Synthesis LiFePO$_4$ at Various Atmosphere Condition

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Abstract. LiFePO$_4$ is considered the most environmentally friendly, inexpensive, abundant, has good cycle stability and thermal stability. However, LiFePO$_4$ has the main disadvantage of potential voltage and conductivity which is relatively lower than other batteries. This can be overcome by adding carbon and reducing particle size. The method used in this research is the rheological phase method. This method was chosen because the material used is easy to obtain and the price is cheap, no requires a lot of tools, and good homogeneity. LiFePO$_4$ is very sensitive to direct air. So in this study an evaluation of the effect of argon gas, hydrogen, and nitrogen on the material. LiFePO$_4$ analyzed its morphology with SEM (Scanning Electron Microscopy), its crystallinity with XRD (X-Ray Diffraction) and functional group of LiFePO$_4$ with FTIR (Furier Transformation Infra-Red). Based on the characterization result, the optimum synthesis product continued battery performance test. LiFePO$_4$ H$_2$-Ar produces the best battery capacity compared to other gases because it uses reducing gas which can increase the carbon content of the material.

1. Introduction
Technology for storing energy has shifted from Lead Acid Battery to Lithium Ion Battery (LIB). LIB is an energy storage device that is reliable in its ability to be used repeatedly [10]. LIB has been used successfully as a portable power source for commercial and transportation electronic devices in the past 30 years. High LIB capacity, high energy density, and good cycle performance are the reasons LIB is the best energy storage at the moment [8]. LIB is the first choice as a storage of new and renewable energy both solar cells, wind power, geothermal and fuel cells so that the advancement of this technology is a concern of many from various groups, especially in industry and government [10].

Several types of LIB cathodes are Lithium Cobalt Oxide (LCO), Lithium Manganese Oxide (LMO), Nickel Cobalt Aluminum Oxide (NCA), Nickel Manganese Cobalt Oxide (NMC) and Lithium Iron Phosphate (LiFePO$_4$). The first commercially available cathode material is LiCoO$_2$ (LCO). This LCO material is difficult to meet the demand for electric vehicle applications which continues to increase every year. This is due to the highly toxic nature of LCO, high cost, thermally unstable, and limited Cobalt resources [2]. The weakness of LCO is what made the researchers look for alternative cathode materials to be studied more deeply in order to be able to meet the requirements of high energy density at a low cost. LiFePO$_4$ is considered the most environmentally friendly, inexpensive, abundant, has good cycle stability and thermal stability [9]. However, LiFePO$_4$ is easily oxidized in
water and air. Long exposure to air causes oxidation of Fe$^{2+}$ to Fe$^{3+}$ which can limit electrochemical ability and reduce battery performance [6]. Improving the performance of LiFePO$_4$ can be done in several ways, namely by choosing the method of synthesis, carbon coating, reducing the size of the particles, and doping with superval cation.

Common LiFePO$_4$ synthesis methods are carbothermal reduction, solid-state reaction, flame assisted spray pyrolysis (FASP), co-precipitation, sol-gel, and hydrothermal. LiFePO$_4$ is one of the cathode materials that has many advantages, namely the type of Li-ion rechargeable battery for high power applications, thermal stability, high power capacity, and long life cycle (> 2000 @ 0.2C rate, IEC Standard) [11]. However, LiFePO$_4$ has the main disadvantage of potential voltage and conductivity which is relatively lower than other batteries. This can be overcome by adding carbon and reducing particle size [1]. The method used to synthesize LiFePO$_4$ is reaction rheological phase, carbothermal reduction method, sol-gel method, synthesis method microwaves, coprecipitation methods, hydrothermal / solvothermal synthesis methods, freeze drying process, ionothermal synthesis and so on [12]. The method used in this research is the rheological phase method. This method was chosen because the material used is easy to obtain and the price is cheap, no requires a lot of tools, and good homogeneity [4].

Based on research on the scale of a demo plant making LiFePO$_4$ batteries using rheological methods and technical raw materials that have never been done. Therefore, in this study using methanol and glucose as a carbon source. Methanol was chosen as a solvent because it has low purity, is easily available and is cheap. LiFePO$_4$ is highly sensitive to direct air situations. For sintering, atmospheric conditioning is quite necessary. In this research the effect of argon gas, hydrogen and nitrogen on the material is evaluated. In previous research, the effect of gas was never discussed.

2. Material and Methods

2.1 Tool
The main tools used in the synthesis of LiFePO$_4$ cathode material consist of Synthetic Equipment and Instrument Characterization of Products. Synthetic equipment includes vacuum oven, 300 mesh filter, beaker, filter paper, bottle flask, measuring cup, dropper pipette, mortar, mixing motor, spoon, automatic thick film coater, hot rolling machine, gloves box, stirrer stove, magnetic stirrer, furnace. While for Product Characterization Instruments include X-Ray Diffractometer(XRD), FTIR spectrometer, and Scanning Electron Microscope (SEM) and Battery Analyzer.

2.2 Material
The main materials used in manufacturing LiFePO$_4$ cathode batteries are LiOH (99,99%, Merck, Germany), FeSO$_4$ technical (CV. Agung Jaya, Indonesia), H$_3$PO$_4$ (85%, Megah Kimia, Indonesia), HNO$_3$ (68%, Multi Jaya Kimia, Indonesia), acetylene black/AB (99,99%, MTI, China), polyvinylidenefluoride/PVDF (99,99%, MTI, China), N-methylpyrrolidone/NMP (99,99%, MTI, China), aluminum foil, argon gas, and LiPF$_6$ (99,99%, MTI, China).

2.3 Synthesis LiFePO$_4$
FeSO$_4$ was extracted first by the distillation of technical FeSO$_4$ in distilled water while processing the LiFePo4 cathode, then 32% technical HCl was added slowly to the technical FeSO$_4$ solution until a green solution was obtained. A vacuum filter separates the residual solution. FeSO$_4$ 1 M was the answer.

Heat 1 liter of 1 M FeSO$_4$ at 60 °C to FeC$_2$O$_4$, and stir at 700 rpm. Put an acid solution oxalate by dissolving H$_2$C$_2$O$_4$ in distilled water and 25% ammonia slowly into the solution. The temperature is maintained for 2 hours at 60 °C and then cooled to room temperature. With the help of a vacuum filter, the precipitate formed is filtered and collected for one night over. The solid is called FeC$_2$O$_4$.

To make LiFePO$_4$ cathode material, LiOH, H$_3$PO$_4$ and methanol are needed. The material is mixed with a stirring motor for 2 hours to form white slurry. FeC$_2$O$_4$ was subsequently put into a slurry for
two hours and stirred again. The homogenous slurry then dried for overnight in an oven at 120 °C. Precursors of LiFePO$_4$ are heated under a gas mixture of oxygen, argon and hydrogen-argon at 700 °C over 12 hours in the tube furnace. The processed LiFePO$_4$ material was mashed and grinded using a mortar and pestle and 100 mesh size [4].

2.4 LiFePO$_4$ Characterization
The LiFePO$_4$ research has studied its morphology with SEM (Scanning Electron Microscopy), its crystallinity with XRD (X-Ray Diffraction), and functional group of LiFePO$_4$ with FTIR (Fourier Transformation Infra-Red). The optimal synthesis material continued battery performance testing on the basis of the characterization analysis. The battery performance testing using a cylindrical battery.

3. Result and Discussion
In this paper the synthesis of LiFePO$_4$ is achieved by a process of rheological phase. This method was chosen because the material used is easy to obtain and the price is cheap, no requires a lot of tools, and good homogeneity. This method is a method of mixing solids with an organic liquid medium. In this study using the organic liquid medium is methanol. Before technical FeSO$_4$ is used it is necessary to reduce it with HCl acid. This is because the technical FeSO$_4$ on the market has been oxidized to form Fe$^{3+}$ ($\text{Fe}_2(\text{SO}_4)_3$ and $\text{Fe}_2\text{O}_3$), causing the raw material to be completely insoluble and reddish yellow, and the Fe content to be uncertain. FeSO$_4$ solution was reacted with oxalic acid solution and ammonia solution. In this case, FeSO$_4$ functions as a source of iron, ammonia as a regulator of pH, and oxalic acid as a precipitant.

![Figure 1. FTIR spectra LiFePO$_4$ of Argon Gas, Nitrogen Gas, and Commercial](image)
observed namely the OH$^-$ bond and the 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$_4$. OH-bonds appear in the antisymmetric stretching mode range 3000-3500 cm$^{-1}$. Whereas the PO$_4^{3-}$ group appears in the antisymmetric stretching mode range of 1000-1200 cm$^{-1}$ and 400-560 cm$^{-1}$ [1].

![XRD analysis of LiFePO$_4$ with Nitrogen Gas, H$_2$-Ar Gas, and Commercial](image)

**Figure 2.** XRD analysis of LiFePO$_4$ with Nitrogen Gas, H$_2$-Ar Gas, and Commercial

The XRD test is used for the analysis of the crests of crystal structures formed from sample particles whether they are in accordance with the peaks in commercial LiFePO$_4$. Diffraction pattern The results of XRD analysis by the rheological method are shown in Figure 2 where the peaks in LiFePO$_4$ products are in accordance with the peaks in commercial LiFePO$_4$ (PDF (81-1173)) [3]. On LiFePO$_4$ (H$_2$-Ar) the peak is clearer. This is because, the higher the carbon content in LiFePO$_4$ products, the lower the intensity so that the peak produced will be lower [5].
Figure 3. SEM images of LiFePO$_4$ Precursor (a) at 5000x magnification, (b) at 10,000x magnification, (c) at 15,000x magnification, (d) at 20,000 magnification.

Figure 4. SEM images of LiFePO$_4$ with Nitrogen (a) at 1000x magnification, (b) at 3000x magnification, (c) at 5000x magnification, (d) at 10,000 magnification.

Analysis of the morphological surface structure and size and diameter of LiFePO$_4$ particles is performed by SEM (Scanning Electron Microscopy). Random analyses of the particles are done. The SEM of LiFePO$_4$ as shown in Figure 3. Similarly prepared with the precursor LiFePO$_4$ morphology (Fig. 4). In magnification of figure 4 taken is at magnification 1000x, 3000x, 5000x, and 10000x. Figure 4 is the SEM test results of a study of Li FePO$_4$ in which many particles are already very obvious from each other in polyhedral shape [7]. In comparison to LiFePO$_4$-N$_2$, the precursor has a greater diameter. The diameter of precursors reaches 5 microns. While the average size of LiFePO$_4$ particles formed is 0.964 microns.
Figure 5. Graph of Specific Capacity of LiFePO$_4$

Based on the picture at the time of filling and releasing which increases the number of needs in the second sample. This is because the ability of Li ions to move decreases due to the conductivity of the material and the ability of the material's diffusivity. The reduction in the capacity of the LiFePO$_4$ Ar sample is far less than that of LiFePO$_4$ H$_2$-Ar, this is due to the higher carbon content increasing the conductivity material [13]. Since the reduction gas contains a lot of hydrogen to enable the sintering method to increase the carbon content [14].

4. Conclusion
Preparation of LiFePO$_4$ cathode material by the rheological phase method can be done by homogenizing FeC$_2$O$_4$, LiOH, H$_3$PO$_4$, on methanol. XRD test shows that the particles produced have formed LiFePO$_4$ crystal structure. FTIR test found that two groups were observed namely the OH-bond and the PO$_4^{3-}$ group had formed. The SEM test shows that the morphology of LiFePO$_4$-N$_2$ has a smaller diameter compared to LiFePO$_4$-precursor. From the results of the characterization that has been analyzed so that it can be concluded that the synthesis of LiFePO$_4$ can be carried out at various atmosphere conditions. LiFePO$_4$ H$_2$-Ar is better than other variations because it uses reducing gas which can increase the carbon content in the material so that the battery capacity is higher.

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