Solid state synthesis of LiFePO$_4$/C: using low cost materials

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Cathode materials have been the most important components of the Li-ion secondary battery research because they generally determine the capacity and safety of Li-ion battery (LIB). In order to decrease the cost of LIBs, main efforts are devoted to the cost reduction of the electrode materials. As a consequence, low cost raw materials are considered for cost reduction. Iron (III) phosphate has recently gained interest as a compatible source of both iron and phosphate in the field of LIB. It is prepared by a precipitation technique from aqueous solution. The starting material is Fe(NO$_3$)$_3 \cdot$ 9H$_2$O, in this study, which is one of the cheapest iron sources for LiFePO$_4$ cathode preparation. The olivine-type LiFePO$_4$/C composites are synthesized by a solid state reaction process using pre-milled Li$_2$CO$_3$ and pre-synthesized amorphous FePO$_4 \cdot x$H$_2$O powders. The pre-synthesized FePO$_4 \cdot x$H$_2$O powders are mixed with pre-milled lithium carbonate and glucose (8 wt.%) using either water or alcohol solvent sequentially via ball-mill process. The main purpose of the present study is to investigate Fe(NO$_3$)$_3 \cdot$ 9H$_2$O as a source material and explore the effect of precursor mixing solvent, if any, on the microstructure and electrochemical property of LiFePO$_4$ cathode materials. The structural characteristics of LiFePO$_4$/C composites are examined by XRD, SEM and TEM. To investigate the mixing solvent effect on the electrochemical property in LiFePO$_4$/C composites, a Li[LiPF$_6$ (ethylene carbonate + dimethyl carbonate)] LiFePO$_4$/C model cell is used. It is demonstrated that the LiFePO$_4$/C synthesize by using alcohol solvent exhibits the better electrochemical performance than that of water one. The reason of such kind of behavior is explicated by their corresponding TEM micrographs.

Key words: Solid state, Iron nitrate, Particle shape, TEM.

Introduction

The world's dependence on non-renewable sources should reduce to meet the growing global demand for preserving the environment. Rechargeable batteries based on lithium ions are at the frontier of this effort, as they play important roles in our daily lives by powering numerous portable consumer electronic devices (e.g., cell phones, PDAs, laptops) [1]. However, in large-scale applications such as automotive transportation or grid-storage, they will require not only new materials with considerably improved performance but also cost effective materials. Efforts must also focus on using earth-abundant and nontoxic compounds so that whatever developments made shall not create new environmental problems. It must be one of the main issues to choose cathode materials in terms of environmental benignness and cost (material and process costs). Lithium iron phosphate (LFP), LiFePO$_4$, with olivine polyoxy anion structure is one of the most promising cathode materials for next generation LIBs. The transition metal employed in LiFePO$_4$, Fe, is

nontoxic hence a better environmental friendliness unlike nickel or cobalt which is used in current LIBs [2]. LiFePO$_4$ materials can be obtained directly via many chemical methods, such as sol-gel method [3], hydrothermal method [4], microwave [5] and spray pyrolysis [6]. In fact, these methods reported are either high cost due to the expensive Fe(II) raw materials in the form of FeC$_2$O$_4 \cdot$ 2H$_2$O or (CH$_3$COO)$_2$Fe, or being impractical owing to complicated synthesis techniques that are difficult to scale up for industrialization. Therefore, it is necessary to use relatively cheaper Fe(III) raw materials and a convenient method. In this study, we focus our concern on the raw materials and processing cost. In the sol-gel method, starting materials are expensive and some additives might be required to control the pH value or chelate complexes into gels, and relatively complicated. Moreover, a large amount of inorganic reagents are consumed which would increase both the cost and the complexity of synthesis. The other methods either require expensive equipments or need to maintain rigorous conditions. The most common and traditional method to manufacture LiFePO$_4$ is still solid-state reaction synthesis, due to its simplicity. It is suitable for the production of LiFePO$_4$ in large scale in which the choice of source materials is an important factor, because not only the overall cost

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Table 1. The price of raw materials of iron salts, lithium salts and phosphorous compounds (2012).

Raw material	Purity	USD/kg	USD/kg of one atom of Fe, Li or P
Iron salts			
$FeC_2O_4 \cdot 2H_2O$	99 wt.%	8.750	8.750
Fe_2O_3	99 wt.%	2.125	1.063
$FeSO_4 \cdot 7H_2O$	98 wt.%	1.563	1.563
$Fe(NO_3)_3 \cdot 9H_2O$	98 wt.%	2.72	2.72
$FeCl_3$	98 wt.%	5.00	5.00
Lithium salts			
$LiOH$	99 wt.%	12.90	12.90
Li_2CO_3	99 wt.%	11.81	5.90
Li_3PO_4	99 wt.%	21.81	7.27
Phosphorus compounds			
$NH_4H_2PO_4$	99 wt.%	3.018	3.018
H_3PO_4	85 wt.%	3.100	3.100
P_2O_5	95 wt.%	37.500	18.750

but also the electrochemical performances vary depending on the source materials [7].

The prices of some raw materials used in commonly for LiFePO₄/C synthesis are listed in Table 1. Fe_2O_3 is the cheapest among the iron salts, but it demands relatively expensive P_2O_5 or unsafe $NH_4H_2PO_4$ as phosphate source. The pollution gas NH_3 is an inevitable by-product when $NH_4H_2PO_4$ is used as a raw material. $FeSO_4 \cdot 7H_2O$ is cheaper than all other iron sources, which has been used for LiFePO₄ fabrication in several previous studies [8, 9]. However, it requires an additional oxidizing agent such as hydrogen peroxide which is blameworthiness for adverse affect to human health. According to the market price, $Fe(NO_3)_3$ is next most low-priced powders. J. Ying *et al*. [10] have synthesized LiFePO₄/C composite cathode with Cr doping by a controlled crystallization-carbothermal reduction method using $Fe(NO_3)_3$. At room temperature, electrochemical tests show that this material has exhibited an initial discharge capacity of 110 mAh g⁻¹ at 1 C. Recently, LiFePO₄/C composites have been prepared by X. Wang *et al*. [11] using same source as the iron precursor and various organics as carbon precursors. When resorcinol-formaldehyde is used as carbon precursor, the cathode material shows the highest initial discharge capacity, 138.4 mAh g⁻¹ at 0.2C and 110 mAh g⁻¹ at 1C. However, the cathode capacities are shown to be low compared to LiFePO₄/C cathodes which are synthesized using other Fe(III) sources. Thus, it is necessary to further study by using this raw material.

In this paper, we have successfully adopted inexpensive $Fe(NO_3)_3 \cdot 9H_2O$ as iron source, to synthesize LiFePO₄/C composites using glucose as a carbon source and reducing agent. Both water and alcohol have been employed sequentially as a mixing solvent in order to compare the effect of these solvents on particle morphology.

Experimental Procedure

Synthesis of amorphous FePO₄ precursor

Amorphous $FePO_4 \cdot xH_2O$ was synthesized by precipitation process from aqueous solutions. The process was conducted by the pH control of solution using NH_4OH at room temperature in order to precipitate $FePO_4 \cdot xH_2O$ same as literature [10], but with modified procedure. H_3PO_4 (85%) solution was gradually added to equal molar amount of $Fe(NO_3)_3 \cdot 9H_2O$ solution under stirring. The aqueous solution was pumped into a continuously stirred tank reactor. An aqueous NH_4OH solution was also pumped into the reactor to control the solution pH. The pH of the solution was kept at 2.0. To assure proper nucleation and the particle growth of the precursor, the concentration (2 M), temperature (50 °C), and stirring speed (1000 rpm) of the resulting mixture were precisely controlled throughout the synthesis process. A white colored precipitate was formed. It was then collected by filtration, and washed with distilled water and isopropyl alcohol. After washing precipitates ($FePO_4 \cdot xH_2O$), a drying process was carried out at 100 °C for 6 hours. XRD analysis revealed that precipitates were of mostly an amorphous state.

Synthesis of LiFePO₄/C composites

LiFePO₄/C composites were synthesized by a solid state reaction process using pre-milled Li_2CO_3 and pre-synthesized amorphous $FePO_4 \cdot xH_2O$ powders. Appropriate amounts of precursors and glucose (8 wt.%) were weighed and ball-milled with a ZrO_2 media in ethanol for 24 hours. The mixture was then dried at 80 °C for 4 hours. The dried powders were then sintered at 700 °C for 4 hours under an N_2 atmosphere to prevent the oxidation of Fe^{2+} and to coat the surface of LiFePO₄ particles with carbon. Similar process was done again but using water instead of ethanol.

Structural and electrochemical characterizations

The powder X-ray diffraction (XRD, Rigaku, D/MAX-2500H) analysis with Cu Kα radiation was used to identify the crystalline phases of the prepared materials. In order to observe the particle morphology and microstructures, e-SEM (FEI, Quanta-400), FE-SEM (Jeol, JSM-6700F) and TEM (Philips CM200) were employed. For electrochemical property assessment, electrodes were fabricated from a mixture of carbon coated LiFePO₄ powders (80 wt.%), carbon black (Super P, 10 wt.%), and polyvinylidene fluoride (PVDF, 10 wt.%) as a binder in N-methyl-2-pyrrolidone (NMP) solution. This slurry was spread onto Al foil and dried in a vacuum at 120 °C for 4 hours. Electrochemical properties were measured for coin cells (CR2016), which were assembled in a glove box under Ar atmosphere.
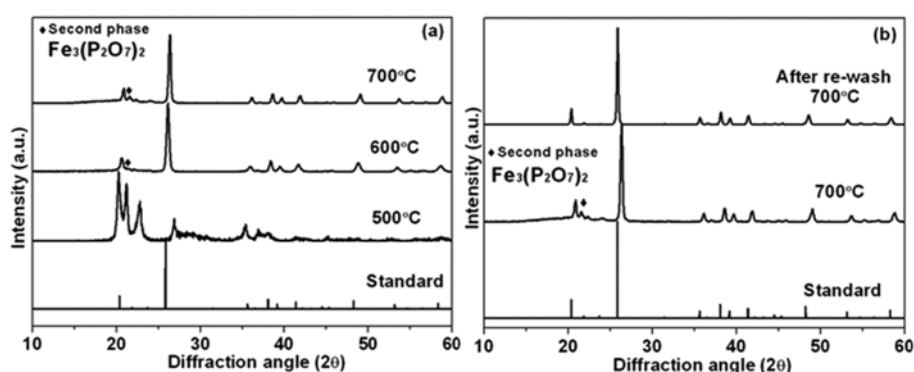
Fig. 1. XRD patterns of synthesized $FePO_4$ after heat treatments; (a) at three different temperatures (b) at 700 ℃ after re-wash.
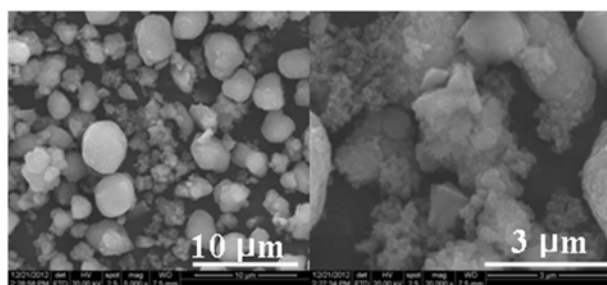

Fig. 2. SEM micrographs of as-synthesized $FePO_4 \cdot xH_2O$ (low and high magnification).

The electrolyte used was 1M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 volume). The cells were galvanostatically charged and discharged between 2.0V and 4.2V versus Li/Li^+ in a battery cycler (Wonatech,WBCS-3000) at room temperature.

Result and Discussion

Phase analysis and powder morphology

$FePO_4 \cdot xH_2O$ precursors are decided to calcine above 500 ℃, 600 ℃ and 700 ℃ for XRD analysis to observe phase information. XRD patterns indicate crystallization of amorphous $FePO_4$ to hexagonal $FePO_4$ as shown in Fig. 1(a). A second phase of $Fe_3(P_2O_7)_2$ appears in the as-synthesized iron phosphate which is removed after further washing by hot water, as shown in Fig. 1(b). Thus phase purity of amorphous as-synthesized $FePO_4 \cdot xH_2O$ powder is confirmed. The $FePO_4 \cdot xH_2O$ powders are composed of well-dispersed spherical particles and each of the spherical particles is made up of a large number of primary particles, as shown in Figs. 2(a-b).

Before synthesizing the $LiFePO_4/C$ composite, both lithium carbonate and $FePO_4 \cdot xH_2O$ are milled in advance in a high energy mill to effectively eliminate possible problems associated with size and shape differences and to enhance reaction activities in starting materials [12]. The XRD patterns of heat-treated $LiFePO_4/C$ composites, which are fabricated with pre-
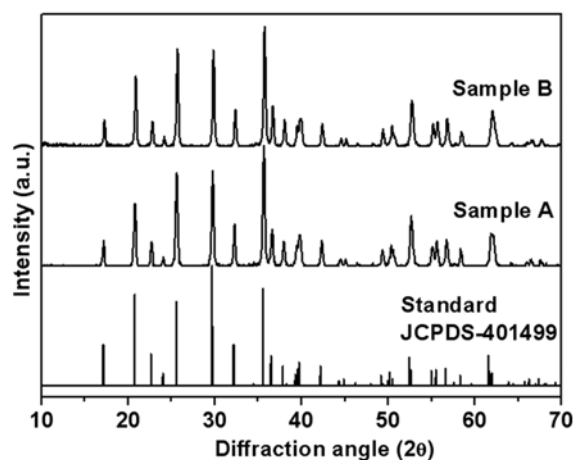

Fig. 3. XRD patterns of $LiFePO_4/C$ composites fabricated with the pre-synthesized $FePO_4 \cdot xH_2O$ through two different solvents.
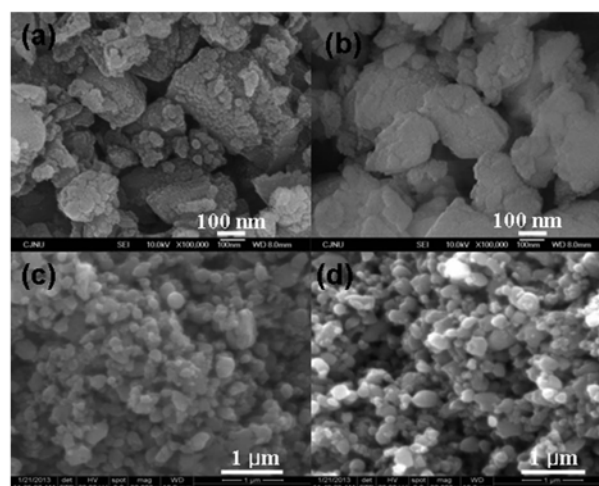

Fig. 4. SEM micrographs of $LiFePO_4/C$ composites: before heat treatment for (a) Sample A, and (b) Sample B; (C) as for (a), and (d) as for (b) but after heat treatment.

synthesized $FePO_4 \cdot xH_2O$ and pre-milled Li_2CO_3, using either ethanol or water (designated as sample A and B, respectively) sequentially are shown in Fig. 3. The patterns show good correspondence with the reference $LiFePO_4$ spectrum, which is also included in the figure.
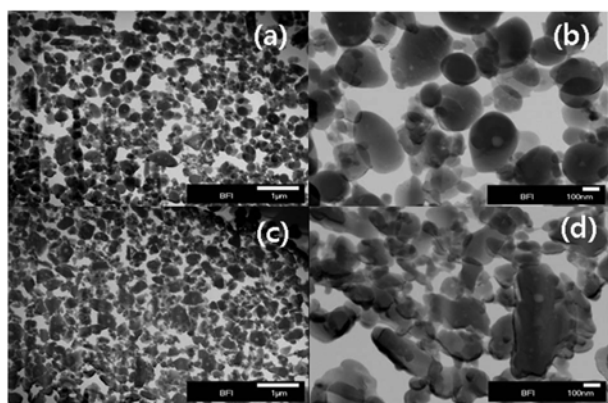
Fig. 5. TEM micrographs of LiFePO₄/C composites after heat treatment: (a) and (b) for Sample A, (c) and (d) for Sample B.

There are no significant peaks arising from any impurity phase in the samples.

The microstructures of the sample A and B (LiFePO₄/C composites) are identified by SEM, which reveal the influence of solvent on the microstructure before heat treatment as shown in Figs. 4(a-b), respectively and those after heat treatment as shown in Figs. 4(c-d), respectively. As shown in Fig. 4(a), sample A bears rough surface morphology with minute sized particles (probably dispersed glucose) accumulate on the large particles. In contrast, apparent and smooth particle surface is readily apparent in case of sample B. SEM micrographs of sample A and sample B after heat

treatment do not demonstrate any significance difference, and there is no clue about the effect of solvent from these figures. To confirm the solvent role within the LiFePO₄ powder microstructure, the LiFePO₄/C powders are further observed under TEM as shown in Fig. 5. A comparative look at the images clearly depicts that particle size after heat treatment in sample B become quite larger, while those in sample A exhibit a restricted growth with a spherical shape distribution. The particle growth in sample B may be due to the dissolution of carbon source (glucose) material in water solvent. Glucose molecules have a lot of –OH groups which can form hydrogen bond with polar water molecules. The glucose molecules are solvated by water molecule, and this occurrence inhibits it from dispersing well in the water. Thus carbon source is restrained from diffusing into deep insides of LiFePO₄ agglomerates during mixing before heat treatment. Carbon source, which is known to prohibit the particle growth during heat treatment [13], is believed not to be coated much on the sample B particles in this study. Since particles in sample A are relatively regular shaped and well dispersed, the carbon source seems to be rather uniformly coated on the surface of individual particles, possibly leading to the retardation of particle growth.

Electrochemical properties

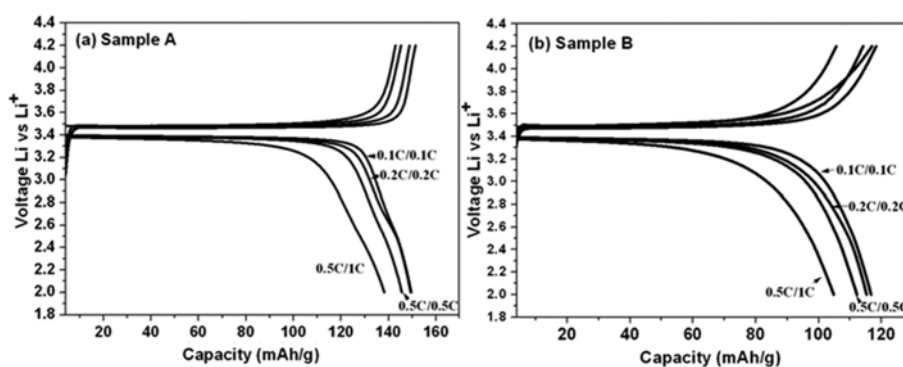Fig. 6(a-b) represent the charge/discharge voltage profiles at various rates from 0.1C to 1C of sample A and

Fig. 6. Charge/discharge profile of (a) Sample A and (b) Sample B, cathodes at different current densities against Li anode.
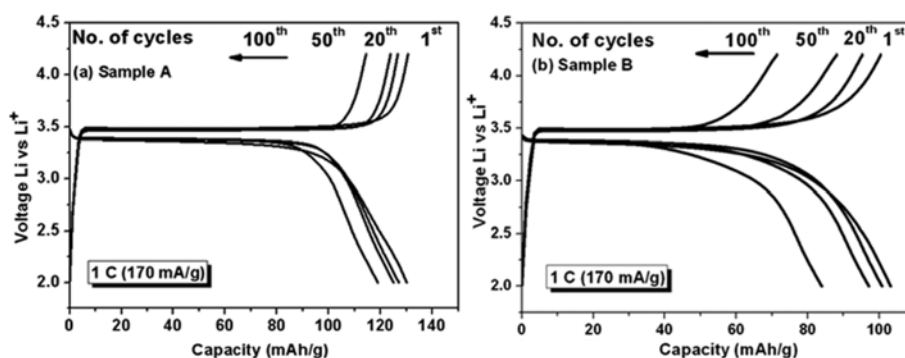

Fig. 7. Discharge curves of the 1st, 20th, 50th, 100th cycles at 1C for (a) Sample A and (b) Sample B cathodes.

B electrodes, respectively. Initial charge and discharge capacity of sample B has 119 and 118 mAhg^{-1}, respectively at 0.1C current rate. For sample A, the charge capacity is 152 mAhg^{-1}, and the discharge capacity is 150 mAhg^{-1} at the same current rate. The charge and discharge capacities decrease with the C-rate increasing for both samples.

In order to clarify the effect of solvent, the cycling behavior of both samples is presented in Fig. 7(a-b) which show the charge/discharge curves of the 1st, 20th, 50th,100th cycle for sample A and B, respectively, at 1C rate. For the sample B, the initial discharge capacity is 102 mAhg^1 and a discharge capacity is 94 mAhg^1 and 85 mAhg^1 after the 50th and 100th cycle, respectively, as shown in Fig. 7(b). As shown in Fig. 7(a), sample A shows the initial discharge capacity of 137 mAhg^{-1} and a discharge capacity of 130.5 mAhg^{-1} and 120 mAhg^{-1} after the 50th and 100th cycle charging/discharging, respectively. The capacity loss in both samples from the initial cycle to the increased number of cycles may be attributed to the formation of a solid electrolyte interface (SEI) on the surface of the electrode. The results indicate that the cycle stability of the prepared composite cathode materials can be further improved. Sample A has relatively higher charge/discharge capacities comparing to sample B. This can be ascribed to the regular and spherical shape of its particle. It is believed that this important clue for the preparation of LiFePO$_4$/C composite supplied a valuable suggestion for the future study.

Conclusions

LiFePO$_4$/C composites are synthesized by a solid state reaction process using pre-milled Li$_2$CO$_3$ and pre-synthesized amorphous FePO$_4 \cdot x$H$_2$O powders. Both ethanol and water are used sequentially as a mixing solvent in order to point out their influence if any on the microstructure and property of synthesized LiFePO$_4$ cathodes. TEM observation of synthesized LiFePO$_4$ cathodes microstructure reveals the effect of two different mixing solvents. After heat treatment, particles size become quite larger when water is used as mixing solvent, while those exhibit a restricted growth with a spherical shape distribution in case of alcohol solvent. The reason of particle growth of former composition is attributed to the poor carbon coating due to the lack of carbon source (glucose) dispersing ability in water solvent in this study. Electrochemical test shows that the later composition has relatively higher charge/discharge capacities comparing to former one. This can be ascribed to the regular and spherical shape of its particle. It is believed that this important clue for the preparation of LiFePO$_4$/C composite supplied a helpful suggestion for the further investigation.

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