P-Fe alloy as anode materials for lithium ion batteries: a first-principles study

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Abstract. In this paper, based on first-principle plane wave method, P-Fe alloy interphases were studied as anode materials for lithium ion batteries. The results show that the incorporation of Fe can effectively reduce the lithium intercalation potential of P-Fe, improve the conductivity of P, and provide more lithium intercalation gap positions to enhance the specific capacity of the P-Fe alloy anode materials.

1. Introduction
Lithium ion battery has become the most important energy storage system\textsuperscript{[1-2]}. However, the capacity of the commercial graphite carbon anode material is close to its theoretical limit (372 mAh/g)\textsuperscript{[3]}, which restricting the further development of lithium-ion battery.

Phosphorus has a high theoretical specific capacity (Li\textsubscript{3}P is 2596 mAh/g)\textsuperscript{[4]}, however, due to the volume effect in the process of charging and discharging, and the poor conductivity of the Li-P compound, it shows poor cycle stability when used as anode material. Adding the second component to form P-M “active-active/inactive” system is considered as an effective solution, such as P-Fe system\textsuperscript{[5]}, P-Cu system\textsuperscript{[6]}, P-Ni system\textsuperscript{[7-8]} and P-Co system\textsuperscript{[9]}. However, due to the lack of mechanism research, great progress has not been obtained in the study of new phosphorus based anode.

In this paper, the first principle plane wave pseudo potential method\textsuperscript{[10-11]} based on the density functional theory is used. Using the CASTEP module in Materials Studio 6.0, the intermediate phase P-Fe alloy is used as the anode material of lithium-ion battery for molecular simulation design, and the comprehensive evaluation of the Fe doped modification of phosphorus anode is carried out.

2. Computation and Structure

2.1. Computation Method
The theoretical simulation involved in this paper adopts the CASTEP module in Materials Studio 6.0. The generalized gradient approximation (GGA) and the modified density functional of PW91 are used in the calculation. In order to obtain their local most stable structures, the BFGS method is used to optimize the geometry of the cells. In the self-consistent calculation, the cut band can be taken as 10 eV, and the k-point is taken as 1*1*1 grid point based on the Monkhorst-Pack method.
2.2. Structure Model

Table 1 the structure parameter and atoms’ sites of P-Fe alloy interphases

| Si-Fephase | Space group | atom | site | coordinate | SOF |
|------------|-------------|------|------|------------|-----|
| P$_2$Fe    | PNNM        | Fe   | 2a   | 0 0 0      | 1   |
|            |             | P    | 4g   | 0.165 0.361 0 | 1   |
| PFe        | PNMA        | Fe   | 4c   | 0.0019 0.25 0.2004 | 1   |
|            |             | P    | 4c   | 0.1915 0.25 0.5686 | 1   |
| PFe$_2$    | P-62M       | Fe   | 3f   | 0.256 0 0 | 1   |
|            |             | P    | 3g   | 0.594 0 0.5 | 1   |
|            |             | P    | 2c   | 0.3333 0.6667 0 | 1   |
|            |             | P    | 1b   | 0 0 0.5 | 1   |

According to ICSD 2009, the relatively stable P-Fe alloy phases are P$_2$Fe, PFe and PFe$_2$, ranking from the lowest to the highest Fe content.

The space group of P$_2$Fe phase belongs to PNNM, which is orthorhombic. The Fe and P atoms are in 2a and 4g positions respectively. The Fe atom occupies the vertex position (0, 0, 0), and the P occupies the coordinate position (0.165, 0.361, 0). According to the spatial symmetry distribution, the lattice constant is $a = 0.49732$ nm, $b = 0.56590$ nm, $c = 0.27235$ nm. The spatial group type of PFe alloy phase belongs to PNMA, the spatial group number is 62, the lattice constant is $a = 0.5191$ nm, $b = 0.3099$ nm, $c = 0.5792$ nm, also belongs to the orthorhombic, the atoms are in 4c position, the Fe atomic coordinates are (0.0019, 0.25, 0.2004), the P atomic coordinates are (0.1915, 0.25, 0.5686). The spatial group type of PFe$_2$ phase is P-62M, and the spatial group number is 189. It belongs to hexagonal system. Fe atom occupies 3f and 3g positions, P atom occupies 1b and 2c positions, Fe atom coordinates are (0.256, 0, 0) and (0.594, 0, 0.5), P atom coordinates are (0.3333, 0.6667, 0) and (0, 0, 0.5), and they are distributed according to symmetry. The lattice structure model is shown in Fig. 1 (a) (c) (e).

According to the kinetics of lithium intercalation, it can be considered that when lithium ion enters into the main material, it first occupies the position of octahedron, and then occupies the position of tetrahedron. If there is no displacement reaction to metal atoms, the lithium intercalation process ends. The lattice structure model after lithium ion intercalation is shown in Fig. 1.

![Structure model of the P-Fe alloy interphases before and after lithium intercalation](image)
The reaction between lithium ion and P-Fe alloy can be defined by equation (1), so the formation energy of intercalation can be calculated by equation (2). Equation (3) is used to calculate the volume expansion coefficient. V is the volume of the material after the lithium insertion, and V\(_0\) is the volume of the material before the lithium insertion. Equation (4) is used to calculate the theoretical lithium insertion capacity, where F is the Faraday constant, the geometric structure coefficient of the system, and M is the relative molecular weight of the negative material.

\[
P_{x}Fe_{z} + xLi^{+} = Li_{x}P_{x}Fe_{z} \quad (1)
\]

\[
E = -\frac{1}{x}[E_{\text{total}}(Li_{x}P_{x}Fe_{z}) - E_{\text{total}}(P_{x}Fe_{z}) - xE(Li_{\text{ion}})] \quad (2)
\]

\[
\eta = \frac{V - V_{0}}{V_{0}} \times 100\% \quad (3)
\]

\[
C = \frac{x \cdot F}{e \cdot M} \quad (4)
\]

\[
U \approx -\Delta E / \Delta x \quad (5)
\]

The lithium intercalation potential can be calculated by equation (5), which \(\Delta E\) refers to the change of total energy after lithium intercalation reaction, and \(\Delta x\) is the change of lithium intercalation capacity.

### 3. Computation Result and Analysis

Table 2 shows the calculation results of Li-P-Fe alloy intermediate phases in this paper, including total energy of the system, formation energy of lithium intercalation, volume before and after lithium intercalation, volume expansion coefficient, theoretical specific capacity and lithium intercalation potential. Among the electrochemical parameters mentioned above, the bulk expansion coefficient, intercalation potential and intercalation specific capacity related to volume expansion, open circuit voltage and endurance of the battery are mainly investigated.

Fig. 2 compares the volume expansion ratio and lithium intercalation potential of P-Fe alloy phase. It can be seen from fig. 2(a) that with the increase of Fe content, the volume expansion ratio of Li-P-Fe alloy phase shows an upward trend. For P\(_{2}\)Fe, the volume expansion ratio of Li-rich phase Li\(_{2}\)P\(_{2}\)Fe is only 85.4905\%, which is far lower than that of P, indicating that the incorporation of Fe is beneficial to reduce the volume effect of P. For Li\(_{2}\)PFe, its volume expansion ratio is as high as 156.4428\%, which is equivalent to Sn and has no practical value. When the lithium content of PFe\(_{2}\) reaches the maximum (x=4), its volume expansion coefficient also reaches 170.9187\%. However, considering the large lithium content and high capacity, based on the perspective of endurance capacity, it can be considered to be modified again in combination with other parameters.

Fig. 2 (b) shows the lithium intercalation potential comparison of three P-Fe phases. It can be seen from the results that with the increase of Fe content, the lithium intercalation potential of P-Fe shows a downward trend, indicating that the incorporation of Fe is conducive to the formation of transport channels in the material, the reduction of energy required for lithium ion intercalation, the reversible intercalation and removal of lithium ions, the avoidance of the formation of "dead lithium phase" \[12\].

| Phase    | Total energy (eV) | Formation energy(eV) | cell volume/10\(^{3}\)nm\(^{3}\) | Expansion ratio (%) | Capacity (mAh/g) | Lithium intercalation potential/V |
|----------|------------------|----------------------|-----------------------------------|---------------------|------------------|----------------------------------|
| P\(_{2}\)Fe | -1228.9437       | ---                  | 37.2480                           | ---                 | ---              | ---                              |
| Li\(_{2}\)P\(_{2}\)Fe | -1609.0257       | 2.0156               | 69.0915                           | 85.4905             | 454.2624         | 2.0156                           |
| PFe      | -1048.5551       | ---                  | 21.9805                           | ---                 | ---              | ---                              |
| Li\(_{2}\)PFe | -1428.4088       | 1.9041               | 56.3674                           | 156.4428            | 616.1260         | 1.9041                           |
| PFe\(_{2}\) | -1915.9028       | ---                  | 31.4284                           | ---                 | ---              | ---                              |
| Li\(_{4}\)PFe\(_{2}\) | -2671.8665       | 0.9668               | 85.1454                           | 170.9187            | 749.6918         | 0.9668                           |

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and the improvement of energy density of the battery. Among the three P-Fe phases, \( \text{Li}_4\text{PFe}_2 \) has the lowest potential value of 0.9668 V.

Fig. 2(c) shows the comparison of lithium intercalation capacity of the P-Fe phases. With the increase of Fe content, the lithium intercalation capacity of P-Fe is also on the rise, which shows that the incorporation of Fe is conducive to the increase of reversible lithium intercalation interstitial site and the increase of specific capacity. For \( \text{PFe}_2 \), the specific capacity of lithium-rich phase \( \text{Li}_4\text{PFe}_2 \) is 749.6918 mAh/g, which is more than twice the limit capacity of graphite.

![Fig.2 Volume expansion ratio, Li intercalation potential and specific capacity of P-Fe alloy interphases](image)

![Fig.3 Band structure and total density of states for P-Fe alloy interphases](image)

Fig. 3 shows the energy band structure and total density of states of P-Fe alloy. It can be seen from Fig. 3 that the energy band structure of the three P-Fe alloy phases intersects the conduction band and valence band at the Fermi level, all of which show metal characteristics. In addition, with the increase of Fe content, the crossing degree of valence band and conduction band near Fermi level becomes stronger, and the conductivity increases with the increase of Fe content. Therefore, the incorporation of Fe has a direct effect on improving the conductivity of P. According to the analysis of the crossing degree between the conduction band and the valence band near the Fermi level, \( \text{PFe}_2 \) show the strongest conductivity, and \( \text{PFe} \) is the second.

The density of states near Fermi level also reflects the same conclusion. With the increase of Fe content, the density of states near Fermi level of P-Fe alloy also increases, and shows a rapid growth trend. The density of state of \( \text{P}_2\text{Fe} \) at Fermi level is only about 0.5 electrons/eV, while that of \( \text{PFe} \) increases to 2.4 electrons/eV, and \( \text{PFe}_2 \) even exceeds 13 electrons/eV, showing strong conductivity.

Therefore, the incorporation of Fe to form "P-Fe" active-inactive system is an effective way to solve the poor conductivity of P.
4. Conclusion

In this paper, based on the first principle of Materials Studio 6.0, the CASTEP module is used to study the mechanism of lithium intercalation and deintercalation of P-Fe alloy as anode material of lithium-ion battery. The results are as follows:

1. With the increase of Fe content, the intercalation potential of P-Fe decreases, which indicates that the incorporation of Fe is conducive to the formation of transport channels in the material, the reduction of energy required for intercalation of lithium ions, the reversible intercalation and removal of lithium ions, and the improvement of energy density of the battery.

2. With the increase of Fe content, the lithium intercalation capacity of P-Fe is also on the rise, which shows that the incorporation of Fe is conducive to the increase of reversible lithium intercalation interstitial sites, and the increase of specific capacity of the anode material.

3. With the increase of Fe content, the conductivity of P-Fe alloy increases rapidly. Adding Fe to form "P-Fe" active-inactive system is an effective way to solve the poor conductivity of P.

Among the three P-Fe phases, Li$_4$PFe$_2$ shows the lowest lithium insertion potential of 0.9668 V, the specific capacity of 749.6918 mAh/g, which is more than twice the limit capacity of graphite. Therefore, PFe2 is the best one among the three P-Fe alloy phases. In addition, the volume expansion coefficient is 170.9187%. Therefore, further measures such as structure design and charge/discharge parameter control should be taken in the later stage, which is expected to meet the commercial requirements.

Acknowledgments

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