Journal of Alloys and Compounds 688 (2016) 386-391

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

LSEVIER journa

Effect of excess Li⁺ in solution on LiFePO₄ preparation via wet chemical method



^a Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China
^b School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, PR China

ARTICLE INFO

Article history: Received 25 April 2016 Received in revised form 21 June 2016 Accepted 3 July 2016 Available online 5 July 2016

Keywords: Lithium iron phosphate Lithium ion battery Wet chemical method Excess Li⁺ Impurity

ABSTRACT

Olivine structure LiFePO₄ has attracted much attention as a promising cathode material for lithium ion batteries, and many approaches have been developed to produce electrochemically active LiFePO₄ at low cost. Here lithium iron phosphate (LiFePO₄) was prepared via co-precipitation method by using FeS- $O_4 \cdot 7H_2O$, LiOH $\cdot H_2O$, and $o-H_3PO_4$ as the raw materials. The effects of Li:Fe:P molar ratios and solution pH value on the synthesis of LiFePO₄ were studied. The results illustrated that besides of the pH value parameter which was reported in many other previous researches, excess Li⁺ in the solution was another essential condition for pure LiFePO₄ preparation. It suggested that excessive LiOH was not only a pH regulator, but also a precipitation promoter. Maintaining a certain excess Li⁺ ion in solution was an efficient measure to avoid the formation of impurities.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, lithium ion battery has become the basis of the huge market for cellular phones and lap top computers, and these mobile communication markets continues to grow at a rapid rate. Even so, intensive efforts are still under way to further improve the technology. The main target of the effort is not only the electric automobile industry by achieving higher energy and higher power, but also the chemical energy storage, which are becoming increasingly important for future environmentally friendly societies, by using rechargeable lithium-ion batteries. Since the pioneering work of Goodenough in 1997 [1], lithium iron phosphate (LiFePO₄) was found to be a particularly attractive cathode material for lithium-ion batteries due to its low cost, nontoxic, high lithium intercalation voltage, high theoretical specific capacity and greater thermal stability [2,3]. Nevertheless, it has suffered with its inherent low electronic conductivity and low lithium diffusion kinetics, which seriously prevent it from being used on a large-scale. Up to now, progressive efforts to eliminate this obstacle by carbon coating on the particle surface [4], developing composites via mixing conductive materials [5], aliovalent cation substitution [6], particle size mini-mization [5], and customizing particle morphologies [7] have been undertaken.

Conventionally, LiFePO₄ powders are prepared by solid-state synthesis with their associated repeated grinding and a long period of high temperature operations. However, this approach has some conspicuous disadvantages such as large particle size, broad particle size distribution, and impurities. In contrast, wet chemical preparation routes, such as hydrothermal [8,9], solvothermal [10,11], sol-gel [12,13], emulsion-drying [14,15] and coprecipitation [16,17] have an indisputable advantage over solid-state reactions in achieving better homogeneity and mixing the starting compounds on the molecular level. Generally, for the wet chemical routes of LiFePO₄ synthesis, it is commonly believed that intermediate precipitates, i.e. $Fe_3(PO_4)_2 \cdot 8H_2O$ and Li_3PO_4 , will be yielded in the initial preparation stage [17,18], and LiFePO₄ will be formed after the following heat treating as equation (1).

$$Fe_3(PO_4)_2 \cdot 8H_2O + Li_3PO_4 = 3 LiFePO_4 + 8H_2O$$
 (1)

According to equation (1), it can be seen obviously that obtaining an equimolar ratio of $Fe_3(PO_4)_2 \cdot 8H_2O(s)$ and $Li_3PO_4(s)$ is a basic prerequisite for preparing pure LiFePO₄. Even so, sometimes it is still difficult to avoid the formation of impurities such as Li_3PO_4 [19,20], $Fe_3(PO_4)_2$ [19] and Fe_2O_3 [21–23] due to the complex physical chemistry properties of the solution system. In general, inactive impurities will decrease the specific capacity of the







^{*} Corresponding author. E-mail address: zhaozw@csu.edu.cn (Z. Zhao).



Fig. 1. XRD patterns of precursors which were synthesized under the conditions of LiOH 0.3 mol L^{-1} , Li:Fe:P molar ratio1:1:1 and labeled as a, b, c, and d, according to different pH values 5.2, 7.3, 8.7, and 10.2, respectively.

material and cause a lower the energy density. It is well known that the formation of impurity phases closely linked to the preparation process of the samples. For example, Liu et al. [24]reported that LiFePO₄ just have been prepared by hydrothermal method at pH value from 6.3 to 9.04, but not at pH value 5.4 and 11.04. Coincidentally, Lee and coworkers' [25] research showed that pure LiFePO₄ was synthesized at pH value 6.5 and 9.22; LiFePO₄, iron oxide and Li₃PO₄ coexisted at pH value 10.62; and a mix of iron oxide (Fe₃O₄) and lithium phosphate (Li₃PO₄) was obtained at pH value 14.32.

Besides the pH value parameter, in our previous thermodynamic study [26], we found that the molar ration of Li^+ :Fe²⁺:PO₄³⁻ in

solution also played an important role for the formation of LiFePO₄ via precipitation method. Therefore, in order to validate this theory predicts, this work concerned with synthesis of LiFePO₄ by coprecipitation, and the emphasis focused on the effects of molar ratio Li:Fe:P and solution pH on LiFePO₄ preparation. Furthermore, the precipitation process of the LiOH-FeSO₄-H₃PO₄-H₂SO₄-H₂O system was also studied, aiming at a better understanding of the precipitation characteristics.

2. Experimental

LiFePO₄ powders were synthesized via co-precipitation method, followed by sintering at 700 °C by using the FeSO₄·7H₂O(A.R. China), LiOH·H₂O(A.R., China), and o-H₃PO₄ (A.R., China) as the starting materials. The co-precipitation process was carried out in a 250 ml three-necked flask equipping with a magnetic stirrer, a thermometer and a pH electrode. Firstly, in order to avoid oxidation of Fe²⁺ to Fe³⁺, the reactants FeSO₄·7H₂O, *o*-H₃PO₄ and proper ascorbic acid were premixed in the three-necked flask containing 100 ml of deionized water. LiOH was also dissolved with 50 ml of deionized water and then added to the previously prepared solution of FeSO₄ \cdot 7H₂O and o-H₃PO₄. The whole processes were carried out under nitrogen atmo-sphere, and the pH value of the solutions was adjusted by 0.1 mol L^{-1} NH₃·H₂O and/or 0.1 mol L^{-1} H₂SO₄. After stirring at room temperature for 2 h, the precipitates were collected by filtration and washed several times with deionized water and alcohol, respectively. The resulting precipitates were mixed with a certain amount of glucose solution. Then the slurry was dried at 60 °C for 8 h in a vacuum oven, and subsequently calcined at 400 °C for 4 h and then sintered at 700 °C for 10 h in nitrogen atmosphere.

X-ray diffraction (XRD) profiles of the sample were measured with TTR-III (Cu K α radiation, Rigaku Corporation) at a speed of 4°/min. The particle morphology was observed by SEM (JXA–8800R, JEOL Ltd.).



Fig. 2. SEM images of the precursors prepared at various pH values: (a)- 5.2, (b)-7.3, (c)-8.7, and (d)-10.2, respectively



Fig. 3. XRD patterns of LiFePO₄ which were labeled as a, b, c, and d, according to different pH values 5.2, 7.3, 8.7, and 10.2 sintered at 700 °C, respectively. (Symbols: ∇ - JCPDS 49-1087 > Graftonite Fe₃(PO₄)₂; \diamond -JCPDS 39-0341 > Sarcopside Fe₃(PO₄)₂).

3. Results

Fig. 1 showed the X-ray diffraction profiles of precipitates synthesized under the conditions of 25 °C, LiOH concentration 0.3 mol L⁻¹, Li: Fe: P molar ratio 1:1:1, pH values 5.2–10.2, drying temperature 60 °C for 8 h in a vacuum oven. It can be seen that at acid conditions, just a single phase of $Fe_3(PO_4)_2 \cdot 8H_2O(JCPDS 30-0662)$ was obtained from the precursor solution. With the pH value increasing from 5.2 to 10.2, the diffraction intensities of (110), (020), (200), (130) peaks belonging to $Fe_3(PO_4)_2 \cdot 8H_2O$ became weaker. In contrast, diffraction intensities of the (020), (101), (021) peaks of Li₃PO₄ phase (JCPDS 15-0760), were generated and became stronger.

Fig. 2 showed the SEM images of the precursors yielded at various pH values. Obviously, the particle morphology changed along with the pH values. At pH = 5.2, the precursor was characterized by thin layers, arranged in alternating and overlapping planes, spreading out radially as a flower corolla (Fig. 2a). With the pH values increasing, the particle was still like a flower corolla, but its "leaves" changed from the "thin layers" to a thicker strips (at pH 7.3, Fig. 2b), and then turned into fusiformis-plate-like crystals (at pH 8.7, Fig. 2c). When the pH value was 10.2, the particles became randomly shaped(Fig. 2d).

The XRD patterns of the LiFePO₄ samples which were sintered at



Fig. 5. XRD patterns of LiFePO₄ samples synthesized under the conditions of 25 °C, LiOH 0.3 mol L⁻¹, and molar ratio Li:Fe:P = 1:1:3 (pH values: a-5.1, b-7.3, c-9.1, and d-11.3, ∇ -Fe₃(PO₄)₂; **□**-Fe₂O₃; **◊**-Li₂CO₃).

700 °C in N₂ atmosphere for 10 h by using the precursors in Fig. 2 as raw materials were shown in Fig. 3. From the X-ray diffraction results, it can be seen that the peaks of the samples synthesized at pH = 5.2 can be indexed as a well-crystallized Fe₃(PO₄)₂ phase, and the space group of the $Fe_3(PO_4)_2$ transformed from $P2_1/c$ (Graftonite-type [27], JCPDS No. 40-1087) to P2₁/a space group (Sarcopside-type [28,29], JCPDS No.39-0341) with the pH value increasing from 5.2 to 7.3. For the phase transformation of Fe₃(PO₄)₂, it can be attributed to the different crystal form of $Fe_3(PO_4)_2 \cdot nH_2O$ precursor. At neutral and slightly basic solution, vivianite $Fe_3(PO_4)_2 \cdot 8H_2O(Space group C 2/m)$ is a stable solid phase in FeSO₄-H₃PO₄-H₂O system. While it will convert to phosphoferrite Fe₃(PO₄)₂·3H₂O (Space group *Pbna*) in an acid environment, which possesses a large domain of stability [30]. Furthermore, with the pH value increasing to 10.2, the X-ray diffraction peaks (020), (011), (131) belonging to LiFePO₄ appeared, and yet containing large amounts of Fe₃(PO₄)₂ impurity. The results seemed to contradict with the general view that pure LiFePO₄ can be synthesized at neutral or slightly basic conditions [26,31,32].

To this confusion, it can be explained by using the solubility product principle. For Li₃PO₄, its dissolution reaction can be expressed as equation (2), with its solubility product constant $K_{sp1} = 3.2 \times 10^{-9}$, which is much larger than that of Fe₃(PO₄)₂·8H₂O ($K_{sp2} = 1.0 \times 10^{-36}$, Eq. (3)). Under acid conditions, phosphate is mainly existed in the form of H₃PO₄ and/or H₂PO₄. For example, at



Fig. 4. Photographs of various precursors prepared at pH values: a-5.1, b-7.3, c-9.1, and d-11.3, respectively (LiOH concentration 0.3 mol L⁻¹, Li:Fe:P molar ratio 1:1:3).



Fig. 6. XRD patterns of LiFePO₄ as-prepared under conditions of LiOH 0.9 mol L^{-1} , and Li:Fe:P = 3:1:1(pH values: (a)- 4.5, (b)-6.7, (c)- 8.9, and (d)-10.6; ∇ -Fe₃(PO₄)₂; \Box -Fe₂O₃; \diamondsuit -Li₂CO₃).

pH 5.0, H₂PO₄ is estimated dominant with 99.23% molar occupancy while only 7.9 × 10⁻⁸% of phosphate is in the form of PO₄³⁻ (calculated from dissociation equilibrium of phosphoric acid: $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 4.8 \times 10^{-13}$). Therefore, the amount of PO₄³⁻ in the solution is insufficient for the precipitation of Li₃PO₄, but sufficient for Fe₃(PO₄)₂·8H₂O precipitation.

$$Li_{3}PO_{4} = 3Li^{+} + PO_{4}^{3-}, \quad K_{sp1} = \left[Li^{+}\right]^{3} \left[PO_{4}^{3-}\right] = 3.2 \times 10^{-9} \quad (2)$$

$$\begin{split} & Fe_3(PO_4)_2 \cdot 8H_2O = 3Fe^{2+} + 2PO_4^{3-} + 8H_2O, \quad K_{sp2} \\ & = \left[Fe^{2+}\right]^3 \left[PO_4^{3-}\right]^2 = 1.0 \times 10^{-36} \end{split} \tag{3}$$

As we know from the above discussion and Eq. (1), obtaining equimolar ratio of $Fe_3(PO_4)_2 \cdot 8H_2O(s)$ and $Li_3PO_4(s)$ is a basic prerequisite for preparing pure LiFePO₄ via co-precipitation method. In order to obtain pure LiFePO₄ product, the key is to improve the precipitation rate of Li_3PO_4 which will react with $Fe_3(PO_4)_2 \cdot 8H_2O$ to form LiFePO₄ in the subsequent heat treatment. One of the measures is to increase the PO_4^{3-} concentration to ensure that Li^+ ions can be precipitated completely.

The photographs of the precipitation prepared at the conditions of LiOH concentration 0.3 mol L⁻¹, Li:Fe:P molar ratio 1:1:3 at various pH values were shown in Fig. 4. The results revealed that the color of the precursors changed from gravish (pH = 5.1), to darkolivegreen (pH = 7.3), to dark green (pH = 9.1), and then to brick red(pH = 11.3) after washing. It proved the existence of Fe(OH)₂ in the basic reaction solution, and it was easily oxidized to Fe(OH)₃ during the washing procedure. Furthermore, the X-ray diffraction profiles of precursors sintered at 700 °C were shown in Fig. 5. The results indicated that a mixture of Sarcopside-type of Fe₃(PO₄)₂ and LiFePO₄ was obtained at pH 5.1–7.3. With the pH values increasing, diffraction intensity of the impurity $Fe_3(PO_4)_2$ phase were becoming weaker, pure and well-crystallized LiFePO₄ was obtained at pH = 9.1. However, a mixture of Fe₂O₃, Li₃PO₄ and LiFePO₄ was obtained at strong basic conditions (pH = 11.3). It can be attributed to the hydrolysis of $FeSO_4 \cdot 7H_2O$ to $Fe(OH)_2$ or Fe(OH)₃ at high pH, and the hydroxides Fe(OH)₂ and Fe(OH)₃ are easily converted to Fe₂O₃ or Fe₃O₄. Obviously, the XRD results were consistent with that of the photographs results listed in Fig. 4.

Nevertheless, pure and single phase of LiFePO₄ powders just was prepared at a narrow pH range after adopting the measure of increasing the H_3PO_4 concentration. Actually, taking the equation (2) into consideration, it can be observed that increasing the Li⁺



Fig. 7. SEM images of LiFePO₄ samples prepared at different pH values: (a)- 4.5, (b)-6.7, (c)- 8.9, and (d)-10.6.



Scheme 1. The process of chemical reaction in co-precipitation synthesis.

concentration may be more efficient. For example, when the Li⁺ concentration increase 10 times, the product value of $[\text{Li}^+]^3 \times [\text{PO}_4^{3-}]$ will increase by an exponent of three, i.e. 1000 times, which is much bigger comparing with the case of increasing the concentration of H₃PO₄ (10 times). So when the concentration product of Li⁺ and PO₄³⁻ becomes above the critical value of K_{sp1} , the reaction (2) is balanced to keep equilibrium by encouraging the reaction from the right to the left side, and then accelerate the Li₃PO₄ precipitation.

Fig. 6 showed the XRD patterns of particles obtained after the LiOH concentration being improved from 0.3 mol L^{-1} to 0.9 mol L^{-1} , with the molar ratio Li:Fe:P = 3:1:1. The results demonstrated that both LiFePO₄ and Fe₃(PO₄)₂ were discovered at pH 4.5. In addition, the impurities Fe_2O_3 and Li_3CO_3 were yielded under strong basic solution (Fig. 6d). Remarkably, a single phase and well-crystallized LiFePO₄ sample was obtained at pH 7–9 (Fig. 6b and c), indicating an efficient improvement on Li₃PO₄ precipitation via maintaining an excess of LiOH in the solution. Furthermore, the SEM images of the samples was displayed Fig. 7, with diamond-shaped particles being those of LiFePO₄. It can be seen that the particle morphology changed depending on the solution pH values. At pH = 4.5, the morphology of the particles was random-irregular, no diamondshaped one was discovered (Fig. 7a). It could be attributed to mixed crystal phenomenon by LiFePO₄ and Fe₃(PO₄)₂, i.e. in the sintering process, the intermediates Fe₃(PO₄)₂·8H₂O and Li₃PO₄ will react with each other to form LiFePO₄ phase, and the excess $Fe_3(PO_4)_2 \cdot 8H_2O$ will dehydrate to generate $Fe_3(PO_4)_2$. Because LiFePO₄ and Fe₃(PO₄)₂ have different crystalline structures, and both of them can be regarded as an impurity for each other. So it is easy to occur a crystal form blending and inhibit the growth and formation of LiFePO₄ and Fe₃(PO₄)₂ crystals, resulting a randomirregular morphology of the particles. With the pH value increasing to 6.7, the morphology of the samples became diamondshaped, and the surface of the particles was smooth, indicating a good crystallization (Fig. 7b). In the case of pH = 8.9, the morphology still kept a diamond shape, but by contrast the particle

surface was rough (Fig. 7c).

4. Discussion

In the prior literature, researches synthesized LiFePO₄ via coprecipitation route or other solution chemistry method constantly emphasised that pure LiFePO₄ only can be prepared at neutral or slightly basic conditions. Therefore, the molar ratio of the starting materials which contain Li, Fe, P resources was always to be LiOH:Fe²⁺:H₃PO₄ = 3:1:1. Under this conditions, triple amount of LiOH can react with H₃PO₄ completely, obtaining a neutral or slightly basic solution with the pH value 7–9. During this process, excess-LiOH was generally reckoned as a pH adjuster.

In fact, this is not entirely true. From the three comparison experiments illustrated in Figs. 3, 5 and 6, we can see that it was hard for us to synthesize pure LiFePO₄ product by using the stoichiometric starting materials of FeSO₄·7H₂O, LiOH·H₂O and o-H₃PO₄ (Li:Fe:P = 1:1:1) at pH 4–10, and the situation was similar in the case of Li:Fe:P = 1:1:3. However, pure and well-crystallized LiFePO₄ particles can be prepared at the Li:Fe:P molar ratio 3:1:1 and pH 7–9.

According to the results of the XRD, the obtained product is different under different pH and Li: Fe: P molar ratio conditions. Therefore, we can roughly calculate the chemical reaction process according to the results of the XRD. In this work, the precipitation processes were based on the LiOH–FeSO₄–H₃PO₄–H₂O system. Fe₃(PO₄)₂·8H₂O was prepared as the first intermediate precipitate by adding LiOH to an aqueous solution of FeSO₄ and H₃PO₄ (3 < pH < 6). When an excess of LiOH was introduced to the equilibration solution of Fe₃(PO₄)₂·8H₂O precipitate with an enough amount of free ions of Li⁺ and PO₄^{3–}, the second intermediate Li₃PO₄ precipitated in the form of small particles on the surface of the pre-formed Fe₃(PO₄)₂·8H₂O particles at neutral or slightly basic conditions (6 < pH < 10). The chemical reaction can be generally written as equation (4), with the processes being shown in Scheme 1.

$$FeSO_4 + H_3PO_4 \xrightarrow{LiOH(3 < pH < 6)} Fe_3(PO_4)_2 \cdot 8H_2O \downarrow \xrightarrow{Excess \ LiOH(6 < pH < 10)} Fe_3(PO_4)_2 \cdot 8H_2O \downarrow + Li_3PO_4 \downarrow \xrightarrow{Sintering \ at \ 700^{o}C} LiFePO_4 \downarrow \xrightarrow{Sintering \ 700^{o}C} LiFePO_4$$

Actually, the experimental research results in this paper were consistent with the thermodynamic analysis of LiFePO₄ precipitation in our previous study [26], i.e., excess-Li⁺ was one of the essential conditions for LiFePO₄ preparation by co-precipitation method, and it was not only a pH adjuster, but also a "precipitation promoter".

5. Conclusions

This work explored the effect of Li:Fe:P molar ratio and pH value on the synthesis of LiFePO₄ via co-precipitation method. At molar ratio Li:Fe:P = 1:1:1, Fe₃(PO₄)₂ was the main phase of the prepared samples, and no pure LiFePO₄ was obtained during the whole experimental pH values range. By increasing the molar ratio Li:Fe:P to 1:1:3, pure LiFePO₄ was synthesized at a narrow pH range (pH value was about 9.0). Especially when the molar ratio of Li:Fe:P adjusted to 3:1:1, pure LiFePO₄ samples were prepared at a wider pH range (pH vales 6.7–8.9). The results illustrated that excess-Li⁺ in solution was an essential condition for pure LiFePO₄ preparation at neutral or slightly basic conditions, and excess-LiOH was not only a pH adjuster, but also a precipitation promoter for intermediate precipitate Li₃PO₄.

Acknowledgements

This work was supported by Science and Technology Bureau of Changsha City (Grant No. 328 K1205034-11) and Hunan Provincial Innovation Foundation for Postgraduate (1105-71380100001).

References

- A. Padhi, K. Nanjundaswamy, J.B. Goodenough, Phospho-olivines as positiveelectrode materials for rechargeable lithium batteries, J. Electrochem. Soc. 144 (1997) 1188–1194.
- [2] M.S. Whittingham, Y. Song, S. Lutta, P.Y. Zavalij, N.A. Chernova, Some transition metal (oxy) phosphates and vanadium oxides for lithium batteries, J. Mater. Chem. 15 (2005) 3362–3379.
- [3] A. Padhi, K. Nanjundaswamy, C. Masquelier, S. Okada, J. Goodenough, Effect of structure on the Fe³⁺/Fe²⁺ redox couple in iron phosphates, J. Electrochem. Soc. 144 (1997) 1609–1613.
- [4] N. Ravet, Y. Chouinard, J. Magnan, S. Besner, M. Gauthier, M. Armand, Electroactivity of natural and synthetic triphylite, J. Power Sources 97 (2001) 503–507.
- [5] H. Huang, S.-C. Yin, L.S. Nazar, Approaching theoretical capacity of LiFePO₄ at room temperature at high rates, Electrochem. Solid-State Lett. 4 (2001) A170–A172.
- [6] S.-Y. Chung, J.T. Bloking, Y.-M. Chiang, Electronically conductive phosphoolivines as lithium storage electrodes, Nat. Mater. 1 (2002) 123–128.
- [7] B. Ellis, W.H. Kan, W. Makahnouk, L. Nazar, Synthesis of nanocrystals and morphology control of hydrothermally prepared LiFePO₄, J. Mater. Chem. 17 (2007) 3248–3254.
- [8] S. Yang, P.Y. Zavalij, M. Stanley Whittingham, Hydrothermal synthesis of lithium iron phosphate cathodes, Electrochem. Commun. 3 (2001) 505–508.
- [9] J. Chen, M.S. Whittingham, Hydrothermal synthesis of lithium iron phosphate, Electrochem. Commun. 8 (2006) 855–858.

- [10] C. Nan, J. Lu, C. Chen, Q. Peng, Y. Li, Solvothermal synthesis of lithium iron phosphate nanoplates, J. Mater. Chem. 21 (2011) 9994–9996.
- [11] H. Yang, X.-L. Wu, M.-H. Cao, Y.-G. Guo, Solvothermal synthesis of LiFePO4 hierarchically dumbbell-like microstructures by nanoplate self-assembly and their application as a cathode material in lithium-ion batteries, J. Phys. Chem. C 113 (2009) 3345–3351.
- [12] Y. Hu, M.M. Doeff, R. Kostecki, R. Finones, Electrochemical performance of solgel synthesized LiFePO₄ in lithium batteries, J. Electrochem. Soc. 151 (2004) A1279–A1285.
- [13] D. Choi, P.N. Kumta, Surfactant based sol-gel approach to nanostructured LiFePO₄ for high rate Li-ion batteries, J. Power Sources 163 (2007) 1064–1069.
- [14] S.-T. Myung, S. Komaba, N. Hirosaki, H. Yashiro, N. Kumagai, Emulsion drying synthesis of olivine LiFePO₄/C composite and its electrochemical properties as lithium intercalation material. Electrochim. Acta 49 (2004) 4213–4222.
- [15] S.-T. Myung, S. Komaba, N. Kumagai, H. Yashiro, H.-T. Chung, T.-H. Cho, Nanocrystalline LiNi_{0.5}Mn_{0.5}O₄ synthesized by emulsion drying method, Electrochim. Acta 47 (2002) 2543–2549.
- [16] J. Ni, H. Zhou, J. Chen, X. Zhang, LiFePO₄ doped with ions prepared by coprecipitation method, Mater. Lett. 59 (2005) 2361–2365.
- [17] M.-R. Yang, W.-H. Ke, S.-H. Wu, Preparation of LiFePO₄ powders by co-precipitation, J. Power Sources 146 (2005) 539–543.
- [18] M.-H. Lee, J.-Y. Kim, H.-K. Song, A hollow sphere secondary structure of LiFePO₄ nanoparticles, Chem. Commun. 46 (2010) 6795–6797.
- [19] K. Dokko, S. Koizumi, H. Nakano, K. Kanamura, Particle morphology, crystal orientation, and electrochemical reactivity of LiFePO₄ synthesized by the hydrothermal method at 443 K, J. Mater. Chem. 17 (2007) 4803–4810.
- [20] Y. Denis, K. Donoue, T. Kadohata, T. Murata, S. Matsuta, S. Fujitani, Impurities in LiFePO₄ and their influence on material characteristics, J. Electrochem. Soc. 155 (2008) A526–A530.
- [21] G. Arnold, J. Garche, R. Hemmer, S. Ströbele, C. Vogler, M. Wohlfahrt-Mehrens, Fine-particle lithium iron phosphate LiFePO₄ synthesized by a new low-cost aqueous precipitation technique, J. Power Sources 119 (2003) 247–251.
- [22] K. Park, J. Son, H. Chung, S. Kim, C. Lee, H. Kim, Synthesis of LiFePO₄ by coprecipitation and microwave heating, Electrochem. Commun. 5 (2003) 839–842.
- [23] A.A. Salah, A. Mauger, K. Zaghib, J. Goodenough, N. Ravet, M. Gauthier, F. Gendron, C. Julien, Reduction Fe³⁺ of impurities in LiFePO₄ from pyrolysis of organic precursor used for carbon deposition, J. Electrochem. Soc. 153 (2006) A1692–A1701.
- [24] J. Liu, R. Jiang, X. Wang, T. Huang, A. Yu, The defect chemistry of LiFePO₄ prepared by hydrothermal method at different pH values, J. Power Sources 194 (2009) 536–540.
- [25] J. Lee, A.S. Teja, Characteristics of lithium iron phosphate (LiFePO₄) particles synthesized in subcritical and supercritical water, J. Supercrit. Fluids 35 (2005) 83–90.
- [26] L.-H. He, Z.-W. Zhao, X.-H. Liu, A.-L. Chen, X.-F. Si, Thermodynamics analysis of LiFePO₄ precipitation from Li–Fe(II)–P–H₂O system at 298 K, Trans. Nonferr. Metals Soc. China 22 (2012) 1766–1770.
- [27] E. Kostiner, J. Rea, Crystal structure of ferrous phosphate, Fe₃(PO₄)₂, Inorg. Chem. 13 (1974) 2876–2880.
- [28] T. Ericsson, F. Khangi, An investigation of Fe₃(PO₄)₂—Sarcopside between 1.6 K–721 K: Comparison with fayalite, Hyperfine Interact. 41 (1988) 783–786.
- [29] B. Robert, Magnetic structure of iron (II) phosphate, sarcopside, Fe₃(PO₄)₂, J. Mater. Chem. 2 (1992) 191–196.
- [30] E. Mattievich, J. Danon, Hydrothermal synthesis and Mössbauer studies of ferrous phosphates of the homologous series Fe₃(PO₄)₂·2H₂O, J. Inorg. Nucl. Chem. 39 (1977) 569–580.
- [31] J. Liu, R. Jiang, X. Wang, T. Huang, A. Yu, The defect chemistry of LiFePO₄ prepared by hydrothermal method at different pH values, J. Power Sources 194 (2009) 536–540.
- [32] J. Lee, A.S. Teja, Characteristics of lithium iron phosphate (LiFePO₄) particles synthesized in subcritical and supercritical water, J. Supercrit. Fluids 35 (2005) 83–90.

(4)