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# The role of impurities on electrochemical properties of $LiFePO_4$ cathode material

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## Abstract

$LiFePO_4$, one of the attractive cathode materials for lithium ion batteries, is obtained by lithiation of pre-synthesized $FePO_4$ using lithium carbonate as lithium source. Inexpensive reducing agent glucose was used for the reduction process. Glucose acted as a conductive additive as well. Lithium ion conductive impurity phase can be attributed to the capacity improvement in $LiFePO_4$ with carbon coating. The off-stoichiometric $Li_xFePO_4$ ($x=1.005$, 1.010) was synthesized to generate a conductive pyrophosphate layer. An electron conductive layer with carbon coating was also concurrently formed by carbothermal reduction of glucose. It is observed that the electrochemical property improves with increasing amount of lithium pyrophosphate impurity phase. This observable fact may be due to accelerating lithium ion diffusion on the lithium ion conductive lithium pyrophosphate layer. XRD and SEM observation show that the $Li_xFePO_4$/C composite has good crystallinity and well-dispersed particles of 200–300 nm size. The $Li_xFePO_4$/C ($x=1.010$) composite shows a high discharge capacity of 150 mAh $g^{-1}$ and 136 mAh $g^{-1}$ at rates of 0.1 C and 1 C respectively with satisfactory capacity retention.

*Keywords:* B. Impurities; B. Composites; E. Batteries

## 1. Introduction

Lithium iron phosphate (LFP) is an attractive choice as cathode material in lithium rechargeable battery. The dominant factors of this material are low price and good safety, compared with conventional cathode materials popularly used in portable electronics applications (e.g. $LiCoO_2$) [1]. Although it has several merits, LFP suffers from its poor electric and ionic conductivities [2,3]. Various strategies have been adopted to overcome the demerits such as decreasing the size of the particles, making an electron conductive carbon layer, making a $Li^+$ conductive impurity phase and doping with various guest ions [4]. It has been proved that decreasing particle sizes and providing conductive carbon coating are beneficial for enhancing the electrochemical property in LFP [5]. However, there are controversial results about the effect of doping by guest element [5]. The electrochemical features of $LiFePO_4$ are strongly influenced by the presence of impurity phases that may be formed during preparation, depending on the synthesis routes [1]. Some of impurities benefit the electrochemical performance while some may deteriorate the performance seriously. Some of them, like $Fe_xP$, $Li_4P_2O_7$ and $Li_3PO_4$ even improve the electrochemical performances which are intrinsically related to $Li^+$ mobility and electron transport [6]. As previously reported, $Li_4P_2O_7$ and $Li_3PO_4$ impurity phases could have benefits for fast charging and discharging by providing a guest ion-conductive surface [7–9].

It is well known that variations in the stoichiometric proportions of the Li content lead to drastic improvements in the conducting behavior of olivine phase materials [10]. Axmann et al. [11] prepared a series of samples by a wet-chemical synthesis with deviation from stoichiometry (a few mol% of Li deficiency or excess in the precursor) and found that excess of lithium only resulted in a $Li_3PO_4$ impurity phase that was inactive but did not poison the electrochemical performance. In contrast, Kim et al. [10] reported $Li_3PO_4$ impurity phase dramatically enhance the

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conducting properties in the materials. An electronic conductivity, six to seven orders of magnitude higher than the pure $LiFePO_4$, was observed [10]. Kang and Ceder [7] recently discovered that non-stoichiometry of the reactants in preparation of $LiFePO_4$ resulted in $Li_4P_2O_7$ phase which drastically increase the electrochemical property. Besides off-stoichiometry and sintering condition, it was observed that the mode of starting material influence material property [12]. From the reviews above, a new strategy has been taken in this study by incorporating impurity phases such as $Li_4P_2O_7$, $Li_3PO_4$ and $Fe_xP$ to the $LiFePO_4$/C composite. A mixture of pre-synthesized iron phosphate and iron pyrophosphate was utilized as a starting material with lithium carbonate and glucose in this study.

## 2. Experimental

### 2.1. Preparation of starting material

A mixture of $FePO_4$ and a condensed phosphate product $Fe_4(P_2O_7)_3$ was synthesized by the temperature controlled precipitation method. This powder mixture was used as a starting material (Fe precursor) for $LiFePO_4$/C composite preparation. $H_3PO_4$ (85%) solution was gradually added to appropriate molar amount of $FeCl_3$ solution and stirred for 1 h. The solution was subsequently aged at 90 °C in a water bath until the precipitate appeared. The white colored precipitates were then isolated by filtration, and washed with distilled water and isopropyl alcohol. After washing precipitates ($FePO_4 \cdot xH_2O$), the drying process is carried out at 100 °C for 6 h. In addition, lithium carbonate was pre-milled using a high energy nano-mill to compensate size and shape differences.

### 2.2. Preparation of cathode materials

$LiFePO_4$/C composites (0.5 and 1 wt% excess Li) were synthesized by a solid state reaction process using pre-milled $Li_2CO_3$ and pre-synthesized amorphous powders of Fe precursor. Appropriate amount of precursors and glucose (8 wt%) were weighed and ball-milled with a $ZrO_2$ media in ethanol for 24 h. The mixture is then dried up at 80 °C for 4 h. The dried powders were then sintered at 700 °C for 4 h under $N_2$ atmosphere preventing the oxidation of $Fe^{2+}$ and coating the surface of $LiFePO_4$ particles with carbon.

### 2.3. Characterizations

X-ray diffraction (XRD, Rigaku, D/MAX-2500 H) analysis with Cu Kα radiation was used to identify the crystalline phases of prepared materials. Preliminary study revealed that precipitates are of mostly amorphous state. $FePO_4$ phase information and $Fe_4(P_2O_7)_3$ phase formation were confirmed by observing crystal structure of heat treated (in air at 600–700 °C for 3 h) amorphous powders by XRD. The quantity of $Fe_4(P_2O_7)_3$ phase was 13%, calculated from XRD data. In order to observe microstructures, e-SEM (FEI, Quanta-400) was employed.

### 2.4. Electrochemical property measurement

For electrochemical property assessment, the cathode was prepared by uniformly coating a mixture of prepared $LiFePO_4$/C, carbon black (Super P, 10 wt%), and PVDF binder onto an aluminum foil sheet with NMP as a solvent. Then, the cathode film was dried under vacuum at 120 °C for 10 h. Electrochemical properties were measured for coin cells (CR2016) which were assembled in a glove box under Ar atmosphere. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume). The cells were galvanostatically charged and discharged at a voltage range of 2.0–4.2 V against the Li anode in a WONATECH (WBCS-3000) battery testing system at room temperature.

## 3. Result and discussion

The XRD patterns of the $Li_{1.005}FePO_4$ (abbreviated as E1) and $Li_{1.01}FePO_4$ (abbreviated as E2) prepared from $FePO_4 \cdot xH_2O$ powders including iron pyrophosphate are shown in Fig. 1. For both XRD patterns, $LiFePO_4$ with Li pyrophosphate impurities as well as $Li_3PO_4$ is detected and do not exhibit peaks of $Fe_xP$. Besides, an unexpected $Fe_2P_2O_7$ phase appears intensively.

Fig. 2 shows the SEM morphology of $LiFePO_4$/C composites (E1 and E2) after sintering at 700 °C. The particles of both composites are well dispersed without any apparent agglomerates. The typical size of these particles is in the range of 200–300 nm.

Electrochemical performance was investigated to examine the effect of impurity in $LiFePO_4$ on Li insertion/extraction behavior. Fig. 3 shows the charge/discharge profiles at 0.1 C of both samples. It is demonstrated that the capacity enhances with increasing Li content. The composite cathode material for sample E2 has a first cycle

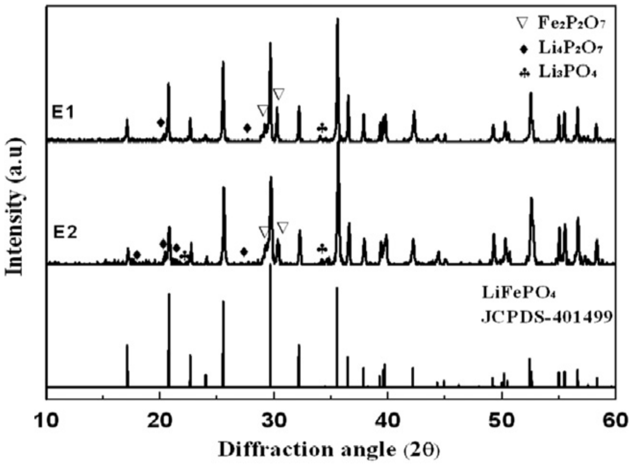

Fig. 1. XRD patterns of E1-$Li_{1.005}FePO_4$/C and E2- $Li_{1.01}FePO_4$/C composite synthesized at 700 °C.

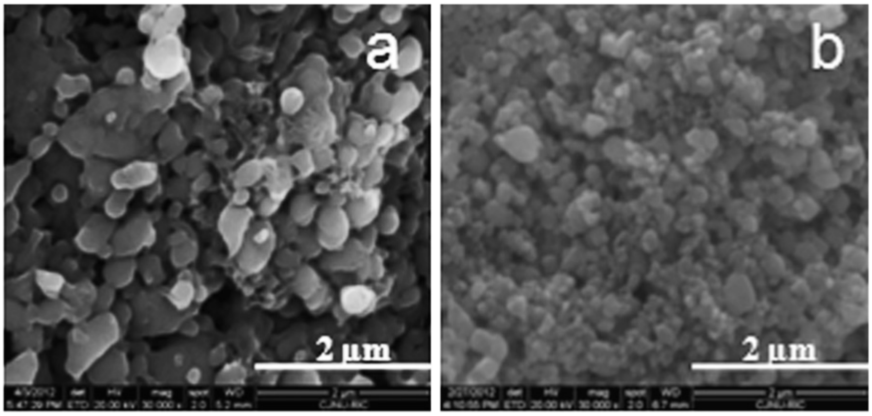

Fig. 2. SEM images of (a) $Li_{1.005}FePO_4/C$ (b) $Li_{1.01}FePO_4/C$.

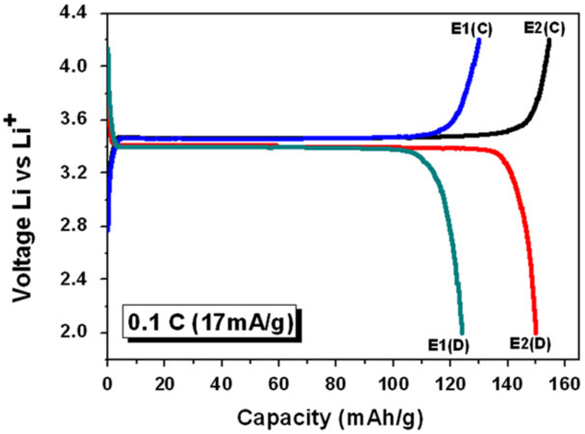

Fig. 3. Initial charge (C) and discharge (D) curves of samples E1 and E2.

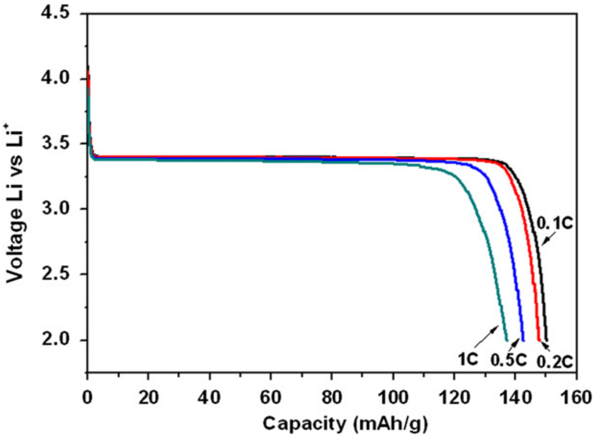

Fig. 4. Discharge capacity of sample E2 at different current densities.

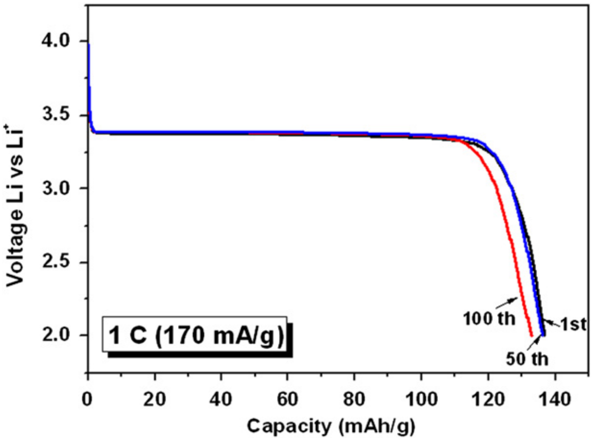

Fig. 5. Discharge curves of sample E2 at different cycle numbers at 1 C rate.

charge capacity of 154 mAh $g^{-1}$ followed by a discharge capacity of 150 mAh $g^{-1}$, which is nearly 88% of the theoretical capacity (170 mAh $g^{-1}$) [2]. $Fe_2P_2O_7$ impurity phase was responsible for capacity decline according to one of the previous investigation by Daheron and MacNeil [13].

Thus, the improved electrochemical performances of sample E2 could be attributed to the presence of $Li_4P_2O_7$ and $Li_3PO_4$ phases. These may be credited to the increase of ionic conductivity in the material.

The initial cycle for the sample E2 shows high columbic efficiency, almost 97.5%. The small voltage difference between the charge and discharge plateaus is representative of its good kinetics.

Another important feature for battery applications is cycling stability. Rate capability studies were performed for E2 samples as presented in Fig. 4. Different current densities from 0.1 to 1 C were performed at room temperature. It is found that the prepared sample exhibits good cycling stability and high reversible capacity. At current of 0.2 C, 0.5 C and 1.0 C, the composite cathode materials have initial discharge specific capacity of 147, 142 and 136 mAh $g^{-1}$, respectively, demonstrating that the synthesized composite can endure high rate charge and discharge during test. The discharge curves of the 1st, 50th and 100th cycles for composite electrode of E2 sample at 1 C are shown in Fig. 5. Cycling capability of sample E2 within the first 100 cycles is superior, with less than 3% of discharge capacity loss between the 1st and the 100th cycle

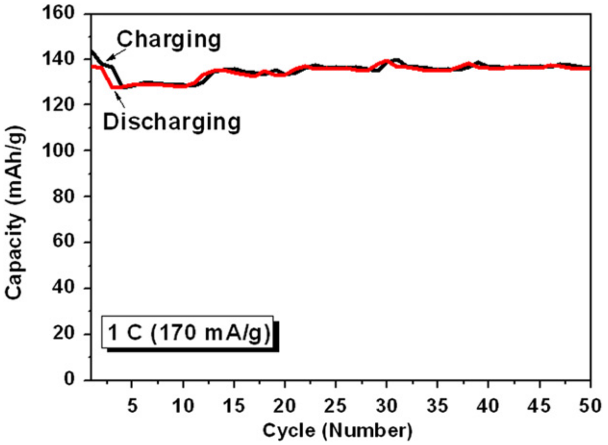

Fig. 6. Cycling behavior of sample E2 at 1C rate between 2.0 V and 4.2 V.

Table 1
Comparison of rate capability and its retention in this paper with those in other literatures.

| Doping element | 0.1 C (mA hg$^{-1}$) | 1 C (mA hg$^{-1}$) | Capacity retention (%) |
|---|---|---|---|
| Mn [14] | 142 | 120 | 84.50 |
| Mn [15] | 142 | 112[a] | 78.80 |
| Mn [16] | 144.5 | 122 | 84.50 |
| Cu [17] | 145 | 109 | 75 |
| Cr [18] | 142 | 110 | 77.50 |
| Co [19] | 150 | 60 | 40 |
| This work | 150 | 136 | 90.66 |

[a] 0.5 C

at 1 C rate. Capacity attenuation is negligible on this cycling test.

After 50 cycles, the reversible discharge capacity is 136 mAh g$^{-1}$ at 1 C, showing the retention of almost 100%, and capacity fading was not observed with cycling as shown in Fig. 6.

The rate performance exceeds those of the previously reported phase of pure $LiFePO_4$/C composites with doping [14–19], as shown in Table 1. This is presumably due to the conductive Li pyrophosphate impurity phase. There is no doubt that single phase olivine $LiFePO_4$ is optimum condition for superior performance as a cathode material in Li ion battery [20], this investigation reveals that formation of conductive impurity phase like $Li_4P_2O_7$ and $Li_3PO_4$ in $LiFePO_4$ is more beneficial than doping by transition elements such as Mn, Co, Cr and Cu regardless of unexpected $Fe_2P_2O_7$ phase incorporated instead of conductive $Fe_xP$.

## 4. Conclusion

A new route for synthesizing lithium iron phosphates with conductive impurity phases and its effect on the subsequent properties of $LiFePO_4$/C have been investigated comprehensively in this study. The $LiFePO_4$/C composite prepared from $FePO_4$ mixture with 13% $Fe_4(P_2O_7)_3$ and 1% excess lithium results in a discharge capacity of 150 mAh g$^{-1}$ which is 88% of its theoretical capacity. It reveals that formation of conductive impurity phases like $Li_4P_2O_7$ and $Li_3PO_4$ with $LiFePO_4$/C composite is more favorable than doping transition elements into $LiFePO_4$/C. High columbic efficiency indicates good reversibility of the prepared composite. The prepared composite including the impurities such as $Li_4P_2O_7$, $Fe_2P_2O_7$ and $Li_3PO_4$ showed good rate capability and capacity retention over cycling in this study.

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## References

[1] D. Jugovic, D. Uskokovic, A review of recent developments in the synthesis procedures of lithium iron phosphate powders, Journal of Power Sources 190 (2009) 538–544.
[2] S.Y. Chung, J.T. Bloking, Y.M. Chiang, Electronically conductive phospho-olivines as lithium storage electrodes, Nature Materials 1 (2002) 123–128.
[3] A.S. Andersson, J.O. Thomas, The source of first cycle capacity loss in $LiFePO_4$, Journal of Power Sources 97–98 (2001) 498–502.
[4] O.K. Park, Y. Cho, S. Lee, H.-C. Yoo, H.-K. Song, Who will drive electric vehicles, olivine or spinel?, Journal of Energy and Environmental Science 4 (2011) 1621–1633.
[5] W.J. Zhang, Structure and performance of $LiFePO_4$ cathode materials: A review, Journal of Power Sources 196 (2011) 2962–2970.
[6] L.X. Yuan, Z.H. Wang, W.X. Zhang, X.L. Hu, J.T. Chen, Y.H. Huang, J. B., Good enough, Development and challenges of $LiFePO_4$ cathode material for lithium-ion batteries, Journal of Energy and Environmental Science 4 (2011) 269–284.
[7] B. Kang, G. Ceder, Battery materials for ultrafast charging and discharging, Nature 458 (2009) 190–193.
[8] P.S. Herle, B. Ellis, L.F. Nazar, Nano-network electronic conduction in iron and nickel olivine phosphates, Nature Materials 3 (2004) 147–152.
[9] K. Sun, S.J. Dillon, A mechanism for the improved rate capability of cathodes by lithium phosphate surficial films, Journal of Electrochemistry Communications 13 (2011) 200–202.
[10] D.K. Kim, H.M. Park, S.J. Jung, Y.U. Jeong, J.H. Lee, J.J. Kim, Effect of synthesis conditions on the properties of $LiFePO_4$ for secondary lithium batteries, Journal of Power Sources 159 (2006) 237–240.
[11] P. Axmann, C. Stinner, M. Wohlfahrt-Mehrens, A. Mauger, F. Gendron, C.M. Julien, Nonstoichiometric $LiFePO_4$: Defects and Related Properties, Journal of Chemistry of Materials 21 (2009) 1636–1644.
[12] F. Gao, Z. Tang, J. Xue, Effect of different iron sources on the electrochemical performance of $LiFePO_4$/C composite cathode materials, Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Material 15 (6) (2008) 802–807.
[13] B. Daheron, D. Macneil, Study of $LiFePO_4$ synthesized using a molten method with varying stoichiometries, Journal of Solid State Electrochemistry 15 (2011) 1217–1225.

[14] K.T. Lee, K.S. Lee, Electrochemical properties of $LiFe_{0.9}Mn_{0.1}PO_4/Fe_2P$ cathode material by mechanical alloying, Journal of Power Sources 189 (2009) 435–439.

[15] Y.C. Chen, J.M. Chen, C.H. Hsu, J.W. Yeh, H.C. Shih, Y.S. Chang, H.S. Sheu, Structure studies on $LiMn_{0.25}Fe_{0.75}PO_4$ by in-situ synchrotron X-ray diffraction analysis, Journal of Power Sources 189 (2009) 790–793.

[16] D.H. Baek, J.K. Kim, Y.J. Shin, G.S. Chauhan, J.H. Ahn, K.W. Kim, Effect of firing temperature on the electrochemical performance of $LiMn_{0.4}Fe_{0.6}PO_4/C$ materials prepared by mechanical activation, Journal of Power Sources 189 (2009) 59–65.

[17] S.B. Lee, S.H. Cho, J.B. Heo, V. Aravindan, H.S. Kim, Y.S. Lee, Copper-substituted lithium rich iron phosphate as cathode material for lithium secondary batteries, Journal of Alloys and Compounds 488 (2009) 380–385.

[18] J. Ying, M. Lei, C. Jiang, C. Wan, X. He, J. Li, L. Wang, J. Ren, Preparation and characterization of high-density spherical $Li_{0.97}Cr_{0.01}FePO_4/C$ cathode material for lithium ion batteries, Journal of Power Sources 158 (2006) 543–549.

[19] D. Shanmukaraj, G.X. Wang, R. Murugan, H.K. Liu, Electrochemical studies on $LiFe_{1-x}Co_xPO_4$/carbon composite cathode materials synthesized by citrate gel technique for lithium-ion batteries, Journal of Material Science and Engineering B 149 (2008) 93–98.

[20] C.M. Julien, A. Mauge, A. Ait-Salah, M. Massot, F. Gendron, K. Zaghib, Nanoscopic scale studies of $LiFePO_4$ as cathode material in lithium-ion batteries for HEV application, Ionics 13 (2007) 395–411.