where U_c is the ion-ion electrostatic interaction energy of growth unit, U_p is the polarization energy of growth unit.

For nonpolar crystal,

$$U_p = 0 \qquad (3)$$

The stabilization energy of growth units can be simplified as

$$U = U_c = \frac{Ne^2}{2m}(1-\frac{1}{n})\sum_{i=1}^{m}\sum_{\substack{j=1 \\ i\neq j}}^{m}[(Z_i Z_j)/R_{ij}] \qquad (4)$$

Here N is Avogadro constant ($6.022\times10^{23}\,\mathrm{mol}^{-1}$), e is electron charge (4.802×10^{-10} electrostatic unit), m is ion number of growth unit, R_{ij} is the inter-ionic distance, Z is ion valence and n is the average value of Bonn index.

For polar crystal,

$$U_p > 0 \qquad (5)$$

The polarization energy of growth unit, U_p, can be decomposed into sum of the interaction energy of equivalent dipole, U_K, induction energy of equivalent dipole, U_D and ion dispersion energy, U_L. That is

$$U_p = U_K + U_D + U_L \qquad (6)$$

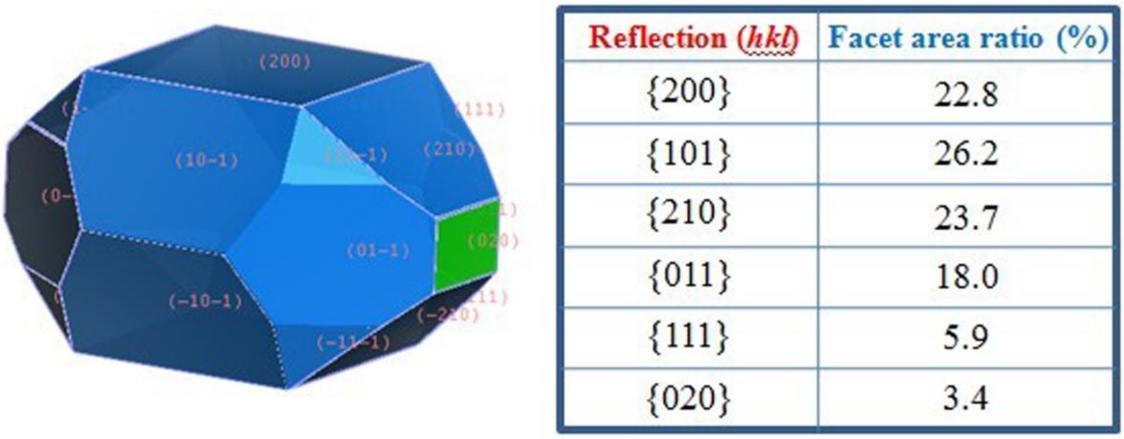
The stabilization energy of combination for growth units follows the formula

$$\Delta U = \Delta U_c + \Delta U_p \qquad (7)$$

Although compared with calculation result by crystal field theory, the stabilization energy may be lower only in view of the ion electrostatic potential, the changed trend of combination energy of growth units should be consistent. In addition, the inter-ionic distance is adopted by the optimization geometry parameters of $LiFePO_4$ crystal. So the combination energy of growth units for $LiFePO_4$ crystal can be expressed as

$$\Delta U = \Delta U_c = U_{c2} - U_{c1} \qquad (8)$$

The crystal morphology of $LiFePO_4$ was predicted by using Bravais-Friedel-Donnary-Harker (BFDH) model (Fig. 3).



Reflection (*hkl*)	Facet area ratio (%)
{200}	22.8
{101}	26.2
{210}	23.7
{011}	18.0
{111}	5.9
{020}	3.4

Figure 3. Crystal morphology and the facet area ratio of olivine-$LiFePO_4$ crystal calculated based on BFDH model.

The calculated crystal morphology of $LiFePO_4$ exhibits the {200}, {101}, {210}, {011}, {111}, {020} faces with the facet area ratio, 22.8%, 26.2%, 23.7%, 18.0%, 5.9% and 3.4%, respectively.

According to the theoretical calculation and Fisher and Islam's exhaustive research [20], the growth habit of $LiFePO_4$ crystal under hydrothermal condition was predicted by the calculated stabilization energy of combination of growth units on the {200}, {101}, {210}, {011}, {020} and {002} faces.

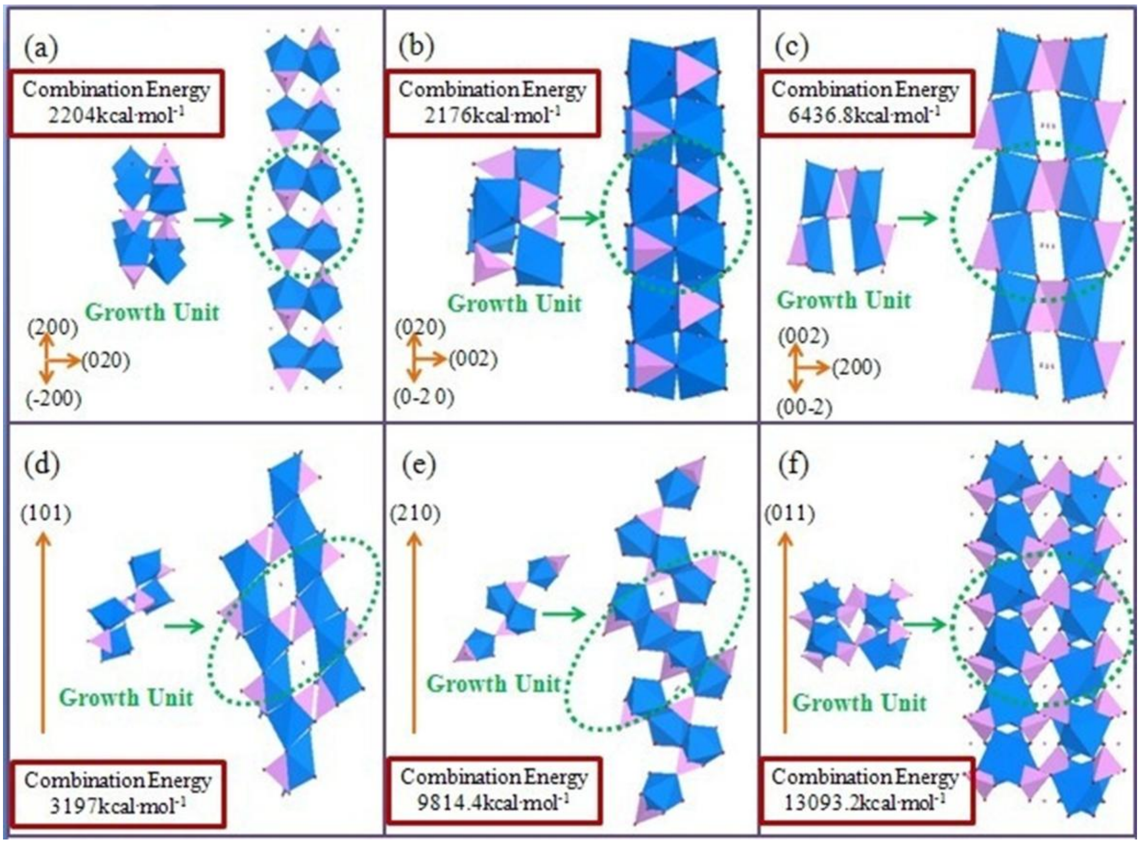


Figure 4. the favorable growth units of various faces and the calculated stabilization energy of combination of growth units

Fig.4 shows the favorable growth units of various faces and the calculated stabilization energy of combination of growth units. Notice that here hydroxyl or H_2O coordinated FeO_6 octahedra and PO_4 tetrahedron were taken into account in order to more accurately describe the combination manners of anionic coordination polyhedra of various crystal faces.

Larger stabilization energy for combination of growth unit means faster growth rate along the direction and the corresponding crystal facet appear poorly or even disappear. As shown in Fig.4, the growth rate of various faces follows the order of $V_{\{011\}} > V_{\{210\}} > V_{\{002\}} > V_{\{101\}} > V_{\{200\}} \approx V_{\{020\}}$. The dominant growth habit exhibits the {020}, {200} and {101} faces under hydrothermal condition in accordance with the results reported in literatures [20-21] and ours.

The combination energies of growth units of {200} and {020} faces are identical nearly. However, according to Dokko and Kanamura's exhaustive research [21], the plate-like crystal obtained from weak acidic solutions of 4<pH<6.5, had a large facet in the ac-plane, while the needle-like particles had a large facet in the bc-plane from acidic solutions (pH≈3.5). The results show that the exposure degree of crystal face or the facet area ratio may bear on not only the growth rate along the direction but also the formation rate and the stability of favorable growth units of various faces at different solution conditions, such as pH, initial concentration and etc. By molecular simulation calculations, the binding energies of the favorable growth units of {200} and {020} faces are -6243.2 $kcal \cdot mol^{-1}$ and -7235.4 $kcal \cdot mol^{-1}$ under acidic condition and -5351.8 $kcal \cdot mol^{-1}$ and -4563.7 $kcal \cdot mol^{-1}$ under weak acidic condition, respectively. Under weak acidic solution, the binding energy of the favorable growth units of {020} face is smaller in the negative than that of {200} face and the stability and number of the favorable growth units of {200} face are better than that of {020} face, so the dominant exposure is {020} face and vice versa.

6. CONCLUSIONS

In this study, the formation mechanism and growth habit of $LiFePO_4$ cathode materials under hydrothermal condition were investigated on the basis of growth unit model of anion coordination polyhedron and molecular simulation. The binding energy of the formation of growth unit and the dehydration reaction between growth units was systematically calculated for revealing the crystal nucleation process. The crystal habit can be explained using the combination energies of growth units of anionic coordination polyhedron on different surfaces during crystal growth. The main points can be summarized as follows:

(1) The $LiFePO_4$ crystal nucleus separated out when the more stable multidimensional structure unit was large enough to overcome dissociation by dehydration and proton reaction between $[Fe(OH)_x(H_2O)_{6-x}]^{2-x}$ and $[H_2PO_4]^-$ or $[HPO_4]^{2-}$ complex compounds.

(2) The growth unit structures of various crystal faces are different and the favorable growth unit of the crystal-liquid interface boundary layer is supposed to be in keeping with those in the crystal face. The exposure degree of crystal face or the facet area ratio may bear on not only the growth rate along the direction but also the formation rate and the stability of favorable growth units of various faces at different solution conditions, such as pH, initial concentration and etc.

(3) The pH of the precursor solution has been confirmed to play an important role on the formation of various growth units of anionic coordination polyhedron, nucleation, morphology and crystal habit of the prepared $LiFePO_4$ particles under hydrothermal condition.

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