

Process Scale-up for Production of Water-Based Lithium-Ion Pouch Cell

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With the aim to promote technology transfer to small and medium-sized enterprises, a scale-up process to synthesize kilos of LiFePO₄ is described. The process allowed the production of a material with a specific capacity of to 150 mAh g⁻¹. Furthermore, a water-based manufacturing process to produce LiFePO₄ electrodes was described. The experimental conditions were widely investigated to obtain homogeneous slurries and cracking free electrode coating, which resulted in flexible electrodes with good mechanical characteristics. These electrodes have been coupled with graphite base anodes to build 50 mAh Li-ion batteries and their electrochemical performance evaluated by galvanostatic cycles.

1. Introduction

Lithium iron phosphate (LiFePO₄ or LFP) with an olivine structure is regarded as one of the most promising cathode materials for Li-ion batteries due to its environmental friendliness, high cyclic performance, and safety features (Wang and Sun, 2015). LiFePO₄ offer several benefits compared to other cathodes for lithium batteries, such as long-life span, high power, high safety, and low-capacity fade (Armand and Tarascon, 2008, Ghadbeigi et al., 2015, Dunn et al., 2011). LFP-based batteries have rapidly occupied various sectors of the market and their future development is still promising. Although they are not used as the first choice for automotive purposes, the Asian market is re-evaluating them to reduce the price of the final product and suppress the overall use of cobalt (Gucciardi et al., 2021). For this application it would be appropriate to further improve the performance of the batteries, reduce their cost, and at the same time to deal seriously with all the environmental problems that may arise from their production and disposal. To this end, new production methods for material synthesis and new formulations for electrode fabrication must be developed (Liu et al., 2021). To achieve these results, it is necessary to design cost-effective manufacturing processes for both materials and electrodes with controlled quality (Valvo et al., 2017). In the past, in our laboratories, LFP with good performance has been synthesized by using an innovative method, whose main strength derived from the fact that the LFP did not need to be produced in ovens with a controlled atmosphere as it was possible to obtain it in air (Prosini et al., 2016). At the same time, a research activity to produce electrodes containing non-fluorinated water dispersible polymers as electrode binders was started (Prosini et al., 2015). Being the polymers dispersible in water, their use allows to eliminate the N-methyl pyrrolidone (NMP) commonly employed as a solvent in the preparation of the electrodes in Li-ion battery technology, replacing it with water. In this way it is possible not only to reduce the dangerousness but also the production costs of the electrode. Indeed, it has been calculated that, evaluating the entire cathode production, 47 % of the total process energy is consumed in the drying process of the electrodes for NMP evaporation and recovery (Wood et al., 2018). Starting from these two processes developed in lab-scale, in this paper we describe the design of a pilot plant able to produce LFP in quantities of kilos and the preparation of water-based electrodes of 26 cm² in size. Although the dimensions of these processes are not comparable with those carried out on an industrial scale, at the same time they are significantly larger than those performed on a laboratory scale.

2. Material and methods

2.1 LiFePO₄ synthesis

De-ionized water (18 MΩ cm⁻¹) was produced by a water production system (Milli-Q, Millipore, Bedford, MA). Ferrous sulphate heptahydrate (FeSO₄·7H₂O, Aldrich, ACS reagent, ≥99.0 %), ammonium phosphate monobasic (NH₄H₂PO₄, Aldrich ACS reagent, ≥98 %), lithium acetate dihydrate (LiCOOCH₃·2H₂O, Aldrich, ACS reagent, ≥99.0 %), and hydrogen peroxide solution 30 % in water (H₂O₂, Aldrich) were used as received. Since the quantities handled were lower than those of a real industrial process, it was not possible to use components designed for industrial processes. So, the choice was addressed to apparatus used in different commercial sectors, such as food, domestic and crafts. Figure 1 shows the equipment adopted for the synthesis, i.e., the vacuum system storage tank (Figure 1a) for washing operation, the drum filtration system capable of using 90 g/m² filter paper as a filter medium (Figure 1b), the digestion reactor with bain-marie heating (Figure 1c), and the ultracentrifuge (Figure 1d, Retsch Model ZM 200, 6,000-18,000 rpm, 1300 W).



Figure 1: a) Vacuum pump with washing water tank, b) drum filter with filter material, c) water bath system for digestion, d) ultracentrifuge mill sieve with 0.15 mm and 0.08 mm meshes.

2.2. Electrode preparation.

Carbon black (SuperP TM, TIMCAL) with dimensions around 20-30 nm was used as conductive filler. The anode active material was graphite (Linyi-Gelon) with 90 % of the particles with a diameter of less than 28-32 μm. Triton X-100 (BASF) was used in the cathode formulation as a non-ionic surfactant. The water-soluble binder was Na-CMC (Sigma Aldrich). A lab scale pouch cell fabrication line was used (MTI Corporation, Richmond, CA). Table 1 reports the main apparatus used to prepare the electrodes.

Table 1: Main apparatus used to prepare the electrodes.

Model	Description	Unitary operation
MSK-SFM-7	Vacuum mixer	Coating slurry preparation
MSK-AFA-III	Compact tape casting	Electrode tapes production, 150 mm (W) x 260 mm (L)
MSK-HRP-01	Hot rolling press	Electrode thickness reduction
MSK-180SP	Pneumatic die cutter	Electrode cutting, electrode area was about 26 cm ²
MSK-800W	Ultrasonic metal welder	Tabs to current collector welding

2.3 Electrochemical testing.

Impedance spectroscopy (IS) was performed with a Solartron 1260 frequency Response Analyzer coupled with a Solartron 1287 Electrochemical Interface in the frequency between 1 MHz and 0.1 Hz. Electrochemical testing was carried out using a Maccor 4000 cycler. Both coin and pouch cells were used. A 1.0 M solution of lithium hexafluorophosphate (LiPF₆) in ethylene carbonate and dimethyl carbonate (EC/DMC=50/50 v/v) was used as electrolyte (LP30, Aldrich) and a glass fiber as separator (GF/B Grade Whatman, Aldrich). The cell characteristics are reported in Table 2.

Table 2: Characteristics of the cell used for the electrochemical characterization.

Coin cell	Diameter	Pouch cell	Dimension	Current collector
Cathode	12 mm	Cathode	56 mm (L) x 43 mm (W)	10 mm (L) x 10 mm (W)
Lithium metal	14 mm	Anode	58 mm (L) x 45 mm (W)	10 mm (L) x 10 mm (W)

3. Experimental

3.1 Material synthesis

To facilitate further implementation on industrial level, the scaled-up process was designed to produce material: (i) with a specific composition and quality; (ii) in discrete quantities, and (iii) by using equipment with the operating characteristics required for a possible and further dimensional scale-up. The production process of LFP is shown in the block diagram in Figure 2. The complete process was divided into four phases: two equal and successive phases of mixing-separation, followed by two other equal and successive phases of firing-grinding. These unitary operations can be easily implemented for further scale-up to bring production to an industrial level.

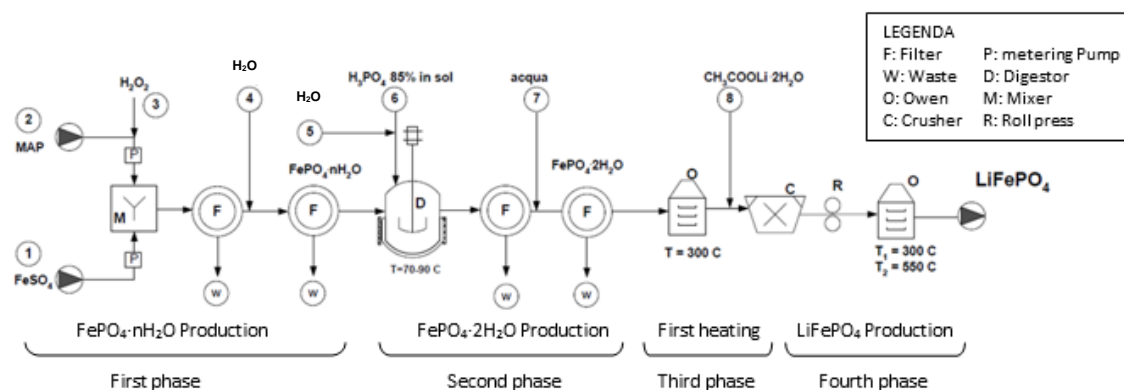
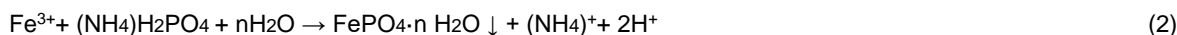
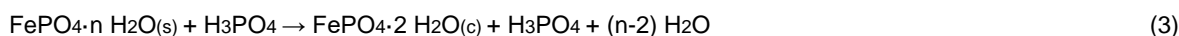


Figure 2: Process diagram to produce battery grade LiFePO_4 .

Phase I. The first phase is the production of amorphous hydrated iron phosphate ($\text{FePO}_4 \cdot n\text{H}_2\text{O}$). A 1.0 M iron sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) aqueous solution and an aqueous mixture of 0.1 M ammonium phosphate monobasic ($\text{NH}_4\text{H}_2\text{PO}_4$, MAP) and 0.6 M hydrogen peroxide (H_2O_2) were slowly mixed (10 mL min^{-1}) under mechanical stirring at room temperature. The thus obtained suspension was left under stirring for two hours. The liquid was then separated by filtration leaving a gelatinous white product which was subsequently washed with demineralized water to eliminate reaction impurities. In this phase iron (II) is oxidised to iron (III) (Equation 1) and this latter reacts with the phosphate ions forming iron phosphate which finally precipitates in its hydrated, amorphous form (Equation 2).

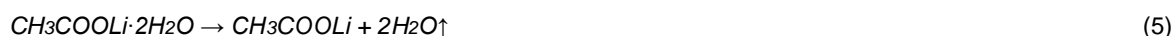


Phase II. The second phase concerns the transformation of amorphous hydrate iron phosphate into crystalline di-hydrate iron phosphate (strengite, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) as shown in Equation 3.



To this end, the solid $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ obtained in the previous phase was added in a single portion to a 0.3 M phosphoric acidic aqueous solution and heated to 75°C . The formation of the crystalline phase is evidenced by a change in the colour of the suspension from creamy yellow to light pink. After the color change, the suspension was allowed to cool down to room temperature and filtered. To eliminate the excess of phosphoric acid, the solid was washed with demineralised water.

Phase III. In the third phase the strengite was dehydrated (Equation 4) by keeping it in a dry room for at least 12 hours and then by heating to 300°C for 2 hours. Commercial lithium acetate hydrate was dehydrated (Equation 5) by heating to 300°C as well.



Phase IV. In the fourth and last phase, the two anhydrous compounds were intimately pulverized and mixed with a Li/Fe ratio 1:1.13. The mixture was put in a crucible, covered with an aluminium foil, and heated in a two-step process. The first step was carried out at 300°C for 30 minutes, followed by a second step at 550°C for 30 minutes. The heating treatments transform the mixture into crystalline LiFePO_4 as shows in Equation 6.



The grinding/blending of FePO_4 and CH_3COOLi was found critical in determining the properties of the final product. Since the ball-milling apparatus used in lab-scale operations was not feasible on a larger scale, an ultracentrifuge mill was tested. By using a 0.08 mm ultracentrifuge mill sieve, a material with specific capacity equal to 150 mAh g^{-1} was obtained. Once the process was set up, the quantities of compound treated were increased until the design target quantity was reached (1.8 kg of LiFePO_4). Table 3 reports the amount of materials used to reach the final target.

Table 3: Amount of materials used to obtain 1.8 kg of LiFePO_4 .

Compound	Weight /kg	Weight %	Weight /kg	MW	Mol	Water/L
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$			4.173	278.02	15.0	15
$\text{NH}_4\text{H}_2\text{PO}_4$			1.725	115.03	15.0	15
H_2O_2	1.020	30	0.306	34.01	9.0	
H_3PO_4	0.864	85	0.734	98.00	7.5	24
$\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$			1.400	102.2	13.7	
CH_3COOLi			0.900	65.99	13.6	
FePO_4			1.800	150.81	12.0	

3.2 Electrode Manufacturing Process.

In the next step, a full Li-ion pouch cell was constructed. The cell preparation was subdivided into four phases: sieving and mixing, slurry preparation, coating, and cell assembly.

Phase I. The electrode components (carbon and active material) were sieved starting with a mesh size of 700 μm down to 250 μm and then mixed for 2 hours by low energy ball milling process, with a ball to powder ratio of 1:10. The so obtained mixture was further sieved starting with a mesh size of 700 μm down to 250 μm .

Phase II. Aqueous slurries were prepared by suspending the mixture of powders with water. Na-CMC (used as the binder) was added to the suspension. In the case of the cathode a small amount of Triton X-100 (used as surfactant) was added to avoid thickening of the solid fraction during the deposition process. Table 4 shows the percentage of the various components in the slurry.

Table 4: Percentage of the various components in the slurry.

Component	Anode Weight %	Cathode Weight %
Carbon	1.9 %	9.4%
Active material	95.5%	85 %
Binder	2.6 %	4.3 %
Triton X-100		1.3 %

Phase III. A copper or aluminium foil was used as current collector for the anode and for the cathode, respectively. The thickness of each current collector was 20 μm . The suspension was deposited on the current collector using the doctor blade technique. The slurries were swept across the metal foil at a constant speed and distance from the foil. The cathode tapes were made by fixing the blade height at 330 μm . This distance has been experimentally determined as the maximum height that can be reached before cracks form on the electrode surface during the drying process. The anodes were made by adjusting the doctor blade height between 70 and 100 μm , to obtain electrodes with various loads of active material. This then will give the possibility to correctly balance the electrodes capacity in the construction of the complete cell. The tapes were initially left to dry in air at room temperature and then in a dry chamber at 120 °C for at least 24 hours. After drying, the electrode tapes were calendered to reduce the height to about 90 % of the initial one. The LFP load of the electrode was about 8 mg cm^2 while the graphite load ranged between 4 and 5 mg cm^2 .

IV Phase. A monopolar cell configuration was chosen for the construction of the battery. Electrodes of approximately 26 cm^2 were punched from the tapes. Aluminium and nickel tabs were welded on the cathode and anode current collector, respectively. Figure 3 shows photos of the rear (a) and front (b) sides of an anode electrode with a Ni tab soldered onto the current collector.

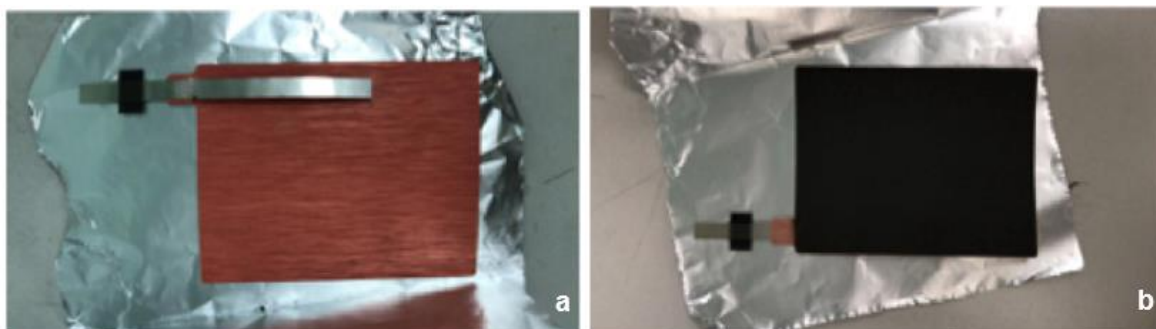


Figure 3: a) rear and b) front images of the anode with the nickel tab welded to the current collector.

A glass fibre was used as the separator. A battery cover of about 10 cm x 10 cm was obtained by folding in two a 10 cm x 20 cm poly-laminate sheet. The electrodes and the separator were housed inside the cover and this latter was thermally welded on the two lateral sides. The cell was filled with the electrolyte just before sealing the last side of the pouch cell under vacuum. The volume of electrolyte necessary for the correct functioning of the pouch cell was determined by calculating the total porosity of the cell components, i.e., cathode, anode, and separator (Long et al., 2016).

4. Results and discussion

To validate the effectiveness of the proposed method, the electrochemical performance of the LFP obtained with the scaled-up process was compared with that of the material obtained by the lab-scale process. Figure 4 shows the voltage profiles as a function of the specific capacity of the two materials when used as the cathode in a lithium metal coin cell.

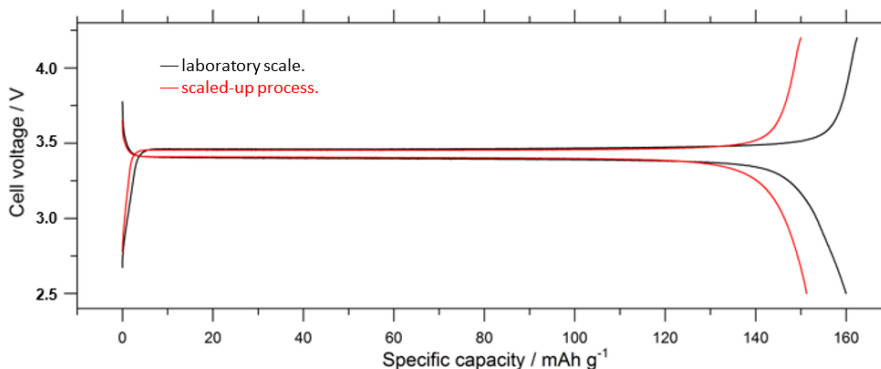


Figure 4: Comparison of the first cycle specific capacities of LiFePO₄ obtained at laboratory scale (black) and the one obtained according to the scaled-up process (red). The test was carried out at C/10 rate.

The performance of the two materials is comparable, with specific capacities of 160 and 150 mAhg⁻¹ for the material produced on a lab scale and one produced using the scaled-up procedure, respectively (and both close to the maximum theoretical capacity of the LFP of 170 mAhg⁻¹).

Before evaluating the performance of pouch cells, the minimum amount of electrolyte required to have a stable and comparable cell behaviour was evaluated. The pouch cells were filled with various amounts of electrolyte and tested. It was found that the cells correctly work only if the ratio between the quantity of electrolyte and the estimated volume of the pores is larger than 3:1. To evaluate the cell resistance, an IS measurement was carried 12 hours after cell assembling. The cells exhibited significantly low resistance values: the electrolyte resistance was about 0.5 ohm, while the charge transfer resistance was about 2.5 ohm. After carrying out the IS measurement, the cells were subjected to five galvanostatic cycles, conducted at C/25. Although the cells had a theoretical capacity of about 30 mAh, they exhibited a practical capacity of only 25 mAh. To make a 50 mAh battery two cells were coupled, and the resulting battery was tested at C/25. The battery exhibited a first cycle capacity of 63.4 mAh and 50.16 mAh in charge and discharge, respectively. In the second cycle the values decreased to 54.7 mAh and 53.6 mAh in charge and discharge respectively, and slowly decreased in the following cycles. The voltage profile is clean, with a rather limited hysteresis between the charge and discharge plateaus, of 0.11 V (Figure 5).

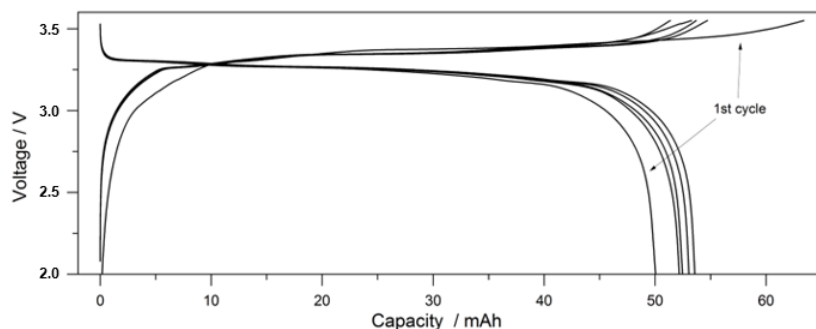


Figure 5: Voltage profiles of a Li-ion pouch cell with a nominal capacity of 50 mAh as a function of capacity.

5. Conclusions

In this work, battery-grade LiFePO₄ production with a scale-up process and its use in Li-ion pouch cells were described. It has been demonstrated that the crystallization of the material can be carried out in air avoiding the use of modified atmosphere furnaces. It was also demonstrated that the electrode production can be done using water as a process fluid. The main advantage of using water in the electrode preparation lies in the possibility of directly discharging harmless water vapour into the surrounding environment without recovery the solvent. This can reduce production costs compared to other methods using organic solvents. The unitary operations necessary for the synthesis of the material and the construction of the pouch cell have been described. These unit operations can be easily scaled up allowing for a further increase in production size up to transfer the process to plants on an industrial scale. For the abovementioned reasons this work stands as a trait-union between the world of research and that of business.

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