JOURNALOF

Ceramic Processing Research

Influence of calcined temperatures on the microstructure and electrochemical properties of LiFePO₄/C nano-particles with a core-shell structure and It's thermal stability study

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Influence of calcined temperatures on the microstructure and electrochemical properties of LiFePO₄/C nano-particles as well as it's thermal stability were studied using HRTEM, XRD, electrochemical workstation and TGA. The results indicated that when calcined at 973 K, the LiFePO₄/C nano-particles consisted of a well-crystalline LiFePO₄ core with size of 58.6-80.1 nm and an amorphous carbon shell with thickness of 2 nm. With the increase of calcined temperature, the electrochemical properties of LiFePO₄/C materials increased first and then decreased, it reached maximum when temperature equaled to 973 K. The initial discharge capacity of the sample was 142 mAh/g, the discharge capacity of it maintained 132 mAh/g with capacity retention of 93.0% after 40 cycles. The decomposition reaction of LiFePO₄/C material calcined at 973 K occurred at 938.38-1194.52 K under 10 K \cdot min⁻¹ in N₂ atmosphere and corresponded to approximately 5.8% of the total weight. The decomposition mechanism of it consisted of three stages: the first stage was controlled by gas diffusion in carbon shell; the second stage was controlled by chemical reaction and gas diffusion; the third stage was controlled by chemical reaction.

Key words: LiFePO₄/C nano-particles, Microstructure, Electrochemical properties, Thermal stability.

Introduction

Olivine structured LiFePO₄ has been studied extensively since it was first reported as a promising cathode material for rechargeable lithium ion batteries [1]. Compared with other cathode materials, LiFePO₄ exhibits the strong advantages of low toxicity, high theoretical capacity $(170 \text{ mAh} \cdot \text{g}^{-1})$, low cost, high reversibility and repeatability [2]. Problems persist, however; specifically, LiFePO4 is an insulator, which seriously limits its rate capability in lithium cells. This compound exhibits strong electrochemical properties only at low charge/discharge rates due to its low electronic conductivity and low lithium ion mobility [3, 4]. In recent years, it was reported that coating with carbon to prepare a core-shell structure and minimizing the particle size of LiFePO₄ are effective methods to improve the power performance of LiFePO₄ [5-7]. Therefore, LiFePO₄/C nano-particles with a core-shell structure have attracted considerable attention and have been synthesized in various ways [8-12].

Carbon used in LiFePO₄/C materials has been carbonized by adding reactants in a synthesized process, such as sugar [13], glucose [14] and polyaniline [15].

E-mail: gaopengzhao7602@126.com (P.Gao) liuwei2013@tsinghua.org.cn (W.Liu) However, these carbon precursors may not carbonize sufficiently at temperatures suitable for synthesizing LiFePO₄/C materials. Therefore, the improperly calcined temperature may result in an insufficiently carbonized of the carbon precursors as well as produce the impurity as LiFePO₄ (triphylite), FePO₄ (heterosite), Li_xFePO₄ in the aimed material [16, 17]. The undesirable compositions would occur complex reactions during the charge/discharge process to reduce the electrochemical properties of LiFePO₄/C nano-particles. Thus, the calcined temperatures plays an important role in the electrochemical properties of LiFePO₄/C materials as well as in its microstructure and composition [18, 19].

In the present paper, influence of calcined temperatures on the microstructure and electrochemical properties of LiFePO₄/C nano-particles as well as it's thermal stability were studied using HRTEM, XRD, electrochemical workstation and TGA. Some interesting results were obtained.

Experimental Process

Raw materials

LiFePO₄/C nano-particles were prepared according to Ref [20]. The calcined temperatures of it ranged from 773 to 1273 K in a N_2 atmosphere with an interval of 100 K, and held 3 h at each of the temperatures, respectively. The obtained particles were labeled as A, B, C, D, E and F as calcined temperatures increased.

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Microstructure characterization

Phase identification of LiFePO₄/C nano-particles calcined at different temperatures were determined by X-ray diffraction (XRD, D5000, Siemens) using nickel filtered Cu K_a radiation produced at 30 kV and 30 mA. The scanning speed was 2 ° \cdot min⁻¹.

The microstructure of LiFePO₄/C nano-particles calcined at different temperatures were characterized by high resolution transmission electron microscopy (HRTEM, JEM-3010).

The cell comprised a lithium metal electrode and a LiFePO₄/C electrode were separated by a micro-porous polypropylene separator. To make LiFePO₄/C electrode, 80 wt% sample, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) were mixed together with N-methyl-2 pyrolidone solvent. Then the obtained slurry was deposited uniformly onto an Al foil. After drying the filmed Al foil at 393 K for 12 h under vacuum, the dried filmed Al foil, worked as cathode, was cut into disks with a diameter of 1.3 cm for assembling coin-type cell. The electrolyte was 1 molL⁻¹ LiPF₆ dissolved in ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) in a molar ratio of 1 : 1 : 1. The test cells were assembled in an argon-filled dry glove box.

Electrochemical performances of the samples were performed on Land-CT2001A (Land, Wuhan, China) automatic battery test system at different current densities in a voltage range of 2.2-4.2 V at 298 K. It was necessary to point out that the electrochemical tests were carried out using active materials with the same weight.

The thermal stability, decomposition kinetics and mechanisms of LiFePO₄/C nano-particles calcined at 973 K were studied using thermogravimetric analysis (TGA) in N₂ atmosphere with a flow rate of 30 ml \cdot min⁻¹ and heating rates of 5, 10, 15 and 20 K \cdot min⁻¹ from room temperature to 1273 K. TGA was performed using a TGA-DSC thermal analyzer (STA 449C, Netzsch Thermische Analyser) with alumina powder as the reference sample.

Model-free kinetics^[21]

Model-free kinetics is based on an iso-conversional computational technique that calculates the effective activation energy (E_{α}) as a function of the conversion (α) of a chemical reaction, $E = f(\alpha)$. Conversion (α) , temperature (T) and time (t) are the three factors influencing the reaction rate of a chemical reaction. The reaction rate represented as function of conversion $f(\alpha)$ is different for each process and must be determined experimentally. The model-free kinetics is a computer program option based on the Vyazovkin and Flynn-Wall-Ozaw theory.

In their approach, no model is applied. The data in this approach is gathered during numerous experiments.

The approach follows all points of conversion from multiple experiments instead of a single one. The theory is based on the assumption that

$$\frac{d\alpha}{dt} = k(T)f(a) \tag{1}$$

where $f(\alpha)$ represents a reaction rate equation, k(T) is the Arrhenius rate constant and the activation energy E_a is constant for a certain value of conversion α (this is called iso-conversional method). Taking the reaction rate equation and dividing by the heating rate b = dT/dt, one obtains:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \Rightarrow \frac{d\alpha}{dT} = \frac{k}{\beta}f(\alpha)$$
(2)

where da/dt is the reaction rate (s⁻¹), *k* is the velocity constant (s⁻¹), *a* is the conversion and β is the heating rate (K · s⁻¹). Substituting *k* by the Arrhenius expression $k = k_0 \cdot e^{-E/RT}$ and rearranging gives:

$$\frac{1}{f(\alpha)}d\alpha = \frac{k_o}{\beta}e^{-E_RT}dT$$
(3)

Integrating up to conversion α (at the temperature *T*) gives:

$$\int_{0}^{a} \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{k_{o}}{\beta} e^{-E/RT} dT$$
(4)

Because E/2RT >> 1, the temperature integral can be approximated by:

$$\int_{T_0}^T e^{-E/RT} dT \approx \frac{R}{E} \cdot T^2 \cdot e^{-E/RT}$$
(5)

Substituting the temperature integral, rearranging and taking the natural log, one obtains the Vyazovkin equation:

$$\ln \frac{\beta}{T_{\alpha}^{2}} = \ln \left[\frac{Rk_{\alpha}}{E_{\alpha}g(\alpha)} \right] - \frac{E_{\alpha}1}{RT_{\alpha}}$$
(6)

Equation (4) can be rearranged as

$$g(\alpha) = \frac{k_o}{\beta} \int_{T_0}^T e^{-E/RT} dT = \frac{k_o E}{\beta R} \int_{\infty}^{\mu} \frac{-e^{-u}}{u^2} du = \frac{k_o E}{\beta R} \cdot P(u)$$
(7)

where

$$u = \frac{E}{RT} dT = \frac{E}{Ru^2} dt$$

According to the Doyle approximation, one obtains:

$$1gP(u) = -2.315 - 0.4567 \frac{E_{\alpha}}{R} \frac{1}{T_{\alpha}}$$
(8)

Combining equations (7) and (8), one obtains the Flynn-Wall-Ozaw equation:

$$1g\beta = 1g\left[\frac{K_0 E_\alpha}{Rg(\alpha)}\right] - 2.315 - 0.4567\frac{E_\alpha}{R}\frac{1}{T_\alpha}$$
(9)

Equations (6) and (9) are defined as dynamic equations, which are used for the determination of the activation

energy for all conversion values (α).

Results and Discussion

Composition of LiFePO₄/C nano-particles calcined at different temperatures

XRD patterns of LiFePO₄/C nano-particles calcined at different temperatures and standard LiFePO₄ (JCPDS 40-1499)-olivine structure exhibited in Figure 1.

From the figure, it can been seen clearly that the main diffraction peaks of LiFePO₄/C nano-particles were all in good accordance with the standard LiFePO₄ crystal when samples were calcined below 973 K. There were no carbon diffraction peaks in these patterns, which indicated that the carbon derived from PANI was amorphous [20]. Using Jade 5 software to estimate the crystallite size of LiFePO₄/C nano-particles, the results was 34.5 nm when sample was calcined at 773 K, 36.6 nm at 873 K and 43.1 nm at 973 K, respectively.

With an increase of calcined temperatures, the main phase of samples D and E was still an olivine structure, while the intensities of corresponding peaks increased and their widths narrowed, indicating that the crystal size of LiFePO₄ increased. In addition, very weak diffraction peaks of Fe₃(PO₄₎₂ and Li₃P can be observed, which indicated that slight impurity existed in sample D and E. When calcined temperature reached 1273 K (sample F), all peaks weaken dramatically, and the peaks of LiFePO₄, Li₃PO₄, Li₃P, FePO₄ and Fe₂O₃ were detected. Combined with Ref [22-25], we suggest that the possible decomposition reactions were as follows:

$$3 \text{ LiFePO}_{4}(s) \rightarrow \text{Fe}_{3}(\text{PO}_{4})_{2}(s) + \text{Li}_{3}\text{P}(s) + 2\text{O}_{2}(g)$$
(1073 and 1173 K) (10)

$$12 \text{ LiFePO}_{4}(s) \rightarrow 2 \text{ Li}_{3}\text{PO}_{4}(s) + 2 \text{ Li}_{3}\text{P}(s) + 8\text{FePO}_{4}(s) + 2\text{Fe}_{2}\text{O}_{3}(s) + \text{O}_{2}(g) (1273\text{K})$$
(11)

Microstructure of LiFePO₄/C nano-particles calcined at different temperatures

TEM images of LiFePO₄/C nano-particles calcined at different temperatures were shown in Figure 2.

The figure illustrated that each primary LiFePO₄ crystallite (black) was completely coated by a carbon shell (gray) to form a core-shell structure (Fig.2-a₂,c₂ and e_2), where the carbon shell was derived from the carbonization of PANI [20]. In addition, the thickness of shell decreased from about 10 nm (a_2) to 2 nm (c_2) when calcined temperatures increased from 773 to 973 K, however, it increased to about 5 nm (e₂) when calcined temperature reached 1173 K. Also, the combination of carbon shell with LiFePO₄ crystallite changed compacter first $(a_2 \text{ to } c_2)$ and then incompact $(c_2 \text{ to } e_2)$. The first change was resulted from the more and more completely carbonization degree of PANI [20], and the second change may derived from the emission of decomposed product (as O₂, XRD results in Figure 1) as well as the mismatch of thermal expansion coefficient of carbon and LiFePO₄.

It also can be seen that all the size of these LiFePO₄/ C particles ranged from 18.2 to 80.1 nm, and shape of it ranged from globular to abnormal cubic shape with well dispersion in Fig.2.a₁, c_1 , e_1 .

Galvanostatic charge/discharge measurements of $LiFePO_4/C$ nano-particles calcined at different temperatures

Initial charge/discharge curves of LiFePO₄/C nanoparticles calcined at different temperature at 0.1 C rate were shown in Figure 3.

Form the figure, it can be seen clearly that the $LiFePO_4/C$ nano-particles calcined at 973 K (sample C) possessed the best charge/discharge properties. The flat part of its voltage profiles was longest than that of other samples, which indicated that the polarization of it was small [26]. The flat part of voltage profiles of sample D was longer than that of sample A, sample B and E owned similar voltage profiles, flat parts of the two samples both were shorter than that of sample A. Voltage profiles of sample F exhibited a very short flat.

The initial discharge capacity of the sample C exhibited the highest value of 142 mAh/g, higher than that of 135 mAh/g calcined at 1073 K (sample D), 116 mAh/g at 773 K (sample A), 113 mAh/g at 873 K



a LiFePO₄; b Fe₃(PO₄)₂; c Li₃P; d FePO₄; e Fe₂O₃; f Li₃PO₄

Fig. 1. XRD patterns of LiFePO₄/C nano-particles calcined at different temperatures.



a Sample A; c Sample C; e Sample E

Fig. 2. TEM images of LiFePO₄/C nano-particles calcined at different temperatures.

(sample B), 110 mAh/g at 1173 K (sample E) as well as 94 mAh/g at 1273 K (sample F).

As we know that the charge/discharge property of LiFePO_4 was mainly affected by its electronic conductivity and lithium ion diffusivity rate. The carbon shell, existed on the outer surface of LiFePO_4 crystallite, can connect with each other to form an electric conductivity rate of LiFePO_4 nano-particles. With the increase of carbonization temperature, the carbon shell changed compacter first to improve the electronic conductivity rate of LiFePO_4/C nano-particles, and then it became loose to reduce the electronic conductivity

rate of this kind of materials [27].

While, the carbon shell also exhibited a negative effect for lithium ion diffusivity rate of $LiFePO_4/C$ nano-particles as the lithium ion threaded loose shell more easier than that of a dense one. Moreover, the electrolyte can easily infiltrate through loose shell to contact with $LiFePO_4$ to increase the lithium ion diffusivity rate. In addition, both the crystalline degree of $LiFePO_4$ as well as existed impurity can lower the lithium ion diffusivity rate.

For these factors abovementioned, we can see that LiFePO₄/C nano-particles calcined at 1173 K (sample D) and 773 K (sample A), owned loose carbon shell, had higher lithium ion diffusivity rate, so it exhibited flatter and longer voltage profiles compare with that of sample B, E and F. While LiFePO₄/C nano-particles calcined at 973 K (sample C) crystallized sufficiently, and coated with high electronic conductivity carbon shell, it exhibited flattest and longest voltage profiles.

Cyclic charge/discharge measurements LiFePO₄/C nano-particles calcined at different temperatures

The first forty discharge capacities of LiFePO₄/C nano-particles calcined at different temperatures at 0.1 C rate were shown in Figure 4.

From the figure, it can be see clearly that the sample calcined at 973 K (sample C) delivered the highest discharge capacity, the value was 142 mAh/g. After 40 cycles, the discharge capacity of it maintained 132 mAh/g, with a capacity retention of 93.0%, which displayed a good cyclic stability. The sample calcined at 1073 K (sample D) owned the second highest discharge capacity. After 40 cycles, the discharge capacity of it maintained 121 mAh/g, with a capacity retention of 92.0%, which displayed relatively good cyclic stability. However, the sample calcined at 773 K delivered the least discharge capacity and its capacity decreased rapidly with cycling, which derived from the imperfect crystalline of LiFePO₄.

As calcined temperature plays an important role on the microstructure as well as electrochemical properties of LiFePO₄/C nano-particles, also the LiFePO₄/C nanoparticles calcined at 973 K exhibited the excellent



Fig. 3. Initial charge/discharge curves of LiFePO₄/C nano-particles calcined at different temperature at 0.1 C rate.



Fig. 4. Cyclic curve of LiFePO₄/C nano-particles calcined at different temperatures at 0.1 C rate.

electrochemical properties. Next step, the thermal stability as well as the decomposed kinetics and mechanism of the material were studied systemly.

Thermal stability of LiFePO₄/C nano-particles calcined at 973K

Figure 5 showed TG-DTG and DSC curves of LiFePO₄/C nano-particles calcined at 973K with a heating rate of 10 K \cdot min⁻¹. From TG-DTG curves, it can be clearly observed that with an increase of temperature, the weight loss process of LiFePO₄/C

nano-particles was divided into three stages. The first stage occurred in the range from room temperature to 598.29 K and was due to the loss of physically adsorbed water, gas, etc.; it corresponded to ca. 1.5% of the total weight of the sample. The second stage occurred at 598.29-938.38 K and was related to the decomposition and evaporation of the chemical bonds of water; it corresponded to approximately 1.9% of the total weight of the sample [28]. The third stage occurred at 938.38-1194.52 K and was derived from the decomposition of LiFePO₄/C and corresponded to ca. 5.8% of the total weight of the sample. The TG curve of the sample showed an increasing trend for a slight oxidation of the decomposition products, where the O₂ was from the decomposition reaction of LiFePO₄ and small amounts from impurities in N₂.

From the DSC curve, we observed that before 1145.83 K, the decomposition process of LiFePO₄/C exhibited an endothermic trend, and it reached a minimum at 889.50 K. Beyond this temperature, the oxidation reaction resulted in an exothermic trend [30].

Decomposed kinetics and mechanism of LiFePO₄/C nano-particles calcined at 973K

Model-free kinetics requires at least three dynamic curves with different heating rates. In the present study, there were four heating curves with heating rates of 5,







Fig. 5. TG-DTG and DSC curves of LiFePO₄/C nano-particles calcined at 973 K.



Fig. 6. TG and DTG curves of LiFePO₄/C nano-particles calcined at 973 K with different heating rates.

	$5 \text{ K} \cdot \text{min}^{-1}$		10 K • min ⁻¹		15 K • min ⁻¹		$20 \text{ K} \cdot \text{min}^{-1}$	
α/%	T/K	da/dT	T/K	da/dT	T/K	$d\alpha/dT$	T/K	da/dT
10	916.95	0.181	917.95	0.156	1003.75	0.185	1019.15	0.179
15	945.55	0.250	944.15	0.136	1027.35	0.242	1044.35	0.259
20	968.35	0.176	962.15	0.197	1045.75	0.304	1061.95	0.323
25	984.35	0.532	977.35	0.239	1060.55	0.401	1076.55	0.367
30	993.35	0.546	990.15	0.308	1072.15	0.473	1090.95	0.381
35	1002.75	0.495	1001.15	0.323	1082.75	0.480	1104.15	0.380
40	1013.75	0.512	1011.15	0.382	1093.35	0.475	1117.15	0.401
45	1022.75	0.578	1019.95	0.418	1103.75	0.513	1129.15	0.448
50	1030.55	0.676	1027.95	0.459	1113.75	0.498	1140.55	0.453
55	1038.75	0.524	1035.75	0.494	1123.95	0.489	1151.75	0.473
60	1048.15	0.574	1043.55	0.544	1134.55	0.484	1161.75	0.573
65	1056.15	0.657	1051.35	0.603	1144.95	0.475	1170.35	0.615
70	1063.75	0.599	1060.15	0.643	1156.55	0.404	1178.35	0.642
75	1072.55	0.586	1069.35	0.639	1168.35	0.461	1186.55	0.603
80	1080.95	0.583	1079.35	0.642	1179.55	0.460	1195.55	0.535
85	1090.95	0.402	1090.95	0.553	1190.75	0.427	1206.35	0.439
90	1106.35	0.164	1104.95	0.514	1204.15	0.343	1219.55	0.314

Table 1. T and $d\alpha/dT$ corresponding to different conversion α under different heating rates.



Fig. 7. E_{α} of the decomposition reaction of LiFePO₄/C nanoparticles calcined at 973 K as a function of α using model-free methods.

10, 15, and 20 K \cdot min⁻¹ shown in Fig. 5. As mentioned above, the thermal decomposed process of LiFePO₄/C nano-particles mainly occurred between 938.38-1194.52 K, when heating rates were 10 K \cdot min⁻¹. Because the heating rate would affect the initial and final temperatures of the decomposition reaction, temperature ranges between 900 and 1250 K were chosen for model-free kinetics calculations.

Table 1 showed data of decomposed reaction of $LiFePO_4/C$ nano-particles obtained from TG-DTG curves in Figure 6.

In accordance with model-free kinetics, for each conversion α , $\ln b/T_a^2$ was plotted versus $1/T_\alpha$ for the Vyazovkin method and $\ln b$ was plotted versus $1/T_a$ for the F-W-O method, giving a straight line with the slope $-E_\alpha/R$. Therefore, the activation energy was obtained as

a function of conversion α .

Figure 7 presented the E_{α} of the decomposition reaction of LiFePO₄/C nano-particles calcined at 973 K as a function of conversion *a*. It can be clearly observed that the value of E_{α} increased first, followed by a plateau, then further increased. It reached a maximum value (81.93 kJ · mol⁻¹) when α equals was 90% and a minimum value (63.77 kJ · mol⁻¹) at the beginning of the decomposition reaction.

Vyazovkin et al. [30-32] have studied the phenomena and proposed the concept of variable activation energy, which is a compromise between the actual complexity of solid state reactions and oversimplified methods of describing their kinetics. They label the variable E_{α} as "effective E_{α} " and propose that the process with variable activation energy not only involves chemical reactions but also physical processes, such as sublimation, adsorption, desorption, diffusion of gaseous products, etc. The variation of activation energy on the extent of conversion is attributed to the relative contribution of each single-step process. Therefore, the effective activation energy of a solid state reaction is generally a composite value determined by the activation energy of various processes and by their influence on the overall reaction rate.

Combining the XRD results in Figure 1 and the data in Figure 6, it was concluded that the decomposed process of LiFePO₄/C primarily consisted of two elementary steps of chemical reaction and gas diffusion. Therefore, the effective E_{α} of LiFePO₄/C decomposition reaction was a composite value (Fig. 6) determined by the E_{α} of the two single-step processes and by their influence on the overall oxidation rate, as follows (12) [21]:

$$\beta \frac{d\alpha}{dT} = f_c(\alpha) k_c(T) + f_d(\alpha) k_d(T)$$
(12)

Where, subscript c and d stand for chemical reaction and gas diffusion, respectively.

According to the dependence of E_{α} on a obtained by the Vyazovkin and F-W-O model-free methods, the decomposition mechanisms of LiFePO₄/C were obtained.

In the first stage of the LiFePO₄/C decomposition process ($\alpha \le 25\%$), an ascending trend of E_{α} indicated a complex process. In this step, although the chemical reaction rate was small for a lower temperature, it was difficult for the decomposed gas (O₂) to diffuse through the dense carbon shell to the environment. In this condition, gas diffusion had an important influence on the whole reaction rate ($f_c(a)k_c(T)$ equals near zero). Therefore, the decomposition process of LiFePO₄/C nano-particles was mainly controlled by the gas diffusion in the carbon shell and the corresponding E_{α} was approximately 63.77 kJ · mol⁻¹.

As the decomposition process proceeds, the dense carbon shell was slightly torn due to the oxidation reaction of the decomposition product with carbon, as well as the decreasing combination of the LiFePO₄ core and the carbon shell. Small cracks were produced in carbon shell gradually. The result was that the O_2 diffuses through the carbon shell more easily than before. At the same time, an increasing temperature led to an increase in the chemical reaction rate. Therefore, the chemical reaction showed an increasing influence on the whole decomposition process of LiFePO₄/C nano-particles. As the E_{α} of the chemical reaction was larger than that of gas diffusion [21], the value of E_{α} apparently increased. Namely, as the conversion a and temperature increased, the influence of the chemical reaction rate on the whole decomposition process increased, which results in an increase in the activity energy.

In the second stage $(25\% < \alpha < 50\%)$, as the temperature increased, the chemical reaction rate increased. At the same time, O₂ diffused through the carbon shell more easily than before because more small cracks were produced in the carbon shell. The integrity of carbon shell wasnot destroyed too much for the small weight loss of LiFePO₄ and the less gaseous product O₂. In this condition, chemical reaction and gas diffusion show similar influences on the whole decomposition process, and a plateau trend of E_{α} was observed. Namely, the decomposition process of LiFePO₄/C nano-particles was controlled by the chemical reaction and gas diffusion together, and the corresponding E_{α} was approximately 74.5 kJ · mol⁻¹.

In the third stage $(50\% < \alpha)$, with the increase in conversion, acute decomposition of LiFePO₄ and reaction of O₂ with carbon produce many cracks in the carbon

shells such that gaseous products can easily diffuse across it. Additionally, due to the non-isothermal heating process, the chemical reaction rate increases rapidly with an increase in temperature. In this condition, the value of E_{α} indicates an increasing trend with a and the decomposition process of LiFePO₄/C nano-particles was mainly controlled by chemical reaction. The maximum value of E_{α} (84.23 kJ · mol⁻¹) lay when a was 90%. Small wave propagation of $E_{\dot{a}}$ (shown in Fig. 6) derives from the change of the decomposition reaction (see equations 10 and 11).

Conclusions

1. Below 973K, with the increase of calcined temperatures, LiFePO_4/C nano-particles consisted of a crystallized LiFePO_4 core and an amorphous carbon shell, also the carbon shell became more and more compacter as the carbonization degree of PANI increased; Above 973 K, with the increase of calcined temperatures, LiFePO_4 begun to decompose and the carbon shell became looser;

2. When calcined at 973K, the obtained LiFePO₄/C consisted of a well-crystalline LiFePO₄ core with size of 58.6-80.1 nm and an amorphous carbon shell with thickness of approximately 2 nm;

3. With the increase of calcined temperature, the electrochemical properties of $LiFePO_4/C$ nano-particles increased first and then decreased, it reached maximum value when temperature equaled to 973 K. The initial discharge capacity of the sample was as high as 142 mAh/g in the potential range of 2.2-4.2 V. The cyclic performances of it delivered the highest discharge capacity, after 40 cycles, the discharge capacity maintain 132 mAh/g with capacity retention of 93.0%;

4 The decomposition reaction of LiFePO₄/C occurred at 938.38-1194.52 K under 10 K \cdot min⁻¹ in N₂ atmosphere and corresponded to approximately 5.8% of the total weight loss. The decomposition mechanism of LiFePO₄/C nano-particles was divided into three stages. The first stage ($\alpha \le 25\%$) was primarily controlled by gas diffusion in the carbon shell and the corresponding E_{α} was approximately 63.77 kJ \cdot mol⁻¹; the second stage (25% < α < 50%) was controlled by chemical reaction and gas diffusion together, and the corresponding E_d was approximately 74.5 kJ \cdot mol⁻¹; the third stage (50% < α) was primarily controlled by chemical reaction, and the maximum value of E_{α} (84.23 kJ \cdot mol⁻¹) lay when a was 90%.

Acknowledgments

This work is supported by the Planning of the Growth of Young Teachers (Hunan University China), the Science and Technology Planning Project of Hunan Province, China (2012WK3023) and the Science and Technology Planning Project of Changsha City, Hunan Province, China (K1109117-11).

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