Available online at www.sciencedirect.com
SCIENCE DIRECT®
Electrochemistry Communications 8 (2006) 855–858
www.elsevier.com/locate/elecom

Hydrothermal synthesis of lithium iron phosphate

Jiajun Chen, M. Stanley Whittingham *

Department of Chemistry and Institute for Materials Research, State University of New York at Binghamton, Binghamton, NY 13902-6000, USA

Received 28 February 2006; received in revised form 9 March 2006; accepted 10 March 2006
Available online 17 April 2006

Abstract

$LiFePO_4$ is a potential cathode candidate for the next generation of secondary lithium batteries. The $LiFePO_4$ was synthesized by a hydrothermal process. Phase-pure material was obtained and the critical synthesis parameters were determined. Iron disorder onto the lithium sites can be eliminated by using temperatures in excess of 175 °C; above this temperature the crystalline unit cell was essentially identical to that of the high temperature material, with a volume of 291.3 ± 0.2 Å^3. The use of a soluble reductant, such as sugar or ascorbic acid, was found to minimize the oxidation of the iron to ferric. The electronic conductivity was enhanced by the deposition of carbon from the sugar, or by the addition of carbon nanotubes to the hydrothermal reactor. The electrochemical behavior of this material showed more than 90% lithium removal on charge and complete capacity retention over 50 cycles.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Iron phosphate; Hydrothermal; Rietveld; Battery cathode; X-ray analysis

1. Introduction

Since the commercialization of $LiCoO_2$ by SONY [1], alternative cathode materials have been pursued to replace the expensive and oxidatively unstable $LiCoO_2$. A good cathode material has to meet the following criteria: high capacity that can be retained for up to 1000 cycles; stability that can withstand fast recharge and discharge and other possible extreme conditions; affordability for consumer electronics and large scale storage, and low toxicity. $LiFePO_4$, with the Olivine structure, reported by the Goodenough group in 1997 [2] when coated with a conductive coating appears to meet many of these requirements.

Many research groups have tried to improve the performance of this material, which has a discharge voltage of about 3.4 V vs. lithium. It shows no obvious fading even after several hundred cycles, and shows power capabilities comparable to that of the mixed layered oxides [3,4]. Its theoretical energy density is 550 W h/kg, higher than obtained in commercial $LiCoO_2$ cells, and moreover it is very stable during discharge/recharge. $LiFePO_4$ can be synthesized by high temperature reactions [2] or under hydrothermal conditions [5]. As this material has a very low conductivity at room temperature, it can achieve the theoretical capacity only at a very low current density [6] or at elevated temperatures [7], as suggested by Padhi et al. [2] due to the low lithium diffusion at the interface. Ravet et al. [8] showed that a carbon coating significantly improves the electrochemical performance of this material; sucrose was proposed [9] as one carbon precursor, and we used it for our initial hydrothermal samples [5]. Nazar et al. have proposed [10] using carbon gels, and Chang et al. [11] proposed addition of metallic dopants (reductants) in the high temperature synthesis process to make a conductive coating on the $LiFePO_4$; both approaches succeeded in increasing the electrochemical capacity. Efforts in this area have been recently reviewed [3,12].

A remaining challenge is how to make this material by a low cost process, ideally involving no energy intensive high temperature firing. We showed in 2001 that $LiFePO_4$ could be formed by a hydrothermal process [5]. However, that material did not behave very well in electrochemical cells.

* Corresponding author. Tel./fax: +1 607 777 4623.
E-mail address: stanwhit@binghamton.edu (M.S. Whittingham).

1388-2481/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2006.03.021

Samsung Ex. 1041, Page 1 of 4
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

A later study showed that it was also resistant to chemical oxidation or reduction. This was shown [13] to be due to disorder of the iron atoms, with around 7% iron atoms on the lithium site as determined from additional electron density on that site from a Rietveld refinement study. A number of studies [14–17] of the hydrothermal process have been made in the last two years, but all those had low capacities or required a high temperature firing of the hydrothermal $LiFePO_4$ in order to attain electrochemical capacity approaching the theoretical value of 169 mA h/g. For example, Dokko et al. [15] recently reported a capacity of 65 mA h/g before heating at 400 °C in argon and 150 mA h/g after. Our initial reports [5] showed a discharge capacity of just under 100 mA h/g for a hydrothermal material prepared at 120 °C; it also showed a high polarization on the first charge. We therefore decided to determine the critical parameters in the hydrothermal process that were controlling the structural and electrochemical properties of $LiFePO_4$. Our emphasis was placed on finding-out how to obtain iron ordering and also how to prevent the oxidation of the desired ferrous to ferric iron.

2. Experimental

The $LiFePO_4$ was prepared by hydrothermal reaction in a Parr reactor as described previously [5]. Specifically the starting materials were $FeSO_4 \cdot 7H_2O$ (98% Fisher), H_3PO_4 (85 wt% solution Fisher), LiOH (98% Aldrich). The molar ratio of the Li:Fe:P was 3:1:1, and a typical concentration of $FeSO_4$ was 22 g/liter of water. Sugar and/or L-ascorbic acid (99% Aldrich) was added as an in situ reducing agent to minimize the oxidation of ferrous to ferric; 1.3 g/liter was used. Multi-Wall carbon nanotubes (95% Aldrich) were also added, 0.8 g/liter. The resulting grayish blue gel was transferred into a 125 ml capacity Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 150–220 °C for 5 h. Precipitates were collected by suction filtration and dried at 60 °C for 3 h in the vacuum oven.

For electrochemical evaluation, the compounds were mixed with carbon black (Cities Service Company) and Teflon (Dupont) in the weight ratio of 75:15:10. The cathode loading was 30–40 mg/cm^2. The sample was hot pressed into a stainless steel Exmet™ grid and wrapped in Celgard 2400 separator (Hoechst Celanese Corp.). Lithium foil (Aldrich) was used as the anode. The cell was soaked in $LiPF_6$ (DMC:EC = 1:1, EM Industries, LP30) electrolyte. The data were collected galvanostatically on a MacPile system and the current density was 0.3 mA/cm^2, the temperature was 20 °C, and cut-off voltages were 2.5 and 4.3 V.

Thermal analysis of all samples was performed on a TA 2950 instrument under oxygen flow at a heating rate of 5 °C/min, to determine the ferrous content. All X-ray studies were done on a Scintag XDS2000 diffractometer, and the Rietveld analysis used the GSAS/EXPGUI refinement program.

3. Results and discussion

An understanding of the synthesis of pure $LiFePO_4$ is important to its utilization as a battery cathode. We have therefore studied the structure and iron ordering as a function of synthesis temperature and organic reductant. The X-ray diffraction pattern of a $LiFePO_4$ material synthesized at 200 °C in the presence of ascorbic acid is shown in Fig. 1. The only phase observed is $LiFePO_4$. The cell parameters obtained from Rietveld refinement are: $a = 10.332(2)$ Å, $b = 6.005(1)$ Å, $c = 4.693(6)$ Å, volume $= 291.2$ Å^3 consistent with previous values $a = 10.329(1)$ Å, $b = 6.007(1)$ Å, $c = 4.691(1)$ Å, volume $= 291.03$ Å^3 from high temperature synthesis [18]. The Rietveld refinement also showed no additional electron density (<0.2%) on the lithium sites, indicating that the iron is completely ordered. Samples prepared at 150 and 190 °C showed 3.6 and 0.6 at.% iron on the lithium site, respectively; this trend is consistent with the earlier value of 7–8% at 120 °C [13].

We made a study of the unit cell parameters as a function of hydrothermal synthesis temperature, as our original data was very different [5]. The cell volumes calculated from this data are shown in Fig. 2. It can be seen that the cell volume decreases with increasing synthesis temperature until 180 °C, when a plateau is reached. This plateau value, 291.0–291.5 Å^3, is the same as that found for $LiFePO_4$ material synthesized at high temperature. The iron disorder was found to similarly decrease with increasing synthesis temperature; thus, determination of the cell volume may be used as a measure of the iron disorder and thus of potentially electrochemically acceptable $LiFePO_4$.

The oxidation state purity of the hydrothermal $LiFePO_4$ was determined by heating the material in oxygen to around 600 °C, which causes a weight gain associated with the complete oxidation of all the iron to the ferric state. If all the iron in the $LiFePO_4$ is ferrous then a weight gain of 5.0% is expected. Fig. 3 shows that a sample prepared at 200 °C is essentially pure ferrous. Similar weight gains were observed whenever sugar or ascorbic acid was used in the synthesis, and the temperature was over 175 °C. It was sometimes observed for samples made at lower temperatures, but not consistently. When both sugar and ascorbic acid were used, lower weight gains, or even weight losses were observed, due to the presence of carbon on the sample. X-ray diffraction did not indicate any second phase even when there was 50% ferric iron in the sample; thus an excellent X-ray pattern does not guarantee a pure ferrous phase.

Fig. 4 shows the first cycle of $LiFePO_4$ synthesized at 200 °C in the presence of ascorbic acid. Carbon nanotubes were added to the reaction medium in an attempt to increase the conductivity of the product formed. The carbon content in the synthesized LiFePO4 was around 6% by weight, as determined by TGA. The charging and discharging was done at 20 °C and 0.3 mA/cm^2. Close to 160 mA h/g capacity was obtained on the

Samsung Ex. 1041, Page 2 of 4
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

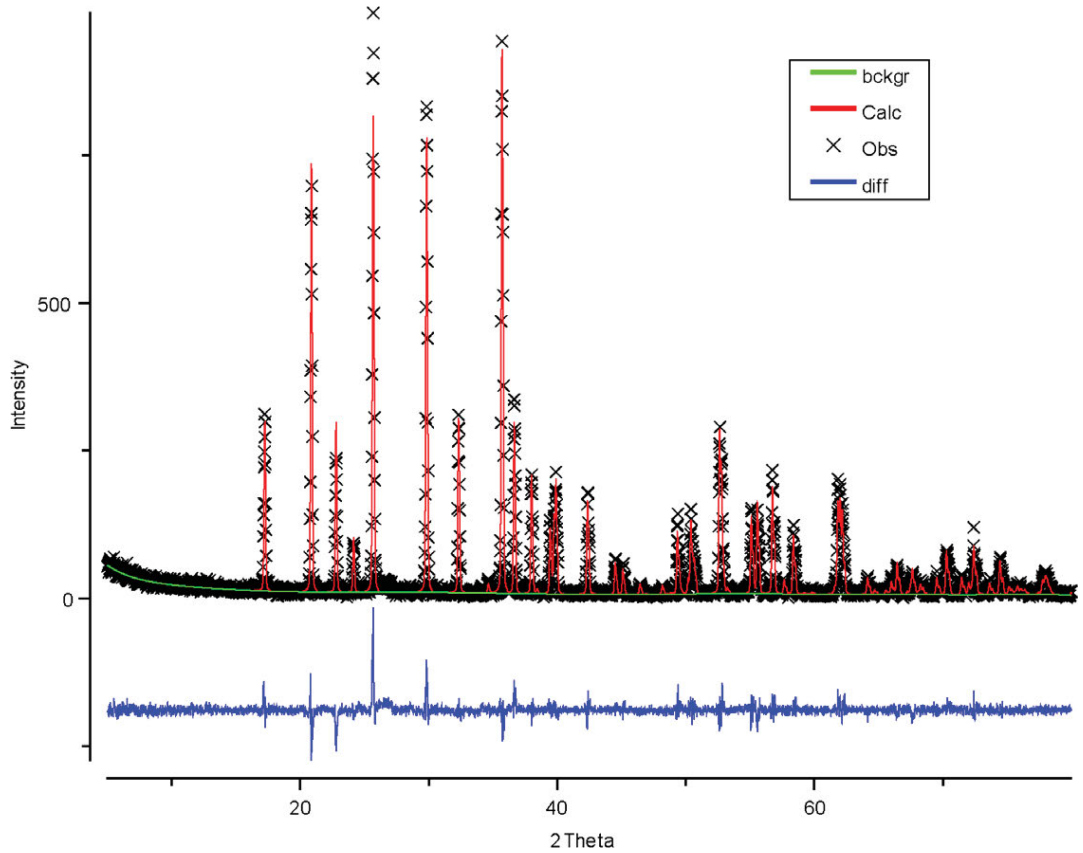

Fig. 1. Rietveld refinement of $LiFePO_4$, formed at 200 °C in the presence of ascorbic acid. No iron was detectable on the lithium site (<0.2%).

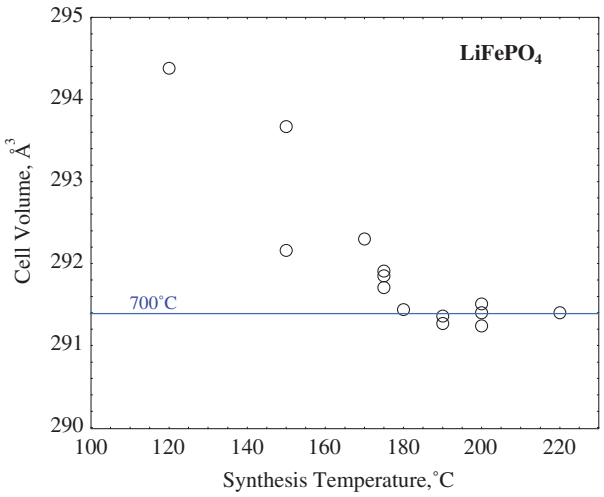

Fig. 2. Unit cell volume of $LiFePO_4$ as a function of the hydrothermal synthesis temperature. The value for syntheses made at 700 °C is also given for comparison.

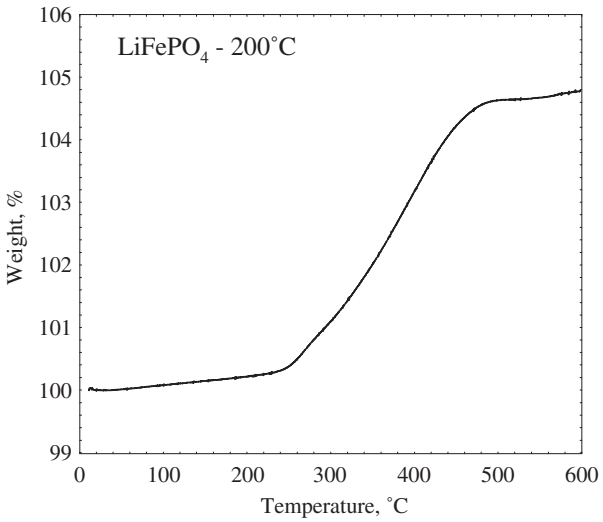

Fig. 3. TGA of pure $LiFePO_4$. If all the iron is ferrous, a weight gain of 5.0% is expected.

charging cycle. This exceeds 94% of the theoretical capacity of 169 mA h/g. On discharge the capacity was over 145 mA h/g, this value was maintained over subsequent cycling. 145 mA h/g is around 86% of the theoretical value and very comparable to the earlier value of 148 mA h/g reported by us [13] in similarly constructed cells for material prepared at 700 °C. Thus, hydrothermal material synthesized at 200 °C has the same performance as material formed at 700 °C. We anticipate that 100% utilization can be obtained by operating at higher temperatures or at lower current densities, as we found for the high temperature material.

Samsung Ex. 1041, Page 3 of 4
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356

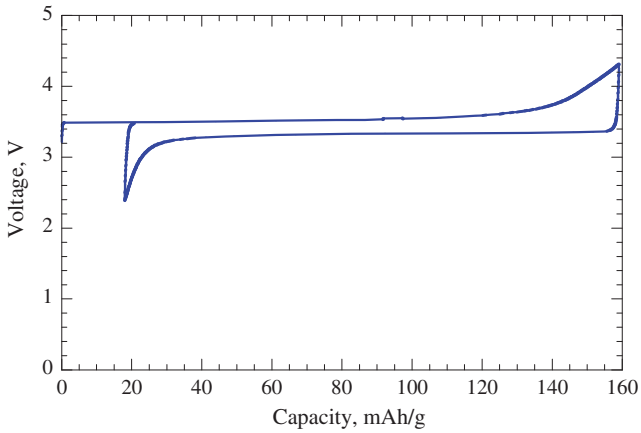

Fig. 4. First electrochemical cycle of hydrothermal $LiFePO_4$ at room temperature. Sample synthesized at 200 °C in the presence of ascorbic acid and carbon nanotubes.

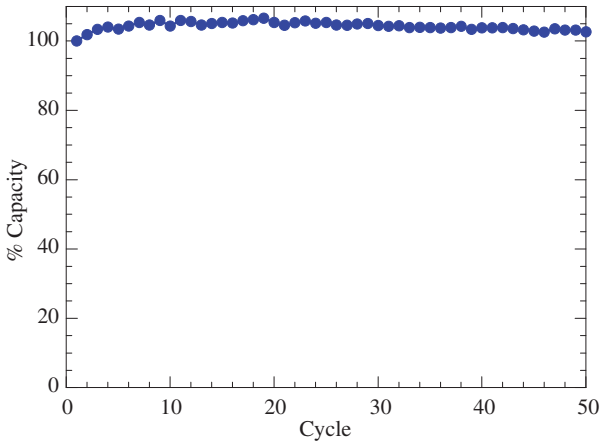

Fig. 5. Cycling capacity of $LiFePO_4$ at room temperature as a function of the first cycle capacity.

We determined the stability of this hydrothermal $LiFePO_4$ to extended cycling, and the data is shown in Fig. 5 as a function of the first discharge capacity. There is no loss of capacity over the first 50 cycles, indicating that this phosphate structure even when prepared at the low temperature of 180–200 °C is extremely stable. This may be associated with the very crystalline nature of the lithium iron phosphate formed. The diamond-shaped crystallites formed are around 3–5 μm on an edge, and up to 1 μm thick. The actual crystal morphology is strongly dependent on the temperature and reductant used. Optimization of the morphology will be needed for high rate and extended life lithium iron phosphate for battery applications; we are presently studying these effects.

4. Conclusions

We have shown that battery acceptable $LiFePO_4$ can be successfully synthesized at low temperatures using a hydrothermal process. The temperature of synthesis must exceed 175 °C to minimize iron disorder and to obtain material with the correct lattice parameters and volume. Reductants, such as sugar or ascorbic acid, in the hydrothermal reactor successfully prevented the oxidation of the iron to the ferric state. The hydrothermal $LiFePO_4$ gave the same discharge capacity as $LiFePO_4$ formed at 700 °C when tested in a similar configuration. Capacity retention on cycling was excellent over the first 50 cycles.

Acknowledgment

We thank the US Department of Energy, Office of Transportation Technologies, for support of this work through the BATT program at Lawrence Berkley National Laboratory. This was part of the opening lecture presented at the Hawaii Battery Conference in Waikoloa, Hawaii, January 9, 2006.

References

[1] K. Ozawa, Solid State Ionics 69 (1994) 212.
[2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[3] M.S. Whittingham, Chem. Rev. 104 (2004) 4271.
[4] S. Yang, Y. Song, K. Ngala, P.Y. Zavalij, M.S. Whittingham, J. Power Sources 119 (2003) 239.
[5] S. Yang, P.Y. Zavalij, M.S. Whittingham, Electrochem. Commun. 3 (2001) 505.
[6] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
[7] A.S. Andersson, J.O. Thomas, B. Kalska, L. Häggström, Electrochem. Solid-State Lett. 3 (2000) 66.
[8] N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, Electrochem. Soc. Abstr. 99–2 (1999) 127.
[9] N. Ravet, S. Besner, M. Simoneau, A. Vallée, M. Armand, J.-F. Magnan, Hydro-Quebec, European Patent 1049182A2, 2000.
[10] H. Huang, S.-C. Yin, L.F. Nazar, Electrochem. Solid State Lett. 4 (2001) A170.
[11] S.-Y. Chung, J.T. Bloking, Y.-M. Chiang, Nat. Mater. 1 (2002) 123.
[12] M.S. Whittingham, Y. Song, S. Lutta, P.Y. Zavalij, N.A. Chernova, J. Mater. Chem. 15 (2005) 3362.
[13] S. Yang, Y. Song, P.Y. Zavalij, M.S. Whittingham, Electrochem. Commun. 4 (2002) 239.
[14] S. Franger, F.L. Cras, C. Bourbon, H. Rouault, Electrochem. Solid State Lett. 5 (2002) A231.
[15] K. Dokko, K. Shiraishi, K. Kanamuraa, J. Electrochem. Soc. 152 (2005) A2199.
[16] S. Tajimi, Y. Ikeda, K. Uematsu, K. Toda, M. Sato, Solid State Ionics 175 (2004) 287.
[17] S. Franger, F.L. Cras, C. Bourbon, H. Rouault, J. Power Sources 119 (2003) 252.
[18] A.S. Andersson, B. Kalska, L. Häggström, J.O. Thomas, Solid State Ionics 130 (2000) 41.

Samsung Ex. 1041, Page 4 of 4
Samsung Electronics Co., Ltd., et al. v. Molecular Rebar Design, LLC
IPR2025-00356