

First-principles Study on LiFePO₄ Materials for Lithium-ion Battery

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Abstract. In this paper, the band structure and density of states of LiFePO₄ are calculated by first principles. It is found that LiFePO₄ is a semiconductor with the band gap of 0.786 eV. The electrochemical properties of LiFePO₄ are mainly influenced by Fe element. The thermodynamic properties of cathode material LiFePO₄ for lithium ion battery were also studied. The entropy S, the specific heat capacity C and the enthalpy H of the LiFePO₄ increased with the increase of temperature and the Gibbs free energy G decreased with the increase of temperature in the paper.

1. Introduction

With the increasing demand of portable electronic products, rechargeable electric vehicles and other traffic equipment, lithium ion batteries have become the most widely used power batteries at present. It is also a hot spot in the research and industry all over the world. Compared with other cathode materials for lithium ion batteries, LiFePO₄ has high theoretical capacity, good cycling performance, stable performance and abundant raw materials. Moreover, LiFePO₄ become one of the first choices of lithium-ion power battery materials because of its Low cost, environmental protection and other advantages [1-4].

In order to improve the utilization of LiFePO₄ material, it is necessary to improve the electrochemical performance of this material. Researchers have done a lot of work in experiments [5-9]. However, the theoretical research of LiFePO₄ is also very important [10]. Therefore, we focus on the properties of LiFePO₄ electronic structure, so as to understand the electronic properties and some chemical bonds of LiFePO₄ materials in this paper. Furthermore, there is important guiding significance for improving the conductivity of and ion diffusivity of LiFePO₄ materials. The results of other researchers provide the conditions and basis for us to understand LiFePO₄ theoretically. Moreover, it can help us improve the performance of LiFePO₄ in theory. Recently, the first principle calculation method combined with molecular dynamics has made great contributions to the design synthetic simulation and performance evaluation of materials. And first principle calculation method

has become the core technology of the science of material computing. In this paper, we use the first principles to study LiFePO_4 materials from solid state physics.

2. Simulation and calculation

2.1. Structures

LiFePO_4 exists mainly in the form of lithium iron phosphate in nature. Its stereoscopic diagram is shown as shown in Figure 1. The crystal structure of LiFePO_4 is olivine type, and it has good regularity. And it is easy to form highly ordered lattice.

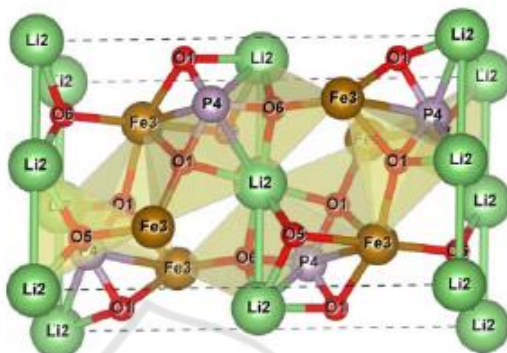


Figure 1. Stereoscopic diagram of LiFePO_4 .

As shown in Figure 1, LiFePO_4 crystal belongs to the $Pnma$ orthogonal space group. The oxygen atoms accumulate densely close to the six parties. And Fe and Li are respectively located 4C and 4A bits in octahedron center of O atom. This leads to the formation of FeO_6 octahedron and LiO_6 octahedron. P atom is located 4C bits in the central position of O atom tetrahedron. In this way, the PO_4 tetrahedron is formed. Li^+ parallel to the c axis forms a continuous linear chain in t 4aposition. And Li^+ moved along the c axis in two-dimensional diffusion. It can embed in charge and discharge process freely. Phosphoric acid has the function of supporting the whole material frame. It makes the material has good thermal stability and cycling performance.

The charge discharge process is carried out between LiFePO_4 and FePO_4 , and the cell parameters of LiFePO_4 are $a=10.6380 \text{ \AA}$, $b=5.9630 \text{ \AA}$, $c=4.5280 \text{ \AA}$. And the volume changes 6.8% during the charge discharge process. At the same time, in the process of lithium ion deintercalation, the crystal structure is not rearranged. It maintains olivine structure. Therefore, LiFePO_4 has excellent cycle performance.

2.2. Structure optimization

The coordinate parameters and are shown in Table 1.

Table 1. Lattice parameters (SpaceGroup: $Pnma$, SG Number: 63, Crvst Sys: orthorhombic).

	atom	x	y	z
1	Li	0	0	0
2	Fe	0.2820	0.250	0.9734
3	P	0.0951	0.250	0.4187
4	O1	0.0922	0.250	0.744
5	O2	0.4547	0.250	0.211
6	O3	0.1626	0.0477	0.2844

After geometric optimization, the most stable structure of LiFePO₄ can be obtained. The parameters of LiFePO₄ crystal after optimization are shown in Table 2. The cell volume increased from 287.231 Å³ to 267.211 Å³.

Table 2. Lattice parameters before and after optimization.

a(Å)		B(Å)		C(Å)	
Pre optimization	After optimization	Pre optimization	After optimization	Pre optimization	After optimization
10.6380	9.8856	5.9630	5.7932	4.5280	4.6658

3. Results and analysis

The band structure and the density states of cathode material LiFePO₄ for lithium ion batteries are calculated. As seen in figures 2 and 3, LiFePO₄ shows the characteristics of semiconductors. And the band gap of is 0.768eV, which is greater than reports of S.Q. Shi [11-12].

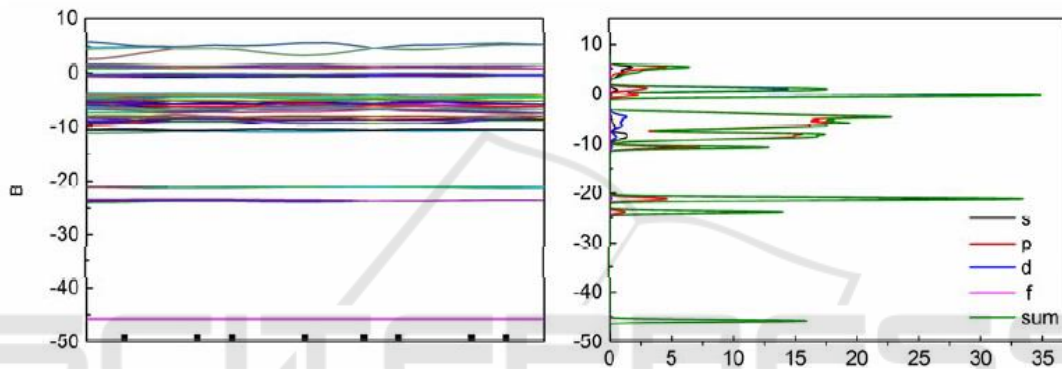


Figure 2. Total Energy band and Density of States of LiFePO₄.

The valence band is mainly composed of the electron on p orbit of O and d orbit of Fe below Fermi surface. FeO₆ octahedron is formed at the same time. The conduction band above Fermi surface is mainly contributed of electrons on d orbital of Fe.

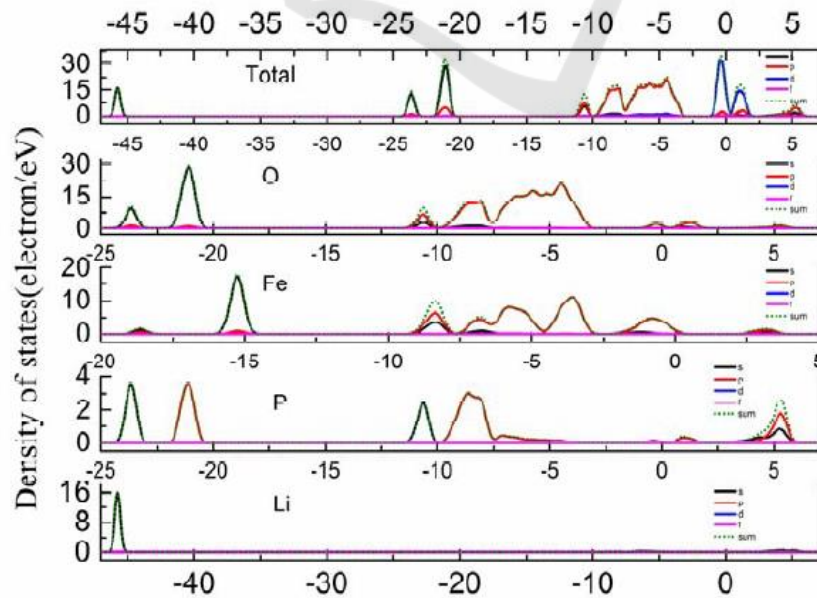


Figure 3. Density of States of Li atoms, P atoms, O atoms, Fe atoms.

Figure 3 indicates that the electrochemical properties of LiFePO_4 are mainly affected by Fe atom. The contribution of electron on s orbital of Li near Fermi level is very small. The conduction band between 2.5eV and 7eV is mainly contributed by the electron on p orbital of Li and electron on p orbit of Fe. But its effect is very weak, which mainly affects the conductivity of LiFePO_4 . But the effect is

Table 3. The thermodynamic properties of LiFePO_4 .

Temperature (T)	Entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	Specific heat capacity ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	Enthalpy ($\text{kJ} \cdot \text{mol}^{-1}$)	Gibbs free energy ($\text{kJ} \cdot \text{mol}^{-1}$)
100	55.671	128.7426	0.25485	0.24928
125	90.3546	183.6702	0.25876	0.24746
150	128.394	234.2802	0.264	0.24473
175	167.958	279.2034	0.27043	0.24103
200	207.8664	318.4902	0.27791	0.23633
225	247.401	352.7622	0.28631	0.23064
250	286.1544	382.7628	0.29551	0.22397
275	323.904	409.1766	0.30542	0.21634
300	360.528	432.5538	0.31594	0.20779
325	395.9886	453.3354	0.32702	0.19833
350	430.2732	471.8742	0.33859	0.188
375	463.407	488.4684	0.3506	0.17682
400	495.4152	503.349	0.363	0.16483
425	526.3398	516.726	0.37575	0.15206
450	556.2228	528.7674	0.38883	0.13853
475	585.1062	539.6328	0.40218	0.12426
500	613.0404	549.4482	0.4158	0.10928
525	640.0674	558.3396	0.42965	0.09361
550	666.2292	566.3994	0.44371	0.07728
575	691.572	573.7242	0.45796	0.06031
600	716.1294	580.3938	0.47239	0.04271
625	739.9476	586.4754	0.48698	0.02451
650	763.0602	592.0278	0.50171	0.00572
675	785.5008	597.114	0.51657	-0.01364
700	807.303	601.776	0.53156	-0.03355
725	828.4962	606.06	0.54666	-0.054
750	849.1098	610.0038	0.56186	-0.07497
775	869.169	613.6368	0.57716	-0.09645
800	888.7074	616.9884	0.59254	-0.11842
825	907.7418	620.0922	0.608	-0.14088
850	926.2932	622.965	0.62354	-0.16381
875	944.391	625.632	0.63915	-0.18719
900	962.052	628.11	0.65482	-0.21102
925	979.293	630.4158	0.67056	-0.23529
950	996.135	632.562	0.68634	-0.25998
975	1012.5906	634.5696	0.70218	-0.2851
1000	1028.6808	636.4428	0.71807	-0.31061

very weak, which mainly affects the conductivity of LiFePO₄. The low energy level lies between -40 and -45eV, mainly composed of electron on s orbit of Li atom.

The thermodynamic properties are calculated at 1 atmospheric pressure. The thermodynamic temperature is 100 to 1000K. And it is measured once each interval of 25K. Thermodynamic data of LiFePO₄ is shown in Table 3. The Gibbs free energy G, entropy S, heat capability C and enthalpy H of LiFePO₄ changed with temperature respectively according to the calculation results shown in Table 3.

At the same time, Entropy S and enthalpy H of LiFePO₄ increase with the increase of temperature, while Gibbs free energy G decreases with the increase of temperature, which is in accordance with thermodynamic law. Gibbs free energy of LiFePO₄ decrease slowly at the beginning. After 250K, Gibbs's free energy decreased linearly with the increase of temperature. The entropy of LiFePO₄ increases linearly with temperature. The enthalpy of LiFePO₄ changed slowly at the beginning stage, and the enthalpy increased rapidly with temperature after 300K. The heat capability increases fast with temperature before 300K. And the heat capability increases with temperature slowly after 300K.

4. Conclusions

In this paper, the electronic structure and thermodynamic properties of LiFePO₄ for lithium ion batteries cathode materials were calculated by first principles calculations based on density functional theory. LiFePO₄ exhibits the characteristics of semiconductors by calculating the band structure and density states of LiFePO₄. The entropy S and enthalpy H of LiFePO₄ increase with the increase of temperature, while the Gibbs free energy G decreases with the increase of temperature, which is consistent with the thermodynamic law. The microstructure and thermodynamic parameters of lithium ion battery cathode material LiFePO₄ obtained in the paper can provide theoretical guidance for the practical application of lithium ion batteries.

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