

Electrospinning synthesis of Li-Fe-P/PAN based micro-nanofibers as precursors for LiFePO₄ cathode material in Li-ion fiber battery applications

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Abstract. The increase popularity of wearable devices and smart textiles are being held back partly by better energy storage systems, which are based on electrochemical phenomena. Research in novel materials with optimal morphologies for better electrochemical performance is one the paths being followed. Micro/nano fibers are interesting morphologies as they present high surface areas, less agglomeration and flexibility, compared to micro/nano particles. In this article, precursor fibers for LiFePO₄ cathode material, defined as lithium-iron-phosphorous/polyacrylonitrile (*Li-Fe-P/PAN*) precursor nanofibers, have been synthesized by the electrospinning method. The influence of electrospinning parameters such as voltage (V), flow rate (F) and distance between the collector and the tip of the syringe needle (D), on the morphology of the fibers have been studied mainly by scanning electron microscopy (SEM). Optimal morphological features such as less formation of beads, small fiber diameter, less polydispersity and high fiber alignment, were observed at V=14 kV, F=0.7 mL/h and D=14 cm. The occurrence of nanofibers on the precursor *Li-Fe-P/PAN* material was observed through SEM, while the energy dispersive x-ray spectroscopy (EDS) confirms the presence of the fundamental elements in the precursor nanofibers.

1. Introduction

Flexible electronics and wearable devices have gained enormous popularity with the emergence of products such as the Google Glasses, Apple Watch and Samsung Bracelet. Perhaps the main aspect holding back this revolution is the need of better energy storage systems. Li-ion batteries are the best energy storage technology currently available, principally because of their size reduction and the energy they can store, as compared with other technologies [1]. Despite its advantages, the current way in which commercial Li-ion batteries are produced, cannot effectively satisfy the working conditions that wearable products require, namely flexibility (bending, folding and stretching [2,3] miniaturization and adaptability. Besides within Li-ion battery components the cost of processing



cathodes are one the major contributing factors [4], the safety and capacity in Li-ion batteries are largely limited by the cathode and research around the globe has mostly concentrated on the development of nanostructured cathode materials to improve their intercalation features [5]. LiFePO_4 (more known as LFP) cathodes are one of the most promising materials for Li-ion batteries due to its excellent electrochemical properties, good energy efficiency, but mainly because of its safety compared to other materials for electrodes [6]. This material stands out for its small change in mechanical properties during lithiation/delithiation, low cost, low toxicity and low environmental impact, which can be an option to meet the previously mentioned conditions for wearable devices [7].

‘Wearable batteries’ is the term used for batteries that can achieve the energy demand for the so-called smart textiles, in particular with applications that combine textiles and electronics (e-textiles) [8]. Ideally, this systems should be directly in the form of a fiber so that it can be integrated naturally during the weaving process [8]. However, the research in this strategic topic is still limited.

Initial attempts to investigate fiber storage focused on using carbon materials (graphene and carbon nanotubes –CNTs-) to develop light, weight and flexible supercapacitors [9–19]. However, compared with supercapacitors, Li-ion batteries have much higher energy density per weight unit. In 2011, Cu’s group in Stanford integrated Li-ion battery electrode materials into a 3D porous textile conductor and obtained capacities of 150 mAh/g with an 88.5% capacity retention after 30 cycles [20]. Since then, several groups have contributed to this field and two thorough complete reviews on wearable fiber-shaped batteries have been published recently [21,22].

Among the morphologies reported previously for light and flexible electrodes, micro/nano fibers offer such possibilities and present advantages such as less agglomeration, high surface area, less diffusion distance for both Li^+ and e^- , among others [23–25]. Electrospinning is a novel and versatile technique, in which a precursor solution is subjected to a high voltage, making elongated jets in the form of micro/nano fibers [26–28]. The formation of fibers is determined by many operating parameters such as applied voltage, solution concentration, viscosity, surface tension, conductivity, and flow rate. The structure of the resulting fiber can be tuned by carefully modifying these parameters.

This paper describes the production of Li-Fe-P/PAN fibers (from here on “precursor fibers”) by electrospinning, that will later be used for the formation of LFP cathode fibers. A detailed study will be shown on how the variation of the equipment parameters (voltage, flow rate and distance from nozzle to substrate), affects the formation of fibers with different morphological features. This is a preliminary step on the synthesis of full LFP cathode fibers, thus after calcination of the Li-Fe-P/PAN precursor fibers here obtained, a LFP stoichiometry with atoms arranged in an olivine structure is expected.

2. Materials and methods

2.1. Precursor solutions

Liquid precursor solution for the electrospinning process is a relevant stage, as its properties, together with the electrospinning parameters, define the final fiber morphology. The viscosity, surface tension and the electric field will determine the stretching of the solution. These properties are defined by a correct choice of the polymer/solvent set [29].

The liquid precursor solution was prepared using stoichiometric amounts of lithium acetate, $\text{C}_2\text{H}_3\text{LiO}_2$, iron (III) nitrate nonahydrate, $(\text{FeN}_3\text{O}_9) \cdot 9\text{H}_2\text{O}$, and phosphoric acid, $\text{H}_3\text{O}_4\text{P}$, as suggested by Toprakci, et al. [30]. These salts were mixed with polyacrylonitrile, $(\text{C}_3\text{H}_3\text{N})_n$ (PAN) and dissolved in a miscible solvent composed of dimethylformamide, $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ (DMF) and acetone, $(\text{CH}_3)_2\text{CO}$. The Li:Fe:P molar ratio in the solution was 1:1:1. The concentration in weight for each component was 4% for the PAN, 8% for the Li-Fe-P precursors, 70.4% for the DMF, and 17.6% for the acetone. All chemicals used were purchased from Sigma Aldrich.

2.2. Electrospinning set up

A scheme of the system used to produce the Li-Fe-P / PAN precursor nanofibers is shown in Figure 1. Here, the prepared solution, which was loaded into a syringe pump, was delivered into a reaction zone in a controlled way. When a high voltage is applied to the solution, the forming spherical droplet becomes deformed into the denoted Taylor Cone [31], due to the repulsion force between the surface charges. When the system reaches a critical voltage, a jet is formed at the apex of this cone. Once optimal conditions involving the solution and process parameters are met (i.e. when the repulsive electrostatic forces overcome the surface tension), this jet is further stretched as a fine fiber which finally reach the substrate holder [27], [29], [32].

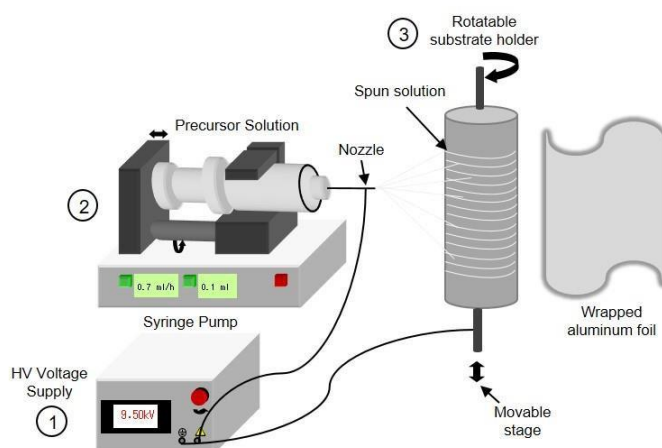


Figure 1. Schematic drawing of the electrospinning setup used to produce the Li-Fe-P / PAN precursor nanofibers. Note that the aluminum foil is rolled around the cylinder, the high voltage terminal is attached to the nozzle, while the ground is attached to the drum collector

2.3. Morphological and compositional characterization

Using the precursor solution described previously, a morphological study was then performed by varying only the parameters related to the electrospinning process. i.e. voltage (V), flux (F), and the distance between the tip of the nozzle and the substrate holder (D). Three levels were considered for each parameter. Table 1 shows the three levels for each electrospinning parameter. One parameter was varied while the other two were fixed. The fixed values were $V=14$ kV, $D=10$ cm and $F=0.6$ mL/h. The precursor fibers were collected on an aluminum foil as substrate. The fiber morphologies for each sample were investigated using a scanning electron microscopy (SEM: JEOL JSM-6010LA) operated at 5 kV. Compositional elemental mapping was investigated using an energy dispersive x-ray spectroscopy (EDS) detector coupled to the SEM (JCM-6000PLUS), operated at 15 kV. For all experiments, parameters such as 19G nozzle (outer diameter=1.07 mm / internal diameter = 0.69 mm), 19 rpm-clockwise drum rotation, temperature between 24-27°C and humidity between 55-65%, were fixed.

Table 1. Levels for each electrospinning parameter

V [kV]	F [mL/h]	D [cm]
14	0.5	10
15	0.6	11
16	0.7	12

3. Results and discussion

3.1. Changing voltage

Figure 3 shows the resulting fibers, using three different voltages in the electrospinning process: 14 kV (3a), 15 kV (3b) and 16 kV (3c). The fixed parameters in this case were the distance from the tip of the needle to the collector and the flow rate, with a corresponding value of 10 cm and 0.6 mL/h, respectively.

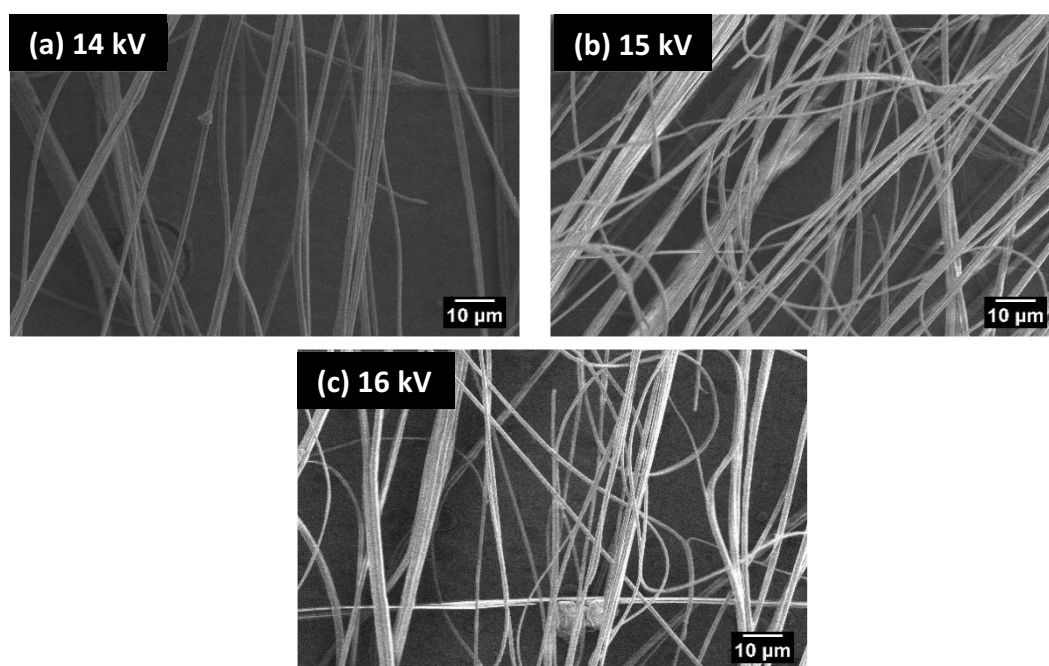


Figure 2. SEM micrographs showing the influence of voltage on the fiber morphology: (a) 14 kV, (b) 15 kV, and (c) 16 kV ($F=0.6$ mL/h; $D=10$ cm)

Fibers obtained at 14 kV have a clear alignment, in contrast with the fibers obtained at 15 and 16 kV, which present a curl-like shape. The curly effect obtained for these two last samples is due to the instability of the jet (whipping effect [33]), at higher electric fields (i.e. higher voltages) compared to the 14 kV sample [34]. Fibers produced at 16 kV confirm that alignment is lost, meaning the jet movement is higher for these conditions.

Regarding fiber diameter, the 14 kV sample have smaller fibers than those at 15 and 16 kV. Mats (the non-woven film of fibers collected on the counter electrode) produced at 14 kV present similar fiber diameters, with an almost monodisperse feature. In contrast, fibers produced at higher voltages present polydispersity in terms of diameter size.

The increase in diameter among samples might occur as the 15 and 16 kV voltages are above the critical voltage. This may cause an incorrect Taylor cone development and a jet instability, which breaks the fibers during their pathway toward the collector, resulting in the formation of small curl-like fibers [28,35].

3.2. Changing distance

Figures 2a, b and c, show the influence in fiber morphology with distance values between the tip of the nozzle and the substrate of 10 cm, 11 cm and 12 cm, respectively. The fixed parameters in this case were the voltage and the flow rate, with a corresponding value of 14 kV and 0.5 mL/h, respectively.

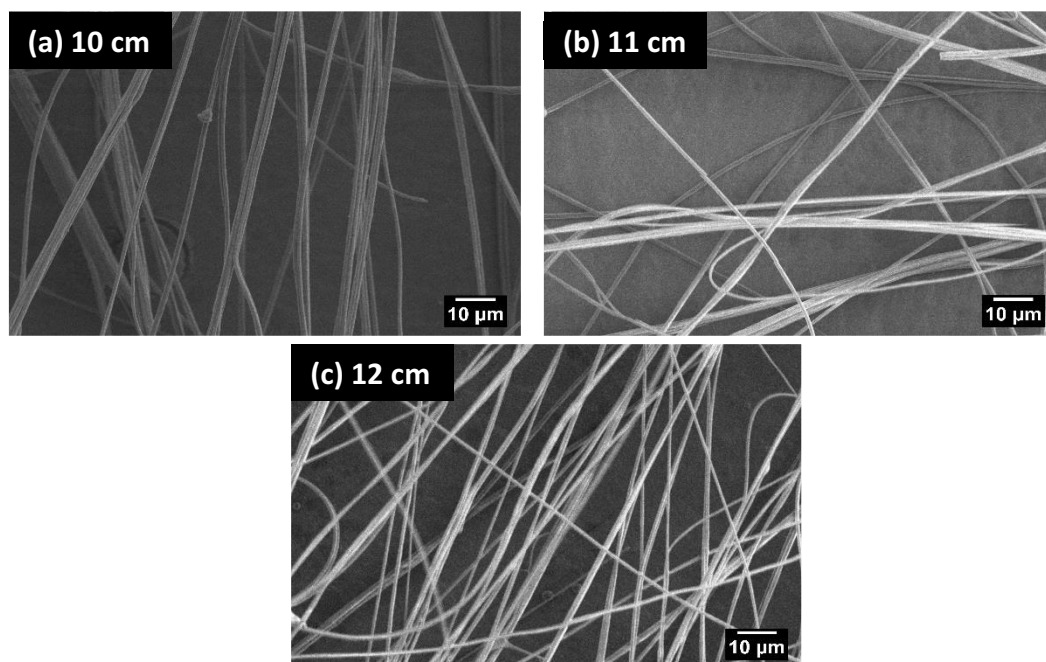


Figure 3. SEM micrographs showing the influence of distance from nozzle to substrate on the fiber morphology: (a) 10 cm, (b) 11 cm, and (c) 12 cm ($V=14$ kV; $F=0.6$ mL/h)

In all three cases, there is a preferential alignment of the fibers, most likely in the direction of the rotation of the cylinder. There are no visible differences regarding the apparent diameter of the fibers. However, it is difficult to determine the diameters of these fibers in the samples done at 10 and 11 cm, as they present more fiber agglomerations than the fibers observed in the sample done with a 12 cm distance. For this reason, the apparent diameter of fibers in 12 cm sample seems to be smaller and more monodisperse than those at 10 and 11 cm distances.

The strength of the electric field (E) depends on both the applied voltage and the distance ($E=\Delta V/d$). The latter also plays an important role on the time of flight of the jet [29], [36,37]. A shorter distance causes the time of flight to be reduced, therefore reduces the time for solvent to evaporate. Thus, fiber diameter is smaller for longer distances and tend to become larger for shorter distances. In addition, at shorter distances, the electric field strength is high, which causes the fiber to accelerate, resulting in a lower evaporation of the solvent [29]. When fibers with a large amount of solvent reach the substrate, the solvent tends to agglomerate the fibers.

In all cases presented previously, even though the solvents created fiber agglomeration, there are no observed droplets, which means that the DMF and the acetone have enough time to partially volatilize while the solution gets from the tip of the needle to the substrate.

3.3. Changing flowrate

The influence in fiber morphology with the variation of the flow rate is shown in Figure 4. Figure 4a corresponds to the sample obtained with 0.5 mL/h, while those of 0.6 mL/h and 0.7 mL/h correspond to Figures 4b and c, respectively. The fixed parameters in this case were the voltage and the distance from the tip of the needle to the collector, with a corresponding value of 14 kV and 14 cm, respectively.

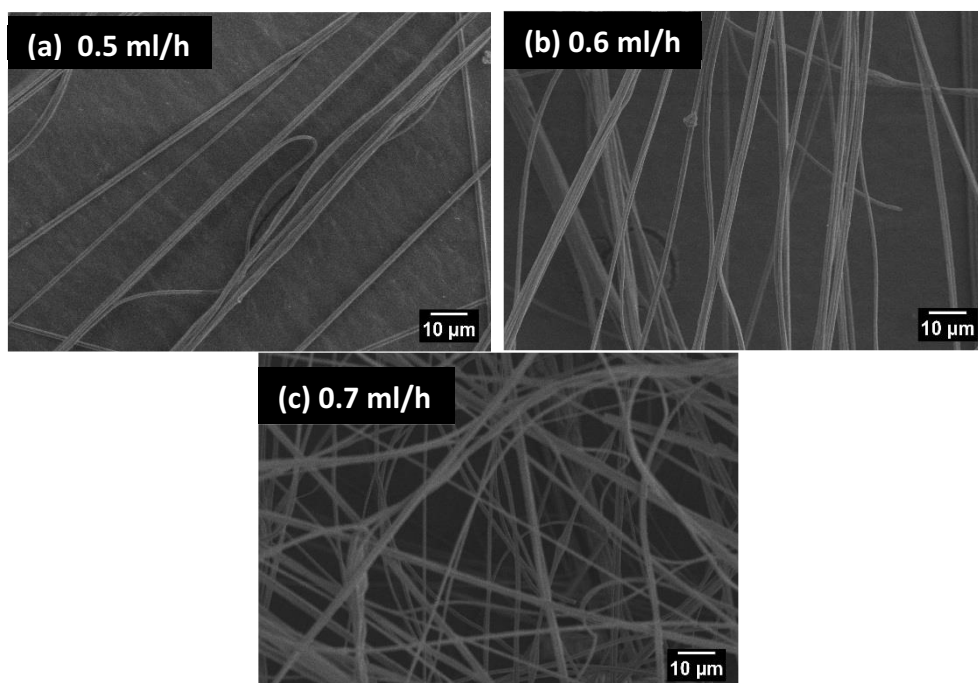


Figure 4. SEM micrographs showing the influence of flowrate on the fiber morphology: (a) 0.5 mL/h, (b) 0.6 mL/h, and (c) 0.7 mL/h ($V=14$ kV; $D=10$ cm)

For the fibers obtained with a flow rate of 0.6 mL/h and 0.7 mL/h, there are no significant changes in the apparent diameter. Conversely, the sample with $F=0.5$ mL/h apparently presents a smaller fiber diameter. According to the literature the flow rate must exceed a critical value in which enough solution is fed to the tip of the nozzle before all the volume is drawn away by the strong electrostatic forces, causing a discontinuous or pulsating jet [38]. On the other hand, exceeding a certain flow rate may cause the formation of beads as there is not enough time for the extra solvent in the stretched fiber to evaporate [39]. As shown in figures 4(a-c), there are no beads, therefore it can be concluded that this upper critical flow rate was not achieved. Also, during the electrospinning process, for all the values investigated, there was no jet discontinuity, which means the flow rate was always above the lower critical flow rate. Moreover, it can be observed how an increase in flow rate leads to larger fiber diameters, which can be attributed to less evaporation of the solvent during flight from needle to collector [39]. Likewise, agglomeration of fibers becomes obvious when the solvent has not enough time to evaporate completely. Also, there is an apparent monodisperse distribution of the fiber diameters for the samples done with a flow rate of 0.5 mL/h and 0.6 mL/h, while that of 0.7 mL/h presents different fiber diameters. However, fibers from the highest flow rate are less agglomerated than those fibers obtained with lower flow rates. Finally, the amount of fibers increases by increasing the flow rate, as the spread volume is higher.

3.4. Energy dispersive spectroscopy (EDS) analysis

EDS analysis was done for the Li-Fe-P/PAN precursor nanofibers. Table 2 shows the mass percentage for the elements present in the precursor nanofibers. It reveals the presence of carbon, oxygen, iron and phosphorus elements, which are the main elements to obtain the LFP active material. It is expected that after calcination of the Li-Fe-P/PAN precursor fibers here obtained, a LFP 1:1:1 stoichiometry with atoms arranged in an olivine structure is expected.

Table 2. Mass percentage of the elements present in the Li-Fe-P/PAN precursor nanofibers

Element	Mass Percentage	Atomic Percentage
Carbon	39,7254576	53,0606366
Oxygen	39,6145313	39,7234625
Phosphorus	5,56017748	2,88059916
Iron	15,0998336	4,33530174

4. Conclusions

Micro-nanofibers based on lithium, iron and phosphorous precursor salts, together with PAN polymer, have been successfully produced. This opens the door to obtain full LFP cathode fibers which will be employed on fiber battery applications.

The morphology and texture can be influenced by adjusting flow rate, voltage and distance from nozzle to sample of the electrospinning technique. According to the results discussed in this paper, to obtain monodisperse, aligned and straight Li-Fe-P/PAN precursor nanofibers, it is ideal to use a distance between the collector and the tip of the syringe of 12 cm, an electrospinning voltage of 14 kV, and a flow rate of 0.5 mL/h. It is important to clarify that these electrospinning parameters are recommended for the specific precursors used here, since properties of the solution such as concentration, viscosity, surface tension and conductivity will vary and hence, the optimal electrospinning parameters will also change.

It is relevant to mention that this is a preliminary step on the synthesis of full LFP cathode fibers. After calcination of the Li-Fe-P/PAN precursor fibers here obtained, a LFP stoichiometry with atoms arranged in an olivine structure is expected. Finally, the applicability of these fibers as cathode material will ultimately depend on their electrochemical performance.

This is an ongoing project and further work is needed.

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