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

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Abstract. In this paper, based on the first principle method, the mechanism of lithium intercalation and deintercalation of P-Cu alloy as anode material of lithium-ion battery was studied. The results followed that the volume expansion coefficient of Li-P-Cu is small, 59.4650% for Li₂PCu₃ and 61.4071% for Li₂P₂Cu, indicating that the introduction of Cu can effectively inhibit the volume expansion of phosphorus. And PCu₃ is superior to P₂Cu in terms of volume expansion coefficient and lithium intercalation formation energy and good conductivity.

1 Introduction

Lithium ion battery has become an indispensable energy storage system[1-2]. However, the capacity of commercial anode materials is close to its theoretical limit (372mAh/g)[3-4], so it is difficult to make a big breakthrough in recent years.

Phosphorus based anode materials are popular because of their theoretical specific capacity of 2596 mAh/g[5-6]. However, due to the volume effect in the charging and discharging process[7], low conductivity and the hidden danger from high activity, they have not been commercialized. The formation of "P-M" binary system by adding the second component is regarded as an effective solution, such as P-Fe system[8], P-Cu system[9] and P-Ni system[10]. However, due to the lack of mechanism, the research progress is slow.

In this paper, the mechanism of intercalation and delithiation of P-Cu alloy as anode material of lithium-ion battery is deeply studied by first-principles method. The key parameters such as volume expansion coefficient, lithium intercalation formation energy and theoretical specific capacity are comprehensively analysed to find out the capacity loss mechanism and provide theoretical basis for experimental research.

2 Computation and Structure

2.1 Computation Method

All the molecular simulations in this paper are carried out by CASTEP module. The Schrodinger equation of single electron can be obtained by using functional variation to calculate the best form of single electron state.

$$\left[-\frac{\nabla^2}{2m} + V_{\text{ext}}(\vec{r}) + V_{\text{xc}}(\vec{r}) + V_{\text{eff}}(\vec{r}, r(\vec{r}))\right]\varphi_n(\vec{r}) = \varepsilon_n \varphi_n(\vec{r}) \quad (1)$$

$$\rho(\vec{r}) = \sum_n a_n |\varphi_n(\vec{r})|^2 \quad (2)$$

Here $-\frac{\nabla^2}{2m}$ is the effective kinetic energy, $V_{\text{ext}}(\vec{r})$ is the field potential, $V_{\text{xc}}(\vec{r})$ is the exchange correlation potential, $V_{\text{eff}}(\vec{r}, \rho(\vec{r}))$ is the effective potential, $\rho(\vec{r})$ is the electronic density of states, a_n is the number of internal electronic states.

Combined with the basic properties of materials, the generalized gradient approximation (GGA) and the modified density functional theory of PW91 are used in the calculation. The electron exchange correlation energy can be defined as a function of charge density and gradient.

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int f_{\text{xc}}[\rho(\vec{r}), |\nabla \rho(\vec{r})|] d\vec{r} \quad (3)$$

And 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

According to ICSD 2009, only PCu₃ and P₂Cu are stable alloy phases. The space type of PCu₃ is P-3C1, space group number is 165, and it is an orthorhombic hexahedral structure. Cu atoms occupy the positions of 2b, 4d and 12g, and the atomic coordinates are (0, 0, 0), (0.3333, 0.6667, 0.17) and (0.69, 0.07, 0.08). P atoms

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occupy the position of 6f, and the coordinates are ($x = 0.38, y = 0, z = 0.25$).

The phase space group type of P_2Cu alloy belongs to P21/C1, space group No.14, monoclinic system, PDF standard card No.18-452, all the atoms are located in 4e position, Cu atoms occupy the vertex position (0.14344, 0.46071, 0.41602), the coordinates of P occupied position are (0.24958, 0.7789, 0.6997) and (0.40648, 0.1139, 0.797), respectively, According to the spatial symmetry distribution, the lattice constants $a=0.58004nm$, $b=0.48063nm$, $c=0.75263nm$. The lattice structure model is shown in Fig.1(a)(c), and the lattice structure diagram after lithium intercalation is shown in Fig.1(b)(d).

Table 1. The structure parameter and atoms' sites of P-Cu alloy interphases.

Phase	Space	Atom	Site		
			x	y	z
PCu_3	P-3C1	Cu	0	0	0
		Cu	0.3333	0.6667	0.17
		Cu	0.69	0.07	0.08
		P	0.38	0	0.25
P_2Cu	P21/C1	Cu	0.14344	0.46071	0.41602
		P	0.24958	0.7789	0.6997
		P	0.40648	0.1139	0.58025

Fig. 1. Structure model of the P-Cu alloy interphases before and after lithium intercalation.

The lithium intercalation reaction of P-Cu alloy is defined by equation (4), and the lithium intercalation formation energy is calculated by equation (5). The volume expansion coefficient is calculated by equation (6). V is the volume after lithium intercalation, and V_0 is the volume before lithium intercalation. Equation (7) is used to calculate the theoretical lithium intercalation capacity, where F is the Faraday constant and M is the relative molecular weight material of negative ions. The lithium intercalation potential can be calculated by equation (8).

$$E = -\frac{1}{x}[E_{total}(Li_xP_yFe_z) - E_{total}(P_yFe_z) - xE(Li_{ion})] \quad (5)$$

$$\eta = \frac{V - V_0}{V_0} \times 100\% \quad (6)$$

$$C = \frac{x \cdot F}{\varepsilon \cdot M} \quad (7)$$

$$U \approx -\Delta E / \Delta x \quad (8)$$

3 Computation Result and Analysis

For Li-P-Cu alloy, the volume expansion coefficient is small. For Li_2PCu_3 , the volume expansion coefficient is only 59.4650%. For Li_2P_2Cu , the volume expansion coefficient is 61.4071%, which is slightly higher than that of graphite anode material. The theoretical specific capacity of P-rich phase P_2Cu is 427.1153 mAh/g. However, the lithium intercalation formation energy of Li_2PCu_3 is 2.36 eV, and that of Li_2P_2Cu is even as high as 2.9853 eV. According to the "dead lithium phase" theory, the high bond energy leads to the lithium ion can not be separated again in the subsequent discharge process, resulting in the loss of active lithium ion. Although P-rich phase P_2Cu has higher theoretical specific capacity, PCu_3 is superior to P_2Cu in terms of volume expansion coefficient and lithium intercalation formation energy.

Table 2. Total energy, formation energy, cell volume, relative expansion ratio, specific capacity and lithium intercalation potential for P-Cu alloy interphases

Samples	Total energy (eV)	Formation energy(eV)	cell volume/ $\times 10^{-3}$ nm ³	Expansion ratio (%)	Capacity (mAh/g)	Lithium intercalation potential/V
PCu ₃	-4614.4750	---	50.2983	---	---	---
Li ₂ PCu ₃	-4995.2458	2.36	80.2082	59.4650	241.9998	2.36
P ₂ Cu	-1838.4128	---	48.1755	---	---	---
Li ₂ P ₂ Cu	-2220.4288	2.9853	77.7587	61.4071	427.1153	2.9853

Fig. 2. Volume expansion ratio, Li intercalation potential of P-Cu alloy interphases.

(a)PCu₃ band structure

(c)P₂Cu band structure

(d)P₂Cu TDOS

Fig. 3. Band structure and total density of states for P-Cu alloy interphases.

In the band structure, the cross of the valence band and conduction band near the Fermi level represents the conductivity of the material. In the total density of states diagram, the density of states near the Fermi level also reflects the conductivity of the material. For the anode material of lithium-ion battery, the conductivity directly affects the transport characteristics of lithium ion in the material, directly affects whether the material has high rate of high current charge and discharge performance, and affects the impedance of the whole battery.

The band structures and density of states of the P-Cu alloy phases are showed in Fig.3. Fig. 3 (a) shows the band structure of PCu₃. The results show that there is a dense cross between conduction band and valence band near Fermi level, which shows the characteristics of conductor, indicating that PCu₃ has good conductivity. Fig. 3 (c) shows the band structure of P₂Cu. The results show that there is also a cross between conduction band and valence band near Fermi level, which shows the characteristics of conductor. However, the weak degree of cross-section indicates that the poor conductivity of P₂Cu. The same conclusion is obtained from the calculation of total density of states. From Fig.3(b), the total density of states (TDOS) of PCu₃ is about 7 electrons/eV at Fermi level, which shows conductor property and relatively good conductivity, while that of P₂Cu is near 1 electrons/eV from Fig.3(d), which shows poor conductivity. PCu₃ is the best choice when used as anode materials for lithium ion battery.

4 Conclusion

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

(1) The volume expansion coefficient of Li-P-Cu is small, 59.4650% for Li₂PCu₃ and 61.4071% for Li₂P₂Cu, indicating that the introduction of Cu can effectively inhibit the volume expansion of phosphorus.

(2) PCu₃ shows the characteristics of conductor with good conductivity, while P₂Cu shows poor conductivity.

(3) PCu₃ is superior to P₂Cu in terms of volume expansion coefficient and lithium intercalation formation energy and conductivity.

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