Research Article

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Facile rheological route method for LiFePO₄/C cathode material production

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Abstract: LiFePO₄/C cathode material is largely used in Li-ion batteries due to its low toxicity, nonhazardous and high stability features. A facile and simple approach is proposed in LiFePO₄/C production using low-cost materials. The effect of carbon addition during the formation of LiFePO₄/C was investigated. Based on the XRD and FTIR analyses, olivine-structured LiFePO₄/C cathode material was successfully obtained via methanol-based rheological method. The SEM result showed that the material has micron-sized polyhedral shape. The electrochemical performance tests were conducted in an 18,650-type cylindrical battery. The charge–discharge performances were tested at a voltage range of 2.2–3.65 V using charge and discharge rate of 1C. Based on the charge–discharge test, LiFePO₄ with 30% carbon addition has the highest specific capacity of 121 mA h/g with excellent cycle and rate performance as a result of successful carbon compositing in LiFePO₄ material. This approach is promising to be adapted for mass production of LiFePO₄/C.

Keywords: LiFePO₄, rheology, composite, synthesis, Li-ion batteries, cathode

1 Introduction

Batteries are an electrochemical device with an ability to alter the chemical energy into electricity and thus often found in wireless electronics as energy storage. Based on its rechargeability, batteries can be classified into two types, namely, primary battery and secondary battery. A secondary battery is rechargeable, meaning it can be repeatedly used with external energy source. At this moment, the most promising secondary battery is lithium-ion battery (LIB) [1–4].

Inside an LIB, four main components are anode, cathode, separator and electrolyte. The capacity of LIBs is largely dependent on the cathode materials as the host network of an Li-ion as the charge carrier. Therefore, high-capacity cathode materials with high volumetric and gravimetric density are highly needed in an LIB cell. Many types of cathodes are used in LIBs, including lithium cobaltate (LiCoO₂) [5], lithium manganese oxide (LiMn₂O₄) [6,7], lithium nickel cobalt aluminum oxide (LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂) [8–10] and lithium iron phosphate (LiFePO₄) [11]. Spinel-type LiMn₂O₄ offers economical features; however, it has low gravimetric and volumetric capacity. Layered structure of LiCoO₂, LiNi₀.₈Co₀.₁₅Mn₀.₃O₂ and LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ has higher capacity and density of all types; however, the safety issues and high-cost raw material are the main concerns in adapting such cathode material. Among other types, LiFePO₄ material is a balanced choice, with features such as high thermal stability, environmentally friendly, long lifespan and inexpensive starting materials, for example, iron and phosphate have high availability with nontoxic properties. On the other hand, it has sufficiently high theoretical capacity (170 mA h/g) [12].

Various synthesis routes to obtain LiFePO₄ have been reported in previous studies, such as (i) solid state reaction, (ii) carbothermal reduction method, (iii) Pechini’s/sol–gel method, (iv) microwave synthesis method, (v) coprecipitation method, (vi) hydrothermal/solvothermal synthesis method, (vii) freeze–drying process, (viii) nonthermal
synthesis and so on [13–15]. Even though numerous studies on LiFePO₄/C synthesis have been performed in the past two decades, large-scale production of LiFePO₄/C is rarely discussed in previous reports. The lack of mass production-oriented studies creates a gap between research and industrial application. The removal of this gap or a research that creates a bridge between lab-scale and industrial-scale application is a crucial step toward a more economically feasible LFP/C product. Therein, in this study, we synthesized LiFePO₄/C via a rheological phase reaction method from pretreated highly available iron sulfate. Rheological phase method utilized solvents such as water and organic solvent to assure raw material distribution during the mixing process; thus, a final homogenous precursor can be easily obtained. The effect of carbon content on the physiochemical characteristics of LiFePO₄ was deeply investigated. The raw materials are in technical grade and the production of LiFePO₄ is in pilot plant scale (150 g per batch). Since low-grade iron sulfate precursor was used, we provide a simple, economical and facile pretreatment process to obtained better characterized and high-purity precursor. The as-produced LiFePO₄/C powders were used as the cathode material in an 18,650-type cylindrical LiFePO₄/artificial graphite battery. Such efforts have never been reported in previous studies.

2 Methodology

2.1 LiFePO₄ synthesis

Technical-grade FeSO₄·7H₂O of 280 g was dissolved in 1 L of distilled water and then technical-grade HCl 32% of 30 mL was added slowly to the technical FeSO₄ solution until the solution turned green under vigorous stirring for an hour and allowed to age for another hour. Iron sulfate and hydrochloric acid were obtained from Hunan, China, and Asahi, Indonesia, respectively. The green solution is filtered using a vacuum filter. One liter of 1 M FeSO₄ solution was heated at 60°C and stirred under 700 rpm speed. Eight hundred millilitre 1 M oxalic acid (Yuanping Changyuan Chemicals, China) and 25% ammonia (Merck, Germany) were slowly transferred into the FeSO₄ solution while maintaining the temperature and pH of 60°C and 2, respectively, under vigorous stirring for 2 h. Yellow precipitate was allowed to settle while brownish solution was carefully removed. The FeC₂O₄ precipitate was washed several times until the pH reached 6–7, filtered using vacuum filter and store in an oven for a night.

To make the cathode material, 157 g of LFP, 42 g of LiOH (Leverton, India), 100 g of H₃PO₄ (Brataco, Indonesia) and 100 mL of methanol (Brataco) were mixed using an overhead stirrer at 700 rpm for 2 h. Next 180 g of FeC₂O₄ was put into the slurry and further stirred for another 2 h. Homogeneous slurry was dried overnight in an oven at 120°C to obtain dried LFP precursor. Various percentages (0, 1, 3, 5, 7, 10 and 30% w/w) of commercial glucose were mixed with the dried precursor using mortar and pestle. The final LFP precursor composite was heated in a tube furnace at 700°C for 12 h under a flow of nitrogen gas. The LFP product produced was ground using mortar and pestle and sieved using 100 mesh filter. The overall steps are displayed in Figure 1.

2.2 Material characterization and electrochemical performance

The crystal structure of FeC₂O₄ and LiFePO₄/C samples was examined using mini-diffractometer (MTI, USA) at 2θ range of 17–67°. The morphology of the particle was investigated using scanning electron microscopy (SEM; JEOL JSM-6510LA, Japan). The surface chemistry of the particles was studied using FTIR spectroscopy (Shimadzu FTIR, Japan). The electrochemical performance tests were conducted in 18,650 cylindrical batteries using graphite as the counter anode. The LFP electrode sheet was
prepared by coating a mixture of LFP:AB:KS6:PVDF of 80:5:5:10 in N-Methyl-2-Pyrrolidone solvent on both sides of Al foil with a cathode coating thickness of 200 µm. The coated sheet was dried and assembled in cylindrical cells using cylindrical cell assembly equipment (MTI). LiPF₆ dissolved in 3:7 EC:DMC was used as the electrolyte. The cells were aged for a day and charge–discharged using 0.1C rate at voltage window of 2.2–3.65 V using Neware Battery Analyzer (Neware, China). Electrochemical impedance spectroscopy (EIS) analysis was performed using NuVant EZ-ware (Nuvant System Inc., USA).

3 Results and discussion

3.1 Iron sulfate purification

In this study, the production of LiFePO₄/C precursors was carried out using the coprecipitation method with materials in the form of technical FeSO₄. But before the technical-grade FeSO₄ was used, it should be reduced with HCl acid. This is because the technical-grade FeSO₄ obtained from local vendor oxidizes to form Fe³⁺(Fe₂(SO₄))₃ and Fe₂O₃ (Figure 2(a)), and the raw material is not completely soluble, becoming reddish yellow, thereby causing uncertainty in the Fe content [16]. The occurrence of reduction reaction is confirmed when a green solution is formed, which is predicted to be similar to the reductive leaching process of metal oxide as seen in equation (1). In the acidic environment, the formation of Fe³⁺ is inhibited; therefore, a stable Fe²⁺ solution is obtained.

Fe²⁺(aq) + Cl⁻(aq) (reddish yellow)
→ FeCl₂(aq) + 1/2Cl₂(g) (green) (1)

3.2 Synthesis of Fe₂C₂O₄·2H₂O powder

FeSO₄ solution of 1 M was reacted with 1 M oxalic acid solution and ammonia solution with continuous stirring and heating for 1 h at 60°C. In this case, FeSO₄ functions as a source of iron, ammonia as a regulator of pH and oxalic acid as a precipitant. During the stirring process, yellow precipitate was formed (Figure 2(b)). The precipitate was filtered and tested for its characteristics by XRD and FTIR tests.

Figure 3 shows the results of the XRD spectra of FeC₂O₄ powder. The peaks in the diffraction pattern correspond to the diffraction peaks of FeC₂O₄ (JCPDS 72-1305) [17]. It can be concluded that the solids formed
are indeed iron oxalate powders. The peaks in the diffraction pattern have a high intensity. This indicates that the solid has highly crystalline properties [18].

Surface properties of the FeC$_2$O$_4$ sample were analyzed using FTIR and SEM. FTIR determined the groups formed in FeC$_2$O$_4$ particles (Figure 4(a)). Based on the result, H$_2$O antisymmetric stretching modes 3,410–3,395/cm; C–C group appears in the range of antisymmetric stretching modes 2,123/cm; C–O appears in the range of antisymmetric stretching modes 1,646–1,655/cm; and C–O–H appears in the range of antisymmetric stretching modes 1,334–1,320, 1,431–1,438, and 665–667/cm, while the C–O group appears in the range of antisymmetric stretching modes 1,382–1,036/cm [19]. The high H$_2$O peak indicates that the precipitate formed is in hydrate form. The overall reaction of FeC$_2$O$_4$·2H$_2$O precursor formation is presented in equation (2). Figure 4b shows the micron size of FeC$_2$O$_4$ particle and is of rod shape.

$$\text{FeSO}_4^{(aq)} + 2\text{NH}_4\text{OH}^{(aq)} + \text{H}_2\text{C}_2\text{O}_4^{(aq)}$$
$$\rightarrow \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}^{(s)} + (\text{NH}_4)_2\text{SO}_4^{(aq)}$$

(2)

3.3 Production of LiFePO$_4$/C cathode materials

The reactions that occur in the formation of LiFePO$_4$ and LiFePO$_4$/C are presented, respectively, in equations (3) and (4).

$$\text{LiOH} \cdot \text{H}_2\text{O}^{(s)} + \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}^{(s)} + \text{H}_2\text{PO}_4^{(aq)}$$
$$\rightarrow \text{LiFePO}_4^{(s)} + 2\text{CO}_2^{(g)} + 3\text{H}_2\text{O}^{(g)} + 3/2\text{H}_2^{(g)}$$

(3)

$$\text{LiOH} \cdot \text{H}_2\text{O}^{(s)} + \text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}^{(s)} + \text{H}_2\text{PO}_4^{(aq)} + a\text{C}_2\text{H}_2\text{O}_6^{(s)}$$
$$\rightarrow \text{LiFePO}_4^{(s)} + b\text{C}_2^{(s)} + c\text{CO}_2^{(g)} + d\text{H}_2\text{O}^{(g)}$$

(4)

3.3.1 Structural analysis of LiFePO$_4$/C samples

The results of the XRD analysis of LiFePO$_4$ by rheological method are shown in Figure 5. The peaks in LiFePO$_4$/C products are in accordance with the peaks in commercial LiFePO$_4$/C (PDF (81-1173)) [14]. The peaks in LiFePO$_4$ 0% C XRD patterns are clearer than the other samples. This is because, the higher the carbon content in LiFePO$_4$/C

Figure 4: (a) Infrared absorption spectra (FTIR) of FeC$_2$O$_4$·2H$_2$O precursor; (b) SEM images of FeC$_2$O$_4$ particle.

Figure 5: Results of XRD LiFePO$_4$/C.
products, the lower the intensity, so that the peak produced will be lower [20].

3.3.2 FTIR analysis

Figure 6 shows the FTIR spectra of LiFePO$_4$/C material. Two function groups can be observed, namely, the OH$^-$ bond and PO$_4^{3-}$ group. But the OH$^-$ bonds that are formed are not so clear that it can be ascertained that the particles formed are really LiFePO$_4$/C. The H$_2$O bond appears in the range of antisymmetric stretching modes 3,000–3,500/cm, while the PO$_4^{3-}$ group appears in the range of antisymmetric stretching modes from 1,000–1,200 to 400–560/cm [21].

3.3.3 SEM analysis

SEM analysis was used to examine the surface morphological properties and the size or diameter of LiFePO$_4$/C particles. Particle measurement was randomly conducted.

Figure 6: FTIR spectra of LiFePO$_4$/C at various carbon additions.

Figure 7: SEM images of LiFePO$_4$/C sample with carbon additions of (a) 0%, (b) 7%, (c) 10% and (d) 30%.
The SEM image of LiFePO$_4$/C at various carbon additions is displayed in Figure 7 at 5,000× magnification. Based on the SEM analysis result, with increasing carbon content addition, the submicron-sized primary particles become smaller. Smaller particle size is favorable, since it has a large surface area increase in the Li-ion diffusivity during intercalation and de-intercalation processes. Several particles appear to be of polyhedral shape with grains that can be clearly observed [22].

### 3.3.4 Specific capacity test of LiFePO$_4$/C samples in a cylindrical cell

Electrochemical performance tests were carried out on cylindrical cells with LiFePO$_4$/C sample as the cathode and graphite as the counter anode. A formation process using 0.05C current rate was applied in every cell before further cycled at higher current rate. The specific capacity of LiFePO$_4$/C at 1C current rate in 18,650 cylindrical batteries can be seen in Figure 8. The resulting capacity of each sample is still low when compared with the theoretical capacity of LiFePO$_4$/C batteries (165 mA h/g). This is due to the fact that tests were conducted using the full-cell method (non-Li-based anode), while the theoretical capacity is obtained by the half-cell method (Li metal as an anode) [23]. The capacity of the samples increases with the increase in the addition of carbon sources of up to 30%. It is predicted that with high carbon content, better LiFePO$_4$ material is achieved. Based on Figure 8, the highest specific capacity of 121 mA h/g is exhibited by LFP 30% C. The specific capacity of commercial LiFePO$_4$ is lower than that of LFP 30% C and LFP 10% C. This phenomenon proves that such method is promising and is ready to be adapted at industrial scale [24]. More carbon addition and surface study are necessary to be investigated in the future projects.

Figure 9a presents the cycle performance of LFP/C samples and commercial LFP at 1C. The capacity retention of LFP 7% C, LFP 10% C and LFP 30% C after 50 cycles is 58.4, 85.2 and 89.5%, respectively. This proves that addition of carbon during the synthesis process significantly improves the cycle performance. Figure 9b presents a comparison of LFP/C with 7, 10 and 30% carbon rate performance with a commercial LiFePO$_4$ obtained from MTI. Based on the picture, the higher the charge and discharge currents, the lower the specific discharge capacity in both samples. At higher charge–discharge rate, the ability of Li ions to move decreases due to the conductivity and diffusivity of the material. The reduction in
the capacity of the LiFePO$_4$/30% C sample is still higher than that of commercial LiFePO$_4$, this is due to the high carbon content increasing the conductivity of the material [25].

3.3.5 EIS analysis

Figure 10 presents the EIS test result in the form of a Nyquist plot. Based on the figure, it can be observed that each sample does form a semicircle curve. However, the sample with the lowest semicircle diameter is LFP 30% C, while LFP 7% C has the largest semicircle diameter. This shows that the LFP 30% C sample has good Li diffusivity and conductivity due to its carbon content [25]. This phenomenon is also the reason that LFP 30% C sample has good cycle and rate performance (Figure 9).

4 Conclusion

A large-scale (pilot-scale) production of LiFePO$_4$/C is successfully conducted via methanol-based rheological method. In this study, the addition of carbon source during the formation of LiFePO$_4$ had an effect on the conductivity of the material. Low-grade cheap FeSO$_4$ can be easily purified by adding HCl into the solution. The formation of FeC$_2$O$_4$·2H$_2$O is ensured using simple batch oxalate precipitation confirmed by XRD and FTIR analyses. The XRD patterns of all LiFePO$_4$/C samples are well indexed to the commercial LiFePO$_4$/C cathode material reference. SEM images show that the particles are of micron size having polyhedral shape. The highest capacity was achieved by LFP/C with 30% carbon addition and excellent cycle and rate performance which exceeds the rate performance of commercial LiFePO$_4$ due to the successful formation of carbon coatings on the LiFePO$_4$ particles. The EIS test shows that LFP with 30% carbon addition has the highest ionic conductivity compared to other samples. It can be concluded that producing LiFePO$_4$ from pretreated poor grade raw material using rheological route can be considered promising to be adapted for mass production.

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Figure 10: Nyquist plot of LiFePO$_4$/C samples in cylindrical cells.
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