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Excessive Iron Source on the Structural and Electrochemical Properties of $LiFePO_4$/C Composite

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Abstract. $LiFePO_4$ is one of the most promising cathode materials for lithium ion battery, especially those used in electrical vehicles and hybrid electrical vehicles. However, its very poor rate performance caused by its low electronic and ionic conductivity limits the wide utilization in high power lithium ion battery. Iron phosphides, such as FeP and Fe_2P, were reported to have positive effect on the improvement of the rate performance. In order to improve the electrochemical properties, $LiFe_{1+x}PO_4$/C (x = 0-0.1) composite with various contents of iron phosphides was synthesized by adding different amount of iron source during a sol-gel process. The amount of iron phosphides increased with the increase of iron source. Electrochemical performance showed that the samples with 1% iron source in excess had better rate performance than the $LiFePO_4$/C sample synthesized with stoichiometric iron source. However, the overall samples with excessive iron source showed relatively low specific discharge capacity. Hence, some balance between the rate capability and discharge capacity should be found and the amount of the in-situ formed iron phosphides should be optimized.

Introduction

Currently, $LiFePO_4$ proposed by Goodenough and co-workers [1] has received intensive attention due to its potential use as a next-generation cathode material for lithium-ion battery in applications such as power tools, electric vehicles (EVs) and hybrid electric vehicles (HEVs). It has many advantages in comparison with conventional cathode materials, such as low cost, environmental benignity and thermal stability. Meanwhile, the poor electronic conductivity (~ 10^{-9} S cm^{-1}) and lithium ion diffusion coefficient (~ 1.8×10^{-14} cm^2 s^{-1}) at room temperature pose a bottleneck for commercial applications. Various approaches have been introduced to improve the poor rate performance, either by surface coating the $LiFePO_4$ particles with carbon [2, 3] or by doping the material [4]. At the same time, synthesis techniques such as hydrothermal, solid-state, sol-gel, and mechanochemical methods have been refined to optimize the active material with good crystallinity, small particle size and uniform particle size distribution.

Herle et al. [5] reported that the nanonet work (or its amorphous phase) of metallic compound, iron phosphide Fe_2P, formed during the doping process led to an increase in conductivity of seven orders of magnitude in the bulk composite phase. Compared to the semiconductive amorphous carbon derived from organic carbon source, Fe_2P is a metal and can play a major role in the improvement of the bulk conductivity of $LiFePO_4$. Iron phosphides were prone to form at high sintering temperature [6] in the presence of organic carbon, due to the carbon thermal reduction, and in reducing sintering atmospheres [7, 8]. In the current study, some other condition for the formation of iron phosphides was investigated. The amount of iron phosphides (FeP and Fe_2P) were quantified by Rietveld analysis and its influence on the electrochemical properties of $LiFePO_4$ was studied.

Experimental

The $LiFePO_4$ cathode material was prepared by a sol-gel method using $FeC_2O_4{\cdot}2H_2O$ (ferrous oxalate), $LiNO_3{\cdot}2H_2O$ (lithium nitrate), and $NH_4H_2PO_4$ (dihydrogen ammonium phosphate) as the starting materials. Ethylene glycol was applied as carbon source. Mixtures of $FeC_2O_4{\cdot}2H_2O$, $NH_4H_2PO_4$ and $LiNO_3{\cdot}2H_2O$ with molar ratio of (1+x):1:1, where x was 0.01, 0.03 and 0.1, were dissolved in an aqueous solution of ethylene glycol to prepare the carbon coated $LiFePO_4$. The molar ratio of ethylene glycol to metal cations was kept at unit. The resulting solutions were heated at 110 ºC in order to obtain gels. Subsequently, the gels were dried firstly at 120 ºC for 24 h and then sintered at 700 ºC for 10 h in a mixture atmosphere of nitrogen with 5 vol.% of hydrogen. The synthesized products were ground with a mortar and pestle for microstructural characterization and electrochemical properties testing.

The phase identification of the synthesized samples was carried out by X-ray diffraction (Thermo ARL X' TRA), using Cu Kα radiation (λ = 1.54 Å). XRD data collected by step-scanning method with a step interval of 0.02° and a count time of 1s per step were analyzed by Rietveld analysis. The surface morphologies and composition of the samples were observed by a field emission scanning electron microscope (Sirion-100, Philips-FEI). The carbon content of the samples was analyzed by a Flash EA1112 (ThermoFinnigan) element analyzer.

The electrochemical performance of $LiFePO_4$ was evaluated using CR2025 coin-type cells. Laminated electrode was prepared by spreading the N-methyl methyl-pyrrolidone slurry containing 83 wt.% active material (the synthesized product), 5 wt.% Kynar poly-vinylidene fluoride (PVDF) binder (Atofina, USA), 6 wt.% synthetic graphite (Super P, Timcal Ltd.) and 6 wt.% acetylene black onto an aluminum foil current collector, and then dried at 120 °C overnight. The active materials loading on the cathode was between 3 mg and 4 mg on 1.54 cm^2 current collector area. Coin cells were assembled in an argon-filled glove box. Lithium metal was used as counter electrode and a solution of 1 M $LiPF_6$ in 1:1 ethylene carbonate/dimethyl carbonate (EC/DMC) was used as electrolyte. Cells were cycled galvanostatically at constant current rates with a voltage region of 2.5-4.2 V vs. Li/Li^+ at room temperature. The calculation of specific capacity of the synthesized samples includes all the phases formed along with $LiFePO_4$, such as the residual carbon from the organic compound and iron phosphides.

Results and Discussion

Figure 1 displays the XRD patterns of the $LiFe_{1+x}PO_4/C$ (x = 0-0.1) samples synthesized with excessive iron source. Table 1 lists the lattice parameters and phase abundance of $LiFe_{1+x}PO_4$ derived from Rietveld analysis. It can be seen that when the iron source are 0.01 and 0.03 in excess, the samples contain about 94 wt.% of $LiFePO_4$ and a little amount of FeP and Fe_2P, which is similar to the sample synthesized with stoichiometric iron source. When the iron source is 0.1 in excess, FeP disappears and much more amount of Fe_2P appears, about 11 wt.%. It can be seen from Table 1 that the excess of iron source has almost no influence on the lattice parameters of $LiFePO_4$. The carbon content of the samples was about 1.5 wt.%, which indicates that the amount of carbon-coating is decided by carbon source and has almost no relation with the carbon in the ferrous oxalate.

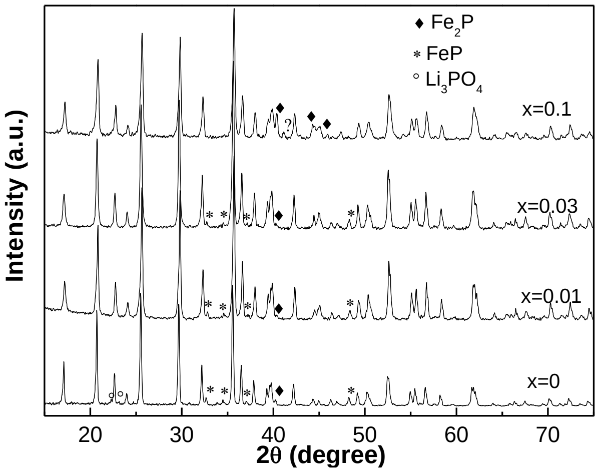

Figure 1 XRD patterns of the $LiFe_{1+x}PO_4$/C (x = 0-0.1) samples

Table 1 Lattice parameters and phase abundance of $LiFe_{1+x}PO_4$ derived from Rietveld analysis

$LiFe_{1+x}PO_4$ x	Lattice parameters				Phase abundance * (wt.%)			
	a (Å)	b (Å)	c (Å)	Cell vol. (Å ^{3})	$LiFePO_4$	FeP	Fe_2P	Li_3PO_4
0	10.319	6.003	4.692	290.6	94.0	3.7	1.3	1.0
0.01	10.317	6.002	4.693	290.6	94.1	4.4	1.5	/
0.03	10.308	5.999	4.690	290.0	94.8	3.2	2.0	/
0.1	10.311	6.005	4.695	290.7	89.0	0	11.0	/

*Goodness of fitting is 3.1-3.4

SEM results reveal that the morphology of the $LiFe_{1+x}PO_4$ samples with x=0, 0.01, 0.03 is similar and the SEM image of the sample synthesized with stoichiometric iron source is shown in Fig. 2(a). It can be seen that most of the $LiFePO_4$ particles are weakly connected. When the iron source is 0.1 in excess, more small bright fragments can be seen in the sample, which might be due to the increasing amount of iron phosphides. And the agglomeration of the particles becomes severer.

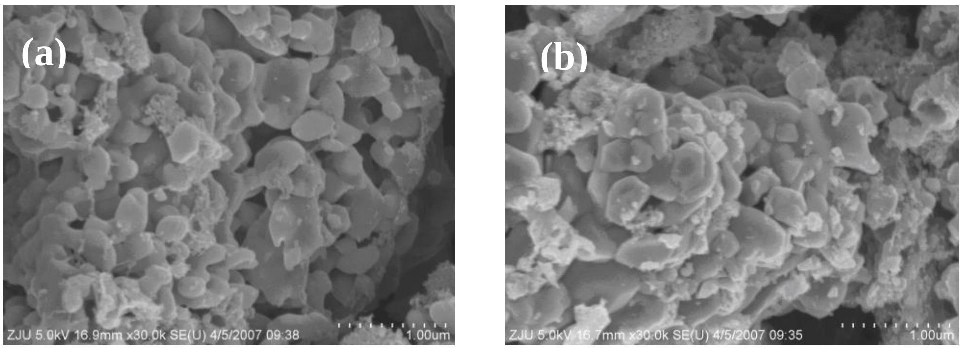

Figure 2 SEM images of $LiFe_{1+x}PO_4$ with excessive contents of iron source: (a) x=0; (b) x=0.1

Figure 3 shows the discharge capacity of the $LiFe_{1+x}PO_4$/C samples at various rates. When discharged at 0.1C, the $LiFe_{1+x}PO_4$ samples with x=0, 0.01 and 0.03 have capacities of 143mAh/g, 140 mAh/g and 125 mAh/g, respectively. While discharged at 1C and 5C, they show similar capacity, about 100 mAh/g and 70 mAh/g, respectively. However, the $LiFe_{1+x}PO_4$ samples with x=0 and 0.01 show relative larger capacity when discharge rate increases to 10 C and 15 C. It can also be seen from Fig. 3 that the $LiFe_{1+x}PO_4$ sample with x=0.1 shows the lowest discharge capacity at various rates. However, its decreasing extent becomes smaller at 15C, which may reveal the slight improvement in kinetics.

Combined with the SEM and XRD results analysized above, it can be derived that the poor high rate performance of the $LiFe_{1+x}PO_4$ sample with x=0.03 may due to the particle agglomeration and relative small amount iron phosphides. The slight improvement in kinetics of the sample with 0.1 iron source excess at 15 C may be mainly ascribed to the fact that it contained relatively more amount of Fe_2P, which enhances the utilization to $LiFePO_4$. Nevertheless, too much iron source in excess could easily lead to the agglomeration of $LiFePO_4$ particles and the increasing amount of non-electrochemical active material, which decrease the electrochemical capacity, especially at low discharge rate. It can be deduced that a little excess of iron source in the synthesis of $LiFePO_4$ can improve its high rate performance.

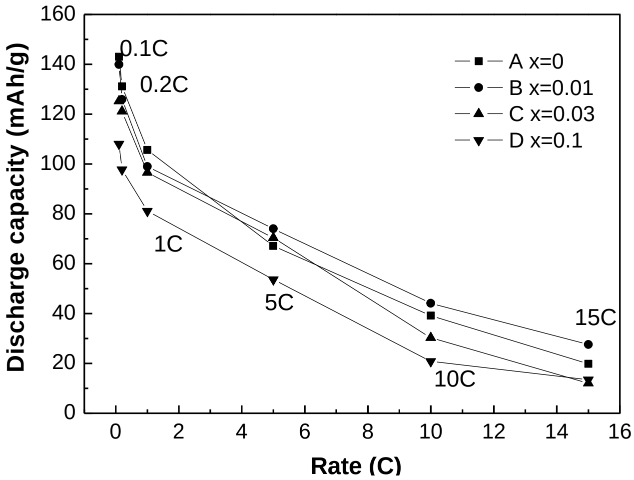

Figure 3 Discharge capacity of the synthesized $LiFe_{1+x}PO_4/C$ samples at various rates

Summary

$LiFe_{1+x}PO_4/C$ (x = 0-0.1) composite with different contents of iron phosphides was synthesized by adding different amount of iron source during a sol-gel process using ferrous oxalate as iron source and ethylene glycol as carbon source. When iron source was stoichiometric and 1-3% in excess, the obtained samples contained 5-6 wt.% iron phosphides and had similar morphology where particles were weakly connected. When iron source was 10% in excess, the agglomeration of the particles became severer and the amount of iron phosphides was about 11 wt.%. The electrochemical results showed that 1% iron source in excess in the synthesis of $LiFePO_4$ can improve the high rate performance, while too much iron source in excess decreased the capacity due to severe agglomoration and large amount of non-electrochemically active material.

References

[1] A.K. Padhi, K.S. Nanjundaswamy and J.B. Goodenough: J. Electrochem. Soc. Vol. 144 (1997), p. 1188

[2] X.L. Li, W.D. Wang, C.W. Shi, H. Wang and Y. Xing: J. Solid State Electrochem. Vol. 13 (2009), p. 921

[3] Y.B. Guan, F. Wu, Y. Bai and C. Wu: New Carbon Mater. Vol. 24 (2009), p. 359

[4] Y. Lu, J.C. Shi, Z.P. Guo, Q.S. Tong, W.J. Huang and B.Y. Li: J. Power Sources Vol. 194 (2009), p. 786

[5] P.S. Herle, B. Ellis, N. Coombs and L.F. Nazar: Nat. Mater. Vol. 3 (2004), p. 147

[6] Y.B. Xu, Y.J. Lu, L. Yan, Z.Y. Yang and R.D. Yang: J. Power Sources Vol. 160 (2006), p. 570

[7] Y.H. Rho, L.F. Nazar, L. Perry and D. Ryan: J. Electrochem. Soc. Vol. 154 (2007), p. A283

[8] Y. Lin, M.X. Gao, D. Zhu, Y.F. Liu and H.G. Pan: J. Power Sources Vol. 184 (2008), p. 444