Furnace Temperature and Atmosphere Influences on Producing Lithium Iron Phosphate ($LiFePO_4$) Powders for Lithium Ion Batteries

Abstract:

New technologies for creating efficient low cost lithium ion batteries are currently being developed for large scale manufacturing. Many methods are researched to show the benefits of using lithium iron phosphate ($LiFePO_4$) as cathode material over other Li-ion based substances such as lithium manganese or lithium cobalt. Solid state synthesis, co-precipitation, and sol-gel are such techniques being used to fabricate $LiFePO_4$ powders. A major flaw found in these powders is its electrical conductivity being only around 10^{-9} S/cm compared with that of lithium cobalt (around 10^{-3} S/cm). By creating smaller sized particles, carbon coating, and adjusting of temperature/atmospheric conditions, improved electrochemical performance can be achieved. This paper will give an overview of furnace firing parameters and methods of $LiFePO_4$ production.

Introduction:

Discovered by John Goodenough at the University of Texas in 1996, lithium iron phosphate is still advancing as a technology that is utilized in computers, cell phones, and hybrid vehicles. A theoretical discharge process with cathode and anode material inside a battery is shown in figure 1.

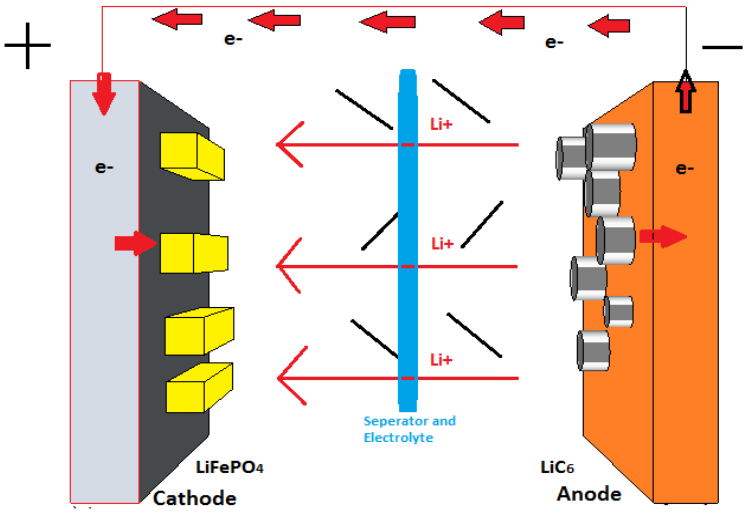

Figure 1. Battery representation and lithium iron phosphate as cathode

The cathode material of lithium iron phosphate is valued for its high theoretical capacity, cycle/thermal stability, and environmental benefits over other Li-ion type batteries. Other materials used for cathode powder material are lithium cobalt ($LiCoO_2$), lithium nickel ($LiNiO_2$), and lithium manganese ($LiMn_2O$). The structure of $LiFePO_4$ is also shown to have an olivine structure providing a safer charging/discharging than other cathode materials [1]. This material shows good theoretical capacity at 170 $\frac{mAh}{g}$ and a flat voltage of 3.4 V, but low conductivity is the major disadvantage of these types of powders. Using additives in the form

of a carbon source such as acetylene black or sucrose increases electronic conductivity of the powders almost to the theoretical capacity [1]. Carbon coating has also been shown to be a way to decrease particle size and in turn improve electronic conductivity [2]. For example, Wang et. Al. obtained carbon coated nanoparticles of LFP/C that delivered a capacity of 134.2 $\frac{mAh}{g}$ at a rating of 1 C. Even though this capacity is lower, the cycling ability and the charge losses were minimal which would be well suited for long term use. Firing temperature and atmospheric conditions are important because every process requires a heat treatment step. For example, a glass type LFP production route is shown to have improved performance when firing in 7% H_2/N_2 rather than air. There are two main categories of techniques involved in creating $LiFePO_4$: solid state based and solution based methods. These methods differ in the technique, temperature, heating rate, and mixture of components.

Solid State Processing Methods

Solid state reaction methods include solid state synthesis, carbothermal reduction, and mechanochemical activation among others. The process of solid state synthesis needs much higher temperatures and longer sintering times than other techniques, but it is able to create an ordered crystal structure in a simplistic way compared to solution methods. This technique is well suited for the mass production of $LiFePO_4$ and other unique forms such as ceramics or piezoelectrics [3]. The process of solid state synthesis involves the mixing of precursors followed by heat treatment. A common example of precursor components used in solid state synthesis for mixing are Li_2CO_3, $FeC_2O_4 \cdot 2H_20$, and $NH_4H_2PO_4$. Atmospheric conditions used are air, argon, nitrogen, or a combination hydrogen/nitrogen. Adding a conductive carbon coating such as graphite or acetylene black to the precursors will be able to increase the conductivity of $LiFePO_4$ as well. During ball milling and mixing, a stoichiometric amount of precursors are stirred together and milled for 3-18 hours. This is followed by heat treatment using equipment such as belt furnaces with temperatures seen up to 700˚C. Heating up to high temperatures can be done in a one or two step process. In the two step process, pre-calcination (pre-firing) is done first involving heat treatment between 250-350˚C to expel gasses and decomposing of precursors [3]. The final step is to bring the product to the final calcination temperature ranging from 400-800˚C [3]. A simple outline of procedures for the popular solid state synthesis is shown in the image below.

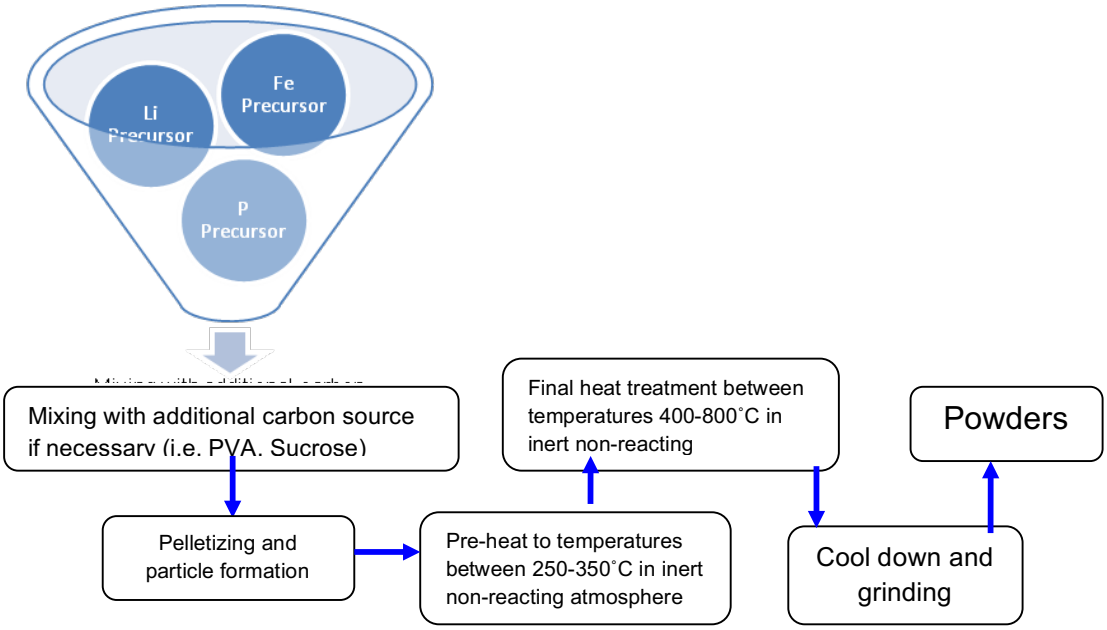

Figure 2. Solid state synthesis method

Many different combinations of temperature and heating rates have been studied to find the most optimal outcome. Yamada et. Al. reports that the highest discharge capacity found was 162 $\frac{mAh}{g}$ at sintering temperatures between 500-600˚C with particle sizes below 30 nm. Impurities can appear during the heat treatment phase because of the $FePO_4$ precursor inability to convert fully to $LiFePO_4$ as seen in studies by Yang et. Al [4] The addition of glucose as a carbon source helps inhibit particle growth during sintering therefore increasing conductivity [4]. Solid state methods give a simple way to create LFP powder with the ability to easily control results. It does not require solvent which can be expensive on an industrial scale. Solution based methods require this solvent but have the advantage of obtaining better results.

A source of carbon is usually added to solve the problem of poor electrical conductivity. For example, Yamada et. Al. prepared asphalt powder of 85.37% carbon content mixed with LiOH and $FePO_4$ in a solid state reaction. The measured discharge capacity was 138.2 mAh/g at .5C rate after 50 cycles. $LiFePO_4$/C with carbon derived from glucose shows smaller crystallite sizes of 25 nm as opposed to bare $LiFePO_4$ with crystal size of 32 nm for [6]. The smaller sizes for $LiFePO_4$/C can be attributed to a lower degree of crystallization. Carbon inhibits particle growth which leads to better electrochemical performance [4] $LiFePO_4$/C has better discharge retention of 100.1% as opposed to bare LiFePO4 that has 52.4% meaning better cycling performance and lifespan for the battery.

Solution Based Processing Methods

$LiFePO_4$ cathodes by solution based methods show higher discharge performance, smaller particle sizes, and more homogenous carbon coating. They also require less time and energy input than solid state reactions. Techniques in this group include hydrothermal, sol-gel, and spray pyrolysis. Co-precipiation is one such method that involves mixing of lithium and phosphate compounds with control of pH values followed by precipitation and heat treatment. This process is able to obtain small particle sizes and good uniformity. According to Jugovic et. Al., crystallite sizes range from 56-140 nm and give a maximum

discharge capacity of 160 mAh/g. In this method the process begins with the mixing of lithium and phosphate precursors in solvent. Common elements of chemicals used are Li_2CO_3, $FeSO_4 \cdot 7H_2O$, and H_3PO_4 mixed in deionized water. The mixture is then precipitated and filtered under an inert atmosphere. Afterwards, heat treatment is performed in a furnace with temperatures ranging from 500-800˚C under a N_2 atmosphere for times as long as 12 hours [3]. A simple outline of the process is shown below.

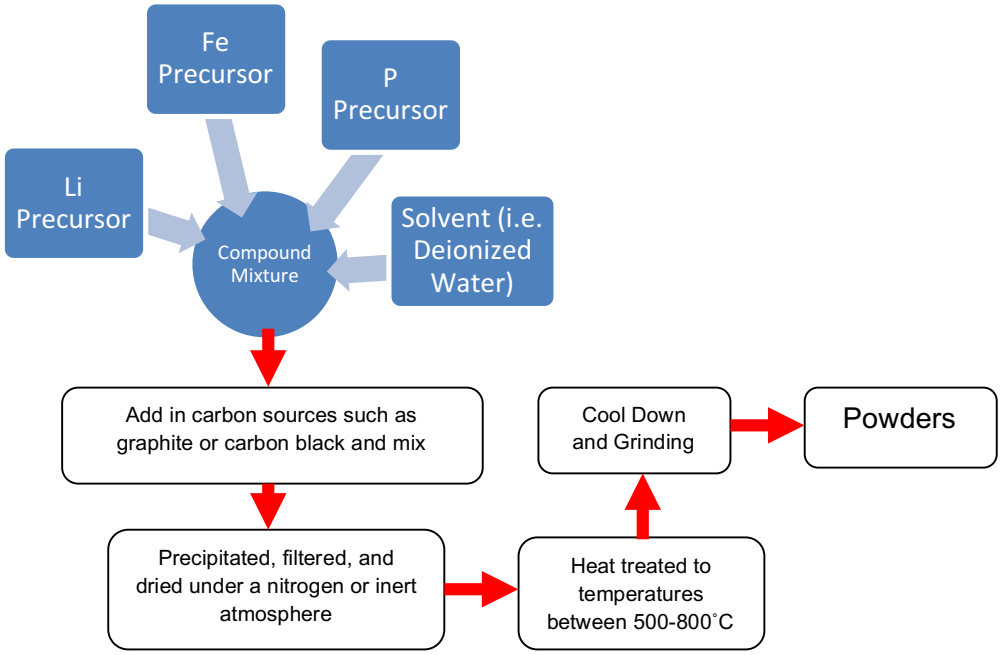

Figure 3. Solution based co-precipitation process method

Co-precipitation can also be combined with other processes such as solid state synthesis discussed before. This is performed by using a two step drying process at 80˚C and a high-pressure filtering method. Powders were obtained with 7 wt% carbon and a gravimetric discharge capacity of 167 mAh/g [4]. This value is nearly the theoretical discharge value of $LiFePO_4$ due to the well homogenized carbon content in the precipitate.

Firing Temperature Influence on Powder Formation

All mechanisms of creating $LiFePO_4$ will require some kind of heat treatment as a final step. Temperature has a significant influence on resulting physical characteristics and electrical properties. High temperatures in solid state reactions are needed in large scale commercial production of $LiFePO_4$ for repeatability in the manufacturing process. In a spontaneous precipitation method, Wang et. Al.[2] created LiFeP/C nanoparticles by heating products to 350˚C for 5 hours to rid the particles of excess gasses. The products are then heated to 700˚C under a N_2/H_2 atmosphere. Temperature was found to be an important factor in the development of the particle growth. Yamada et. Al.[5] found that the highest discharge capacities obtained were heat treated between 500-600˚C using a solid state synthesis method. These samples gave discharge capacities of 162 mAh/g. Temperatures higher than 600˚C create uncontrollable particle growth, while temperatures lower than 500˚C create unwanted oxidation of unstable Fe^{2+} ions [5].

In co-precipitation, heat treatment up to 800˚C can be used. Firing temperatures of 600, 700, and 800˚C are studied by Jugovic et. Al. to compare the properties obtained at each firing temperature. Samples obtained at 600˚C were the smallest in size but showed high agglomeration as seen in figure 1. At 700˚C the morphology of the compounds does not have any significant change. At 800˚C the morphology of the product changes dramatically creating more crystallization and growth of particles [6].

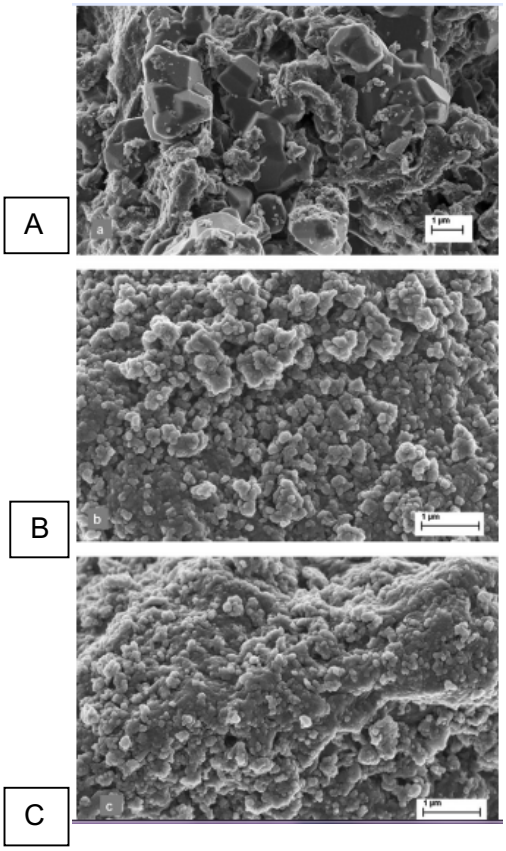

Figure 1. SEM micrographs of powder obtained from firing at a) 600˚C, b)700˚C, and c)800˚C [6]

700˚C is the optimum temperature for an aqueous precipitation method because of good crystallinity, small powder particles, and exceptional iron ordering [6]. Depending on the homogeneity of the carbon content and the precursor ingredients, temperature control is of importance.

In another solution based method called sol-gel, high temperatures play an important role in the curing process. Liu et. Al. created a mixture containing lithium hydroxide monohydrate, ferric nitrate, phosphoric acid, with added ascorbic acid as carbon source. It was prepared and mixed in different annealing temperatures of 500, 600, 700, and 800˚C. The heating rate was at 2˚C/min. An increase in crystallinity and grain size has been shown with a rise in temperature. Crystallite sizes obtained from experiments by Liu et. Al. are shown in table 1.

Temperature (°C)	Crystallite size (nm)
500	16.1
600	19.4
700	21.1
800	30.8

Table 1. Temperature in relation to crystallite sizes.

The structure can be controlled through the annealing process. The optimum temperature for heat treatment was found to be 600˚C. At this temperature, the initial discharge capacity was 312 mAh/g for the initial cycle and stays at 218 mAh/g after 20 cycles [3]. A higher performance seen here is due to the large surface to volume ratio and poor crystallinity which provides a less packed structure leaving space for more lithium ion intercalation [3]. The comparison of various annealing temperatures can be seen in figure 2.

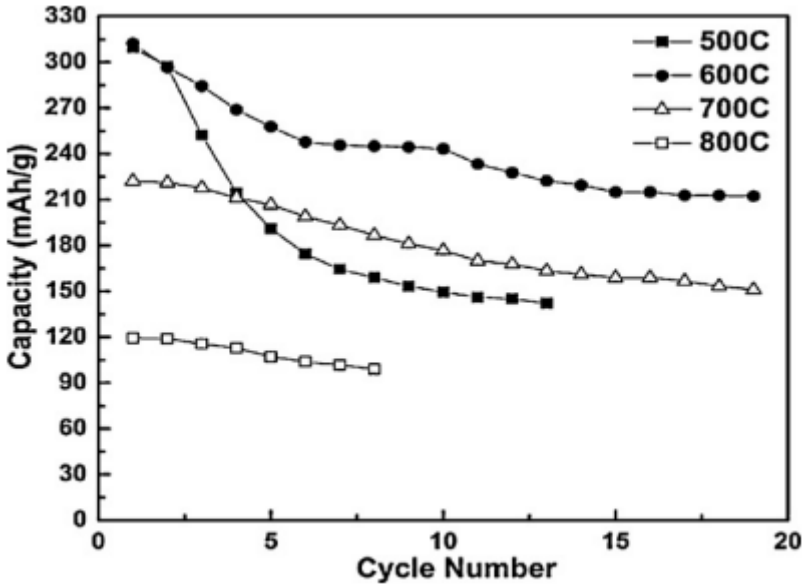

Figure 2. Number of cycles vs Capacity at different annealing temperatures

Influence of Atmospheric Conditions on Characteristics of LiFePO4

Atmospheric conditions play an essential role during annealing. Controlling heat treatment atmospheres is important in avoiding oxidation of chemical compounds such as Fe_2O_3 or $LiFe_2(PO_4)_3$ [3]. Atmospheres used include air, nitrogen, argon, argon/hydrogen, and argon/nitrogen. Negamine et. Al.[7] found that hydrogen gas in atmosphere was shown to have influence on iron ions especially in the small particle size range of less than 2 um. Molar fractions of $LiFePO_4$ are important in determining the final makeup of compounds. As seen in table 2, air results in a molar fraction of 25 mol%, while 7% H2/Ar shows a much higher product efficiency of 49 mol% [7].

		X_{LiFePO_4} (mol%)		
Particle size (μm)	Quenching type	Air	Ar	7% H_2/Ar
63–40	Rapidly	25	49	49
<2	Rapidly	4	72	81
63–40	Slowly	—	—	58

Table 2. Molar weight percent in different atmospheres

In this experiment, products were heat treated between 400˚C and 600˚C at its crystallization peak temperature with a heating rate of 10˚C/min. The heating in air shows much less efficiency because of the oxidation of Fe^{2+} ions taking place. Reduction of Fe^{3+} to Fe^{2+} ions takes place in the H_2/Ar atmospheres enhancing the formation of $LiFePO_4$.

Furnace for $LiFePO_4$ Manufacturing

The HSA series furnace is an efficient furnace designed and used for heat treatment for processes such as $LiFePO_4$. It features a low mass refractory heating chamber equipped with ceramic FEC (Fully Enclosed Coil) heating board. The HSA furnace has 6 independent zones able to reach 1150˚C, temperatures high enough to heat treat lithium iron phosphate. The temperature profiles are able to run at the desired heating rate to meet the required sintering temperatures under controlled atmosphere. Gas is independently controlled for the adjustment of air, nitrogen, hydrogen, and argon inflow. Temperature control zones allow the furnace to run at the proper heating rate to meet the needs for firing and curing. The conveyor system allows proper heating across the belt with little temperature variations. The furnace is monitored by type K thermocouples with each zone monitored by single loop PID temperature controllers. This enables precise and stable temperature control throughout the heating process to the cool down.

The furnace is large enough to handle manufacturing processes for $LiFePO_4$ applications. It has a 14” (35cm) belt width and a 130” (330cm) heated length. The conveyor system can run at speeds of 1-8 Inches/min. The HSA furnace is protected from overheating, over loading, and low gas pressures. It also comes equipped with anti shock protection on the doors during maintenance. Technical information and training will be given upon installation of the furnace to ensure proper practice for continued use. Emergency buttons and removable collection traps are also located on each end of the furnace. For the cleaning system, there is a rotating motor metal brush that cleans the belt so future products will not be contaminated. Below is a complete list of the HSA series specifications.

Summary:

An efficient Li-ion material must have characteristics of high charge/discharge ability, stable life cycle, and low cost for manufacturing. Furnace firing parameters are important in controlling the atmospheric conditions in order to protect from contamination at high temperatures. Reactions between the precursors need to be regulated with temperatures not exceeding the point where powder particles begin to increase in particle size and shape. Carbon coating must also be used in order to obtain good electronic conductivity within the system. It is often difficult to reproduce these methods with all the desired electrochemical performance necessary. Solid state reaction methods require long processing times with high temperatures which could cost in efficiency. Solution based methods can be used instead with better results but with added costs and extra complexity. Furnace heat

treatment can well be used for large scale manufacturing procedures to obtain optimum lithium iron phosphate products.

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