Research Article

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Facile rheological route method for LiFePO_4/C cathode material production

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Abstract: LiFePO_4/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 LiFePO_4/C production using low-cost materials. The effect of carbon addition during the formation of LiFePO_4/C was investigated. Based on the XRD and FTIR analyses, olivine-structured LiFePO_4/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, LiFePO_4 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 LiFePO_4 material. This approach is promising to be adapted for mass production of LiFePO_4/C .

Keywords: LiFePO_4 , 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 (LiCoO_2) [5], lithium manganese oxide (LiMn_2O_4) [6,7], lithium nickel cobalt aluminum oxide ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) [8–10] and lithium iron phosphate (LiFePO_4) [11]. Spinel-type LiMn_2O_4 offers economical features; however, it has low gravimetric and volumetric capacity. Layered structure of LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 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, LiFePO_4 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 LiFePO_4 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

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synthesis and so on [13–15]. Even though numerous studies on LiFePO_4/C synthesis have been performed in the past two decades, large-scale production of LiFePO_4/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 LiFePO_4/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 LiFePO_4 was deeply investigated. The raw materials are in technical grade and the production of LiFePO_4 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 LiFePO_4/C powders were used as the cathode material in an 18,650-type cylindrical LiFePO_4 /artificial graphite battery. Such efforts have never been reported in previous studies.

2 Methodology

2.1 LiFePO_4 synthesis

Technical-grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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 FeSO_4 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 FeSO_4 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 FeSO_4 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 FeC_2O_4 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 H_3PO_4 (Brataco, Indonesia) and 100 mL of methanol (Brataco) were mixed using an overhead stirrer at 700 rpm for 2 h. Next 180 g of FeC_2O_4 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 FeC_2O_4 and LiFePO_4/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

Figure 1: Flow diagrams of LiFePO_4 electrode production.

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). LiPF_6 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 LiFePO_4/C precursors was carried out using the coprecipitation method with materials in the form of technical FeSO_4 . But before the technical-grade FeSO_4 was used, it should be reduced with HCl acid. This is because the technical-grade FeSO_4 obtained from local vendor oxidizes to form $\text{Fe}^{3+}(\text{Fe}_2(\text{SO}_4)_3 \text{ and } \text{Fe}_2\text{O}_3)$ (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 Fe^{3+} is inhibited; therefore, a stable Fe^{2+} solution is obtained.

3.2 Synthesis of $\text{Fe}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powder

FeSO_4 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, FeSO_4 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 FeC_2O_4 powder. The peaks in the diffraction pattern correspond to the diffraction peaks of FeC_2O_4 (JCPDS 72-1305) [17]. It can be concluded that the solids formed

(a)

(b)

Figure 2: (a) FeSO_4 precursor and (b) pretreated yellow FeC_2O_4 precursors.

Figure 3: XRD pattern of FeC_2O_4 precursors.

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_2O_4 sample were analyzed using FTIR and SEM. FTIR determined the groups formed in FeC_2O_4 particles (Figure 4(a)). Based on the result, H_2O 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_2O peak indicates that the precipitate formed is in hydrate form. The overall reaction of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor formation

(a)

(b)

Figure 4: (a) Infrared absorption spectra (FTIR) of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor; (b) SEM images of FeC_2O_4 particle.

is presented in equation (2). Figure 4b shows the micron size of FeC_2O_4 particle and is of rod shape.

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).

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 5: Results of XRD LiFePO_4/C .

Figure 6: FTIR spectra of LiFePO_4/C at various carbon additions.

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_2O 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 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 $5,000\times$ 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 cells 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

Figure 8: Specific charge-discharge capacity of LiFePO_4/C samples.

Figure 9: (a) Cycle performance and (b) rate performance test of LiFePO_4/C at various carbon additions.

LiFePO_4 30% C and LiFePO_4 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

Figure 10: Nyquist plot of LiFePO_4/C samples in cylindrical cells.

the capacity of the $\text{LiFePO}_4/30\% \text{ C}$ sample is still higher than that of commercial LiFePO_4 , this is due to the high carbon content increasing the conductivity of the material [24].

3.3.5 EIS analysis

Figure 10 presents the EIS test result in the form of 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 $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ 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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