Alternative approaches for the fabrication of electrodes based on LiFePO₄ as cathodes in LIBs

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We hereby certify that the thesis entitled “Alternative approaches for the fabrication of electrodes based on LiFePO4 as cathodes in LIBs” submitted by Zahilia Caban Huertas in partial fulfillment of the requirements for the degree of Doctor of Philosophy was carried out under our supervision and we authorize it submission for oral defense.

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Bellaterra, June, 15, 2017
To:

Every Nerd, Geek, Metal, Goth, Punk and member of the LGTBQ community.

All the women in the STEM field, especially those with Turner Syndrome.
The “Matrix” concept of energy generation might not be the most plausible one. But dreaming, even wrong things, can be a good way to seed the beginning of good things to come.
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Abstract

Lithium ion batteries are the power sources of choice for portable electronics, power tools and electric base transportation and they are ready to take over other niche and mainstream applications (from wearables to smart grid support to electric vehicles). Yet, this implies new requirements such as a combination of high energy and power densities, longer cycling life and, last but not least, substantially reduced costs.

The European Project SOlid MAterials for high power Li polymer BATteries (SOMABAT) aimed to develop more environmentally friendly, safer and better performing Li batteries. Most of the work presented in this thesis corresponds to our contribution to this project, consisting of the optimization of low-cost and ecofriendly methods for the preparation of LiFePO₄ (LFP) and the development of nanostructured and hybrid composites based on this cathode material and conductive polymers or conductive nanocarbons like graphene.

Indeed, olivine-type LFP has been recognized as one of the most promising cathode materials for rechargeable Li batteries. Its advantages include high capacity, high stability, nontoxicity, and low cost. We used low-temperature methods for synthesizing nanocrystalline LiₓFePO₄ with the olivine structure and different morphologies and microstructures are described. In order to overcome the well-known insulating nature of LFP, different methods, alternative to the conventional carbon-coating, were proposed and tested.

Chapter three describes the development of a low-cost hydrothermal (200°C) synthesis method. We were able to control the morphology using Poly-ethyleneimine (PEI) and characterize the corresponding Li⁺ diffusion coefficients for the various LFP samples. These materials exhibit a fractal morphology, high tap density and relatively high surface area. These characteristics could increase the point of contact between the LFP and the electrolyte. As a consequence of these properties the rate capability and discharge capacity of these samples were satisfactory, 164 mAh/g and a Li⁺ of $2.2 \times 10^{-13}$ cm²/s.

The development of a solvothermal method (200°C, ethylene glycol), described in chapter four, allowed us to prepare LFP with a small particle size (ca. 60 nm) with only 5% of surfactant (pluronic acid). The performance of the corresponding carbon-coated
Alternative approaches for the fabrication of electrodes based on LiFePO₄ as cathodes in LIBs. The material was optimal (168 mAh/g) and close to the theoretical capacity of LFP. Using this method, we synthesized LFP/RGO hybrids (also described in chapter four). The electrochemical performance of the optimal LFP/RGO hybrid (with small LFP particles of ca. 40 nm) was quite similar to that of the carbon-coated standard. In this chapter, we also explored the synthesis of hybrid LFP/PPy-Nanopipes, which showed reasonable electrochemical performance but only at low C-rate.

The studies described in chapter five deal with the use of a reflux method to synthesize LFP and LFP/RGO composites. Pure LFP crystallized with a nanoplatelet morphology, but with the large crystal faces (parallel to bc plane) not optimal for Li⁺ diffusion and leading to a specific charge of 150 mAh/g. When grown on RGO the morphology of LFP changed and led to better electrochemical performance 165 mAh/g. The reflux approach not only turned out to be simple, but also highly reproducible and cost-effective.

As an alternative design of LFP electrodes, we developed electroactive LFP nanofluids based on the solid samples described before with the intention to use them as part of novel redox flow cells. The nanofluids were prepared by dispersing the solids into suitable electrolytic base fluids (aqueous Li₂SO₄) containing RGO stabilized in dispersion by addition of diaminobenzoic acid (DABA) as conducting component. Aqueous electrolytes (pH controlled) were selected for simplicity, high-conductivity and eco-friendly advantages. Nanofluids with LFP and RGO separately dispersed in the liquid and nanofluids with hybrid LFP/RGO nanoparticles were prepared and studied. The best electrochemical performance was found for the former, with a discharge capacity of ca. 130 mAh/g at 2C for a remarkable material in which RGO plays in the nanofluid the role that conventional carbon coatings play in solid electrolytes.
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuate Total reflectance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner, and Halenda</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DABA</td>
<td>3,5-Diaminobenzoic acid</td>
</tr>
<tr>
<td>EDS</td>
<td>Electron Disperse Spectroscopy</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>LCO</td>
<td>Lithium Cobalt Oxide</td>
</tr>
<tr>
<td>LFP</td>
<td>Lithium Iron Phosphate</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium Ion Battery</td>
</tr>
<tr>
<td>MO</td>
<td>Methyl Orange</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethyleneimmine</td>
</tr>
<tr>
<td>PEIS</td>
<td>Potentiostatic Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>Py</td>
<td>Pyrrole</td>
</tr>
<tr>
<td>RFBs</td>
<td>Redox Flow Battery</td>
</tr>
<tr>
<td>RGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD or PXRD</td>
<td>X-ray Diffraction or Powder X-ray Diffraction</td>
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</table>
1 Introduction
1.1 Energy and Sustainability

The demands for advanced energy storage devices have dramatically increased during the past years. They are fostered by a variety of different needs in multiple technologies like portable and miniaturized electronics, aerospace-military applications, transportation, and reliable power supplies for grid and off-grid needs\(^1,2\).

These needs are the current driving force to develop energy storage devices, with batteries being the main player, rooted in the blooming of smart mobile devices developed during the present information revolution. This is likely to continue if we consider the information technology advances during the last decade. Big Data, Internet of Things, Artificial Intelligence, and Autonomous Vehicles are now every day concepts. With technologists and consumers accustomed to the exponential rate of improvement in computer operations, the need for long cycle life and faster batteries is growing. And mobile devices are not the only players in this information revolution. This leads us to talk about the data centers, which have different energy requirements than mobile devices. The amount of energy consumed by the world’s data centers will triple in the next decade\(^3\), putting an enormous strain on energy supplies and dealing a hefty blow to efforts to contain the climate change.

Autonomous vehicles are not the only transportation method that will demand new ideas in energy production, storage, and distribution. Electric cars are a reality, and require a new infrastructure that allows the fast charging of the vehicle or hydrogen fueling station. The conversion of the light vehicle fleet from gasoline and diesel to electricity has benefits in terms of climate change and human health in urban areas. However, the driving range and slow recharge time of EVs is typically raised as a problem for which the solution is to make EVs replicate liquid-fuel vehicles, in order to provide a 500 km range and a refill time of five minutes\(^4\).

These devices also provide a new opportunity for energy distribution and smart grids. However, this idea will take time to be fully applied. High EV market penetration rates are necessary for EVs to become a “battery” for the electric grid. This brings other concerns not related to energy storage that are beyond the scope of this work.
This leads us to think about the infrastructure of our energy delivery network, and the requirements needed in a not too distant future. For the most part, the electric power infrastructure functions largely as a just-in-time inventory system, in which a majority of energy is generated and then transmitted to the user as it is consumed. This constant increase in global energy demand, together with the knowledge about the finite supply of fossil fuels, as well as the necessity to decrease the greenhouse gas emission (specially \( \text{CO}_2 \)), requires taking advantage of renewable energy sources. There are many kinds of renewable resources of energy available to replace fossil fuels, such as wind, hydro, nuclear, geothermal and solar power. However, most renewable energy sources are intermittent in their nature, which presents a great challenge in energy generation and load balance maintenance to ensure power network stability and reliability. Unfortunately, we currently only have the capacity to store around 1% of the energy consumed worldwide, most of which (98%) is through pumped-storage hydroelectricity\(^5\) (ca. 100,000 MW 100GW). For comparison, only ca. 200 MWs of Li-ion batteries were installed globally for grid applications in 2014\(^6\).

Thus, energy storage is expected to play an important role in the future of a sustainable electrical grid. Energy storage may serve as a solution to the integration challenges of intermittent renewable energy, reduce greenhouse gas emissions, and increase grid reliability\(^7\).

Options for grid-connected energy storage vary greatly, including conventional batteries, flow batteries, compressed air, or flywheels in addition to pumped-storage hydroelectricity. Not only do the grid benefits vary greatly across technologies, the
design, manufacturing, deployment, and operation of energy storage systems may also lead to significantly different environmental impacts.

1.2 Electrochemical energy storage (EES)

Energy storage technologies available for large-scale applications can be divided into five types: mechanical, thermal, electrical, chemical, and electrochemical, Figure 1-2 (a). Electrochemical Energy Storage (EES) technology refers to the process of converting energy from one form (mainly electrical energy) to a storable form (chemical or physical form), so that the stored energy can be converted back into electrical energy when needed\textsuperscript{8}. This storage technique benefits from the fact that both electrical and chemical energy share the same carrier, the electron. Energy storage offers a well-established approach for improving grid reliability and utilization. Whereas transmission and distribution systems are responsible for moving electricity over distances to end users, the EES systems involve a time dimension, providing electricity when it is needed. By decoupling generation and load, grid energy storage would simplify the balancing act between electricity supply and demand, and on overall grid power flow.

Many kinds of EES technologies, such as batteries, supercapacitors, and even regenerative fuel cells, have been developed. The characteristics for several of these EES systems in terms of power rating, which identifies potential applications, and duration of discharge are illustrated in Figure 1-2. In general, electrochemical energy storage possesses several desirable features, including high efficiency, pollution-free operation, flexible power, and energy characteristics to meet different grid functions, long cycle life and low maintenance. Each storage technology has specific operating characteristics which make it suitable for a particular grid application.

Electrochemical energy storage approaches can be distinguished by the mechanisms used to store energy. Batteries, regardless of their chemistry, store energy within the electrode structure through charge transfer reactions. By comparison, fuel cells, which are usually not reversible, store energy in the reactants that are externally fed to the cells. These devices generally use Pt as catalyst. These differ from redox-flow cells, which store energy in the redox species that are continuously circulating through the cells.
Supercapacitors offer yet another different energy storage mechanism, via a capacitive process arising from an electrical double layer at the electrode-electrolyte interface.

![Energy storage systems](image)

**Figure 1-2 (a)** Overview of different energy storage technologies. **(b)** Ragone plot with specific energy and power for different energy storage devices.

We are unlikely to find, at least in the short-term, a single technology that can repeatedly and efficiently store large quantities of electric energy at low cost. On the other hand, a portfolio approach that is based on using a combination of technologies may be the most effective means to introduce and integrate energy storage. The usefulness of EES stems from the operational characteristics of the grid as a supply chain of a commodity, electric power.

Storage solutions based on the technologies we have today are so expensive that historically it has been far more cost-effective to expand generation as well as transmission and distribution to serve the peak load and provide sufficient operating margin to meet consumer demands for reliability. The cost of these technologies needs to be reduced, in order to couple them to the electricity grid. For example, the use of other catalysts instead of Pt in FC, the development of new materials using more abundant and high capacity materials, and more cost-efficient synthesis methods.

### 1.3 Fundamentals of battery

A battery is a device that efficiently converts chemical energy into electrical energy. The chemical energy is released by oxidation-reduction reactions at the electrodes leading to the transfer of electrons from the oxidizing electrode to the reducing electrode via outside circuit. More precisely, a battery consists of two or more cells connected in
series or parallel, but the term is normally used for a single cell. Such a cell contains an anode, an electrolyte which conducts ions, a separator (allow ion transport) and a cathode.

As example let look into the following reaction of the Daniel cell battery\textsuperscript{11,12}:

\begin{align*}
\text{Anode: } & Zn \rightarrow Zn^{2+} + 2e^- \quad E_o = -0.76 \text{ V} \\
\text{Cathode: } & Cu^{2+} + 2e^- \rightarrow Cu \quad E_o = 0.34 \text{ V} \\
\text{Cell: } & Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu \quad E_o = 1.1 \text{ V}
\end{align*}

Batteries can be divided into two main categories: primary and secondary batteries. In primary batteries, the electrode reactions are not reversible and the cells are therefore not rechargeable. In secondary batteries, the electrode reactions are reversible and the cells are rechargeable.

There are three major characteristics in energy conversion and storage devices:

1. Operating voltage, which is related to power output
2. Current related to charge rate
3. Capacity related to how long it can last

1.3.1 Energy density

The available energy stored in a fully charged cell depends on the Voltage and the charge and may be obtained by measuring the time $\Delta t (I_{dis})$ for its complete discharge at a constant current $I_{dis}$ ($I_{dis} = dq/dt$\textsuperscript{13}):

$$E = \int_0^{\Delta t} IV(t) dt = \int_0^Q V(q) dq \quad \text{Equation 1-1}$$

The energy of a cell can be obtained by the relationship of the cell voltage multiplied by the electricity equivalent to 1 mol (96500C or 26.8 Ah) as follows \textsuperscript{11,14}:

Energy of a cell [W h] = Cell voltage [V] x Electricity \quad \text{Equation 1-2.}
We conventionally refer to specific energy (normalized per mass of active material) in units of [WhKg\(^{-1}\)] and to energy density (normalized per volume of active material) expressed in units of or [WhL\(^{-1}\)].

### 1.3.2 Theoretical capacity

The theoretical capacity can simply be calculated by the electricity equivalent to 1 mol divided by molecular weight of active material, as in the following:\(^{14}\):

\[
\text{theoretical capacity} = n \times F \times \frac{1}{\text{molecular weight of the active material}} \quad \text{Equation 1-3}
\]

The actual output capacity is less than the theoretical capacity because the theoretical capacity can only be obtained in an ideal process.

### 1.3.3 Efficiency of the cell

The perfect energy efficiency of a cell to store energy at a fixed current I is

\[
Q = \int_0^t I \, dt = \int_0^Q dq \quad \text{Equation 1-4}
\]

where Q is the total charge per unit weight (Ah kg\(^{-1}\)) or per volume (Ah L\(^{-1}\)) transferred by the current on discharge or charge. Q can be limited by the use of high currents because the rate of transfer of ions across electrode/electrolyte interfaces becomes diffusion-limited at high currents\(^{13}\). The percent Coulombic efficiency of a single cycle associated with a capacity fade is:

\[
100 \times \frac{Q_{\text{dis}}}{Q_{\text{ch}}} \quad \text{Equation 1-5}
\]

### 1.4 Rechargeable Batteries

#### 1.4.1 Historical technologies

There are various types of rechargeable batteries developed long ago, such as the Lead-Acid battery, Nickel-Cadmium and Nickel-Metal Hydride (Ni-MH). The Lead-Acid battery
has been traditionally used as Starting-Lighting-Ignition system in vehicles and was initially used as power supply for the EVs and HEVs. Even though the Lead-Acid Battery is highly reliable, it is an outdated technology, which is not adequate for the application of EVs because of its low gravimetric and volumetric energy density. Furthermore, using materials such as sulfuric acid and lead also hinder the lead-acid battery for using in green energy applications. The same could be said about the Ni-Cd battery. The Ni-MH battery is composed of active materials such as nickel oxyhydroxide and hydrogen-absorbing alloy. Ni-MH replaced the Ni-Cd battery and has twice the capacity of Ni-Cd. Characteristic comparisons of these three types of batteries are listed in Table 1-1.

**Table 1-1 Comparisons of three typical rechargeable batteries adapted from** \(^{15}\).

<table>
<thead>
<tr>
<th>Items</th>
<th>Ni-MH</th>
<th>Ni-Cd</th>
<th>Lead-acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working voltage (V)</td>
<td>1.2</td>
<td>1.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Power density (W/Kg)</td>
<td>200</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Energy density (W·h/Kg)</td>
<td>50</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Cycle life (cycles)</td>
<td>400</td>
<td>1500</td>
<td>300</td>
</tr>
<tr>
<td>Capacity self-discharge rate (% per month)</td>
<td>30%</td>
<td>20%</td>
<td>10%</td>
</tr>
<tr>
<td>Energy efficiency (Cdischarge/Ccharge)</td>
<td>70%</td>
<td>70%</td>
<td>75%</td>
</tr>
<tr>
<td>Reliability</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

1.4.2 Emerging technologies

1.4.2.1 Redox flow cells Batteries and nanofluids

The rechargeable nanofluid technology is a transformational advancement of redox flow battery concepts, where energy is stored and released through a reversible electrochemical reaction in two electrolytes.

1.4.2.1.1 Redox Flow Batteries

Redox Flow Batteries (RFBs) are not new technologies, but they are re-emerging, thrusted by the need of high-power energy storage. Among them the all-vanadium redox flow battery being the most popular.
A flow battery is an electrochemical device that converts the chemical energy in flowing electro-active solutions directly to electrical energy, similarly to a conventional battery. The electro-active materials in a flow battery, however, are mostly stored externally in an electrolyte and are introduced into the device only during operation. Flow batteries have all the reactants and products of the electro-active chemicals stored externally to the power conversion device.

The modular design distinguishes RFBs from other solid-electrode based electrochemical energy storage systems: decoupled energy capacity owing to the external circulating sub-system, and quick response arising from fast mass/charge transfer between the electrodes and intimate liquid–solid interface between active species and current collector\textsuperscript{16}. This is the most attractive characteristic of the RFBs.

Flow batteries have more complicated system requirements of pumps, sensors, flow and power management, and secondary containment vessels, thus making them more suitable for large-scale storage applications.

All vanadium\textsuperscript{17} (1.26 V) and Zn/Br\textsuperscript{18} (1.85 V) flow cells are the most advanced systems and have reached the demonstration stage for stationary energy storage. Interest in the all-vanadium system, Figure 1-3, is based on having a single cationic element, so that the cross-over of vanadium ions through the membrane on long-term cycling is less important compared with other chemistries\textsuperscript{19}.

However, the limitations are obvious: low energy density arising from low working potential limited by electrolysis to ca. 1.5 V cell voltage, and low ion concentrations (typically 1–2M), yielding only 40 Wh/L energy density for the fluids alone\textsuperscript{16}. 
1.4.2.1.2 Nanofluids

Nanofluids are engineered by dispersing nanometer-sized particles in conventional base fluid and were first introduced by Choi \(^\text{20}\) for thermal nanofluid application. Nanofluids feature improved properties compared to their base fluids making of them ideal candidates for a host of industrial and consumer applications.

A novel flow battery has been developed by scientists from Argonne National Laboratory and Illinois Institute of Technology, \(^\text{21}\) as well as in our own laboratory based on electroactive nanofluids \(^\text{22}\). The ANL-IIT technology, was dubbed nanoelectrofuels flow battery (NFB). These novel systems use nanofluids made of electro-active particles dispersed in a liquid electrolyte as flowing materials alternative to the solutions conventionally used in RFB.

A wide range of nanoparticles could be used in electrochemical energy conversion and storage devices. However, it is noted that suitable nanofluids are needed to achieve an optimal energy density.

The unique combination between RFBs and nanofluids offers excellent properties unlike those found in the conventional accumulator and solid battery. Leveraging the excellent nanofluid properties and the established flow battery technology, a rechargeable battery with effectively liquid electrodes could be created. The nanofluids, stably dispersed, are used as cathodic and anodic electronanofluids with the primary challenge of maximize nanoparticle concentrations. However, there are more challenges for the
final use of nanofluids as electroactive materials, including intrinsic performance, effective charge and discharge, pumpable and durable electroactive materials.

We have recently shown that even at low concentrations of nanocarbon particles, nanofluids can deliver effective and fast charge transfer through the bulk of the dispersion. Thus, a stabilized dispersion of RGO in aqueous sulfuric acid solution can deliver energy storage capacities similar to those of solid electrode supercapacitors (169 F g\(^{-1}\) (RGO)), but working up to much faster rates (from 1 mV s\(^{-1}\) to the highest scan rate of 10 V s\(^{-1}\)) in nanofluids\textsuperscript{22}.

1.4.3 Other re-emerging lithium systems

Despite the fact that Lithium-sulfur (Li-S) or Li-air (Li-O\(_2\)) batteries are not new systems they are a couple of representative examples of technologies based on Li that have been intensely revisited recently. The hope is that the use of novel enabling tools such as nanotechnology could help surpass the drawbacks that hindered their implementation in the past.

1.4.3.1 Li-O\(_2\)

Li–O\(_2\) batteries have theoretical energy densities about 10 times higher than most batteries in the market today, but the improvements needed to use this technology are far from being accomplished. The Li–O\(_2\) has the highest theoretical specific energy (energy per unit mass) of any battery technology, 3,500 Wh/kg. Practical energy storage reported are variable, since many determining factors are poorly controlled, but values in the range 500 to 1,000 Wh/kg\textsuperscript{23,24} have been reported.

The reaction paths leading to the final Li\(_2\)O\(_2\) discharge products can be greatly affected by the operating conditions or environment, which often results in major side reactions. Recent research findings have begun to reveal how the reaction paths may be affected by the surrounding conditions and to uncover the factors contributing to the difficulty in achieving the reactions of lithium and oxygen.
To avoid the problems associated to the parasitic reactions between the electrodes and the electrolyte, several approaches have been proposed during the last decade. Nazar et al. have reported 2,3-dimethyl-2,3-dimethoxybutane as an improved electrolyte, greatly enhancing performance\(^{25}\). Bruce’s group, recently succeeded in achieving more than 100 cycles with excellent capacity retention, high coulombic efficiency, and low polarization using a porous gold electrode\(^{26}\).

1.4.3.2 Li-S
Elemental sulfur, abundant and inexpensive, has become one of the most actively researched cathode material in the last few years. Sulfur, with a theoretical capacity of 1,675 mAh/g, makes this technology attractive. Its high theoretical specific energy (2,567 Wh/kg)\(^{6}\) is based on a redox reaction that reversibly interconverts sulfur and Li\(_2\)S via intermediate lithium polysulfide species, which solubility represents a major problem for the reversible cycling of these cells. The chemistry is fundamentally different from the intercalation process that governs Li-ion cells and has higher energy density, but it comes with several challenges.

Aurbach et al. have elucidated the mechanism behind the process that passivates Li when LiNO\(_3\) is used as additive, showing that it creates a protective film of LixNO\(_y\) and/or Li\(_2\)SO\(_3\) on the negative electrode\(^{27}\).

On the other hand Kazda and collaborators found that the obtained S powder by cryogenic grinding result in a cathode with better capacity and better stability\(^{28}\).

1.4.4 Beyond Lithium
Discussing other options for “beyond Li-ion batteries” usually includes Na-ion and magnesium batteries. In fact, the plethora of relevant Na-ion insertion cathodes available today is a pleasant surprise, especially as many of them demonstrate excellent kinetics. However, Na-ion systems do not compete with Li-ion battery systems in terms of energy density. Instead, Na-ion systems may be relevant in the context of a possible future scarcity of lithium, benefiting from the high abundance of Na in earth crust. The
knowledge gained from developing Li or Lithium ion electrodes is being applied to this and other battery technologies.

However, the larger size and different bonding characteristics of sodium ions influence the thermodynamic and kinetic properties of NIBs, and can lead to unexpected behavior in terms of electrochemical performance or reaction mechanism. The lower operating voltage of Na-ion cells results in enhanced stability of the non-aqueous electrolyte, but it also manifests itself in lower energy density. The majority of the proposed electrode materials for NIB show similar or slightly lower specific capacity and redox potential than when used in Li-ion cells. Moreover, the accommodation of sodium in traditional host materials is difficult because the ionic radius and reduction potential of sodium are strikingly larger than that of lithium. Therefore, the (de)sodiation process induces large distortions in the host lattice that ultimately lead to pulverization of the electrode and the impending failure of the cell.

Some researchers argue that the next generation of cells should switch to heavier elements such as magnesium. Doubly charged magnesium ions shuttle two electrons at a time — instantly multiplying the electrical energy that can be issued for the same volume. Also, Mg raw material is significantly cheaper and more abundant than Li. Magnesium comes with its own challenge, however: whereas lithium move easily through electrolytes and electrodes, magnesium with its two charges have difficulties moving through the electrolyte and the electrodes. Furthermore, the extremely high volumetric capacity (3832 mA h cm$^{-3}$) makes it an ideal prospective anode material for mobile devices and electric vehicle batteries. A critical characteristic of magnesium, unlike lithium, is that its deposition occurs without the formation of dendrites.

There are several technical problems that have hampered the commercialization of MIBs. While most of the concepts are identical, Li-ion research cannot be easily extrapolated to Mg-ion electrochemistry. On Mg battery systems, excellent work was done so far on the anode. Several families of electrolytes with wide electrochemical windows, in which Mg anodes are fully reversible were demonstrated.

On the other hand, prospective work on cathode materials working properly in the electrolytes in which Mg anodes are fully reversible has not been so successful. The
second major problem is also related to cathode materials, which suffer from either slow solid-state diffusion kinetics or low total energy density.\(^\text{33}\)

Finally, Calcium is an especially attractive alternative as it is the fifth most abundant element in the Earth’s crust, and its standard reduction potential is only 170 mV above that of lithium, enabling a significantly larger cell potential than that achievable with magnesium.\(^\text{35}\) Moreover, Ca\(^{2+}\) holds the promise for faster reaction kinetics than Mg\(^{2+}\) (and thus better power performance), owing to its lower polarization character. Pioneering research work by Aurbach et al.\(^\text{36}\) led to the conclusion that the electrochemical behavior of calcium electrodes in conventional organic electrolytes is surface-film-controlled, but that calcium deposition was virtually impossible, which was attributed to the absence of calcium ion transport through the surface passivation layer formed.

To develop viable calcium metal anodes, the electrolyte must contain Ca\(^{2+}\) ions and allow reversible calcium metal plating/stripping (on reduction/oxidation). Palacin et al demonstrated the feasibility of calcium plating at moderate temperatures using conventional organic electrolytes and a reversible cycling process.\(^\text{35}\) This can be considered the first step to developing a calcium rechargeable technology.

To summarize, batteries are advancing on two fronts, reflecting an increased specific energy for longer runtimes and improved specific power for high-current load requirements. Improving one characteristic of a battery may not automatically strengthen the other and there is often a compromise.

### 1.5 Lithium Ion Batteries

#### 1.5.1 Operation principles

The operation principle of lithium-ion batteries is based on reversible de/intercalation processes of Li\(^+\), into the electrode materials in order to compensate for electrons transferred. During discharge the lithium ions move from the anode to the electrolyte and from the electrolyte to the cathode of the battery where they then diffuse into the active material.
The first commercially used lithium-ion battery consisted of a cell is composed of a graphite anode (e.g. lithiated graphite LixC₆ in its charged form), a cathode formed by lithium metal oxide (e.g. LiCoO₂ in its discharged form) and electrolyte (e.g. LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate mixture) embedded in a separator felt. During discharge, Li⁺ ions are extracted from the layered graphite, and intercalate between the LiCoO₂ (LCO) layers (Figure 1-4). The process is reversed during charge:

\[ yC + LiCoO₂ \rightarrow Li_xC_y + Li_{1-x}CoO_2, \ x \approx 0.5, \ y = 6, \ V_{oc} \approx 3.7 \ \text{V} \]  

Reaction 1-4

Figure 1-4: Schematic drawing of a lithium ion battery

The energy density in a lithium-ion battery is a product of its cell potential, \( V_{oc} \) and the capacity of reversible charge transfer per unit weight or unit volume. The values of \( V_{oc} \) are linked directly to the intrinsic properties of the materials that form the positive and negative electrodes. Furthermore, the cycle-life and lifetime of a lithium-ion battery are dependent on the nature of the interfaces between the electrodes and electrolyte, while safety is the function of the stability of the electrodes and electrode/electrolyte interfaces.

1.5.2 Market

Since its commercialization by Sony Corp. in the early 1990s, the lithium-ion battery became the most important secondary battery, produced by a billion units per year and thus triggered the revolution of portable electronic devices.
Lithium Ion Batteries (LIBs) are the current choice for high energy density and lightweight energy storage devices. Industry experts expected lithium-ion batteries to be the promising energy storage of the global market for use in hybrid electric vehicles (HEV)s because light-weight lithium ion batteries with high power density and energy density can store electricity significantly. Actually, LIBs market are presently ready to grow from portable electronics to electric vehicles (EV) industry.

In particular, the market value of lithium ion batteries as power suppliers for EV is estimated at $15.9 billion in 2019, which is 5 times more than the value of $3.4 billion in 2013, according to the estimation report by JP Morgan. The value of $15.9 billion as mentioned above is only about the market of lithium ion batteries for EVs. The performance of lithium ion battery has been greatly improved. However, for the application of a power supply for EV there are still many research requirements for designing lightweight, high energy density and high-power density material, with a consideration of safety under severe conditions, in order to use the batteries all around the world. Above all, reducing costs is a key point for the application of lithium ion batteries. As it was mentioned before, the first marketed lithium ion cathode material was lithium cobalt oxide, LCO, and it has been currently used as a cathode material due to the fact that LCO has a high theoretical capacity of 280 mAhg\(^{-1}\). Although LCO is the principal cathode material for commercial LIB, it suffers from many disadvantages such as toxicity, high cost of the rare Co mineral resources, and unreliability from explosive reactions at high temperatures.

1.5.3 Electrode materials

1.5.3.1 Negative electrode

The most obvious material, metallic lithium is not practically used anymore when liquid electrolytes are concerned. Lithium metal exhibits the disadvantage in that lithium dendrites can be formed during the charging process (during fast lithium electroplating). These dendrites are subsequently able to grow through the separator to the cathode, resulting in a bypass and from there to damage of the battery (short circuit).
Carbonaceous materials are currently the preferred materials for producing anodes in the Li-ion battery. For instance, graphite (Li_xC_6), with a theoretical capacity of 372 mAh/g, can avoid the problem of Li dendrite formation by reversible intercalation of Li into carbon host lattice, and this provides good cyclability and safety for Li ion battery anodes. To increase the energy and power densities of Li-ion batteries, nanostructured carbonaceous anode materials, such as one dimensional (1D), two-dimensional (2D), and porous carbon based anodes, have been developed to create more active sites for Li storage\textsuperscript{41}.

**1.5.3.2 Positive electrode**

For a successful application as cathode material in lithium-ion batteries the materials should show some specific characteristics, such as:\textsuperscript{42}

1. the material should contain an oxidizable/reducible ion, such as a transition metal.
2. the reaction of the material with lithium is reversible.
3. the material and lithium react with each other in a reaction with a high free energy.
4. a rapid reaction with lithium during insertion and removal.
5. being a good mixed (electronic-ionic) conductor.
6. no change in structure or other degeneration during charge/discharge.
7. low cost and environmental acceptability.

Figure 1-5 shows some examples of anode and cathode materials with indication of their capacity and voltage range.
1.5.3.2.1 Some examples of materials used as positive electrode in LIBs

In a Li-ion battery, Li\(^+\) is the guest ion and the host network compounds are metal chalcogenides, transition metal oxides, and polyanion compounds. These intercalation compounds can be divided into several crystal structures, such as layered, spinel, olivine, and tavorite.

LCO introduced by Goodenough\(^{37}\) is the first and the most commercially successful form of layered transition metal oxide cathodes. The Co and Li, located in octahedral sites, occupy alternating layers and form a hexagonal symmetry. LCO is a very attractive cathode material because of its relatively high theoretical specific capacity of 274 mAh\(\cdot\)g\(^{-1}\), high theoretical volumetric capacity of 1363 mA\(\cdot\)h cm\(^{-3}\), low self-discharge, high discharge voltage, and good cycling performance. The major limitations are high cost, low thermal stability, and fast capacity fade at high current rates or during deep cycling. While the thermal runaway issue is general to transition metal oxide intercalation cathodes, LCO has the lowest thermal stability of any commercial cathode material\(^{44}\).

LiMnO\(_2\) (LMO) can also be promising because Mn is much cheaper and less toxic compared to Co or Ni. However, the cycling performance of LMO was still not satisfactory (i) because the layered structure has a tendency to change into a spinel...
structure during Li ion extraction\textsuperscript{45}, and (ii) because Mn leaches out of LMO during cycling\textsuperscript{44}. Spinel Li$_2$Mn$_2$O$_4$\textsuperscript{46} benefits from the abundance, cost, and environmental friendliness of Mn. Li occupies tetrahedral 8a sites and Mn is located in octahedral 16d sites in a cubic close-packed (ccp) array of oxygen anions. Li$^+$ can diffuse through vacant tetrahedral and octahedral interstitial sites in the three-dimensional structure.

Polyanion-based compounds, Li$_x$M$_y$(XO$_4$)$_z$ (M = metal, X = P, S, Si, Mo, W), are now regarded to be the most promising cathode materials for future lithium-ion batteries. Among them, LiFePO$_4$ (LFP) has been by far most studied since its discovery. The first reports of Li$^+$ intercalation in LFP have been published by Padhi \textsuperscript{47} from the John B. Goodenough group in 1997 in the University of Texas, Austin.

1.6 Lithium iron phosphate

1.6.1 Crystal growth and crystal structure

For the synthesis of LFP, many possible combinations of starting reagents have been used as well as high-temperature (ceramic synthesis) and lower-temperature procedures reported. These will be discussed in more detail in chapter 2. The initial reagents are dissolved and reacted and nucleation takes place. Some of the nuclei can grow greater than a critical radius, and will not disappear again. The amount of surface energy leads to the growth in a certain direction of the crystal, which is the second stage during the crystal formation. Thus, the reaction conditions determine the shape of the crystal formed. If the surface energy of the nuclei is high in only one direction, the crystal will grow and form a platelet. Sometimes the nucleation process occurs while the nuclei grow, leading to particle size distributions which are not uniform. Finally, the reaction will stop when the concentration of the complex ions in the medium are lower than the critical super-saturation concentration \textsuperscript{48}.
LiFePO₄ crystallizes in the orthorhombic space group Pnma belonging to the olivine structure.

There are two slightly different octahedral sites in this crystal structure: M1 and M2. The M1-O bonds have a length of around 2.16 Å and the M2-O bonds are slightly longer (2.19 Å) and distorted from the regular geometry. M2 is the usual site for Fe²⁺ ions, with the Fe²⁺ ions in the center of the FeO₆ unit. Each FeO₆ distorted octahedron is connected to four other FeO₆ via vertices, forming a layered network perpendicular to the a-axis of the crystal. Successive Fe²⁺ layers are separated by PO₄ tetrahedra and LiO₆ octahedra. On the other hand, the M1 positions are usually occupied by lithium ions, while oxygen atoms are in a slightly distorted, hexagonal close-packed array (Figure 1-7).

Additionally, the oxygen atoms are strongly covalently bonded by phosphorus atoms in the (PO₄)³⁻ clusters (calculated interatomic distance is rP-O = 1.512 Å), leading to a robust stable structure at relatively high temperatures. Furthermore, there is no
evidence of potentially troublesome reactions between the commonly used electrolyte and LFP under charged and discharged conditions up to 85°C, guaranteeing no O₂ release and no likely pressure build-up inside the battery.

However, it is well known that Fe²⁺ in LFP can be quite unstable under oxygen and water, as is the case in the atmospheric air. As a result, long-term air exposure of LFP can lead to severe oxidation (Fe²⁺ to Fe³⁺ conversion on the surface of the particles) limiting its electrochemical performance⁵³. LFP and FePO₄ atomic coordinates, cell parameters, and interatomic distances were reported using the Rietveld refinement of X-ray powder diffraction (Table 1-2). The difference in the unit-cell volume between the two phases was found to be 6.8%⁵⁴.
Table 1-2: Atomic and unit cell parameters for LFP and FePO₄ obtained via Rietveld refinement of the X-ray powder diffraction data.

<table>
<thead>
<tr>
<th></th>
<th>LiFePO₄</th>
<th>FePO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(A)</td>
<td>10.3290(3)</td>
<td>9.8142(2)</td>
</tr>
<tr>
<td>b(A)</td>
<td>6.0065(2)</td>
<td>5.7893(2)</td>
</tr>
<tr>
<td>c(A)</td>
<td>4.69080(2)</td>
<td>4.7820(2)</td>
</tr>
<tr>
<td>B(A²)</td>
<td>9.8142(2)</td>
<td>4.7820(2)</td>
</tr>
<tr>
<td>X</td>
<td>Li</td>
<td>Fe</td>
</tr>
<tr>
<td>y</td>
<td>0</td>
<td>0.2822(3)</td>
</tr>
<tr>
<td>Z</td>
<td>0</td>
<td>0.9716(7)</td>
</tr>
<tr>
<td>X</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Y</td>
<td>0.0954(5)</td>
<td>0.4179(12)</td>
</tr>
<tr>
<td>z</td>
<td>0.4179(12)</td>
<td>0.7403(21)</td>
</tr>
<tr>
<td>X</td>
<td>O₁</td>
<td>O₁</td>
</tr>
<tr>
<td>Y</td>
<td>0.0946(11)</td>
<td>0.7403(21)</td>
</tr>
<tr>
<td>z</td>
<td>0.7403(21)</td>
<td>1.74(3)</td>
</tr>
<tr>
<td>X</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Y</td>
<td>0.4538(13)</td>
<td>0.2056(15)</td>
</tr>
<tr>
<td>z</td>
<td>0.2056(15)</td>
<td>0.2861(11)</td>
</tr>
<tr>
<td>X</td>
<td>O₃</td>
<td>O₃</td>
</tr>
<tr>
<td>Y</td>
<td>0.1615(8)</td>
<td>0.0521(12)</td>
</tr>
<tr>
<td>z</td>
<td>0.0521(12)</td>
<td>0.2861(11)</td>
</tr>
</tbody>
</table>
1.6.2 Electrochemical properties

LFP is a typical material with a two-phase reaction mechanism at \( V = 3.45 \) \( \text{V vs. lithium} \) over a large composition range. Upon charging, \( \text{Li}^+ \) ions are extracted from LFP and the \( \text{Fe}^{2+} \) ions in the structure lose electrons and are oxidized to \( \text{Fe}^{3+} \), accompanied by the formation of \( \text{FePO}_4 \) phase. When all lithium ions are extracted from the host structure, all the LFP (known as triphylite) transforms into \( \text{FePO}_4 \) (known as heterosite). Upon discharge, the reverse process takes place. \( \text{Li}^+ \) ions are inserted into \( \text{FePO}_4 \) structure and the \( \text{Fe}^{3+} \) ions gain electrons and are reduced to \( \text{Fe}^{2+} \). The flat voltage profile indicates, by Gibbs’ phase rule, that the extraction/insertion involves a two-phase reaction:\(^1\)

\[
\text{LiFePO}_4 \leftrightarrow x\text{FePO}_4 + (1-x)\text{LiFePO}_4 + x\text{Li}^+ + xe
\]

Figure 1-8 shows the voltage and current during charge and discharge of a LFP cathode cycled vs. lithium at a C/10 rate. In the assessment of the rate capability of the material, Padhi et al. noted that increasing the current density does not lower the OCV, but it reversibly decreases the cell capacity. Cycling again at lower rates restores the capacity, indicating that the loss in capacity is a diffusion-limited phenomenon associated to the two-phase nature of the insertion process or the low electrical conductivity of the material.\(^3\)

**Figure 1-8: Voltage profile for LFP cathode cycled vs. lithium metal.**

Lithium has been found to diffuse more quickly in the \( b \) direction than in the \( a \) or \( c \) directions. First principle electronic structure calculations suggest that the activation energy for diffusion is much lower along the \( b \)-axis (the direction of lithium chains in the structure) and much higher in other directions (270 meV compared to 2.5 eV and 1 eV,
for \( x = 1 \) in \( \text{LiFePO}_4 \))\(^2\). Therefore, lithium diffusion is essentially restricted to the tunnels along the b-axis, so that this material is a one-dimensional ionic conductor. Therefore, it would be important to synthesize materials with crystals thinner in the b-axis direction, in order to optimize it by increasing the percentage of electroactive ac faces of the crystals; Figure 1-9 illustrates this phenomenon.

**Figure 1-9:** a,b, The crystal structure of LFP projected along the [010] (a) and [001] (b) directions. c,d, Possible Li diffusion pathways are parallel to these directions\(^3\).

1.6.3 Lithium ion intercalation/deintercalation

The mechanism of \( \text{Li}^+ \) intercalation/deintercalation in the LFP has not been completely elucidated. In 1997, Padhi *et. al.* \(^1\) proposed a model, where they concluded that the flat charge/discharge profile of LFP arises from the motion of a two-phase interface. The second phase was identified to be orthorhombic \( \text{FePO}_4 \), which crystallizes in the same space group as LFP (Pnma), Figure 1-10 (a).

Delmas *et. al.* \(^4\) developed a “domino-cascade” model which takes into account structural constraints as well as the influence of the reaction interface. The “domino-cascade” model claims that the speed of the phase boundaries is extremely high, so that no particles with the mixing phases can be identified during reaction process; therefore, single particles are either \( \text{LiFePO}_4 \) or \( \text{FePO}_4 \).

Ramana *et. al.* \(^5\) introduced a “spinodal-decomposition” model, which suggests that the movement of the phase boundaries is relatively slow, and multiple domains and phase interfaces should be observed in the partially delithiated particles.
An alternative model, the “mosaic model”, invokes a mosaic character within each particle. The idea here is that lithium extraction/reinsertion can occur at many sites within a given particle. On discharge, lithium re-enters the major part of FePO₄, leaving the core as FePO₄. At the same time, the inactive LFP is left entrapped by a coating of amorphous material.

Although many studies support the two-phase mechanism of LiFePO₄/FePO₄, the specific model still remains controversial, including the core–shell, domino cascade, spinodal decomposition, and mosaic model. Because the delithiation/lithiation kinetics and phase compositions strongly depend on the particle size, morphology and physical properties of the studied LFP material, the above disagreement, may be attributed to the specific experimental conditions. In recent years, with the advancement of microscopic and spectroscopic experimental techniques, a solid solution reaction and intermediate phase have been detected in LFP, which also provide another possible phase transformation mechanism for this material.

Recent research has suggested that in an electrode assembly, all LiFePO₄ particles are not (de)lithiated simultaneously, but rather sequentially via a particle-by-particle intercalation pathway. The inhomogeneous LiFePO₄/FePO₄ phase distribution at the entire-electrode scale was confirmed by ex situ STEM. At the mesoscale, a core–shell phase distribution with a preferential pathway along the porosities was found. At a larger scale, the (de)lithiation process occurs via a “stratum-by-stratum” pathway, from the electrolyte side to the current collector.
1.6.4 Improving performance of LFP Electrodes

One major concern about the performance of this cathode material is its low intrinsic electrical conductivity.\(^1\),\(^19\) Pristine LFP (in the absence of carbon) has an electrical conductivity of \(10^{-9}\) S cm\(^{-1}\), which is a quite low value compared to the \(10^{-3}\) S cm\(^{-1}\) conductivity of LCO.\(^28\) Many efforts have been made to improve the electrochemical properties of LFP. There have been different ways for obtaining enhanced electrochemical performances.

1.6.4.1 Carbon-coating and conducting additive addition

Since LFP is an insulating material, it was initially found to have poor rate capability as an electrode material, even when mixed with carbon additives. However, several methods of carbon coating have been shown to be useful in promoting higher rate capability, allowing electrochemical cycling at almost the theoretical capacity of LFP at room temperature.

Carbon coating provides the electron paths and compresses the particle growth as shown in Figure 1-11. Thus, in case of homogeneous carbon coating on LFP particles, electrons can flow well without blockage, and the small particle size can help Li\(^+\) ion diffusion. As a result, electrochemical properties can be enhanced.

![Carbon-coating and conducting additive addition](image)

Figure 1-11: Schematic of comparison of partial and homogeneous carbon coating as electrons path\(^{11}\).

The first carbon coating was shown by Ravet et al., with almost the full theoretical capacity achieved at 80°C in a polymer electrolyte cell.\(^{12}\) When synthesized in situ, it offers intimate contact between inorganic and organic phase, where carbon acts as an electronic wiring system interconnecting LFP particles.
The electrochemical properties of the final LFP/C composites are strongly dependent on the quality of the carbon coating – its amount, morphology, degree of graphitization, and the distribution on the surface \(^{13}\). The optimization of coating carbon thickness can also significantly influence the electrochemical performances of LFP. In addition, the structure of carbon is also a key point for improving electrochemical performance of LFP. It has also been reported that carbon can change the surface conditions of LFP by controlling the spin of iron ions in the amorphous surface layer\(^{14}\).

Carbon sources like glucose and sucrose are advantageous in forming a homogeneous carbon-coating layer and in having a good control of the carbon-layer structure (thickness, homogeneity, full coverage) during the pyrolysis process at high temperatures, but the carbon quality (conductivity, graphitized degree) is hard to control.

Achieving a uniform carbon nanolayer with full coverage on LiFePO\(_4\) is a challenge. Some in situ carbon-coating methods, such as the self-polymerization of dopamine \(^{15}\) or resorcinol–formaldehyde gel\(^{16}\), can result in a uniform carbon and three-dimensional coating layer on LiFePO\(_4\); however, a more economic and feasible method is still highly desirable.

A recent research trend in carbon coating has been to develop a porous carbon structure on LFP which enables the storage of sufficient electrolytes to maximize the electrode reaction interface, and most importantly, to provide a fast lithium-ion transfer pathway. The C-LiFePO\(_4\)-PC composites reported by Fan display a high initial discharge capacity of 152.3 mA h g\(^{-1}\) at 0.1 C, good cycling stability, as well as excellent rate capability\(^{17}\). Other example of this approach was reported by Hongde. The material synthesized with citric acid shows the particle size of 2–3 μm with a refined carbon coating layer and delivers a discharge capability of 152.7 mA·h g\(^{-1}\) at 0.1 C\(^{18}\).

Huang et al. reported that 16 wt. % of polymer polypyrrole (PPy) coated LFP, and 7 wt. % of polymer polyaniline(PANI) co-coated LFP showed a discharge capacity of 145 mAh/g and 140 mAh/g, respectively \(^{19}\). Another example of these efforts can be found in the work published by Fedorkova et al., in which a simple chemical oxidative polymerization of pyrrole (Py) with PEG as additive directly onto the surface of LFP particles was applied to the synthesis of (PEG-PPy)-LFP powder \(^{20}\).
When carbon nanotubes and graphene are used as carbon sources, the entire LiFePO₄ electrode can be composed of a 3D conductive network, but local conductive paths in individual LiFePO₄ particles (particle surface) may lack a proper contact with the carbon source.

Other concerns regarding the CNTs–LFP composites include that the CNTs can be randomly incorporated with LiFePO₄, which may not make full use of the CNTs conductive network because of the poor dispersion of CNTs in solution. Therefore, some functionalization methods have been developed on carbon nanotubes to improve the dispersion in LFP. For example, poly(ethylene glycol) (PEG) was used to functionalize CNTs for LFP²¹. In addition to improved dispersion of CNTs in LiFePO₄ particles, lithium-ion diffusion in a PEG-modified CNTs–LiFePO₄ electrode increased.

Graphene, a monolayer of sp² bonded carbon atoms or multiple layer graphene, has attracted considerable attention as an advanced carbon additive. The first challenge is the easy aggregation and poor dispersion of 2D graphene sheets in common solvents, due to its hydrophobic nature, which significantly decreases its advantages. To improve graphene dispersion in solution, similar to carbon nanotubes, application of a functionalization treatment with strong oxidizing agents is a common strategy.

Rhodamine-acetic acid–pyrene (RAAP) was recently used to functionalize graphene nanosheets. As a result, of the strong interaction between RAAP and graphene, RAAP molecules were well dispersed on the graphene nanosheets, and the resulting graphene was negatively charged. Through charge attraction, Fe²⁺ ions and PO₄³⁻ were adsorbed on to the RAAP-modified graphene, and subsequently formed FePO₄/graphene hybrids. After mixing with Li acetate, the final LFP/graphene composite was obtained by a thermal reduction process. With this strategy, LFP particles can be directly grown on graphene, with a good electronic contact²². However, these processes are too complex and expensive.

### 1.6.4.2 Particle size minimization

Particle size and size distribution are very important factors for Li⁺ ion diffusion. Due to the relatively low rate capability of LFP, many processing methods have been attempted in
order to improve its performance. Particle size minimization is a way to reduce the length of ionic diffusion pathways of lithium. Optimization of the synthesis method is a key point. Yamada et al.\textsuperscript{23} experimented with the sintering temperature, finding that, although the pure olivine phase could be formed at much lower temperatures (around 300°C), the cathode performance depended strongly on sintering temperatures, and the capacity was maximized when the sintering temperature was 500–600°C. In these studies, at 550°C the material had a 160 mAh/g specific capacity with particles with radii of less than 30 microns. They concluded that sintering above 600°C could result in an abrupt particle growth, which was clearly linked to a decrease in rate capability and capacity. However, the material also included 20% of conductive carbon, and probably was cycled at low rates. In order to improve even further on rate capability, many further studies have gone in the direction of nanoscale particles, down to as low as 50 nm diameters \textsuperscript{24}. Guihua reported the preparation of single crystalline LiFePO\textsubscript{4} nanosheets with a large percentage of highly oriented \{010\} facets, which provide the highest pore density for lithium-ion insertion/extraction\textsuperscript{25}.

However, the size reduction also adversely affect the tap density and the volumetric density, and the high surface area increases the undeseriable electrode/electrolyte reactions, which lead to a poor cycling performance.

1.6.4.3 Morphology control

It was found that the solvent plays an important role in controlling the antisite defects. Some solvents with low dielectric constants (such as ethylene glycol and ethanol) can reduce the concentration of Fe–Li antisite defects. In addition to suppressing the antisite defects, the orientation of LFP particles tailored by morphology control also plays an important factor in improving the kinetics of the lithium-ion extraction/insertion process. the preference of crystal facets in LFP is also linked to the properties of the solvent. Currently, most control of the LFP (010) crystal facets are achieved with the solvothermal conditions, typically with ethylene glycol as the solvent\textsuperscript{26}. An example of this technique was reported in 2010 by Zhaoping et al. They did selectively synthesize LFP with different morphologies using a mixture of water and polyethylene glycol. The
carbon coated nanoparticles and nanoplates could deliver a discharge capacity of 155 mAh g\(^{-1}\) at 0.1C rate\(^27\).

1.6.5 Use of LFP in flow cells

A redox flow lithium battery (RFLB) based on LFP as active (but static) material was developed using an approach proposed by Grätzel et al., by introducing the concept of shuttle redox molecular solutions with suitable redox potentials, solubility, stability, and kinetics to transfer the charge to solid particles stored in a separate reservoir \(^28\). Other examples based on the concept, is the full flow cell design using suitable pairs of redox mediators (one for each active material), and LFP and TiO\(_2\) as part of the catholyte and the anolyte, respectively, in RFLB \(^29\). These two examples use the conventional LiPF\(_6\) electrolyte of LIBs. In 2016, a Li anode LFP RFLB cell based on iodide, a single 2-electron redox mediator has been reported, greatly simplifying the catholyte composition. Upon charging, LFP is delithiated with the oxidation of polyiodide; upon discharging, FePO\(_4\) is lithiated with the reduction of iodide\(^30\). As recently as April 2017 Wang reported a redox flow lithium battery, which operates via the redox targeting reactions of LFP with a bifunctional redox mediator, 2,3,5,6-tetramethyl-p -phenylenediamine\(^31\).

1.7 Objectives

This thesis was developed under the framework of the European Project SOlid MAterials for high power Li polymer BATteries (SOMABAT). The aim of the project was to develop better, greener and high-power Li-ion cells to use in EVs.

Part of the specific goals of this project, and constituting the initial objectives of the present Thesis, were to develop new, environmentally friendly ways to make LFP at reduced costs, and to explore their use to prepare nanocomposites with conducting polymers, and/or carbons.

In order to accomplish the general objective, the following specific goals were considered:
1. Developing and optimizing synthesis methods at low temperatures, in order to accomplish the goal of developing an eco-friendly low-cost material to be used as cathode in LIBs. These synthesis methods should be simple, and should allow the easy tailoring of the LFP nanoparticles.

2. To prepare LFP conductive nanocomposites to unleash the full potential of the active material. For this several approaches were considered: i) conventional ex-situ carbon coating, ii) development of hybrid nanocomposites with Polypyrrole and iii) development of hybrid nanocomposites with Reduced Graphene Oxide

3. Finally, to push the boundaries of the state of the art of LFP use as an electrode, we decided to include as a novel objective (not related to SOMABAT) the development of electroactive nanofluids based on LFP nanoparticles in order to carry out preliminary studies of its use in novel flow cells for energy storage.
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2 Experimental procedures and characterization methods
2.1 General consideration on the synthesis and the material used

An important share of the work included in this Thesis was part of the development of a European Project with very focused and practical objectives. Among these objectives, the reproducible synthesis of LFP as the cathode material was one of them. The synthesis had to fulfill a series of requirements which could lower the cost of preparation while maintaining the excellent performance of this phase reported in the literature.

In order to do this our strategy considered several actions, including

1. Low-temperature synthesis to lower fabrication energy costs.
2. Low-cost starting materials.
3. Eco-friendly conditions such as the preferred use of aqueous solvents.

All of this had to be implemented while getting high-quality pure LFP phases with optimized microstructures in order to maximize performance. One specific challenge along this line was the development of nano-micro structures combining high surface area with large tap density.

All of the above considerations are made to emphasize the importance of synthesis and synthetic procedures in this Thesis. In the following chapter, we will discuss the generic conditions used for the synthesis of LFP which could be grouped into the following categories:

1. Hydrothermal.
2. Solvothermal.
3. Reflux.

2.2 LiFePO₄

The main synthetic challenges for LFP synthesis are the control of impurities combined with eco-efficiency of the processes. Some impurities, such as Fe₂P, not only can enhance the electrochemical performance of LFP due to their high conductivity but also
can diffuse into the electrolyte. On the other hand, most of the impurities likely to appear during the synthesis of LFP (Li$_3$Fe$_2$(PO$_4$)$_3$, Li$_2$P$_2$O$_7$, FeP, FePO$_4$, depending on the precursor, preparation mode and growth parameters) have detrimental effects on the final electrochemical performance of the electrode.

Among all the common methods of LFP synthesis, solid-state reaction is the most popular one. The process of solid state synthesis involves the mixing of precursors followed by heat treatment. A typical example of precursor components used in solid state synthesis are Li$_2$CO$_3$, FeC$_2$O$_4$·2H$_2$O, and NH$_4$H$_2$PO$_4$. During ball milling and mixing, a stoichiometric amount of precursors are mixed together and milled for hours followed by thermal treatment. Zhang’s et. al. choose to decompose the intimately ground mixture of the starting materials at ca. 350-380°C for 5 hours. Then, the mixture was reground and put back in the furnace at a higher temperature around 800°C for 3-10 hours under inert atmosphere. The main disadvantages of solid-state method include easy formation of Fe$^{3+}$ and its compounds (Fe$_2$O$_3$, Li$_3$Fe$_2$(PO$_4$)$_3$), due to the presence of residual air (oxidation of Fe$^{3+}$), as well as uncontrollable particle growth and agglomeration, resulting in non-pure final materials with limited surface area and a less than satisfactory particle size distribution. Besides, solid state synthesis requires high temperatures and therefore implies an intrinsically greater energy used to prepare a given amount of material.

Compared to solid-state methods, solution chemistry routes such as solvothermal, sol-gel, co-precipitation, spray-pyrolysis, emulsion-drying and novel ionothermal route, are capable of tailoring the size and morphology of LFP powders which is important for the electrochemical performance. All of the solution routes start from a precursor in a liquid solution which provides intimate mixing of the ingredients at an atomic level, leading to rapid homogeneous nucleation and uniform particle formation. A wide range of iron reactants are available for this synthesis type, including sulfate and chlorides which are not suitable for solid-state reactions due to removal problems. In all solution methods, most of the reactant and reaction produced impurities can be easily removed by washing. This allows to reduce fabrication costs (reactants of lower purity can be used). Similarly, to the solid-state route, some of the solution methods require further calcinations of obtained materials at high temperature for a certain amount of time in order to enhance crystallinity or to better control the Li/Fe positions in the LFP lattice.
Solvothermal methods use the same principles as hydrothermal methods (autoclave reactor treatment at (180 – 200°C), employing different organic solvents and solvent mixtures. The hydrothermal synthesis would be discussed below.

The ionothermal method is a special type of solvothermal approach. It is based on the special solvent characteristics of ionic liquids such as high thermal stability, negligible volatility and tunable solvation properties depending on the cation-anion pairs they are made of. This procedure was proposed by Tarascon et al.²

![Synthesis methods to obtain LFP](image)

Figure 2-1 Synthesis methods to obtain LFP³⁴.

Hydrothermal reactions were carried out with water as a solvent in an autoclave (Figure 2-2) under a given temperature and the corresponding autogenous pressure. The solubility of the reacting materials under these conditions is normally higher than in a reflux reaction. Thus, under such harsh conditions, precursors that are not soluble in water at normal atmosphere can be made soluble easily. In addition, a saturated solution of the precursors can be formed by adjusting the ratio and amount of raw materials. The properties of the product formed using hydrothermal synthesis can be controlled readily. The parameters of hydrothermal synthesis (in addition to the solution composition) are just the temperature, pressure, and the reaction atmosphere. As a result, the advantages of this method are:

1. Equilibrium conditions a relative low temperature growing process induces low density of defects
2. Sealed autoclave can isolate the reaction from air which can decrease the possibility of side reactions
3. Convection of solvent in auto-clave can speed up the diffusion rate of ions to accelerate the crystal growth.

As a conclusion, a hydrothermal method and others related to this procedure were considered to be the best choice to control the crystallite size in combination with a good electrochemical behavior. A further advantage of this method, compared to other syntheses, is also their environmental friendliness, easy scale-up, and high energy efficiency.

Figure 2-2 Photograph of an autoclave reactor and a schematic representation.

2.3 Reduce graphene oxide synthesis

Graphene was considered as an optimal material to prepare some composites with LFP, given its conductive and capacitive properties. The derivative chosen was reduced graphene oxide (referred to as RGO below). The reduction of graphene oxide (GO) to produce RGO is an extremely important process as it has a large impact on the quality of the RGO produced, and therefore will determine how close RGO will come, in terms of structure and properties, to pure graphene. In large scale as applications, like for instance energy storage, RGO is the most obvious choice, due to the relative ease in producing sufficient quantities of graphene to desired quality levels.

In the past, scientists have prepared RGO from GO by:

1. Treating GO with hydrazine hydrate and maintaining the solution at 100°C for 24 hours.
2. Exposing GO to hydrogen plasma for a few seconds.
3. Heating GO in distilled water at various temperatures and times.
4. Directly heating GO to very high temperatures in a furnace.

Reducing GO by using chemical reduction is a very scalable method, but unfortunately the RGO produced has often resulted in relatively poor results in terms of surface area and electronic conductivity. Thermally reducing GO at temperatures of 1000°C or more leads to RGO that has been shown to have a very high surface area, even close to that of pristine graphene. Taking into consideration the quality of the product obtained by thermally reduce GO, this method was chosen to prepare RGO.

2.4 Polypyrrole synthesis

The last decade of conducting polymer research has been characterized by increasing interest in the control of their morphology at the nanoscale. Among conducting polymers, polypyrrole (PPy) has been studied with particular interest on its microstructural versatility. In particular, one-dimensional structures, such as nanorods, nanotubes or nanofibres are promising due to their possible uses in energy storage, electrocatalysis, and electromagnetic interference shielding. They are better suited for charge transport than globular forms and also their larger specific surface area is of benefit in many applications.

There are two basic approaches to the preparation of one-dimensional conducting polymer nanostructures: (1) hard template methods using solid inorganic membranes or fibers for the deposition of conducting polymers, (2) soft template methods employing supramolecular assemblies of auxiliary organic substances, such as surfactant micelles or aggregates of dyes as structure-guiding agents.

PPy, when prepared by the oxidation of pyrrole with inorganic oxidants, such as Fe(III) salts, is obtained in globular morphology. An acid base indicator, methyl orange (MO), represents a simple and easily accessible structure-guiding agent in the preparation of PPy nanostructures. The synthesis of PPy in the presence of MO was initially introduced by Yang et al., and resulted in nanotubes with inner diameter of 50 nm. The mechanism of PPy nanotubes formation was explained by creation of self-degraded template, a complex of iron(III) chloride with MO. In this Thesis, a modified procedure
for the synthesis of PPy nanopipes in order to prepare hybrid composite materials has been used and will be described below.

2.5 LFP RGO and Polypyrrole synthesis procedure

2.5.1 Reactants

The starting materials were iron sulfate heptahydrate FeSO$_4$·7H$_2$O (99%, Sigma-Aldrich), Phosphoric acid H$_3$PO$_4$ (85%, Sigma-Aldrich) and Lithium acetate dihydrate CH$_3$COOLi·2H$_2$O (reagent grade, Sigma-Aldrich), LiOH·H$_2$O (ACS reagent, ≥98.0%, Sigma-Aldrich), FeC$_2$O$_4$·2H$_2$O (≥99%, Sigma-Aldrich), D-(+)-Glucose (≥99.5%, Sigma-Aldrich), Pluronic® F-127, a surfactant details of the structure etc. would be given in chapter 4, (Sigma-Aldrich) and Ethylene Glycol (anhydrous, 99.8%, Sigma Aldrich) were all used as received. Polyethyleneimine (PEI) branch, solutions in water (50 w/v wt%) was also purchased from Sigma-Aldrich, we proceeded to dilute this solution to 5% PEI, this solution was pre-warmed to 70°C for faster precursors dissolution. Sodium Nitrate (NaNO$_3$, (ReagentPlus®, ≥ 99.0%, Sigma Aldrich); Sulfuric Acid (H$_2$SO$_4$), (99.999% Sigma Aldrich); Potassium permanganate (KMnO$_4$), (Sigma Aldrich, ACS reagent, ≥99.0%); Graphite powder, <150 μm, (99.99% trace metals basis, Sigma Aldrich); Pyrrole, this material was distilled under vacuum at 130°C (reagent grade, 98%;Sigma Aldrich), Methyl Orange, (Sigma Aldrich ACS reagent, 85%). Iron(III) chloride (Sigma Aldrich, reagent grade, 97%).

For most of the syntheses described in this work deionized water was used which will be indicated as DI water throughout the text. Occasionally pure double distilled water (DDW) was used.

2.5.2 Reduce graphite oxide synthesis

Graphite oxide (GO) was prepared from natural graphite using a modified Hummers method as follows$^{14}$. NaNO$_3$ (5g) and H$_2$SO$_4$ (225mL) were added to graphite (5g) and stirred for 30 min in an ice bath. KMnO$_4$ (25g) was added to the resulting solution, and then the solution was stirred at 50°C for 2h. Deionized (DI) water (500 mL) and H$_2$O$_2$ (30
mL, 35%) were then slowly added to the solution, and the solution was washed with HCl (750 mL, 10%). Additional washing with concentrated HCl (500 mL, 37%) afforded the GO product as a powder. The reduced graphene oxide was prepared by high temperature treatment of graphene oxide sample at 800°C in N\textsubscript{2} atmosphere. We get 3.6 g of black powder, which is a 72% reaction yield. The characterization of this material would be discussed in the appendix number 1.

2.5.3 Polypyrrole synthesis

A 5 mM solution of Methyl Orange (MO) (sodium 4-[40 (dimethylamino)phenyldiazo]phenylsulfonate ((CH\textsubscript{3})\textsubscript{2}NC\textsubscript{6}H\textsubscript{4}-N=NC\textsubscript{6}H\textsubscript{4}SO\textsubscript{3}Na) and 1.5 mM FeCl\textsubscript{3} (0.243 g) were dissolved in 30 ml double distilled water (DDW) leading to the immediate formation of a flocculent precipitate. In the next step, 0.1 ml (1.5 mM) pyrrole monomer was added to the above solution and the mixture was stirred at room temperature for 24 h. After that time, the formed precipitate was filtered-off and repeatedly washed with a mixture of DDW and ethanol to get neutral pH and finally the filtered product was dried overnight under vacuum at 60°C. The characterization would be discussed in the appendix number 2.

2.5.4 LiFePO\textsubscript{4} Synthesis

Three different synthetic approaches were tested to obtain LFP. A series of parameters were tested in order to optimize various microstructures and the corresponding electrochemical properties of the final electrodes. Those electrodes should meet the criteria propose in this Thesis to achieve the scope of the project and obtain electrodes that can be use in an emergent market as the electric vehicles.

To obtain different morphologies through the hydrothermal method we studied how the solvent affect the product obtained. We used a EG and a solution of 5% PEI in water, we change the ratio of the solvents; we use 50 % of each solvent, 20%-80% ethylene glycol-5% PEI solution in water and finally 100% solution of 5% PEI in water. Concentration of the Li, Fe and Phosphate precursors were the same through the experiments, a molar ratio of 3:1:1 was used. Time, temperature and volume of the
solution did not change through the synthesis procedure, the values of these parameter were 24 hours, 200°C and 140 mL respectively. This samples were coated with carbon using glucose as carbon source and thermally treated under N₂ atmosphere, detail of the sintering and coating will be discussed in the sections below. Details of this synthesis and also the physical and electrochemical properties are going to be discuss in chapter three.

The focus of the experiment during the solvothermal synthesis was to observe how surfactants and carbon additives modified the morphology and the electrochemical properties of LFP. Surfactants as Pluronic® F-127, carbon materials as RGO and PPy were added, we test different amounts of this additives to determine what was the optimal quantity to release the theoretical capacity of LFP material (1% w/w, 2.5% w/w and 5% w/w). Other variables as reactant concentration, temperature, time and volume of the solution did not change through the experiments. The values of these parameters were 3:1:1 molar ratios of Li^{1+}, Fe^{2+}, PO_{4}^{3-} dissolve in 140 mL. 200°C was chosen as the temperature value, 24 hours as time for the reaction to take place. Discussion of the synthesis and the physical/electrochemical characterization take place in chapter four.

Reflux is a less explore method to obtain LFP. This method has shown that is possible to obtain LFP with some unique morphologies that are difficult to obtain by traditional method, especially by solid state synthesis. Also, the advantage to use this method in an industrial scale make this synthetic route attractive, as example we can consider the publication by Guo et. alt. Base in this information and a vast literature research we consider trying this synthesis method to obtain LFP particles with a novel morphologies and good electrochemical properties. Variables like concentration 0.03 mol of each precursor in 70 mL of ethylene were the same through the synthesis. Temperature, 200°C and time/72 hours, for the reaction to take place did not change. However, we decided to add RGO as additive to observe how this affect the morphology and the electrochemical performance, see chapter five for details.
To generate the name of the samples, we decide to use the molar ratio of Iron, Phosphate and Li, followed by the synthesis method, solvent and solvent volume ratio (Ethylene glycol-water). Finally, we indicate the additive use and the amount, if that was the case.

Name = molar ratio – synthesis method – solvent – solvent ratio - additive – additive amount.
## Table 2-1 Materials list nomenclature and synthesis conditions

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<th>Sample Code</th>
<th>Fe molar ratio</th>
<th>P molar ratio</th>
<th>Li molar ratio</th>
<th>Method</th>
<th>Solvent</th>
<th>Additive</th>
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<tr>
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<td>1</td>
<td>3</td>
<td>Hydrothermal</td>
<td>Water</td>
<td>5% PEI</td>
</tr>
</tbody>
</table>

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2.6 Sintering and carbon coating process

2.6.1 Carbon Coating

The LFP materials prepared as described above were pure and of good quality. Nevertheless, in many cases it was necessary or advisable to carry out certain treatments involving their sintering and their coating with conducting carbon materials. Sintering helps in improving their crystallinity and intergrain connections, whereas carbon-coating has been shown in the literature to be a necessary step for providing the necessary conductivity to the electroactive LFP particles in order to form effective high-performing electrodes.

2.6.2 Sintering

LFP particles in the sample were coated with carbon using glucose as carbon source. A solution of 10w% glucose and 90w% LFP in water was prepared. Usually 100 mg of LFP and 10 mg of glucose were dispersed in 1.5 mL of water. This solution was stirred for 5 hours, and then sonicated (oven sonicator model 4000-00301) for 10 minutes, evaporated by putting the sample at 90°C in an oven. Finally, the sample was dry under vacuum at 90 degrees overnight. The sample was initially calcined at 300°C for 3 h and then sintered at 700°C for 10 h, all under nitrogen atmosphere. In case RGO was used the sample were sintered for 3 hours at 700°C.
2.7 Nanofluids

Different compositions of nanofluids were tested, including composition using triton x-100 and CSP. Then a different amount of LFP were added to the nanofluid. We compare this nanofluid composition with one made of Diamino benzoic acid and RGO, with different mass ratio of 20/1, 30/1 and 40/1, then different amounts of LFP was added. We use 1M Li$_2$SO$_4$·H$_2$O as electrolyte. To control the pH we use LiOH·H$_2$O, the amount of the LiOH·H$_2$O depends of the composition of the solution, we use the amount necessary to obtain a pH around 7, see chapter 6 for details.

3-5 Diamino Benzoic (Acid Sigma Aldrich ACS reagent, ≥99.5%), and Li$_2$SO$_4$·H$_2$O (≥98% Sigma Aldrich), triton x-100, a surfactant (laboratory grade Sigma Aldrich) were used as received.
2.8 Characterization Methods

2.8.1 X-ray photoelectron spectroscopy

X-Ray photoelectron spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a surface-sensitive spectroscopy tool that provides information about the chemical state and concentration of elements comprising the outermost surface layers of a solid. XPS is typically accomplished by exciting a sample surface with mono-energetic Al Kα x-rays causing photoelectrons to be emitted from the sample surface (if their binding energy is lower than the X-ray energy). Only the photoelectrons at the extreme outer surface can escape the sample surface, the average depth of analysis for an XPS measurement is approximately 5 nm. An electron energy analyzer is used to measure the energy of the emitted photoelectrons. The spectrum is recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in the spectrum from atoms emitting electrons of a particular energy. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of a detected element can be determined.

XPS analysis in the present study was carried out using a Perkin-Elmer system, equipped with cylindrical analyzer and a highly monochromatic Al Kα (1486.6 eV) X-ray source. The compact pellets of these materials were made using hydraulic press at high pressure and mounted on sample holder using double sided carbon tape. The chamber was maintained at a pressure ~ 10\(^{-9}\) torr during the experiment. The instrument is located at the Institut Català de Nanociència i Nanotecnologia (ICN2).

2.8.2 Raman

The majority of the photons are elastically scattered (Raleigh scattering) while a very small fraction (1 in about 10\(^6\)) of the incident photons lose energy (red shifted) that goes into exciting the molecular vibrations of the lattice, and thus the inelastically scattered light carries the information about the characteristic (finger print) vibrational modes of the lattice/molecule.
A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. The scattered light from the sample is collected and analyzed using a spectrometer which disperses the scattered light frequencies and produces a spectrum of the scattered light.

Raman spectra for this study were collected using a Jobin–Yvon Horiba Triax 550 spectrometer located in the Centres Científics I Tecnològics Universitat de Barcelona (CCITUB) equipped with a liquid-nitrogen cooled charge-coupled device (CCD) detector, an Olympus model BX41 microscope using a 100× objective, and a Modu-Laser (Stellar-Pro-L) Argon-ion laser operating at 514.5 nm. The power of the laser was 10 mW. The Raman-scattered light from the sample was collected with the same microscope objective and focused on the entrance slit of a spectrometer with a 1200 lines/mm diffraction grating. A notch filter placed in front of the entrance slit to block the Rayleigh scattered laser light.

### 2.8.3 Specific surface area

The surface area was characterized by using Quantachrome NOVA 1200, located at MATGAS, which enables to measure N2 gas sorption on particle surfaces. Prior to gas adsorption, the powder sample is degassed and dried in a vacuum. The specific surface area (SSA) measurements use multipoint Brunauer-Emmett-Teller (BET) method.

The concept behind this method is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer.

### 2.8.4 Mercury porosimetry

A pore size distribution determination method, which is typically applied to nitrogen desorption data measured at 77 K on mesoporous materials. It uses the modified Kelvin equation to relate the amount of adsorbate removed from the pores of the material, as
the relative pressure \((P/P_0)\) is decreased from a high to low value, to the size of the pores.

The mercury porosimetry measurements were performed in the MATGAS on a Quantachrome NOVA 1200, located at MATGAS, which enables to measure \(N_2\) gas adsorption on particle surfaces, for the characterization of mesopores the pressure range was from 1 - 2000 bar. Prior to gas adsorption, the powder sample is degassed and dried in a vacuum. The pore size distribution was calculated for a cylindrical system.

2.8.5 Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) is an experimental technique in which the weight of a sample is measured as a function of sample temperature in the scanning mode or as function of time in the isothermal mode. It is used to characterize the decomposition and thermal stability of materials and to examine the kinetics of the physicochemical process occurring in the sample. The mass change characteristics of a material are strongly dependent on the experimental conditions employed. The choice of the temperature program will depend upon the type of information required about the sample. Additionally, the atmosphere used in the TGA experiments plays an important role and the analysis can be performed under \(N_2\), in the presence of air or another reactive atmosphere, for example \(O_2\).

The thermogravimetric analyzer consists of a sensitive analytical balance to measure the weight accurately, a micro furnace to change the temperature in a controlled fashion at specified rate and purge gas system for providing the atmosphere needed. The sample is placed in a pan held in a microbalance supporting a platinum or alumina crucible for a specimen and another one as control. The pan and the sample are heated in a controlled way and weight is measured throughout the heating cycle. The data recorded by a TGA are presented as thermograms of weight or weight percent versus temperature. Sample were analyzed in Pt crucibles under air flow at 20mL/min by increasing the temperature from 25 to 800°C at heating rate of 5°/min. the nominal sample mass was around 5mg (±1mg).
Thermogravimetric Analysis (TGA) of our samples were performed using a TA Instruments Q5000 located in the Institut Català de Nanociència i Nanotecnologia (ICN2).

2.8.6 FTIR

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a vibrational fingerprint of the sample. The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it. The signal can be measured very quickly, usually on the order of one second.

Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.

This means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements.

Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier Transform.
The instrument used in this Thesis was equipped with an Attenuated Total Reflection (ATR). An ATR accessory operates by measuring the changes that occur in an internally reflected IR beam when the beam comes into contact with a sample. An IR beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. In regions of the IR spectrum where the sample absorbs energy, the evanescent wave will be attenuated. The attenuated beam returns to the crystal, then exits the opposite end of the crystal and is directed to the detector in the IR spectrometer. The detector records the attenuated IR beam as an interferogram signal, which can then be used to generate an IR spectrum.

The FTIR from Bruker (Bruker Tensor 27) was provided with an ATR sample holder, which was used to measure the spectrum of the samples. The spectrometer is located in the Institut Català de Nanociència i Nanotecnologia (ICN2).

2.8.7 Atomic Force Microscopy

The atomic force microscope (AFM) is one kind of scanning probe microscopes (SPM). SPMs are designed to measure different sample properties, such as height, friction, magnetism, with a probe. To acquire an image, the SPM raster-scans the probe over a small area of the sample, measuring the local property simultaneously.

AFMs operate by measuring force between a probe and the sample. Normally, the probe is a sharp tip, which is a 3-6 um tall pyramid with 15-40 nm end radius. Though the lateral resolution of AFM is low (~30nm) due to the convolution, the vertical resolution can be up to 0.1 nm.

To acquire the image resolution, AFMs can generally measure the vertical and lateral deflections of the cantilever by using the optical lever. The optical lever operates by reflecting a laser beam off the cantilever. The reflected laser beam strikes a position-sensitive photo-detector consisting of four-segment photo-detector. The differences between the segments of photo-detector of signals indicate the position of the laser spot on the detector and thus the angular deflections of the cantilever.
Chapter 2: Experimental procedures and characterization methods

Agilent 5500 AFM/SPM Microscope or AFM Asylum Research MFP-3D were used to conduct the experiments. Both instruments are located in the Institut Català de Nanociència i Nanotecnologia (ICN2). The sample was transferred to a mica substrate to conduct the AFM measurement. This experiment was done in tapping mode, using a NCHR (Non-Contact - High Resonance Frequency - Reflex Coating) tip known as PointProbe® (PPP).

2.8.8 Tap density

The tap density was determined using a measuring cylinder and put 500 mg of the sample. Then we proceed to tap the cylinder 40 times in one minute, to finally record the volume.

2.8.9 Rheology

Rheology is the science dealing with deformation and flow of matter. Viscosity is one of the building blocks of the rheology. Viscosity is a measure of a fluid’s resistance to flow. When a fluid starts to flow under the action of a force, a shearing stress arises everywhere in that fluid that tends to oppose the motion. As one layer of the fluid moves past an adjacent layer, the fluids molecules interact to transmit momentum from the faster layer to the slower layer tending to resist the motion. These experiments were carried out in a RheoStress 600 from Hacker at the Institut de Ciència de Materials de Barcelona (ICMAB).

2.8.10 XRD

X-ray diffraction (XRD) is a very powerful tool for determining the crystal structure of a material and to identify a given phase and the presence of impurities, even in polycrystalline samples like ours. Diffraction is based on constructive interference of a monochromatic x-rays beam interacting with the sample material, a diffraction peak is obtained whenever the scattered x-ray beam from a set of lattice planes in the crystal satisfies the Bragg’s condition¹:

\[ 2d_{hk\ell} \sin \theta = n\lambda \]  

Equation 2-1
where, \( d_{hkl} \) is the interplanar spacing between lattice planes characterized by Miller indices \((h\ k\ l)\); \( \Theta \) is the diffraction angle, \( \lambda \) is the wavelength of the x-rays and \( n \) is the order of diffraction. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and their intensity determined. By scanning the powder sample through a range of 2\( \Theta \) angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the crystalline phases present because each one has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard database patterns.

We can also find the crystallite size \((D)\) by using the Scherrer equation\(^1\):

\[
\beta \cos \theta = \frac{k \lambda}{D}
\]

Equation 2-2

where, \( \beta \) is the full-width-at-half-maximum (FWHM) of the XRD peak and \( k \) is the Scherrer constant which depends on how the width is determined, the shape of the crystal, and the size distribution. The value of \( K \) varies from 0.62 to 2.08 \(^2\).

X-ray diffractometers consist of three basic elements: X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. A detector record and processes this X-ray signal and converts the signal to a count rate.
The XRD patterns were collected in the angular range $10^\circ \leq 2\theta \leq 80^\circ$ at a scan speed of 2 theta 0.017° 2 theta per s, by using a PANalytical X’Pert PRO diffractometer, ($\lambda = 1.5418 \text{ Å}$) with Cu Kα radiation operated at 40 kV and 45 mA, located in the Institut Català de Nanociència i Nanotecnologia (ICN2).

2.8.11 Electron microscopy

The maximum resolution $r_d$ of any optical system is the diffraction limit imposed by the wavelength of the radiation, $\lambda$, the aperture angle of the objective lens, $\alpha$, and the refractive index, $n$, and can be formalized through the Abbe’s equation

$$ r_d = \frac{k\lambda}{n \sin\alpha} \quad \text{Equation 2-3} $$

Thus,

Previously

stronger

2.8.11.1 Scanning electron microscopy

Scanning

The

A

We
2.8.11.2 Transmission Electron Microscopy, Scanning Transmission Electron Microscope, Energy Dispersive Spectroscopy, Selected Area Electron Diffraction

2.8.11.2.1 Transmission Electron Microscopy (TEM)

The TEM TEM TEM High-

Figure
2.8.11.2.2 Scanning Transmission Electron Microscope

Scanning Like Beam

2.8.11.2.3 Energy Dispersive Spectroscopy (EDS)

EDS When The

2.8.11.2.4 Selected Area Electron Diffraction (SAED)

SAED The

Figure
The separation of the diffraction spots on the diffraction pattern can be directly used to determine the interplane d spacing in crystals. To do so, we need to use what is called “c a m e r a .”
When a beam of electrons impinges on a crystalline specimen, some of the electrons pass through it without interaction, and hit the screen which is at distance $L$ from the specimen, at point $y$. Other electrons are diffracted with an angle $2\theta$ by the crystal planes of spacing $d$, and these electrons hit the film at point $x$, which is the distance $R$ from $y$. From simple geometry, we see that for a small angle of diffraction,

$$\sin \theta \approx \tan \theta \approx \frac{1}{2} \tan 2\theta$$  \hspace{1cm} \text{Equation 2-4}

By the geometry of Figure 2-10,

$$\tan 2\theta = \frac{R}{L}$$  \hspace{1cm} \text{Equation 2-5}

which we substitute in to the $\sin \theta \approx \tan \theta \approx \frac{1}{2} \tan 2\theta$ Equation 2-4 and the in $2d_{hkl} \sin \theta = n\lambda$ to get

$$2d \frac{R}{2L} = \lambda$$  \hspace{1cm} \text{Equation 2-6}

and

$$Rd = \lambda L$$  \hspace{1cm} \text{Equation 2-7}

is the camera equation. It allows us to determine an interplane spacing, $d$, by measuring the separation of diffraction spots, $R$.

We performed TEM studies using a JEOL-2010 TEM operating at 200 KV. The applied acceleration voltages were in the range of 5 - 10 keV for the TEM and 25 keV for the EDs.
measurements, the microscope is located at the Institut Català de Nanociència i Nanotecnologia (ICN2). In order to perform the TEM studies, our specimens were dispersed in absolute ethanol, and a drop was then put onto a conventional carbon-coated Cu grid and allowed to evaporate slowly under ambient conditions before being introduced in the sample holder for TEM.

2.8.12 Electrochemical Measurements

The electrochemical performance and analyses were conducted using the common techniques including: Electrochemical Impedance spectroscopy (EIS), cyclic voltammetry (CV), and constant current charge-discharge testing.

2.8.12.1 Cell assembly

The cathodes were prepared by pressing a mixture of the active materials with Carbon Super-P (Timcal) and Polyvinylidene fluoride (PVDF, Kynar) binder in a weight ratio 85/10/5. They were mixed in a mortar for 5 minutes and then dispersed in N-Methyl-2-pyrrolidone and coated onto Al foil, using a doctor blade technique, which is used as a current collector and substrate. We used Hand Coater with a stainless-steel bar corresponding to a nominal 60µm thickness. Then, the cast Al sheets were dried in a vacuum oven at 120 °C for 12hr. The electrodes were punched into disc shape with 1.0 cm diameter and the press for 1 minute at 7 tons. Electrochemical test cells (Swagelok-type) were assembled in an argon-filled glove box (Jacomex II-P) with the coated Al disk as working electrode, lithium metal foil as the counter/reference electrode, and 1 M solution of LiPF₆ in a 1:1 vol/vol mixture of ethylene carbonate and diethyl carbonate as the electrolyte (Sigma-Aldrich). A glass microfiber separator was used. The electrochemistry experiments were carried out using a multichannel Biologic VMP-3 potentiostat.
2.8.12.2 Flow cell assembly

Commercial Electrolysis Cell was used (BASi Bulk) a container with a porous glass frit of 4-6 μm pore diameter was used for the charge and discharge test. Working and counter electrode used for this experiment were Pt. Reference electrode Ag/AgCl KCl 3.5M was used. The cell was cycled between -0.2V to 1V vs. Ag/AgCl KCl 3.5M. The dispersion was stirred during the experiment.

2.8.12.3 Galvanostatic Characterization

Galvanostatic charge/discharge or Chronopotentiometry is an electrochemical technique in which a constant current is applied (charging) and the potential is recorded as function of the time or total charge passing through the system. In this experiment, the current direction is reversed (discharging) once the pre-set maximum potential difference is reached. The shape of such curves is related to the reaction mechanism,
transport of the reactants from the bulk of the phase to the interface, and transport of the product in the opposite direction. In this technique, the C-rate performance is used to calculate the capacity of the electrode at different charge/discharge current densities. Charge/discharge the cell at C/h rate means complete charge/discharge of the cell within h hours.

In this thesis, the room temperature galvanostatic charge and discharge measurements were performed at different current densities within the voltage range of 2.5 – 4.0 V versus lithium counter electrode. The charge and discharge plateaus observed in chronopotentiometric profile correspond to the redox peaks observed in the CV curves.

2.8.12.4 Cyclic Voltammetry

Cyclic Voltammetry (CV) is a common electrochemical technique for studying the properties of an electrochemical system, a cyclic linear potential sweep is imposed onto the electrode (with respect to a reference electrode) while the current passing between the working electrode and a counter electrode is recorded. Within the scanning potential range, a current peak occurs at a certain potential indicating an occurrence of an electrode reaction. If the electrode reaction is reversible, a peak will be observed in the reverse scanning direction. In case of LFP electrode, the two peaks, observed around 3.45 V vs. Li/Li⁺, corresponded to the two-phase charge – discharge reaction of the Fe²⁺ / Fe³⁺ redox couple, as can be seen in Figure 2-13

![Figure 2-13 Typical CV profile of LFP sample.](image-url)
By analyzing the resulting current versus potential profiles, information on the kinetics and thermodynamics of the electrode reaction can be obtained.

In lithium battery systems and generally solid-state electrochemistry, diffusion of electroactive species occurs inside the electroactive films. In the realms of solid-state electrochemistry, solid-state diffusion within the electroactive film predominantly controls the electrochemical system.

Thus, when referring to the diffusion coefficient, it is related to the solid-state diffusion, not diffusion inside the electrolyte solution.

On the other hand, diffusion inside the electroactive film is no longer one-dimensional; instead they have a complicated three-dimensional diffusion channels, towards accessible active sites for insertion/extraction process.

The classical Randles–Sevcik equation

\[ I_p = (2.69 \times 10^5)n^{3/2}aDCv^{1/2} \quad \text{Equation 2-8} \]

Where \( I_p \) = maximum current, \( n \) = number of electrons transferred in the redox event, \( a \) = electrode area, \( D \) = Diffusion coefficient, \( C \) = concentration and \( v \) = scan rate.

This equation describes the effect of scan rate on the peak current \( i_p \). The diffusion coefficient of the electroactive species can be determined, using the relationships defined by the equation. However, it is indeed a common mistake in the electrochemical literature, use this equation without considering essential assumptions; as equations developed in the electrochemistry textbooks are directly used for solid-state electrochemistry.

Equation 8 has been derived with the following assumptions:

1. Diffusion is one-dimensional from bulk solution towards electrode surface.

2. Electrode surface is ideally smooth.

As stated before, the classic Randles–Sevcik equation is based on an assumption that the electrode surface is entirely smooth; however, electroactive films like metal oxides are known to have significantly rough surfaces. For rough surfaces, the classic Randles–
Sevcik should be modified as a new parameters replaces the power of scan rate\(^5\), modified Randles–Sevcik equation:

\[
i_{\text{peak}} = \frac{\Gamma(1-\alpha) \Gamma(a) \left(\frac{\lambda}{\gamma}\right)^{\frac{1}{2}} n F A D^{-1} c_0^a x_{\max}(\alpha)}{\Gamma^2\left(\frac{1}{2} R T \lambda\right)^a}
\]

where \(i_{\text{peak}}\) is the peak current, ‘\(\Gamma\)’ the gamma function, \(\gamma\) is a fractal geometry factor, ‘\(\alpha\)’ is a geometrical factor close to \(\pi^{-1}\), \(\lambda\) the length corresponding to the outer cut-off of the fractal electrode, ‘\(n\)’ the number of transferred electrons per atom, ‘\(F\)’ Faraday’s constant, ‘\(v\)’ the scan rate, \(C\) the concentration of the electrolyte, \(x_{\max}\) a dimensionless function of the fractal parameter given in Ref.\(^6\), \(R\) the gas constant, and \(T\) the temperature. ‘\(n\)’ is equal to number of electrons transfer.

The initial scan voltage was set at 2.5 V, scan to 4.0 V then scan back from 4.0 V to 2.5 V vs. Li/Li\(^+\). The CVs were recorded at different scan rates of 5mV/s, 2mV/s, 1mV/s, 0.5mV/s, 0.1 mV/s.

2.8.12.5 Electrochemical Impedance Spectroscopy (EIS)

EIS is a powerful tool in investigating the mechanisms of electrochemical reactions, measuring the dielectric and transport properties of materials, exploring the properties of porous electrodes, and for investigating passive surfaces\(^7\). The EIS is based on the application of a sinusoidal voltage (or current) signal to an electrochemical cell. The response of the cell to the sinusoidal perturbation is a sinusoidal current (or voltage), which has the same frequency as the perturbation and is normally shifted in phase. Measurements in this research were carried out in the frequency range of 0.1 – 100 kHz with amplitude of 5 mV.

An electrochemical cell can be modeled using the Randles equivalent circuit as shown in Figure 2-14 (a)Randles Circuit (b) Nyquist Plot. It consists of an ohmic resistance (\(R_s\)), which is corresponding to the total resistance of the electrolyte, a constant phase element (CPE) which stands for the double layer capacitance and passivation film capacitance\(^8\), a charge transfer resistance (\(R_{ct}\)) through the electrode/electrolyte...
interface, and a Warburg impedance ($R_w$) which is associated to lithium ion diffusion in the LFP particles.

![Randles Circuit](image)

![Nyquist Plot](image)

**Figure 2-14 (a) Randles Circuit (b) Nyquist Plot**

The initial intercept of the semi-circle at highest frequency indicates the electrolyte resistance ($R_s$). The semicircle part at high frequency region corresponds to the charge transfer resistance ($R_{ct}$). Finally, the inclined line in the lower frequency is representing the Warburg impedance ($R_w$).

It is known that an apparent exchange current density $I_0$ which measures the kinetics for an electrochemical reaction, can be used to measure the enhanced reaction rate of electrodes.

When overpotential is very small, it can be calculated using the following formula$^{9,10}$

$$I_0 = \frac{RT}{nR_{ct}F}$$  \textbf{Equation 2-10}

where, $R$ is universal gas constant (J mol$^{-1}$ K$^{-1}$), $T$ is the absolute temperature (K), $n$ is charge-transfer number (mol), $F$ is Faraday constant (C mol$^{-1}$) and $R_{ct}$ is charge transfer resistance (Ω). The calculated values of $I_0$ help determine the enhanced reaction rate of the electrodes and the kinetics of the electrochemical reaction.

At low frequency region, the real part Warburg impedance of the cell can be written as follows$^{11}$
\[ Z_{re} = \sigma w^{-1/2} \]  \hspace{1cm} \text{Equation 2-11}

where, \( \sigma \) is the Warburg factor. From the linear relationship between \( Z_{re} \) and \( w^{-1/2} \), \( \sigma \) can be calculated as the slope of the fitted line. As a result, the lithium-ion diffusion coefficient of the material can be calculated according to the following equation\(^{11}\):

\[ D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \]  \hspace{1cm} \text{Equation 2-12}

where, \( R \) is the gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)), \( T \) is the absolute temperature (298.5 K), \( A \) is the effective working electrode area, \( n \) is the number of electrons involved in the reaction of the redox couple (for Li\(^+\) it is 1), \( F \) is Faraday’s constant (96,480 C mol\(^{-1}\)), \( C \) is the molar concentration of Li ions, and \( \sigma \) is the Warburg factor.
2.9 References


3 LFP synthesized by hydrothermal method
3.1. Overview

The hydrothermal route for the synthesis of LFP presents important advantages in comparison to other approaches like solid-state reactions. First of all, it requires lower temperatures and therefore is less energy-intensive. But in addition, this wet chemistry technique allows for a wide variety of conditions and additives which can direct the growth of particular microstructures for this material.

In this chapter, we will present our systematic study of this synthesis, the optimization of reaction conditions and the use of selected additives, which were able to influence the structural properties of the resulting crystalline material (such as microstructure, morphology, particle size etc.).

Polyethylenimine (PEI) is a polymer with repeating unit composed of the amine group and two carbon aliphatic, CH₂CH₂, spacer. It can be found as linear chains, branched chains or even as dendrimers. Branched PEIs contain primary, secondary and tertiary amino groups. This makes its pH more basic, hindering the reduction of Fe(III). In this work, we have used exclusively branch PEI corresponding to the formula:

![Figure 3-1 PEI molecule](image)

On the other hand, the presence of EG can reduce the solubility and mobility of the metal ions during synthesis. Hence, it can inhibit the crystal growth so that smaller particles are obtained¹. Wang et al. proposed that reducing the water content by adding alcohol and/or introducing nucleation sites during the hydrothermal reaction has a significant effect on the specific surface area and electrochemical performance of LFP materials². The concentration of PEI and EG could play a key role on the morphology and particle size of the prepared materials during the hydrothermal process.
3.2. Synthesis

3.2.1. LFP113HTEGH2O2-8-1

In a typical reaction, 6.7900 g (0.0665 moles) of lithium acetate dihydrate (CH₃COOLi·2H₂O) was added to 28 mL of ethylene glycol and stirred for 10 minutes. 6.6232 (0.0238 moles) of iron sulfate heptahydrate (FeSO₄·7H₂O) was dissolved in 112 mL of a 5% (w/v) aqueous solution of polyethyleneimine and stirred for 2 minutes. Then we slowly added 1.65 mL (0.0240 moles) 85% phosphoric acid (H₃PO₄) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO₄ solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200°C for 24 h. The resulting suspension was filtered-off, washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 5 and we obtained 3.6214 g of powder which represents 96% yield. The sample was treated thermally as described in chapter 2. To obtain a carbon coated sample we used the procedure describe in chapter 2.

Scheme 3-1 Illustration of the formation mechanism of various self-assembled LFP samples during the hydrothermal reaction.
3.2.2. LFP 113HTEGH2O5-5-1

In a typical reaction, 6.6007 g (0.0647 moles) of lithium acetate dihydrate (CH₃COOLi·2H₂O) are added to 70 mL of ethylene glycol and stirred for 10 minutes. 6.6065 (0.0234 moles) of iron sulfate heptahydrate (FeSO₄·7H₂O) are dissolved in 5% polyethyleneimine (70 mL) and stirred for 2 minutes. Then we slowly added 1.65 mL (0.0240 moles) 85% v/v phosphoric acid (H₃PO₄) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO₄ solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200°C for 24 h. The resulting suspension was filtered-off, washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 5 and we obtain 3.3432 g of powder which represents 90% yield. The sample was treated thermally as described in chapter 2. To obtain a carbon coated sample we used the procedure describe in chapter 2.

3.2.3. LFP 113STH₂O-1

In a typical reaction, 6.6618 g (0.0652 moles) of lithium acetate dihydrate (CH₃COOLi·2H₂O) are added to 70 mL of a preheated 5% polyethylene imine solution in water and stirred for 10 minutes. 6.6175g (0.0238 moles) of iron sulfate heptahydrate (FeSO₄·7H₂O) are dissolved in 5% w/v polyethyleneimine (70 mL) and stirred for 2 minutes. Then we slowly added 1.65 mL (0.0240 moles) 85% v/v phosphoric acid (H₃PO₄) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO₄ solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200°C for 24 h. The resulting suspension was filtered-off, washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 8 and we obtain 3.4932 g of powder which represents 93% yield. The sample was treated thermally as described in chapter 2. To obtain a carbon coated sample we used the procedure describe in chapter 2.
3.3. Effects of the solvent composition in the crystal structure of LFP and CLFP (carbon coated samples)

The first step in the characterization of this material was to confirm its crystal structure by recording its powder X-Ray Diffraction pattern (XRD), Figure 3-2. All the samples discussed in this chapter show diffraction patterns corresponding to the orthorhombic olivine crystal structure Pnma. The diffraction pattern did not show any impurities that could be detected using this technique. This is in contrast with some previous reports on solvothermal synthesis making use of water or organic solvents leading to detrimental impurities. Some researchers reported impurities such as iron phosphides (FePx) which often form at high temperatures (> 600 °C) or LiFe(P2O7), Fe (II, III) pyrophosphates or phosphates Li3Fe2(PO4)3 and Li3PO4. Moreover, all diffraction peaks are intense and narrow for our samples, indicating a high degree of crystallinity of the LFP phase prepared both before and after carbon-coating. Table 3-1 summarizes crystallite size data for each of sample. Other remarkable observation is that the crystallite size of the carbon coated sample are smaller compare to the respective pristine sample. This is an indication of the effectiveness of the carbon coating in constraint the crystallite size. These crystallite size were calculate using 020 peak.

![Figure 3-2 (a) X-Ray Diffraction patterns of different pristine LFP materials and (b) Diffraction patterns of the corresponding C-coated LFP materials](image.png)
### Table 3-1 of the LFP and LFP hybrids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP 113STH2O1</td>
<td>35</td>
</tr>
<tr>
<td>C/LFP 113HTH2O1</td>
<td>32</td>
</tr>
<tr>
<td>LFP 113HTEGH2O2-8-1</td>
<td>33</td>
</tr>
<tr>
<td>LFP 113EGHTH2O5-5-1</td>
<td>38</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O5-5-1</td>
<td>33</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O2-8-1</td>
<td>33</td>
</tr>
</tbody>
</table>

3.4. Effects of the solvent composition on the morphology of LFP and CLFP

To study the morphology of the obtained LFP structures; SEM images of various LFP samples prepared with different solvent compositions are displayed in Figure 3-3. The images show microstructures that are hierarchically constructed from smaller primary nanoparticles. These tiny building blocks grow side by side in an ordered arrangement.

We obtain different microstructures, from spheres for the EG-free synthesis, to haystacks to fan-like formations for the materials prepared with a higher EG/water ratio. These microstructures are composed of rectangular nanoprisms of various thicknesses and sizes.

The spheres, samples LFP113HTH2O-1 and C/LFP113HTH2O-1, were prepared with 5% PEI (w/v) in H₂O were formed by primary pebble-shaped nanoparticles with homogeneous size around 200 nm conforming microspheres of ca. 10 μm in diameter.

It should be noted that this fractal granularity is retained after the pyrolysis treatment for carbon-coating. In this case, there is no noticeable effect from the carbon coating on the morphology of these structures. These particles show pores as can be seen in the inset of the Figure 3-3 a and b. The pores on the surface of the particles can increase the surface area of these materials. The configuration could be described as fractal for sample LFP113HTH₂O-1 and the respective carbon-coated sample,

Figure 3-4. LFP with haystack morphology, sample LFP113HTEGH2O2-8-1 with a solvent composition of 20% (v/v) of EG and 80% (v/v) of 5% PEI in H₂O, are formed by nanoparticles with different sizes. The haystack has a length of 3-6 μm and these
microstructures are inconsistent in size (Figure 3-3 c). The contact between the particles in these haystacks is robust. The primary nanoparticles have a size around 100-400 nm. In this case, the C-coating process affects the size of the nanoparticles. It seems that the sintering process decreases the size of these nanoparticles and produces microstructures that are more homogeneous. The size of the microstructure in the case of C/LFP113HTEGH2O2-8-1 (Figure 3-3 d) is 5 μm and the nanoparticles that form these structures have a size of around 150 nm. Even under the high temperatures involved in the carbon-coating process (700°C), carbon deposition on the surface of LFP particles can effectively suppress further particle growth\(^9\). Rods like particles form a hand fan, sample113HTEGH2O5-5-1, Figure 3-3 e. The size of this microstructure is 3 μm, and uniform. The nanoparticles that form this structure are uniform in the size of their section but not in length. The lengths of the rods range between 200 nm and 700 nm. In the case of the C-coated sample C/LFP 113HTEGH2O5-5-1, (Figure 3-3 f) the size of the handfan is smaller, and uniform. Also, the size of the nanorods is constant and smaller than before 400 nm (Figure 3-3 f). In Figure 3.3 we have collected individual examples of isolated crystal formations in order to describe their typical morphologies. On the other hand, these microstructures tend to appear systematically agglomerated as shown in Figure 3-4 which shows how the secondary microstructures formed by primary nanoparticles are effectively sintered together to form a kind of tertiary microstructure resulting in an overall hierarchical structure which could be described as featuring fractal granularity. Despite this, and actually derived from this hierarchical structure, it is possible to observe pores of different dimensions in these structures, which can provide a high contact area with the electrolyte (Figure 3-4).
Figure 3-3 SEM images of the LFP and carbon coated LFP. (a) LFP113STH₂O₂-1 (b) C/LFP 113STH₂O₂-1 (c) LFP113HTEGH₂O₂-8-1 (d) C/LFP113HTEGH₂O₂-8-1 (e) LFP113HTEGH₂O₅-5-1 (f) C/LFP113HTEGH₂O₅-5-1
Alternative approaches for the fabrication of the electrodes based on LiFePO₄ as cathodes in LIBs

Zahilia Caban Huertas – June 2017

Figure 3-4 (a) SEM image of C/LFP 113HTH₂O-1, showing the fractal granularity and the pores formed by this morphology (b) the corresponding close up to the pores generated by the fractal morphology

HRTEM images and the inset in Figure 3-5 a-f illustrate the structure of the building blocks of pristine and carbon coated LFP obtained from different synthesis methods. The images are consistent with those from SEM. The SAED analysis also shows evidence of the crystal structure for this LFP materials obtained by the different synthesis methods.

We can see in the inset of Figure 3-5 some individual nanoprisms that form the secondary spheres and the fractal morphology for sample LFP113HTH₂O-1, the size of this building block is around 200 nm. The HRTEM image shows a well-defined crystal morphology and a d spacing in good agreement with the results obtained by XRD, Table 3-2. The big difference between sample LFP113HTH₂O-1 and C/LFP113HTH₂O-1, Figure 3-5 b, is the amorphous layer in sample C/LFP113HTH₂O-1 with a thickness of 3 nm. It is important to mention that this layer is very homogeneous and obviously associated to the carbon-coating through glucose pyrolysis and thermal process, Figure 3-5 b. This image also shows the SAED pattern. The miller index obtained through this analysis correspond to two different planes, the miller indexes are 011 and 200 for LFPHTH₂O-1. For C/LFPHTH₂O the obtained miller indexes are 111 and 101. Figure 3-5 c-d from TEM, showing samples LFP113HTEGH₂O₂-8-1 and C/LFP113HTEGH₂O₂-8-1. The HRTEM image confirms that the building blocks of these samples are crystalline and have similar microstructure. There as difference between the pristine sample and the carbon coated sample is that the latest have an amorphous layer. This layer is homogeneous. We
calculated the d parameter for these samples and assign a miller index to it. The miller index obtained by HRTEM for both samples are in accord with the XRD pattern, Table 3-2. Figure 3-5 c-d from TEM, showing samples LFP113HTEGH₂O₅-5-1 and C/LFP113HTEGH₂O₅-5-1. The HRTEM images confirm that the building blocks of these samples are crystalline and have the same microstructure, a rod like shape. Inset of Figure 3-5 f also shows the morphology of the microstructure that form sample C/LFP113HTH₂O-1. The difference between the pristine sample and the carbon-coated sample is the conspicuous amorphous carbon layer, which shows as a homogeneous coating of ca. 3nm. The spacing between planes measured in these HRTEM for both samples are in accord with the XRD pattern (Table 3-2).

The thickness of the carbon layer did not only affect the bulk density of the composite material but also its reversible capacity. With thicker carbon coating the reversible capacity also decreased, partly due to increasingly hindered electrolyte transport\(^{10}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>D space (nm)</th>
<th>Miller index</th>
<th>Carbon thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113STH2O-1</td>
<td>0.34</td>
<td>111</td>
<td>N/A</td>
</tr>
<tr>
<td>C/LFP113STH2O-1</td>
<td>0.34</td>
<td>111</td>
<td>3.0</td>
</tr>
<tr>
<td>LFP113HTEGH2O2-8-1</td>
<td>0.30</td>
<td>211</td>
<td>N/A</td>
</tr>
<tr>
<td>C/LFP113HTEGH2O2-8-1</td>
<td>0.35</td>
<td>111</td>
<td>3.0</td>
</tr>
<tr>
<td>LFP113HTEGH2O5-5-1</td>
<td>0.30</td>
<td>211</td>
<td>N/A</td>
</tr>
<tr>
<td>C/LFP113 HTEGH2O5-5-1</td>
<td>0.30</td>
<td>211</td>
<td>2.94</td>
</tr>
</tbody>
</table>
Figure 3-5 TEM images of the LFP and carbon coated LFP. (a) LFP113STH$_2$O-1 (b) C/LFP 113STH$_2$O-1 (c) LFP113HTEGH$_2$O$_2$-8-1 (d) C/LFP113HTEGH$_2$O$_2$-8-1 (e) LFP113HTEGH$_2$O$_5$-5-1 (f) C/LFP113HTEGH$_2$O$_5$-5-1
3.5. Surface Area

The fractal granularity of LFP detected in the SEM images of Figure 3-4 leads to a characteristic porosity formed by the primary nanosized crystals. These inter-particle pores extend from the surface to the inner of the spheres and in principle can facilitate deep penetration of liquid electrolyte into the microspheres, thus providing an improved interface area between the electrode and electrolyte.

Gas adsorption isotherms were measured in order to quantify this porosity. The results for N$_2$ adsorption isotherm for the carbon-coated samples are summarized in table 3-3, whereas Figure 3-6 (a) shows a representative example, featuring a type IV curve with an H3 hysteresis loop, indicating mesoporous character. The measured active surface areas range from only 10 to 14.8 m$^2$/g for C/LFP113HTH$_2$O-1. The average pore diameter ranged from 10.9 nm to 18 nm, calculated from the desorption branch of the nitrogen isotherm with the BJH method (Figure 3-6 (b)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area m$^2$/g</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/LFP113HTH$_2$O-1</td>
<td>14.8</td>
<td>18</td>
</tr>
<tr>
<td>C/LFP113HTEGH$_2$O2-8-1</td>
<td>13</td>
<td>16</td>
</tr>
<tr>
<td>C/LFP113HTEGH2O5-5-1-1</td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

Figure 3-6 (a) nitrogen adsorption and desorption isotherms (b) Barret-Joyner-Halenda (BJH) pore distribution curves for C/LFP113HTH$_2$O-1.
3.6. Carbon characterization in carbon coated materials

In this section, we are going to explore the characteristics of the carbon obtained by the pyrolysis/sintering treatment on the various carbon-coated LFP materials. This analysis is based in techniques like Raman, XPS and TGA.

Raman spectroscopy provides an excellent tool to determine the nature and physical-chemical properties of carbon materials. The crystal quality of our samples was good enough to observe sharp phonon lines in the Raman spectra. As shown in Figure 3-7 Raman spectra LFP113HTH2O-1 and C/LFP113HTH2O, two intense broad peaks located at 1344.9 cm⁻¹ and 1600.6 cm⁻¹ are attributed, respectively, to the A₁g vibration mode of the disordered carbon (D-band), due to an activation of an otherwise symmetry forbidden mode by the defects in sp³ network¹¹,¹², and the E₂g vibration mode of the ordered graphitic carbon (G-band). Fundamental geometric difference between defects related to the size of a nanocrystallite and point defects in the sp² carbon lattices, resulting in a different intensity ratio of the D and G bands dependence on the amount of disorder. The ratio of intensities ID/IG is 0.87, indicating sp² carbon, which would enhance the electronic conductivity of the inorganic phase¹³. The band near 1600 cm⁻¹ for carbon-coated sample is very well known and assigned to the presence of the graphitic carbon layer covering the LFP particles¹³. In addition to these two peaks it was also possible to detect a peak at 949 cm⁻¹ corresponding to PO₄³⁻ anion¹⁴. The external modes (lattice vibrations), that occur below 800 cm⁻¹ which arise primarily due to the vibrational motions related to FeO₆ and LiO₆ octahedra¹⁵.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PO₄⁻³ cm⁻¹</th>
<th>D cm⁻¹</th>
<th>G cm⁻¹</th>
<th>D/G intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/LFP 113HTH2O-1</td>
<td>953.4</td>
<td>1344.9</td>
<td>1600.6</td>
<td>0.87</td>
</tr>
<tr>
<td>C/LFP113HTEGH2O2-8-1</td>
<td>946.5</td>
<td>1345.7</td>
<td>1592.0</td>
<td>0.80</td>
</tr>
<tr>
<td>C/LFP113HTEGH2O5-5-1</td>
<td>950.0</td>
<td>1346.3</td>
<td>1593.5</td>
<td>0.86</td>
</tr>
<tr>
<td>LFP 113HTH2O-1</td>
<td>949.0</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>LFP113HTEGH2O2-8-1</td>
<td>947.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>LFP113HTEGH2O5-5-1</td>
<td>948.4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
XPS measurements allow to discern the oxidation states of iron, Li, P and O. Also provide a useful information of C oxidation state, C bonds and crystallinity. The chemical composition and valence state of the as-prepared C/LFP113HTH₂O-1 composites was confirmed by XPS analysis and results for the sample synthesized at 700 °C are shown in Figure 3-8. Figure 3-8(a) shows the wide range scanning spectrum and it can be seen that this sample consists of Li, Fe, P, O and C elements. Figure 3-8 (b) illustrates the XPS narrow spectra of the Fe 2p and it is evident that the Fe 2p signal derives from the contribution of two peaks, due to the spin-orbit coupling. The peaks of the binding energy (BE) at 710.9 and 724.2 eV represent the Fe^{2+} valence state, suggesting that the product contains only one valence state of iron. Indeed, the two peaks could be ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, which is characteristic of the valence of Fe^{2+} state in the olivine-type LFP products

Since the fine structure of C KLL transition is strongly affected by the sp²/sp³ configuration, the parameter $D$, can be considered as a fingerprint of the arrangement of carbon atoms related to the moiety of C in sp² and sp³ hybridization, D parameter for sp³ carbon is 13.7 eV and D parameter for sp² is 21.2 eV. This “D” parameter is the binding energy difference (D) between the most positive maximum and most negative minimum obtained from the first derivative of the Auger transition (C KLL) spectra recorded. The C/LFP113HTH₂O-1 composite shows a D= 16.3 eV which indicates an intermediate composition, corresponding to a mixture of ca. 2/3 sp³ and 1/3 sp² C in the sample Figure 3-8 (d). As we expected the contribution to the C 1s are the same for all the C-coated samples.
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

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Table 3-5 Binding energies of the contributions to the Fe$^{2+}$ signal of the pristine LFP and their hybrids materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Signal (eV)</th>
<th>Fe$^{2+}$ 2p$_{3/2}$</th>
<th>Fe$^{2+}$ 2p$_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113STH2O-1</td>
<td>710.7</td>
<td>724.4</td>
<td></td>
</tr>
<tr>
<td>C/LFP113STH2O-1</td>
<td>710.2</td>
<td>724.7</td>
<td></td>
</tr>
<tr>
<td>LFP113STEGH2O2-8</td>
<td>710.5</td>
<td>724.6</td>
<td></td>
</tr>
<tr>
<td>C/LFP113STEGH2O2-8</td>
<td>711.7</td>
<td>725.1</td>
<td></td>
</tr>
<tr>
<td>LFP113HTEGH2O5-5-1</td>
<td>710.4</td>
<td>724.2</td>
<td></td>
</tr>
<tr>
<td>C/LFP113HTEGH2O5-5-1</td>
<td>711.3</td>
<td>725.2</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-8 (a) XPS spectra (b) narrow range Fe 2p (c) narrow range C 1s (d) 1rts derivate of the C auger peak of the sample C/LFP113HTH$_2$O1
Table 3-6 Binding energy of the contributions to C-1s signal in the pristine LFP and LFP hybrids materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Signal (eV)</th>
<th>O-C=O</th>
<th>C-O-C</th>
<th>C-C</th>
<th>D parameter (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113STH2O2</td>
<td>289.3</td>
<td>N/A</td>
<td>284.8</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>C/LFP113STH2O2</td>
<td>289.0</td>
<td>286.2</td>
<td>284.4</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>LFP113STEGH2O2-8</td>
<td>288.0</td>
<td>N/A</td>
<td>284.4</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>C/LFP113STEGH2O2-8</td>
<td>289.9</td>
<td>285.7</td>
<td>284.4</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>LFP113HTEGH2O5-5-1</td>
<td>288.5</td>
<td>N/A</td>
<td>284.4</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>C/LFP113HTEGH2O5-5-1</td>
<td>298.0</td>
<td>285.8</td>
<td>284.4</td>
<td>16.4</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-9 shows TGA curves of pristine LFP and LFP/C113HTH2O-1 composite under flowing air atmosphere. These experiments were carried out to study the thermal stability of the materials and to determine the exact amount of carbon coated on the active inorganic phase. After an initial weight loss associated to loss of water the TGA curves show a weight gain of 5.0% for LFP and 2.4% for LFP/C between 250-650°C. The weight uptake of pristine LFP can be explained by the following oxidation reaction:

\[
\text{LiFe}^{II}\text{PO}_4 + \frac{1}{4}\text{O}_2 \uparrow \rightarrow \frac{1}{3}\text{Li}_3\text{Fe}^{III}_2\text{(PO}_4)_3 + \frac{1}{6}\text{Fe}^{III}_2\text{O}_3
\]  

Reaction 3-1

The amount of carbon in LFP/C was calculated by the difference between the two samples. In this case the amount of carbon was 2.6%. This result is in agreement with the result obtained by elemental analysis.

Table 3-7 Carbon amount in the LFP carbon coated samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon % TGA</th>
<th>Carbon % Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/LFP113STH2O2</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>C/LFP113STEGH2O2-8</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>C/LFP113HTEGH2O5-5-1</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>
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3.7. Electrochemistry

3.7.1. Cyclic Voltammetry

Cyclic Voltammograms (CVs) were recorded to investigate the electrochemical behavior of the LFP electrodes as a preliminary characterization step, before testing their electrochemical performance in two-electrode cells by means of charge-discharge cycles. Thus, CVs were carried out in three-electrode cells, using LFP electrodes as working electrodes, and Lithium metal as counter and reference electrode. Voltage was cycled between 2.5 – 4.0 V vs. Li/Li⁺. As representative examples, we will discuss in detail the electrodes made from samples LFP113HTH₂O-1 and C/LFP113HTH₂O-1. The cell assemble was described in chapter 2.

The symmetry of the sharp oxidation and reduction waves in the CV curve (Figure 3-10 a) confirms the good reversibility of the Li⁺ extraction-insertion reaction for the carbon-coated sample. The well defined reduction and oxidation peaks at ca. 3.34 V and 3.51 V are assigned to the Fe²⁺/Fe³⁺ redox couple reaction corresponding to the Li insertion (Fe³⁺ to Fe²⁺) and extraction (Fe²⁺ to Fe³⁺) in the LFP crystal structure, respectively. In contrast, the cyclic voltammogram recorded for the pristine LFP, does not show the sharp oxidation and reduction peaks but more sepaarated broader waves centered at 3.26 and 3.55 V vs Li. That shape and the increased polarization is related to the low
conductivity and slow Li diffusion of the pristine phase. This behavior was observed for all the samples prepared.

3.7.2. Galvanostatic Cycling with Potential Limitation

Figure 3-10 b shows the charge/discharge curves at various C rates, from 0.1C to 10C, for C/LFP113HTH$_2$O-1 used as positive electrode vs. lithium negative electrode. The C/LFP113HTH$_2$O-1 exhibits high specific discharge capacities at 0.10C charge discharge rate, 164 mAh/g (ca. 94% of the theoretical capacity of 170 mAh/g). In contrast, positives electrodes made of the pristine LFP do not show a high specific discharge capacity. At 0.10C rate the LFP113HTH$_2$O-1 shows a discharge capacity of 45 mAh/g which correspond to 27% of the theoretical capacity. It is possible to observe that both samples show good stability at different C-rates (Figure 3-10c). The discharge capacity for the C/LFP113HTH$_2$O-1 at 10C correspond to 31% of the initial capacity, whereas for the pristine LFP the discharge capacity at 10C represents a 22% of the initial capacity (Figure 3-10c). The pristine LFP113HTH$_2$O-1 material was stable during extensive cycling at 1C; the capacity retention over 40 cycles is 99%, which is remarkable. Figure 3-10d shows the very good cyclability of C/LFP113HTH$_2$O-1 material. This sample was stable over 100 cycles with a 98% retention of capacity.
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

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Figure 3-10 (a) Cyclic Voltammetry of pristine LFP and C/LFP at 0.1mV/s (b) Charge and discharge curves at various C-rates for C/LFP (5th cycle) (c) Discharge capacity at different C-rates of pristine LFP and C/LFP. (d) Cycling performance of pristine LFP and C/LFP at 1C.

In general all the samples studied in this chapter achieve more than 90% of the theoretical capacity when the samples were treated with glucose as a precursor to obtain carbon, Table 3-8. It is important to mention that in general the samples discussed in this chapter were very stable independently of whether coated or not with carbon.

The C/LFP113EGH$_2$O$_2$-8-1 exhibits a high specific discharge capacity of 157 mAh/g at 0.10C charge discharge rate, (ca. 94% of the theoretical capacity of 170 mAh/g). At 0.10C rate the pristine LFP113EGH$_2$O$_2$-8-1 shows a discharge capacity of 100 mAh/g which correspond to 58% of the theoretical capacity. The discharge capacity for the C/LFP113EGH$_2$O$_2$-8-1 at 10C correspond to 24% of the initial capacity, whereas for the LFP113EGH$_2$O$_2$-8-1 the discharge capacity at 10C represents a 15% of the initial capacity (Figure 3-11 a). The rate capability of LFP113EGH$_2$O$_2$-8 decreases dramatically at high C-rates. In order to understand why fast charging is not practical for this sample we should remember that this method did not generate a monodispersed particle size distribution. Particle sizes ranged from 3 to 6 µm. Thus, contrary to other methods this leads to a
greater portion of large particles which would result in longer diffusion paths for ions and therefore not so good rate capabilities.

Sample C/LFP113LFP113HTEGH₂O-5-5-1 exhibit high specific discharge capacities at 0.10C charge discharge rate, 150mAh/g (ca. 88% of the theoretical capacity of 170 mAh/g). Cathodes of the pristine LFP do not show a high specific discharge capacity. At 0.10C rate LFP113EGH₂O5-5-1 shows a discharge capacity of 45 mAh/g which correspond to 27% of the theoretical capacity. The discharge capacity for C/LFP113EGH₂O5-5-1 at 10C correspond to 37% of the initial capacity, whereas for the pristine LFP113EGH₂O5-5-1 the discharge capacity at 10C represents a 22% of the initial capacity (Figure 3-11 a).

A gradual decrease in discharge capacity with increase in the C rate is evident, as is generally the case for any electrode. This is attributed to increased IR voltage loss; a higher concentration polarization at the electrode/electrolyte interface to meet the fast reaction kinetics at higher C rates. The discharge capacity decreases while the overpotential increases with increasing C rate. At higher C rate, the supply of electrons from the interface electrochemical reactions becomes a problem leading to lower specific capacity.

Figure 3-11 b shows that samples C/LFP113HTEGH₂O-2-8-1 and C/LFP113HTEGH₂O-5-5-1 show a significant difference between the charge and discharge capacities. This could be a result of an irregular size of the microstructure that generate these complex morphologies.

To recapitulate the electrochemical characteristic of the pristine LFP and carbon coated LFP, the next table summarizes some electrochemical properties of these samples. Clearly, these results indicate that the conductivity of the C/LFP is higher than that of the bare LFP, with the carbon coating favoring charge transfer in C/LFP.

### Table 3-8 Electrochemical properties
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

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<table>
<thead>
<tr>
<th>Sample</th>
<th>Epc (V)</th>
<th>Epa (V)</th>
<th>OPC (V)</th>
<th>Discharge capacity (mAh/g) at 0.10 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP 113STH2O1</td>
<td>3.55</td>
<td>3.26</td>
<td>3.0</td>
<td>45</td>
</tr>
<tr>
<td>C/LFP 113STH2O1</td>
<td>3.51</td>
<td>3.34</td>
<td>3.1</td>
<td>164</td>
</tr>
<tr>
<td>LFP 113HTEGH2O2-8-1</td>
<td>3.57</td>
<td>3.35</td>
<td>3.3</td>
<td>100</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O2-8-1</td>
<td>3.52</td>
<td>3.31</td>
<td>3.2</td>
<td>157</td>
</tr>
<tr>
<td>LFP 113HTEGH2O5-5-1</td>
<td>3.53</td>
<td>3.33</td>
<td>3.3</td>
<td>47</td>
</tr>
<tr>
<td>C/LFP 113STH2O5-5-1</td>
<td>3.41</td>
<td>3.39</td>
<td>3.2</td>
<td>150</td>
</tr>
</tbody>
</table>

Figure 3-11 Charge and discharge curves at 0.10 C-rates LFP hybrids (5th cycle).

These results show an improvement over various other reports in the literature, for example Chen et. al. reported a discharge capacity of 150 mAh/g at 0.1C rate and 100 mAh/g at 1C$^{20}$. Our work also improves upon previous reports specifically developing porous materials such as those prepared by Yang et al., reporting 140 mAh/g for porous graphene/LFP$^{21}$, or Yu et al. using a template to obtain porous LFP particles$^{22}$ and reporting 140 mAh/g at 0.10C-rate.

3.7.3. Characterization of electrode fractality

In order to get a better understanding of the Li$^+$ transport in this type of insertion electrodes it is important to correlate it with their microstructure. In particular, given the hierarchical microstructure described in previous sections, which we have described as fractal granularity, it would be necessary to understand and determine the fractality of these electrodes. SEM images in Figure 3-12 and Figure 3-13 show LFP113H$_2$O-1 and C/LFP113H$_2$O-1 electrodes. From these SEM micrographs, it was clearly observed that LFP113H$_2$O-1 deposited on Al substrate had a rougher surface than the C/LFP113H$_2$O-1
film deposited on the same substrate. The film thickness of the slurry was between 15 µm and 20 µm for LFP113H₂O-1 and 8 µm for C/LFP113H₂O-1.

All the LFP particles packed irregularly and formed highly porous structure, which permits large interface between the electrolyte and active materials and allows fast intercalation and transfer of Li ions and electrons. The well coated carbon on LiFePO₄ particles enhanced the transfer of the electrons leading to improved electrochemical properties of LFP raw material. Meantime, the homogeneous carbon dispersion in the film formed a network, which should provide an excellent connection between each LiFePO₄ particles, resulting in effective conductive pathways.

With the purpose of determining the elemental distribution in our electrode, we perform a cross sectional EDS from the electrodes. The approximate cross-sectional atomic distribution of LFP113H₂O-1 and C/LFP113H₂O-1 was determined from EDS elements distribution from the top to the bottom of the film cross-section. Li cannot be detected by this method because of the low atomic weight of this element. The elements O, P, Fe and C were quite regularly distributed over the surface of Al in both samples.

Increasing the amount of carbon additives increases the electrical conductivity of the electrode; however, it also lowers the packing density. Polarization of the discharge curve is correlated with the ohmic resistance of the electrode, and the discharge capacity is affected by the transport of Li ions into the electrode.
Figure 3-12 SEM images of the (a) LFP113HTH₂O-1 electrode and (b) element lining analysis.

Figure 3-13 SEM images of cross section electrode C/ LFP113HTH₂O-1 and (b) elements distribution
Chapter 3: LFP synthesized by hydrothermal method

Table 3-9 Electrode thickness

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113HTH₂O-1</td>
<td>14</td>
</tr>
<tr>
<td>C/ LFP113HTH₂O-1</td>
<td>8</td>
</tr>
<tr>
<td>LFP 113HTEGH₂O₂-8-1</td>
<td>14</td>
</tr>
<tr>
<td>C/LFP 113HTEGH₂O₂-8-1</td>
<td>6</td>
</tr>
<tr>
<td>LFP 113HTEGH₂O₅-5-1</td>
<td>15</td>
</tr>
<tr>
<td>C/LFP 113HTEGH₂O₅-5-1</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 3-14 (a) (b) illustrates the surface morphology on the polished substrate of the LFP113HTH₂O-1 and the C/ LFP113HTH₂O-1 film electrode, respectively, as studied by AFM. It is worthwhile to note that the C/LFP113HTH₂O-1 film electrode showed the surface morphology less rough, while the LFP film electrode showed the surface morphology with much roughness.

To quantitatively characterize the surface roughness of the LFP film electrodes, root mean square (rms) roughness and the fractal dimension of the specimens were evaluated by analyses of the AFM images and the resulting values are listed with the scan size in Table 3-10.
Table 3-10 Root mean square (rms) roughness fractal dimension of LFP and C/LFP electrode determined from AFM images (Figure 3-14 AFM image (a) LFP113HTH2O-1 electrode (b) C/LFP113HTH2O-1 electrode)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fractal dimension</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113HTH2O-1</td>
<td>2.38</td>
<td>252 (64)</td>
</tr>
<tr>
<td>C/ LFP113HTH2O-1</td>
<td>2.02</td>
<td>207 (15)</td>
</tr>
<tr>
<td>LFP 113HTEGH2O2-8-1</td>
<td>2.43</td>
<td>286 (10)</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O2-8-1</td>
<td>2.12</td>
<td>200 (10)</td>
</tr>
<tr>
<td>LFP 113HTEGH2O5-5-1</td>
<td>2.39</td>
<td>293 (20)</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O5-5-1</td>
<td>2.16</td>
<td>203 (13)</td>
</tr>
</tbody>
</table>

We can think that the fractal dimension is the sums of widths and the heights of the primary particles that form the microstructure, the addition of this factors form a well defined length equal to 2. In some cases, the wide of the height exceeded by such wide margin, that is possible to obtain values between 2 and 3. A shape with a fractal dimension between 2 and 3 can be describe as a “line like” shape and can achieve different configurations. We can conclude that this “line” are thicker in the pristine sample. This is a result of the roughness of the pristine and carbon coated electrode.

As we can see in table Table 3-10 the values of the RMS roughness confirm the first assessment of the AFM images, Figure 3-14, the pristine sample is rougher that the carbon coated sample.

Since these structures appear to be fairly similar on various scales, this surface can be regarded as a self-similar fractal. The procedure to determine the self-similar fractal dimension by the triangulation method used in this work was introduced in previous
Figure 3-15(a) and (b) gives on a logarithmic scale the dependence of the scaled surface area SSA on the projected triangle size TS obtained from the LFP113HTH$_2$O-1 and C/LFP113HTH$_2$O2-1 film electrodes on the substrates, respectively.

For comparison with those film electrodes, the dependence of the SSA on the TS obtained from the LFP113H2O-1 and C/LFP113H2O-1 is presented in Figure 3-15(a) and (b), respectively. For all of the specimens, one can find clearly a linear relationship between the logarithm of SA and the logarithm of TS, indicating the self-
similar scaling property of the surface. It is generally accepted that the self-similar fractal dimension $D_{f,ss}$ of the surface is given in terms of the slope of the straight line, $s = \frac{d(\log SSA)}{d(\log TS)}$ as 27.

\[ D_{f,ss} = -s + 2 \quad \text{Equation 3-1} \]

From Figure 3-15, the outer cut-offs for their fractalities were also determined to be 6.5 and 5.4 $\mu$m, respectively. This concept of outer cut-off is a limit size of fractal structure\textsuperscript{25}, in this case that might be the diameter of the primary spheres. These spheres could be the limit of the large size that fit in the structure. Here, it should be stressed that although both LFP film electrodes show self-similar scaling properties, the spatial outer cut-offs for their fractalities are different from each other.
Chapter 3: LFP synthesized by hydrothermal method

Figure 3-15 Dependence of surface area $SA$ on triangle size $TS$ obtained from AFM images of: (a) LFP113HTH$_2$O-1 electrode and (b) C/ LFP113HTH$_2$O-1 electrode. The slope $s$ means $(d \log SSA/d \log TS)$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Outer cut off (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113HTH2O-1</td>
<td>4.8</td>
</tr>
<tr>
<td>C/ LFP113HTH2O-1</td>
<td>4.1</td>
</tr>
<tr>
<td>LFP 113HTEGH2O2-8-1</td>
<td>5.1</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O2-8-1</td>
<td>4.3</td>
</tr>
<tr>
<td>LFP 113HTEGH2O5-5-1</td>
<td>5.9</td>
</tr>
<tr>
<td>C/LFP 113HTEGH2O5-5-1</td>
<td>4.7</td>
</tr>
</tbody>
</table>
3.7.4. Lithium ion diffusion

Now let us consider ionic diffusion towards the self-similar fractal electrode by using cyclic voltammetry. Figure 3-16 shows the CVs obtained from LFP113H2O-1 and C/LFP113H2O2-1 electrode at various scan rates. The CVs clearly showed one pair of well-defined current peaks.

Strømme et al.\textsuperscript{28,29} suggested the peak/current method to determine the fractal dimension of the electrode surface by using cyclic voltammetry: when the recorded cyclic voltammetric current is limited by diffusion of the electroactive species to and away from the electrode surface, the fractal dimension D\textsubscript{f} of the reaction site distribution on the surface can be obtained by the following equation

\[ I_{\text{peak}} \propto v^\alpha \]  

\textit{Equation 3-2}

Figure 3-16 (a) Cyclic voltammograms obtained from the LFP113HTH\textsubscript{2}O-1 electrode (b) Cyclic voltammograms obtained from the CLFP113HTH\textsubscript{2}O-1 electrode. (c) Dependence of anodic peak current I\textsub{peak} on scan rate n obtained from the cyclic voltammograms of LFP113HTH\textsubscript{2}O-1 and C/ LFP113HTH\textsubscript{2}O-1. The slope a is d log I\textsub{peak}/d log n.

Hence, the films must be treated as fractal electrodes. The slope is denoted \( \alpha_f \) and called the fractal parameter, which is related to the fractal dimension \( d_f \) of the surface through:

\[ \alpha_f = \frac{d_f-1}{2} \]  

\textit{Equation-3-3}

Figure 3-16 is also used to provide information of the ion diffusion coefficient using an improved Randles–Sevcik equation applicable for fractal electrodes\textsuperscript{28},

\[ i_{\text{peak}} = \frac{\Gamma(1-\alpha)\Gamma(\alpha)(\frac{R}{2nF\sigma})^{\frac{1}{2}}(nFv)^{\alpha}nFAD^{-1}C_0X_{\text{max}}(\alpha)}{\Gamma(\frac{1}{2}RT)\alpha} \]  

\textit{Equation-3-4}
where $I_P$ is the peak current, $\Gamma$ the gamma function, $\gamma$ a geometrical factor close to $\pi^{-1}$, $\lambda$ the length corresponding to the outer cut-off of the fractal electrode, $n$ the number of transferred electrons per atom, $F$ Faraday’s constant, $\nu$ the sweep rate, $C$ the concentration of the electrolyte, $\chi_{\text{max}}$ a dimensionless function of the fractal parameter given by Stroome et al., $R$ the gas constant, and $T$ the temperature, $n$ is the number of $e^-$ involved in the reaction. Equation 3-4 gives an estimate of the diffusion coefficient, which is found to be $7.32 \times 10^{-14}$ for LFP and $2.18 \times 10^{-13}$ cm$^2$/s for carbon coated LFP113HTH$_2$O-1.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Diffusion coefficient (cm$^2$/s) obtained by CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113HTH$_2$O-1</td>
<td>$7.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>C/LFP113HTH$_2$O-1</td>
<td>$2.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>LFP113HTEGH$_2$O2-8-1</td>
<td>$7.9 \times 10^{-14}$</td>
</tr>
<tr>
<td>C/LFP113HTEGH$_2$O2-8-1</td>
<td>$2.7 \times 10^{-13}$</td>
</tr>
<tr>
<td>LFP113HTEGH$_2$O5-5-1</td>
<td>$8.1 \times 10^{-15}$</td>
</tr>
<tr>
<td>C/LFP113HTEGH$_2$O5-5-1</td>
<td>$3.5 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

3.8. Final remarks

In this chapter, we have shown the effects of solvent composition on the microstructure, morphology and electrochemical performance of LFP and C/LFP samples prepared hydrothermally.

Thus, comparison of SEM images from different samples allow us to conclude that sample LFP113HTH$_2$O2 (Fe:P:Li, with molar ratios 1:1:3, hydrothermal in PEI-containing water) more uniform and better crystallized particles thanks to the presence of PEI. Among the three carbon-coated samples studied in this chapter, this LFP113HTH$_2$O1 sample also shows the best electrochemical performance with a specific capacity of 164 mAh/g at 0.1 C rate, compared to sample LFP113HTH$_2$OEG5-5 (C-coated) which led to the minimum value of 150 mAh/g. The improvement could be mainly attributed to the optimization of the morphology and microstructure of the material which facilitates Li$^+$ ion extraction/reinsertion in the LFP crystallites. Thus, we have developed here a uniquely simple method to induce the growth of fractal microstructures of LFP.
nanoparticles using mainly water as solvent (+5% PEI). In order to accomplish the goal of tuning the morphology of LFP we used small amounts of polyethyleneimine (PEI, 5% w/v in water), which plays a triple role as a reducing agent, a surface modifier and a polymer host. On the other hand, partial substitution of this water-PEI solvent by Ethylene Glycol did not lead to better results. Figure 3.17 shows the relationship between the amount of EG and the discharge capacity. As we can see, the use of EG is slightly detrimental for the final capacity obtained. This can be associated to the distinct morphology of the nanoparticles obtained as the amount of EG is increased, which crystallize in increasingly elongated nanorods, departing from the prismatic primary nanoparticles obtained in the absence of EG which present active faces (Table 3-2) and morphologies (Figure 3-4) which are better suited for total utilization of Li-insertion capabilities of LFP even at high C rates.

![Figure 3-17 Discharge capacity (0.10C) as function of the amount of EG](image)

Finally, an important parameter for LIBs is the Li\(^+\) diffusion coefficient. The optimization of this parameter enhances LIBs performance in terms of capacity, rate capability and coulombic efficiency of the device. The development of universal methods for the determination of such a parameter is complicated by factors like the geometry of the electrode active particles. Thus, fractal structure comes to complicate the task. Nevertheless, we have applied a previously proposed method in order to determine the fractal dimension and diffusion coefficient in the best of our materials. This is the first
time that such method has been applied to battery electrodes and resulted in a Li$^+$ D of $1.83 \times 10^{-13}$ cm$^2$/s for a granular geometry with a fractal dimension of 2.
3.9. References


(16) Xiangcheng Sun  Caiyun Chen, H. S., Bo Cui, Kai Sun International Journal of Materials and Chemistry 2012, 2.


Chapter 3: LFP synthesized by hydrothermal method


Nanocomposites of LFP and conducting carbons or polymers synthesized by solvothermal methods
4.1. Overview

Pure LFP is an extraordinary electroactive material but it lacks the conductivity required to work as an electrode. In the previous chapter, we explored the conventional method for turning LFP into a useful electrode material, namely the growth of a C coating onto the surface of LFP particles. In this chapter, we will present our work related to the development of several hybrid nanocomposite materials making use of alternative conductive components such as conducting polymers (PPy in our case) or graphenes (RGO).

Polypyrrole (PPy) was used to take advantage of previous experience with this conducting polymer. The PPy coating is expected to reduce the particle-to-particle contact resistance and facilitates the transport of electrons from the current collector due to its electronic conductivity. In this way, the polypyrrole acts as an electronically conducting network which increases the rate of electron exchange in the depth of the electrode. Furthermore, PPy can also contribute to the specific capacity of the electrode by participation in lithiation/de-lithiation reactions.

Graphenes are also potentially useful partners for LFP composites since in principle they could provide electronic conductivity and improved inter-grain connections. Reduced Graphene Oxide (RGO) was chosen among various possible graphene derivatives because it represents a middle-term material with enough functional groups to provide activity and hydrophilicity while still featuring adequate electronic conductivity, both of which are essential for the pursued application. Other reason to choose RGO is that Single Layer Graphene (SLG) has a limited capability of uptaking Li ions.

For the synthesis of these nanocomposite electrodes we were eventually led to use a solvothermal method avoiding the use of water and leading to the growth of LFP nanoparticles which turned to be best suited in morphology and size for the combination with PPy or RGO.

The conducting coating onto LFP particles is of major importance. It serves the purpose of increasing the electrical conductivity of the material, but also helps inhibiting the particle growth during cycling. It has been found that the electrochemical properties of LFP are strongly influenced by the nature of the carbon coating, which in turn depends
on the amount of carbon, the degree of graphitization, morphology, the distribution of the carbon on the LFP surface and in the grain boundaries.

We have analyzed the effects of using alternative conducting materials on the electrochemical performance of the resulting nanocomposite cathode. PPy and RGO can increase the conductivity of LFP.

For the preparation of these complex hybrids we tried various approaches generally involving the growth of LFP onto pre-formed PPy or RGO. This approach led to the growth of nanoparticulate LFP materials. In order to get an LFP material without conducting component but with similar morphology, we tested the use of surfactants during the solvothermal synthesis of LFP with positive results. We are going to proceed to discuss the syntheses, microstructures, morphologies, physical end electrochemical properties of these electrode materials.

It is important to mention that some samples obtained using the synthesis methods that are going to be discussed here (specifically LFP113STEG-2) was finally selected to be used in the preparation of electroactive nanofluids which will be discussed in the final chapter of this Thesis.

4.2. Synthesis and characterization of pristine and carbon-coated LFP

4.2.1. Synthesis of LFP113STEG

In a typical reaction 3.0055 g of Lithium Hydroxide monohydrate, (LiOH·H$_2$O, 0.0716 moles) was added to 70 mL of preheated ethylene glycol, at 70 °C, and stirred for 10 minutes. 6.3878 g (0.0229 moles) of Iron Sulfate heptahydate (FeSO$_4$·7H$_2$O) was dissolved in ethylene glycol (70 mL) and stirred for 2 minutes. Then we slowly added 1.65 mL (0.0241moles) 85% phosphoric acid (H$_3$PO$_4$) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO$_4$ solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200 °C for 24 h.
solution was filtered-off, washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 9 and we obtained 3.8840 g of LFP powder which represents 98% yield. This sample was sintered and carbon-coated as described in chapter two.

4.2.2. Synthesis LFP113STEG-2

The difference between this sample and the one above was the addition of pluronic acid. Thus, 0.0078g of Pluronic® F-127 was dissolved in 140 mL of ethylene glycol. At this point the solution was divided in half. 2.9808 g (0.0710 moles) of lithium hydroxide monohydrate (LiOH·H₂O) were added to 70 mL of preheated EG (at 70 °C) with Pluronic® and stirred for 10 minutes. In parallel, 6.8837 g (0.024 moles) of FeSO₄·7H₂O were dissolved in the other half of the Pluronic® solution (70 mL) and stirred for 2 minutes. Then we slowly added 1.65 mL (0.0241 moles) 85% phosphoric acid (H₃PO₄) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO₄ solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200 °C for 24 h. The solution was filtered-off and washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 5 and we obtained 3.2478 g of powder which represents 83% yield. This sample was sintered and carbon-coated as described in chapter two.

The nominal chemical formula of Pluronic is HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H, triblock copolymers based on poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) are known generically as poloxamer. Poloxamers have behaviors similar to those of hydrocarbon surfactants, and will form micelles when placed in a selective solvent such as water. They are capable of forming both spherical and cylindrical micelles.
4.2.3. Characterization of LFP and C/LFP

4.2.3.1. Structure Characterization

We recorded powder X-Ray diffraction patterns of all samples. Sample LFP113STEG shows sharp XRD peaks well crystalline all of which can be indexed confirming single-phase olivine LFP without detectable impurity phases (Figure 4-1). On the other hand, sample LFP113STEG-2 shows the same major LFP phase but with very weak peaks between 22-25° which correspond to very small amounts of impurities, most likely from pluronic acid. Correspondingly, the carbon-coated samples are impurity-free in the case of C/LFP113STEG, whereas the sample derived from pluronic (C/LFP113STEG-2) shows weak and broad peaks at ca. 22-25 and 35°, which, nevertheless do not represent a serious detrimental factor for electrochemical performance.

On the other hand, we note differences in intensities between pluronic-derived and pluronic-free sample. Thus, the intensities of peaks from sample LFP113STEG-2 (with pluronic) are greater than those for the pluronic-free LFP113STEG, indicating greater crystallinity for the former. This is also the case for the corresponding carbon-coated samples. This shows that the addition of surfactants has no major detrimental influence on the formation of LFP crystal structure in these samples (Figure 4-1).
4.2.3.2. Microstructure

We decided to study the microstructure and particle morphology of our samples obtained by different synthetic methods by SEM and TEM. We studied the morphology, particle size and confirmed some of the crystal properties of these samples using SAED technique coupled with TEM.

Figure 4-2 shows SEM pictures of pristine LFP and C/LFP. These SEM images did not show great differences between samples and the incorporation of carbon-coating films on LFP were not apparent. Therefore we decided to record TEM images which will be discussed later.

The particles of pristine LFP113STEG (no surfactant used) Figure 4-2 (a) are more irregular in size and shape than those of LFP113STEG-2 (prepared with 5% (w/v) pluronic acid) (Figure 4-2 (c)), which shows a more monodispersed particle size distribution and more homogeneous (thick plates) morphology. Sample C/LFP113STEG, Figure 4-2 (b), shows few abnormal particles that did not match in size and shape with the bulk of the specimens observed for this sample. However, this sample looks more homogeneous.

Figure 4-1 Powder X-ray diffraction patterns of LFP113STEG and LFP113STEG-2 (left) C/LFP113STEG and C/LFP113STEG-2 (right)
than LFP113STEG. The shape of this nanoparticles look like rubbles. Carbon coated nanoparticles from sample C/LFP113STEG-2, also show a more regular size, Figure 4-2 (d).

However, is difficult to carefully analyze the images to fix the size of these nanoparticles in all cases due to the agglomeration of the particles. Although is clear that the amount of surfactant used to prepare LFP plays a crucial role in controlling the grain shape, and hence the electrochemical properties. This will be discussed latter.

Figure 4-2 SEM images of (a) LFP 113STEG (b) C/ LFP 113STEG (c) LFP 113STEG2 (d) C/LFP 113STEG2

Figure 4-3 shows TEM and HRTEM images of the four samples we are discussing, LFP113STEG, C/LFP113STEG, LFP113STEG-2 and C/LFP113STEG-2. With this technique, we were able to show the nanoparticles size of these samples. We also analyzed SAED patterns obtained for these samples to confirm the information obtained by XRD. Figure 4-3 a, shows a TEM image of LFP113STEG (sample without surfactant) with a representative particle shown in the inset. The average particle size for this sample is 150 (20) nm (determined from measurements of 6 different single particles of 6 different images). The d spacing of pristine LFP113STEG measured on the micrograph of
Chapter 4: Nanocomposites of LFP and conducting carbons or polymers synthesized by solvothermal methods

Figure 4-3 (a) is 0.31 nm, corresponding to (211) Miller indices. SAED analyses reveal planes (210) and (101) of the olivine LFP phase. This agrees with the XRD patterns recorded for this sample (section 4.2.3.1).

The TEM image for the corresponding C-coated sample (Figure 4.3 (b)) clearly shows an amorphous shell homogeneously covering each particle with a thickness of ca. 2.7 nm. In this particular case, the sample particles were agglomerated which made it difficult to isolate individual particles. However, the size to this particle appears to be circa 100 nm. This agglomeration could be a result of electrostatic forces. The micrograph shown corresponds to a single-crystalline fragment. The d spacing measured (0.34 nm) corresponds to the (111) family of planes. SAED analysis confirmed the good crystallinity of this sample and helped identify the (211) family of planes, in good agreement with reference 01-081-1173 (JCPDS) (Figure 4-3 (b)). The following step was to analyze the images of the sample prepared with 5% w/v of surfactant. Figure 4-3 (c) shows particles of the sample LFP113STEG-2. The average size of this particle is 56 (3) nm. We used 6 images of this sample displaying a single particle to obtain the average particle size. These particles are more homogeneous in size and 63% smaller than samples without surfactant. Concerning particle size, a small amount of Pluronic F-127 has the desired effect to decrease the size of the nanoparticles. The d space for LFP113STEG-2 sample is 0.25 nm, corresponding to a plane 311, listed in reference 01-083-2092. SAED analysis reveals Miller indices of 101 and 001, which agrees with the XRD pattern. The d spacing revealed by the HRTEM images for sample C/LFP113STEG-2 is about 0.43 nm. This image also shows another plane with a d parameter of 0.37 nm. These correspond to a family of planes (010) and (011) (list in JCPDS 01-083-2092). This sample also shows an amorphous layer with a thickness of 2.9 nm. The SAED analysis of this particles shows that this sample has a well crystalline structure and a Miller indexes of 111 and 210. The average particle size of this carbon-coated sample is 53(2) nm. For this analysis, we analyzed 6 different images of 6 different single particles of this sample. The use of surfactant did not affect only the morphology and size of the particle, but also the overall microstructure of the sample was affected which in principle could lead to a better electrode active material.
Table 4-1 crystal parameters obtained by HRTEM images

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>d space (nm)</th>
<th>Plane</th>
<th>Carbon thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113STEG</td>
<td>0.31</td>
<td>211</td>
<td>N/A</td>
</tr>
<tr>
<td>C/LFP113STEG</td>
<td>0.34</td>
<td>111</td>
<td>2.72</td>
</tr>
<tr>
<td>LFP113STEG-2</td>
<td>0.25</td>
<td>311</td>
<td>N/A</td>
</tr>
<tr>
<td>C/LFP113STEG-2</td>
<td>0.43</td>
<td>010</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
<td>011</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-3 TEM images of (a) LFP 113STEG (b) C/LFP 113STEG (c) LFP113STEG-2 (d) C/LFP113STEG-2
4.2.3.3. Carbon Characterization

This analysis is based on techniques like TGA and elemental analysis. Surface techniques such as XPS can also help to understand the nature of this carbon, especially in relation to the conductivity of this material. The amount of carbon was determined by TGA (the analysis procedure was discussed in the previous chapter section 3.6 and we compare the information obtained with the values obtained by chemical analysis. The values obtained by this method agree with each other. Table 4-2 presents the carbon % values obtained from the two samples obtained by both methods.

These samples were carbon-coated using glucose. Raman and XPS were also used to characterize these samples. The results were identical to those obtained for samples described in chapter 3 and will not be discussed here. The fact that the same carbon source, procedure, and conditions were used to coat these new samples, as those used for samples in chapter 3 is the most likely reason why no difference in the nature of the carbon obtained was observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon % (TGA)</th>
<th>Carbon Chemical analysis%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/LFP113STEG</td>
<td>2.1</td>
<td>2.3</td>
</tr>
<tr>
<td>C/LFP 113STEG 2</td>
<td>2.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

4.2.3.4. Electrochemistry

The electrochemical properties of these samples will be discussed in detail in this section. The analyses were carried out by CV and potentiometric charge/discharge cycles at constant currents. As the optimal case example, we will discuss in detail samples LFP113STEG-2 and C/LFP113STEG-2. Some details of sample LFP113STEG and the corresponding carbon coated material will also be discussed for comparison.
4.2.3.4.4. Cyclic Voltammetry

These voltammograms were recorded in a 3 electrode cell using metal Li as reference and counter electrodes. The voltammogram of this sample (Figure 4-4 a) shows a well-defined redox peak at $E_0 = 3.45\text{V}$ vs. Li, characteristic of LFP. As expected, the carbon-coated sample C/LFP113STEG-2 shows more intense, better defined redox waves. Furthermore, carbon-coating also reduces the difference between the potentials of reduction and oxidation peaks with respect to pristine samples (Table 4-3). This confirms that in fact that carbon coating serves to increase the electronic conduction of the LFP material and has a major role in terms of enhancing the electrochemical performance. The difference between the peaks for the carbon coated samples are smaller that for the non coated samples, see Table 4-3.

Table 4-3 shows the values of the open circuit potential and the oxidation and reduction peak of the samples. From the obtained results, it can be concluded that with the decrease of particle size in LFP, the cell voltage also decreases. Similar behavior is observed for carbon coated samples. Is important to remark the fact that the difference between the anodic and cathodic peaks are smaller for the carbon-coated samples as compared with the corresponding uncoated materials. These results are consistent with slower kinetics and larger overpotentials exhibited by pristine LFP and LFP113STEG-2 sample compared with the carbon-coated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{pa}$ (V)</th>
<th>$E_{pc}$ (V)</th>
<th>Difference (V)</th>
<th>OCP (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP 113STEG</td>
<td>3.59</td>
<td>3.33</td>
<td>0.26</td>
<td>3.38</td>
</tr>
<tr>
<td>C/LFP 113STEG</td>
<td>3.52</td>
<td>3.34</td>
<td>0.20</td>
<td>3.26</td>
</tr>
<tr>
<td>LFP 113STEG-2</td>
<td>3.54</td>
<td>3.29</td>
<td>0.25</td>
<td>3.19</td>
</tr>
<tr>
<td>C/LFP 113STEG-2</td>
<td>3.55</td>
<td>3.34</td>
<td>0.216</td>
<td>3.13</td>
</tr>
</tbody>
</table>

4.2.3.4.4. Galvanostatic Charge discharge

Potentiometric charge discharge cycles were carried out at various constant currents and show that sample C/LFP113STEG-2, has a capacity of 168 mAh/g, (at C/10) very close
to the theoretical capacity of LFP (170 mAh/g). The improvement of the carbon-coated sample compared to the uncoated sample (18% of the theoretical capacity at C/10) is remarkable. This improvement can be attributed to the quality of the carbon obtained during the coating process and a homogeneous coating shown in section 4.2.3.2. The quality of the carbon obtained by the thermal decomposition process was discussed in the previous chapter 3.6.

The rate capability of this sample is excellent as can be seen in Figure 4-4 (c). The C-coated LFP material shows outstanding capacity retention without much degradation in the capacity upon cycling, Figure 4-4 (d). It is important to mention the small polarization of the cell used to test sample C/LFP113STEG-2 at low C rate, although the polarization increases at high scan rates that increase still corresponds to an excellent performance. Figure 4-4 (b).

Figure 4-4 (a) Cyclic Voltammetry of pristine LFP113STEG-2 and C/ LFP113STEG-2 at 1mV/s (b) Charge and discharge curves at various C-rates for C/ LFP113STEG-2 (5th cycle) (c) Discharge capacity at different C-rates of pristine LFP113STEG-2 and C/
The next graph, Figure 4-5, summarizes the performance of all four samples studied in this section. First of all, as it is well known, the carbon coating (which in our case provides a relative high abundance of sp2 carbon atoms) increases the conductivity of the electroactive material.

On the other hand, our work shows how a small amount of surfactant can greatly influence the particle size and therefore the final performance of our electrode materials. Thus, the maximum discharge capacity depends on the size of the nanoparticles. Smaller particle size (induced by the use of pluronic acid) leads to smaller Li ion diffusion paths and high discharge capacity. We also observe an increment in the amount of carbon in the sample with a smaller particle size (prepared with pluronic acid). All these favorable conditions increase the discharge capacity of the samples grown under the influence of this surfactant copolymer.

![Figure 4-5 Discharge Capacity of the four LFP samples discussed in this section](image)

4.3. LFP reduced graphene oxide (RGO) hybrid composites

The choice of RGO among different graphene materials was based on its partially hydrophilic nature, offering the possibility of a better interaction with LFP than pure graphene while avoiding the strongly oxidizing nature of graphene oxide. However, even RGO was too strong an oxidizing agent for reduced LiFe(II)PO4. In particular, we should mention here that we tried to carry out a synthesis of LFP/RGO hybrid composites in...
aqueous media, with negative results. The presence of water and RGO result in the oxidation of Fe(II) in LFP. We have decided to skip the details of that work while still mentioning these negative results for the sake of including full information. On the other hand, the use of ethylene glycol (EG) instead of water was enough to prevent this undesired reduction. That was indeed the main reasons to use only EG in order to obtain a LFP/RGO hybrid as we will describe below.

4.3.1. Synthesis of the series LFP113STEGRGOx% (x = 1, 2.5, 5 %)

0.1078 g of RGO (prepared as detailed in appendix 1) was sonicated for 15 minutes in 140 mL of ethylene glycol. This solution divided by half. In a typical reaction 2.7537 g (0.066 moles) of lithium hydroxide monohydrate (LiOH.H\textsubscript{2}O) was added to 70 mL of a preheated (70 degrees) RGO/EG and stirred for 10 minutes. 6.6714 g (0.0241 moles) of iron sulfate heptahydrate (FeSO\textsubscript{4}.7H\textsubscript{2}O) was dissolved in the other half of the RGO solution (70 mL) and stirred for 2 minutes. Then we slowly added 1.65 mL (0.024 moles) 85% phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO\textsubscript{4} solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200 °C for 24 h. The solution was filtered-off and washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 9 and we obtained 3.7222 g of powder which represents 97% yield. We also carried out two other syntheses with different amounts of RGO and using the same procedure described above, in order to optimize the electrode material. The corresponding amounts of RGO used were 0.2044 g and 0.0408 g and the resulting samples were labeled according to the %RGO nominally used (1, 2.5 and 5 %). All three samples were sintered by the method described in chapter two.
4.3.2. Structural characterization

The first assessment of these samples, made by the analysis of powder XRD, shows an olivine crystal structure and no sign of RGO or crystalline impurities. There are no obvious carbon diffraction peaks at 2θ 26° in the LFP113STEGRGO hybrids, which could be due to its low content and a well-exfoliated morphology. Hence, the addition of RGO to the active materials has no negative effect on the formation of LFP olivine crystal phase. The x-ray diffraction patterns shown below (Figure 4-6) reveal well-crystallized phases in all cases. All peaks can be indexed according to JCSPD card 01-083-2092.

![X-ray diffraction patterns of the 3 different LFP113STEGRGO hybrids](image)

4.3.3. Microstructure and morphology

To get information on the morphology of sample LFP113STEGRGO2.5%, we carried out STEM, EDS, TEM and SAED analyses. Figure 4-7 shows images obtained by each of these techniques. It should be noted that RGO provides active sites for LFP nuclei, thereby restricting the aggregation and in-situ crystallite growth of anchored LFP nanoparticles. Figure 4-7 (a) corresponds to a STEM image showing grains with an average particle size of 45 (4) nm. The average and standard deviation were determined from the sizes...
measured for the six crystals indicated in Figure 4-7 a. The high contrast of these nanoparticles is a first indication that they correspond to LFP. EDS analysis shown in Figure 4-7 b confirms the LiFePO$_4$ composition. This image also exhibits a curled morphology of RGO sheets, consisting of thin, wrinkled ‘paper-like’ structures.

Figure 4-7 (c) shows a HRTEM image of the LFP113STEGRGO2.5% sample. Crystal lattice fringes can be detected with a d-spacing of 0.35 nm, corresponding to the 111 plane of orthorhombic LFP crystals. We can conclude that these nanoparticles have a high crystallinity, which has been further confirmed by the SAED pattern, Figure 4-7 (d). The calculated Miller indices are (200) and (111), in good agreement with the JCPDS reference 01-083-2092.

Sample LFP113STEGRGO1% has an average particle size of 46 (8) nm (average of 6 single particles (images not included)). In this particular case it was possible to isolate individual particles, which were attached to RGO sheets much smaller in size than those curling layers shown in Figure 4-7 (a). We should note the big deviation in the particle size of this sample. This can be attributed to the small amount of RGO used during this synthesis process.

Finally, we observe a significant change in the particle size for sample LFP113STEGRGO5%. In this case it was not possible to isolate a single particle. As occurs for sample LFP113STEGRGO2.5%, we also observed a curly RGO layer over the LFP particles. It was difficult to obtain HRTEM images for this sample due RGO amount in the sample and the small size of these particles.
After presenting the results of LFP – RGO nanocomposites in this section we would like to comment here on our use of surfactant for the growth of isolated LFP nanoparticles, as it was described in section 4.2.3.2. In the absence of surfactant, LFP particle sizes were
larger than 100nm, whereas the use of surfactant led to nanoparticles of size ca. 60 nm, much closer to the ones obtained in the LFP-RGO materials we have just discussed.

4.3.4. Chemical and spectroscopic characterization

4.3.4.1. Carbon amount in the composite

Elemental analysis (% C, N, H, S) was carried out for selected samples among the ones prepared during this Thesis. Within the series of compounds LFP-RGO, elemental carbon was analyzed for the sample leading to the best electrochemical performance, which, as it will be shown later, was LFP113STEGRGO2.5%, with a nominal C composition of 2.5%. The real amount of carbon in this sample was determined to be 2.7%. The amount of hydrogen, nitrogen and sulfur was in less than 0.1%. In this case, we did not explore TGA analysis because RGO decomposition interferes with the profile and carbon amount determination for LFP.

4.3.4.2. Raman

Reduced graphene oxide in the hybrid was confirmed by Raman spectroscopy, as displayed in Figure 4-8 (a). Two peaks at 1329 and 1596 cm\(^{-1}\) are assigned to the D and G bands of graphene, respectively. It has been suggested that a high I(D)/I(G) ratio in the carbon Raman spectra of LFP-RGO hybrids (i.e. a high disorder in the RGO component) can be associated to good electrochemical properties\(^9\). This could be understood in terms of greater porosity and Li\(^+\) diffusion paths associated to defects. In our case the I(D)/I(G) ratio of intensities measured for sample LFP113STEGRGO2.5% was 1.1, which is a little bit higher than the intensity ratio obtained for RGO, which was 1.0 (see appendix 1).

The 2D band originates from a two phonon double resonance Raman process\(^10\) was not clearly observed. For SLG, the 2D band can be fitted with a sharp and symmetric peak while that of graphite can be fitted with two peaks. The 2D band becomes broader and blue shifted when the graphene thickness increases from SLG to multilayer graphene.
The intensity and broadness of the 2D band for the LFP-RGO nanocomposite (Figure 4-8 a) is consistent with the multilayer nature described just above, and it was similar to the parent RGO 2D band (appendix 1).

As the Raman bands in D and G region of the spectra are broad, the intensity profiles are often deconvoluted using four Gaussians or Gaussian-Lorentzian lines\textsuperscript{11}. Deconvolution analysis of the D and G peaks provide us data about the $sp_2/sp_3$ ratio. We have fitted the Raman intensity profiles using four Gaussian lines, see Figure 4-8(b), and have estimated intensity ratios $I_{sp_2}/I_{sp_3} = (I_{1354} + I_{1591}) / (I_{1250} + I_{1500}) =5$. This value is evidence of the predominance of planar, graphitic layers, thus indicating a material with a good conductivity. A band corresponding to $PO_4^{3-}$ was also detected in this sample at 946.1 cm$^{-1}$

4.3.4.3. XPS Spectroscopy

X-Ray Photoelectron Spectroscopy was also used selectively for the representative characterization of the best sample of this series, namely, LFP113STEGRGO2.5%. The XPS spectrum in the Fe 2p region (Figure 4-8 (c)) shows the typical 2 peaks related to iron in a formal Fe(II) oxidation state, Fe2p3/2 and Fe2p1/2. Indeed, this result is similar to the other LFP samples discussed previously in chapter 3. This is an indication that the nature of the LFP phase is not affected by the presence of RGO during synthesis. Figure 4-8 (d) shows the binding energy profile of carbon in the hybrid measured by XPS. The observation of C 1s binding energies at 289.0 eV (C=O) and 286.5 eV (C–O), suggests that some oxygen-containing functional groups remain in RGO. These oxygen groups were also detected in the Carbon XPS spectra of pure RGO (see appendix 1).
4.3.5. Electrochemistry of the series LFP113STEGRGOx% (x = 1, 2.5, 5 %)

4.3.5.1. Cyclic Voltammetry (CV)

The electrochemical properties of the three members of this series were measured. The main focus here, however, will be a more detailed discussion of the electrochemical studies for sample LFP113STEGRGO2.5%. Of course, the electrochemistry of other LFP/RGO hybrids will be discussed, especially as comparative analysis, but in a less detailed way.

Figure 4-9 (a) shows the CV of sample LFP113STEGRGO 2.5 as measured in a three-electrode Swagelok cell using LiPF$_6$ in a carbonate solvent mixture and Li metal as counter and reference electrode (1 mV/s). Two well-defined redox waves were recorded.
which are assigned to the well-known Fe(II)/Fe(III) redox couple in LFP, corresponding to lithium extraction and insertion in the LFP crystal structure. The Eap (anodic peak) for this positive electrode is 3.55 V and the Ecp (cathodic) 3.33 V vs. Li, Figure 4-9 (a). It is important to mention that the difference between the oxidation and reduction peaks is 220 mV. These values is smaller than the one found for the non-coated LFP sample LFP113STEG-2 (260 mV), and similar to the carbon-coated sample C/LFP113STEG-2 (210 mV). This low polarization of the hybrid LFP-RGO electrode demonstrates that RGO provides a good conducting framework to facilitate the redox processes in LFP even without the coating of individual particles with carbon.

4.3.5.2. **Galvanostatic charge-discharge**

LFP-RGO electrodes prepared as described in chapter two were assembled in a two electrode Swagelok cells with metal lithium anodes and LiPF₆ electrolytes. The cells were cycled at constant current and various C rates in the voltage range 2.5–4.0V. Figure 4-9 (b) shows the results of the cell made with LFP113STEGRGO2.5% sample. This sample does not show a large polarization, only 0.2 V at 10C, which is a good characteristic for an intrinsically insulating positive LFP electrode material. It can be seen from Figure 4-9 (c) that the sample exhibited attractive rate capabilities and then remained stable when the rate was returned to 1 C. The cyclability was good (Figure 4-9 (d) ) with capacity values of 120 mAh g⁻¹ (at 1C rate) being maintained after 100 cycles.

The sample with 1% RGO (LFP113STEGRGO1%) did not have a good rate capability, the stability of the sample and the general efficiency of the sample was poor, whereas the sample with a 5% of RGO (LFP113STEGRGO5%) showed a higher polarization during the cycling test, as can be seen in Figure 4-9 (e and f). Overall, the best performance was shown by LFP113STEGRGO2.5%.
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Figure 4-9 (a) Cyclic Voltammogram at 0.1 mV/s. (b) Capacity vs potential profile (c) Rate capability (d) Stability, cycling performance at 1C of LFP113STEGRO2.5% (e) rate capability of LFP113STEGRO 1% and 5% (f) C-Rate vs. discharge capacity of LFP113STEGRO 1%, 2.5% an 5%.

This result shows how it is possible to get a good performance for LFP-based electrodes with the use of small amounts of additives through less energy intensive processes. Thus, with just a 2.5% of RGO we get a good electrochemical response, comparable to the coating by pyrolysis of a 15% w/w glucose at 700°C leading to a 2.5% carbon-coating.
4.4. LFP PPy hybrid

4.4.1. LFP 113STEGPPY Synthesis

0.0110 g of polypyrrole (PPy) was sonicated for 15 minutes in 140 mL of ethylene glycol (EG). In a typical reaction 3.0002 g (0.081 moles) of lithium hydroxide monohydrate (LiOH·H₂O) was added to 70 mL of the PPy/EG solution (preheated at 70°C) and stirred for 10 minutes. 6.6107 g (0.024 moles) of iron sulfate heptahydrate (FeSO₄·7H₂O) was dissolved in the other half (70 mL) of the PPy/EG solution and stirred for 2 minutes. Then we slowly added 1.65 mL (0.0241 moles) 85% phosphoric acid (H₃PO₄) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO₄ solutions and stir for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave) and the reactor put in the oven and heated up to 200°C for 24 h. The suspension was filtered-off with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 9 and we could isolate 3.078 g of powder, accounting for 81% yield. The sample was subjected to a thermal process at 700°C, as described in chapter two.

4.4.2. Powder X-Ray Diffraction Pattern

The XRD assessment of this sample shows a pattern that corresponds to olivine crystal structure and no substantial contributions from PPy or crystalline impurities. Hence, the addition of PPy during the synthesis of the cathode material has no negative effect on the formation of LFP olivine crystal phase,

Figure 4-10. The x-ray diffraction pattern below reveals a well crystalline phase; all peaks can be indexed according to the JCPD card 01-083-2092. This sample has a crystallite size of 21 nm as calculated from the width of 020 peak.
4.4.3. Morphology

The SEM images presented in Figure 4-11 shows the morphology and microstructure of sample LFP113STEGPPy2.5%. As we can see this sample has a homogeneous size and morphology. The nanoparticles of this samples look like rubbles, the particles does not shown any sing of a PPy in these SEM images. We did not see any sing of N-CN Pipes or PPy Nanopipes in these images.

The images obtained by TEM, Figure 4-12, provide more information. We observed a thin amorphous layer coating the main nanoparticle. The average size of these particles is 60 (1) nm. We used six different micrographs of six different isolated particles to obtain this average size. It is important to mention that the coating for these particles was not homogeneous, Figure 4-12 (a). The measured thickness of this layer was 2.5 nm, for this specific case, Figure 4-12 (b). This analysis also reveals that the d spacing is 0.30 nm corresponding to 301 Miller indices. It was also possible to confirm the crystallinity of the sample through the analysis of the SAED images. In this case the profile of the pattern corresponds to a family of 301 indices. However, looking in details this SEAD image we get to the conclusion that this image corresponds to two different particles that are over impose each other. In both cases the information obtained is in agreement with the obtained XRD pattern. Elemental analysis of this sample gave 1.4% C and 0.4% N. These values represent an atomic ratio C/N of 3.5, somewhat lower than the value of 4 expected for PPy, which might indicate a partial decomposition of PPy with loss of C.
or the incorporation of N to the final material from the N\textsubscript{2} atmosphere used. The hydrogen and sulfur content was 0.8 and less than 0.1 % respectively.

![General view of the LFp113STEGPPy2.5% morphology by SEM](image)

**Figure 4-11** General view of the LFp113STEGPPy2.5% morphology by SEM

![TEM image (a) HRTEM image and SAED picture of LFP113STEGPPy2.5%](image)

**Figure 4-12** (a) TEM image (b) HRTEM image and SAED picture of LFP113STEGPPy2.5%

4.4.4. Chemical composition and surface composition

4.4.4.1. Infrared Spectroscopy

FTIR is an efficient tool to investigate molecular vibrations and thus it is a good means of studying the local structure of samples. FTIR spectra of PPy, LFP and LFP113STEGPPy hybrid are showed at Figure 4-13 (a). The PPy spectrum shows bands at 1680, 1116 and 1034 cm\textsuperscript{-1} confirming the presence of PPy which correspond to C=C stritching vibration,
C-N in-plane deformation vibration and C-C out-of-plane asymmetric vibration, respectively.

The spectra of LFP is mainly dominated by vibrational modes from the PO$_4$ group, which can be easily detected in the region between 400 ~1200 cm$^{-1}$. It is well known that the fundamental vibrations (v1–v4) of PO$_4$$^{3-}$ polyanions of LFP are split in many components due to the coupling with the Fe-O units in the solid state$^{12}$. The v$_1$ and v$_3$ modes involve the symmetric and antisymmetric stretching vibration of the P-O bonds, whereas v$_2$ and v$_4$ involve mainly O-P-O symmetric and antisymmetric bending mode with a small contribution of the P vibration$^{13}$. The stretching and bending mode regions are well separated from each other. The stretching modes are identified at v$_1$ (A1) = 931 cm$^{-1}$ and v$_3$ (triplet F2) in the region of 1034–1136 cm$^{-1}$; and the bending modes at v$_2$ (doublet E) = 471–502 cm$^{-1}$ and the v$_4$ (triplet F2) in the region of 551–652 cm$^{-1}$ $^{14}$.

Detail observation of the LFP113STEPPPy 2.5% show the changes observed in the spectra when LFP is coated with a little content of PPy. In the range of 1600 ~ 1200 cm$^{-1}$, the bands assigned to C-H and C-N in LFP113STEPPPy can be seeing, this bands are a result of the PPy component in the hybrid. We notice a little band displacement in the LFP113STEPPPy 2.5%, specifically those peaks at 931cm$^{-1}$ and between 1000 and 1100 cm$^{-1}$, this bands are related to a vibration modes of PO$_4$. The band at 1034cm$^{-1}$ of PPy and the band at 1032 cm$^{-1}$ of LFP overlap in the LFP/PPy hybrid composite. The absent of the band at 735 cm$^{-1}$ in PPy and the hybrid composite LFP/PPy is an indication of a 2D structure of the polymer where the h bond is between the carbon layers$^{15}$. This morphology has been described in more stable and conductive PPy materials.

4.4.4.2. Raman Spectroscopy

The hybrid LFP-PPy sample was analyzed by Raman spectroscopy. The spectra of this sample (Figure 4-13 b) show three prominent bands that correspond to PO$_4$$^{3-}$ (950 cm$^{-1}$), and D and G bands (1353 and 1612 cm$^{-1}$) assigned to carbon. We estimated the ratio of intensities between these bands to be I$_D$/I$_G$ = 1.1. We can obtain information about the relative abundance of sp$^2$ and sp$^3$ C atoms by deconvolution of the D and G bands. We obtain 2 bands at 1390 and 1610 cm$^{-1}$ that correspond to sp$^2$ C. Two additional bands
at 1320 and 1520 cm\(^{-1}\) were needed in order to get a satisfactory fit of the overall intensity profile. These later bands are assigned to sp\(^3\) type carbon, which are often observed in amorphous carbonaceous materials. The intensity ratio between the sp\(^2\)/sp\(^3\) is 2.7. According to Diez et al. the carbon material around LFP particles contains more carbon sp\(^2\) which would predictably lead to a more conductive material\(^{11}\). When we compare this spectra with the spectrum of pure PPy NPipes (appendix2), we observe a shift of the G band indicative of a highly oriented carbon which can be assigned to the presence of graphite. The 2D band, associated to graphitic/graphenic carbon, can be detected in the Raman spectra of LFP113STEGPPy2.5% and this is another evidence of the chemical and structural changes with respect to the starting PPy NPipes, this band was absent in the Raman spectra of pure PPy NPipes.

4.4.4.3. XPS Spectroscopy

The XPS of this sample does not show significant changes with respect to other samples discussed in this chapter, section 4.2.3.3; and this is true for iron core spectra, Figure 4-13 (e). However, as it could be expected, we detect a band that corresponds to nitrogen. The analysis and proper fitting of the core N spectra shows two distinct peaks at 398 and 402 eV. Among them, the peak with binding energy 398 eV corresponds to the ‘pyridinic’ nitrogen while peak at 402 eV attributed to the ‘graphitic’ nitrogen. Thus, the peak at 398 eV is contributing to the p-conjugated system with a pair of p-electrons whereas that at 402 eV is observed only when the carbon atoms are substituted by the nitrogen to form the ‘graphitic’ nitrogen. While for PPyNPipes N core spectra only consist of a single peak at 400 eV (appendix 2). This observation is a result of a thermal treatment and was observed by Dubal and colaborators\(^{16}\), Figure 4-13 (f). The narrow scan spectrum of C1s for LFP113STEGPPy2.5% is presented in Figure 4-13 (d), which can be primarily fitted as three peaks centered at binding energies of 284.7, 285.9 and 288.6 eV. In detail, the peak at the binding energy of 284.6 eV confirms the presence of graphitic carbon, corresponding to the energy of sp\(^2\) C-C bond in C1s spectrum. Further the small signals at higher binding energies corresponds to C-O or C-N (285.9 eV\(^{17}\) and C=O(288.6 eV) species in the LFP/PPY hybrid composite, respectively.
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4.4.5. Electrochemistry

4.4.5.1. Cyclic Voltammetry

Figure 4-14 (a) shows a cyclic voltammogram of sample LFP113STEGPy2.5%. We used a three-electrode Swagelok cell to perform the cyclic voltammetry, the counter and reference electrode used were Li metal and the electrolyte was conventional LiPF$_6$ in carbonate solvents. The voltammogram shows two peaks that are a little broad and slightly asymmetric as the cathodic peak height is somewhat smaller than that of the anodic reaction. The redox peaks appear at 3.58 V (oxidation) and 3.32 V (reduction), with $E_0$ centered at 3.5 V. The difference in the peak potentials ($\Delta E_p$) for LFP113STEGPy2.5% cathode is 270 mV whereas for the pristine LFP cathode at the same scan rate of 1mV/s, it was 260 mV (Table 4-3) which implies an electrode with a similar polarization to the pristine sample.
4.4.5.2. **Galvanostatic charge/discharge**

The constant-current discharge curves (Figure 4-14 b,c,d) for the LFP113STEGPPy2.5% composite sample show a flat voltage plateau centered around 3.5 V, which is a characteristic for LFP. At the lowest applied discharge rate of C/10, the highest specific capacity in our experiments was 158 mAh/g, this cell also shows low polarization and good efficiency at this rate. This polarization as well as the effective capacity of the sample, get worse as rates increase. Thus, capacity suffers a substantial reduction, going from 158 mAh/g at C/10 to 70 mAh/g at 1C and 23 mAh/g at 10C. This reduction to just 13% of the initial capacity (C/10 vs. 10C), indicates of a poor rate capability. On the other hand, the stability of this material was very satisfactory during at least 100 cycles at 1C. These results are relatively good but leave room for improvement, especially concerning the optimization of microstructures in order to improve rate capabilities.

![Figure 4-14 Cyclic Voltammetry of LFP113STEGPPy 2.5 at 1mV/s (b) Charge and discharge curves at various C-rates for CLFP113STEGPPy2.5 (5th cycle) (c) Discharge capacity at different C-rates of pristine LFP113STEGPPy2.5 (d) Cycling performance of LFP113STEGPPy2.5 at 1C.](image-url)
4.5. Final remarks

During this chapter, we have discussed the syntheses of various kinds of LFP composites with different conductive materials, in order to study their effect on the morphology, microstructure and the resulting electrochemical performance. We have compared the microstructure and properties of pristine LFP with those of composites of LFP/RGO and LFP/PPy. For comparison, we also prepared and analyzed a sample of conventionally coated LFP with carbon from the pyrolysis of glucose.

In terms of morphology, the first observation was that the particle size of LFP prepared in the presence of RGO or PPy is much smaller than the particle size of pure, pristine LFP. The morphology for LFP/RGO composite looks more like grains covered by a curly layer or RGO as compared with rubble-like morphology of pristine LFP particles.

With the purpose to obtain a morphology and particle size more similar to those obtained for the LFP/RGO and LFP/PPy composites, we tested the use of Pluronic as additive in the synthesis of LFP. Addition of surfactant has a major advantage since it serves as an inhibitor for particle growth, leading to the formation of smaller and more uniform sized nanoparticles and more regular shape, like rubbles. The size of the nanoparticles obtained using this additive is 63% smaller than the pristine particle.

For the sample C/LFP113STEG-2 (surfactant) the capacity obtained was 168 mAh/g at 0.10 C, which is almost the theoretical capacity of LFP (170 mAh/g). This sample also shows an excellent rate capability and stability up to 100 cycles. If we compare this sample with C/LFP113STEG (no surfactant) in terms of electrochemical performance, the sample with the additive shows a better performance, however that does not mean that the performance of sample C/LFP113STEG was mediocre. This sample was stable and we obtained a capacity of 150 mAh/g at 0.10C. The improved performance of the surfactant-assisted product is ascribed to a more effective Li-ion diffusion through the smaller particulate electrode.

LFP particles (LFP113STEGRGO2.5%) are strongly anchored onto the surfaces of the RGO sheets. It is remarkable that a small amount of RGO is capable of reducing the particle size of LFP particles to circa 50 nm. LFP113STEHPPy2.5% sample shows a morphology and particle size comparable to those of C/LFP113STEG-2. More importantly, the
presence of RGO in LFP113STEGRGO2.5% improves the electrochemical properties (163 mAh/g) and the sample has an electrochemistry comparable to that of C/LFP113STEG-2, (168 mAh/g) both at 0.10C. It is very important to mention that in order to obtain a C/LFP with good electrochemical properties, a 15% w/w of glucose is necessary as a sacrificial C source and also a pyrolysis process of 10 hours is needed. However, when RGO is used only a 2.5% of RGO is needed and the sample was treated thermally for 3 hours instead of 10, which decreases the cost of this material.

Unfortunately, we did not found the optimal synthesis conditions that could lead to a LFP/PPy hybrid material with improved electrochemical properties with respect to C-coated LFP. TEM images show that the PPy coating is not homogeneous, which can be detrimental to obtain an excellent electrochemical performance. The electrochemical characteristics, specifically those extracted from the CV, agree perfectly well with those of LFP. Unfortunately, the rate capability and the polarization of this cell are not optimal. The maximum capacity of this sample is 158 mAh/g at 0.10C but only 23 mAh/g at 10C. However the cell with LFP113STEGPPy2.5% electrode shows an excellent stability at 1C. After 100 cycles the capacity of this sample was practically the same. We can conclude for the analysis of this sample that there is room for improvement and optimization of the LFP113STEGPPy-hyrid.
4.6. References


5 LFP synthesis by reflux and their hybrids
5.1 Overview

LFP suffers intrinsic limitations concerning low electronic conductivity and slow lithium ion diffusion rate across the LiFePO$_4$/FePO$_4$ interface. As we have discussed before, low electronic conductivity can be overcome with carbon-coating or hybridization with conducting polymers, RGO, etc. One approach to improve lithium diffusivity is to control the size and morphology of LFP particles$^{1,2}$. This chapter includes our efforts with an alternative synthesis procedure for the isolation of nanosized LFP particles with a morphology clearly departing from what has been described so far.

On the other hand, nanometer-sized particles lead to electrodes suffering an intrinsic limitation concerning tap density, which will affect commercial applications, due to the unique properties of nanoparticles possessing large surface area and low volumetric density$^{3,4}$. Based on these demands, a control of morphology with the crystal structure of the electrode material in mind might be a promising strategy to solve these problems and thereby simultaneously satisfy the requirements of improved tap-density and shortened lithium ion diffusion path length.

Reports on the addition of structure-directing agents or templates to produce LiFePO$_4$ cathodes with specific morphologies that favor improved electrode performances are also available$^{5,6}$. However, such procedures may tend to make the synthesis more complicated and/or expensive. On the other hand, the regulation of simple but crucial parameters such as precursors, sequence of precursor addition, precursor concentrations, solvents, reaction temperature and reaction time also aids in tuning the particle morphology of LiFePO$_4$$^{7,8}$.

Generally, wet-syntheses offer good opportunities to control particle morphologies of nanomaterials at low temperatures provided nucleation and crystal growth processes are monitored and controlled. Among the known solution techniques, hydro/solvothermal and refluxing processes are two of the most promising approaches to obtain morphological tailored nanoparticles$^{9,10}$.

Solvothermal methods can lead to well crystallized products with uniform and small particle sizes. Yet, these methods require high temperature and high pressure reactors which greatly limit the scaling up and the industrialization of LFP production. On the
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

other hand, reflux conditions are more flexible and prone to design and exploitation at industrial scale, although not many reports have appeared in the literature. Thus, we decided to explore the possibilities of these techniques taking advantage of our previous experience with this type of synthesis.$^{11}$

The studies described in this chapter include the use of the reflux method for exploring the synthesis of LFP with different morphologies, and the characterization with special emphasis on the electrochemical properties of the resulting lithium iron phosphate electrode materials. As it will be shown, the reflux approach not only turned out to be simple, but also highly reproducible and cost-effective. For these reactions we used ethylene glycol as solvent, given its capability to dissolve all the reagents but also taking into account its known stabilizing and anti-oxidizing characteristics. Applying this method, we synthesized an LFP material with a novel platelet morphology, which could be used as active cathode material.

We considered that the morphology obtained by this method could be ideal to develop a hybrid integrating LFP and RGO. We will discuss the optimization process to obtain functional LFP/RGO hybrids, we will compare the electrochemical properties of these materials with those of conventional LFP and will discuss the characteristics that make of this material and process good candidates for the development of cathode materials for LiBs.

Finally, we want to note that the samples discussed in this chapter were selected for the formulation of electroactive LFP/RGO nanofluids which will be discussed in chapter 6.

5.2 Synthesis and characterization of LFP prepared by Reflux and its carbon-coated derivative

5.2.1 LFP 111REG Synthesis

Stoichiometric amounts (0.03 mmol each) of, Fe(CO$_2$CO$_2$)$_2$·2H$_2$O (iron oxalate dihydrate) (5.3907 g) 85 %v/v H$_3$PO$_4$ (Phosphoric acid) (2.05 mL) and Li(CH$_3$COO)·2H$_2$O (lithium acetate dihydrate) (3.0606 g) were dissolved in 70 mL of ethylene glycol. The liquid reaction mixture was kept at 70°C until total dissolution of the reactants. The resulting
solution was placed in a round-bottom flask open only at the top, connected to a condenser, and refluxed vigorously for 72 h at 200°C. The final pH of this solution was 8. The resulting greenish-gray solid was filtered-off, washed several times with water and ethanol, and dried overnight at 80°C. We obtained 3.4214 g of powder which represent 92% yield. This sample was subject to a thermal treatment and carbon-coating procedure as described in chapter 2.

5.2.2 Powder XRD characterization

All diffraction patterns can be properly indexed on the orthorhombic olivine LFP crystal structure (space group: Pnma), without detectable impurity phases. Figure 5-1 includes representative patterns for pristine and carbon-coated LFP samples. The peaks of the carbon-coated sample are more intense as it could be expected as a result of the thermal treatment and in both cases Bragg’s reflections are in total agreement with reported LFP patterns. On the other hand, it is important to mention that the relative intensities of the peaks do not agree with any of LFP phases described in the Inorganic Crystal Structure Database, a discrepancy which hinted a possible morphological variation.

Figure 5-1 X-ray diffraction pattern LFP111REG and C/LFP111REG.
5.2.3 TEM analyses. Morphology and electron diffraction

In order to discern the morphology and microstructure of this sample, we carried out Transmission Electron Microscopy (TEM) studies which revealed very thin platelets quite homogeneous in size and shape (Figure 5-2 (a)). The inset of this figure shows an isolated sheet of ca. 150 nm with the plate face corresponding to the bc plane, as confirmed by the Selected Area Electron Diffraction (SAED) pattern. A high resolution image of the squared-shaped platelet shown in the inset was taken (Figure 5-2 (b)) and showed three different lattice distances. This implies an overlap between two different crystals of LFP. Thus, although the crystals are apparently well crystallized, the thin platelets tend to stack together. The SAED pattern shown in Figure 5-2 (c) (also corresponding to the same platelet) reveals that this particle has a zone axis corresponding to [100], indicating that in this specific form, LFP crystals grow faster along the b and c axes leading to platelets with a thin dimension along a. TEM images for the corresponding carbon-coated sample C/LFP111REG are shown in Figure 5-2 (d-f). The coating procedure does not substantially alter the morphology of these particles, although it seems that carbon-coating of the platelets leads to more agglomeration and a less homogeneous particle distribution (Figure 5-2 (d)). The inset of this image shows a single isolated particle of ca. 136 nm. The high-resolution image of this particle clearly showed an amorphous (carbon) coating layer with a thickness of 3 nm, Figure 5-2 (e). The d spacing calculated for this particle was 0.30 nm and corresponds to a (211) Miller index. After indexing the SAED image, Figure 5-2 (f), obtained for this particle of C/LFP111REG we get to the conclusion that this particle has a [100] zone axis, indicating that plates grow easily along the bc plane with slow growth along the a axis.
Chapter 5: LFP synthesis by reflux and their hybrids

5.2.4 Electrochemistry

5.2.4.1 Cyclic Voltammetry

We are going to start with the discussion of the CV. The two cyclic voltammograms shown in
Figure 5-3 (a) were recorded for pristine LiFePO$_4$ (LFP111REG) and for carbon-coated LiFePO$_4$ (C/LFP111REG) at 1mV/s in a three-electrode cell, using Li metal as reference and counter electrode and a commercial (LiPF$_6$/organic carbonates) electrolyte. Both voltammograms show the typical LFP profile, but the carbon-coated sample exhibits a greater intensity and narrower peaks. The exact values of the $E_{pa}$ $E_{pc}$ $I_{pa}$ and $I_{pc}$ are shown in Table 5-1. It was interesting to observe that sample LFP111REG shows a smaller difference between the peaks (0.08 V) compared to C/LFP111REG (0.16V). Also the intensities of the cathodic and anodic peaks are not symmetrical, which might indicate a low coulombic efficiency.

5.2.4.2 Galvanostatic charge-discharge

The analysis of the charge-discharge recorded at different C-rates is presented in Figure 5-3 (b, c and d), the materials were mounted as cathodes in two-electrode cells with metallic Li used as negative electrode. The discharge capacity of the carbon-coated sample at 0.10C was unstable, oscillating between 141 and 133 mAh/g, which is ca. 82% of the theoretical capacity. The stabilization of the discharge capacity was achieved at
0.5C between cycle 12 and 18. At 10C the capacity of this sample was 60 mAh/g, which was 42% of the capacity obtained at 0.10 C, Figure 5-3 (b). LFP111REG sample showed a discharge capacity of 109 mAh/g at 0.10 C, which is 77% of the capacity observed for the carbon-coated sample at 0.10 C. At 10C we obtained 66 mAh/g from this sample which is 60% of the capacity obtained at 0.10 C. We can conclude that this sample shows a relative good cyclability based on the evidence shown in Figure 5-3 (b). Finally, the cycling test was returned to 1C, getting back 92% of the initial capacity obtained at 1C. Figure 5-3 (c) shows the cycling stability of these samples at 1C, as we can find out CLFP111REG does not exhibit a very stable behavior. An interesting observation is that sample LFP111REG shows better cyclability, rate capability and stability. The pristine sample shows a better stability, with a discharge capacity between 72 and 63 mAh/g. As we can observe in Figure 5-3 (d) CLFP111REG show signs of a poor coulombic efficiency, especially at high C-Rates. The good news about the behavior of the carbon coating sample is that this cell does not show large polarization, which can be attributed to a good conductivity of the carbon material. This can be observed in Figure 5-3 (d) when we examine the charge-discharge profile.
5.2.5 Surface and Chemical Characterization

Although carbon-coating improved the capacity of LFP, it did so to a lesser extent that could be expected. In order to understand the disappointing electrochemical performance of the C/LFP111REG sample, we studied the surface properties of these materials, by Raman, XPS and chemical analysis, with an eye on the quality of the carbon layer.

The first step was to find out the quantity of carbon in the coated sample, which is important to understand the electrochemical performance. The amount of carbon in this sample was determined to be 2.8 % using elemental analysis. Other elements detected by this technique were N, S, and H; this sample has less than 0.1% of each of these elements.

Let us continue with the discussion of the Raman spectra. The PO$_4$ band was detected at 958 cm$^{-1}$, in an uncoated sample with the typical D and G bands from carbon absent. In the carbon-coated sample PO$_4$ band was not observed due to the prominent presence of carbon D and G bands, which were located at 1352 and 1592 cm$^{-1}$ respectively. The intensity ratio ($I_D/I_G$) in this case was 0.87, Figure 5-4 (a). Both the values of Raman shifts and the intensity ratio are very similar to other carbon-coated samples described in previous chapters which rules out the quality of the carbon-coating as the major factor in limiting the capacity of these sample at high C rates.

Finally, we will conclude the studies of carbon coating and surface analysis with the analysis of XPS data. Figure 5-4 (b) displays the XPS narrow spectra of the Fe 2p of pristine and c-coated LFP. This figure clearly shows two peaks at 724.09 and 711.0 eV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Epa (V)</th>
<th>Ipa (mA)</th>
<th>OPC (V)</th>
<th>Epc (V)</th>
<th>Ipc (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113STEG</td>
<td>3.45</td>
<td>0.157</td>
<td>3.28</td>
<td>3.37</td>
<td>-0.137</td>
</tr>
<tr>
<td>C/LFP113STEG</td>
<td>3.51</td>
<td>0.475</td>
<td>3.26</td>
<td>3.35</td>
<td>-0.341</td>
</tr>
</tbody>
</table>
The double-peak shape assumes a symmetrical linear Gaussian distribution. The peak at 724.09 eV corresponds to Fe\(^{2+}\)(2p\(^{3/2}\)), while the other corresponds to Fe\(^{2+}\)(2p\(^{1/2}\)). The fitted and experimental curves do not superimpose well, which indicates that a few Fe\(^{3+}\) ions exist. By analyzing the fitted result, two weak peaks at 714.6 eV and 726.5 eV can clearly be seen. The peak at 714.6 eV corresponds to Fe\(^{3+}\)(2p\(^{3/2}\)), while the other peak corresponds to Fe\(^{3+}\)(2p\(^{1/2}\)). In this case, it is very important to notice that the pristine sample also shows a similar profile in the XPS spectra, meaning that the Fe \(\text{III}\) was present before the thermal treatment. The core XPS spectrum carbon, Figure 5-4 (c) shows that the carbon obtained by this method presents three major contributions: C-C bond at 284.8 eV, C-O-C bond at 285.7 eV and C=O bond at 289.0 eV. The D parameter is calculated using the first derivative of the carbon Auger peak as explained in chapter 3 section 6, the value of the D parameter for this sample was 16 eV, which indicates one third of sp\(^{2}\) carbon. We should remember that the D parameter of diamond is 13 eV and the D parameter of graphite is 20 eV\(^{14}\). This fraction could contribute to a sizeable conductivity and is similar to that estimated for our other c-coated samples described in earlier chapters. Therefore, these XPS results support Raman in concluding that the nature and quality of the carbon coating in this particular sample is not substantially lower to those reported in previous chapters.
Rietveld refinement

The studies presented so far (Raman, XPS) have dealt with the nature of carbon (coated) on our LFP sample but have not been able to correlate the relatively poor electrochemical performance of our electrode materials with the chemical nature of the carbon coating. Therefore, we decided to pursue further studies on the nature of LFP nanoplatelets in order to find correlations. In particular, we performed Rietveld refinements of coated and pristine LFP in order to detect preferential orientation and confirm the morphology of the platelets by indexing the platelet face. It is well known that Li$^+$ ion diffusion in LFP is quite anisotropic, taking place more easily along the [010] b axis and therefore platelet faces corresponding to the ac plane would be optimal.

We carried out powder XRD measurements both with a capillary tube (in order to avoid preferential orientation) and letting the particles settle on a flat sample holder (in order to foster preferential orientation). The Rietveld Refinements using the Pnma space group provided acceptable fitting base on the $\chi^2$ factor of 2.2 for “capillary” and 3.5 for
“preferential”. Atomic positions in the crystal structure of LFP are well known and therefore were fixed and not refined. The lattice parameter obtained for LFP111REG “preferential” were \(a=10.28\ \text{Å}, \ b=5.98\ \text{Å}, \ c=4.70\ \text{Å}\), and a volume of \(289\ \text{Å}^3\) in good agreement with the values reported in the literature\(^{15}\). The crystallite size of LFP111REG was 57 nm, this value was obtained using the peak at \(2\theta = 30^\circ\) and the Scherrer equation. The preferential analysis led to essentially identical parameters \(a=10.26\ \text{Å}, \ b=5.96\ \text{Å}, \ c=4.69\ \text{Å}\) and a volume \(288\ \text{Å}^3\), the crystallite size of C/LFP111REG was 53 nm using the same peak at \(2\theta = 30^\circ\).

Figure 5-5 (a) shows the results of the Rietveld refinement for LFP111REG “preferential”. As we can see the Bragg’s reflections agree with the peaks of LFP. The difference in intensity between the calculated and the experimental pattern in the case of the reflexions at 27° and 32° are very prominent. It is known that the intensity of the peaks can be modified due to preferential orientation. Preferred crystallographic orientation produces a non-random distribution in the orientation of the crystallites, and the intensity of the peaks will vary systematically. Based on that observation, we decided to use the equations available in FullProf to model the preferred orientation. Using this equation, we conclude that these particles have a preferred orientation, layer habit. Figure 5-5 (b) compares the XRD pattern obtained with a “capillary” and the XRD pattern obtained by the “preferential” method. Kanamura et al.\(^{16}\) suggested that if the ratio of \(I(020)/I(200)\) is greater than that of the standard reference (in our case the “capillary”), platelet-type structures with preferential direction along the ac facet would be seen. Larger stabilization energy of growth units means faster growth rate along the direction. The combination energies of growth units of (200) and (020) faces are similar\(^{17}\). However, Dokko and col found that the pH can affect the facet of LFP crystals due to change in the binding energies of the (200) and (020) faces\(^{16,18}\). In our case we observe a different situation. In fact, the \(I(020)/I(200)\) ratio of “preferential” and “capillary” experiments are 2.1 and 3.0, respectively, implying preferential orientation of bc-plane platelets.
The same analysis was carried out for the carbon-coated sample (C/LFP111REG). The goodness of fit parameter $\chi^2$ (5.08) of this analysis shows that this fitting is acceptable. The lattice parameter obtained for C/LFP111REG “capillary” were $a=10.32\ \text{Å}$, $b=6.00\ \text{Å}$, $c=4.69\ \text{Å}$, and a volume of $291\ \text{Å}^3$ in good agreement with the values reported in the literature\textsuperscript{15}. The crystallite size of C/LFP111REG “capillary” was 46 nm, this value was obtained using the peak at $2\theta = 30^\circ$ and the Scherrer equation. The carbon-coated “preferential” sample led to essentially identical parameters $a= 10.31\ \text{Å}$, $b= 6.00\ \text{Å}$, $c= 4.69\ \text{Å}$ and a volume $290\ \text{Å}^3$, the crystallite size of C/LFP111REG “preferential” was 54 nm using the same peak at $2\theta = 30\ ^\circ$. The value of the $\chi^2$ was 6.6, with indicate an acceptable fitting. In this case, the Rietveld refinement also shows a big difference between the intensity of the experimental and the calculated pattern. The difference of the intensity calculated and the experimental intensity of the peak at 30 and 25° are very prominent, this is an indication of preferential orientation. Using the equations available to calculate the theoretical pattern, we conclude that this sample has a preferential orientation in a layer habit. The ratio of $I(020)/I(200)$ in the case of the “capillary” experiment was 2.6 and in the case of “preferential” experiment was 1.6. Thus, we can conclude that this sample also has a preferred orientation of the plane $bc$ platelets, Figure 5-6.
Figure 5-6 (a) Results of the Rietveld refinement of C/LFP111REG “preferential” xrd pattern. (b) Comparison between the XRD pattern of LFP111REG “capillary” and “preferential” orientation.

5.2.7 Morphology evolution and formation mechanism

To understand the formation mechanism of LFP, powder XRD patterns (Figure 5-7) and TEM (Figure 5-8) images were taken for intermediate stages of the reflux reaction mixture (solid samples collected after 2, 12, 24 and 48 h).

Figure 5- (a) shows the diffraction pattern corresponding to a solid collected right after the 70ºC pre-treatment of the reaction mixture. The precursors iron oxalate and lithium acetate were detected together with some Fe(II)3(PO4)2. After 2 hours of reflux at 200ºC a second sample was collected, the solid present filtered-off, washed and dried. The corresponding pattern is shown in Figure 5-7 (b) and corresponds to a mixture of the same compounds just mentioned plus a small amount of LFP already formed. Figure 5-7 (c) corresponds to the solid collected after 12h and shows already essentially pure LFP. Similarly, Figure 5-7 (d,e,f) correspond to samples after 24h, 48h and 72h respectively. The patterns are all essentially identical and corresponding to LiFePO4 with no impurities detected. However, as it will be shown below, different reaction times led to different microcrystal morphologies. The evolution of those was followed by TEM microscopy.
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

Figure 5-7 XRD patterns of at (a) 0 hrs (b) 2 hrs (c) 12 hrs (d) 24 hrs (e) 48 hrs (f) 72 hrs of the collected samples.

Figure 5-8 (a) shows a TEM image of the solid collected at 70ºC, corresponding to the initial state of the reaction solution (t=0). These particles are quite heterogeneous elongated plates of different sizes. The particles shown in this figure contained Fe, P and O, as analyzed by EDS and therefore must correspond to the iron(II) phosphate detected by XRD, resulting from the reaction between iron oxalate and phosphoric acid during the first stage of the reaction.

As we can observe in Figure 5- (b) after two hours of reflux the sample is still heterogeneous, formed by rods, platelets, and even spherical particles. A careful observation of this and other images of this sample indicates that agglomerated rod particles are most abundant. An EDS of the particles shown in this figure reveals that they contain Fe, O, and possibly C (interference from the grid) and therefore they could correspond to iron oxalate in accordance with XRD analyses.

The sample collected after twelve hours, Figure 5- (c), shows agglomerates, and it is difficult to discern individual particles. EDS and XRD pattern show that LFP was finally synthesized, without impurities, but the morphology is not well defined.
After twenty-four hours, the particles have grown with respect to the twelve hours sample and look different to the previous stages Figure 5- (d). No regular shape can be described for the particles at this time. EDS detects C, O, P and Fe, confirming LFP formation in combination with the XRD data.

We found that after forty-eight hours of reflux Figure 5- (e) almost all the particles observed have a plate morphology, and they are thinner and less agglomerated than before. Finally, at seventy-two hours Figure 5- (f) we can observe that the particles present their final platelet shape and are very thin. The PXRD pattern confirms that we synthesized LFP with platelet shape.

Figure 5-8 TEM images at (a) time 0 (b) 2 hours (c) 12 hours (d) 24 hours (e) 48 hours and (f) 72 hours of the collected samples.

In the final part of this section we will propose an overall picture for the growth of LFP in the form of platelets as described above. First of all, we should realize that Ethylene Glycol not only plays a role as solvent but also appears to work as a capping agent with the characteristic effect of a soft template directing the growth of the particles in preferred directions. Furthermore, we have only detected Fe(II) phases during the
intermediate stages of the reaction, thus, confirming the proposed effect of EG as an anti-oxidant component.\textsuperscript{20}

The growth of LFP platelets doesn’t seem to follow a straightforward path. In Scheme 5-1 we present a plausible sequence of the process beginning with the formation of nuclei (in principle Fe(II) phosphate intermediate) the reaction with Li to grow LFP after just 2h, a reaction apparently complete after 12 hours and then recrystallization (12-48h) and crystal growth processes (possibly including a final Ostwald ripening stage leading to the final large platelet morphology for LiFePO$_4$.

![Scheme 5-1 Schematic illustration of the LFP crystal formation under the refluxing method.](image)

5.3 LFP-RGO hybrid material

5.3.1 Synthesis of a series of LFP113REGRGOx\% (x=1, 2.5 and 5)

RGO-LFP samples were prepared by reflux method. Different amounts of RGO were used (0.0400g, 0.0979g and 0.2000g of RGO) in order to obtain samples with 1\% RGO, 2.5\% RGO and 5\% RGO respectively. As an example, 0.0978g of RGO were added to 70 ml of
ethylene glycol and heated at 70°C for 15 minutes. Stoichiometric amounts (0.03 mol) of, Fe(CO₂CO₂)·2H₂O (iron oxalate dihydrate) (5.3968g), 85% v/v H₃PO₄ (phosphoric acid) (2.01mL) and Li(CH₃COO)·H₂O (lithium acetate hydrate) (3.0920g) were dissolved in 70 ml of ethylene glycol. The resulting liquid reaction mixture was placed in a round-bottom flask open only at the top. This flask was connected to a condenser and refluxed vigorously for 72 h at 200 ºC. After cooling down to room temperature, the resulting LFP pale-green powder was filtered-off and washed with deionized water and ethanol before being dried at 80 ºC in a vacuum oven overnight. The final pH of this solution was 5 and we obtained 3.6214 g of powder which represent 96% yield. See chapter 2 section for sintering details.

5.3.2 Powder XRD pattern and Rietveld refinement

Figure 5-7 (a) shows the powder X-ray diffraction pattern of the hybrids obtained by the synthesis method describe above. As we can see no impurities were detected by this method. The crystal phase detected for the three samples prepared agreed with the LFP diffraction pattern reported in the literature. Based on that observation, we can conclude that the addition of RGO during this synthesis method does not affect the crystal phase formation.

The Rietveld refinement of sample LFP111REGRGO5% shows that there is not systematic difference between the calculated XRD pattern and the experimental pattern. To be more precise the Rietveld refinement seems to indicate that the addition of RGO counteracts and contributes to eliminate the preferred crystal orientation. Crystallite size of this sample is 40 nm, this number was obtained using the Scherrer equation and the peak 020. Unit cell parameters are a= 10.35 Å b= 6.02 Å c= 4.70 Å and V= 291.48 Å, these results confirmed that we obtain LFP with an olivine structure in the presence of RGO. Considering the 2D structure of graphene a “face to face” contact between the graphene sheets and the supported important properties of graphene²¹.
5.3.3 Electrochemical performance

Figure 5-8 (a) shows the CV at 1 mV/s, the profile corresponds to a LFP111REGRGO5% active material. The redox peaks are symmetric and well defined with an oxidation wave centered at 3.6 V and the reduction wave at 3.3 V. The electrochemical characteristics of all samples LFP111REGRGOx% are summarized in Table 5-2.

Charge and discharge curves (Figure 5-8 (b)) show the typical plateau for LFP at about 3.45 V. These curves also show a large polarization at fast C rates, especially at 5C and 10C. The maximum capacity of 168 mAh/g (measured at 0.10C rate) is essentially 100% of the theoretical capacity. The minimum capacity obtained for this sample was 80 mAh/g (at 10 C), this is a 47% of the theoretical capacity. The polarization between the charge and discharge plots (average charge–discharge potential) is about 0.06, 0.1, 0.13, 0.32 and 0.41 V at rates of 0.1, 0.25, 1C, 5C and 10 C respectively. This sample shows a larger polarization than the one with carbon coating, however, it is appropriate to remark that these values are lower that other polarization values reported in the literature for LFP/RGO composites\textsuperscript{22}. This polarization could be an effect of the capacitive behavior of RGO.

Figure 5-8 (c) shows rate capability measurements by cycling the cell at increasingly fast rates, beginning at 0.10 C, up to 10 C and then going back to 1C charge/discharge. The discharge capacity obtained was almost the same initially obtained at 1C and the
performance was stable for at least 100 cycles Figure 5-8 (d). These data indicate of a good rate capability and cycling performance.

The next step is to discuss how the amount of RGO affects the electrochemical performance of the LFP. We can determine that indeed the amount of RGO is critical for the good performance of LFP. Too small amounts of RGO might not provide enough conductive network to the material. The sample with 1% w/w of RGO shows a maximum discharge capacity of 160 mAh/g at 0.10C and minimum capacity of 20 mAh/g at 10C. Figure 5-8 (e) shows the rate capability plot of this sample, as we can see this sample does not show a stable rate capability especially at high C-rates, the capacity decreases dramatically at these rates. The sample with 2.5 w/w of RGO have a maximum discharge capacity of 170 mAh/g at 0.10C and minimum capacity of 40 mAh/g. Although, the stability shows by this sample is very poor. Figure 5-8 (f) shows that maximum discharge capacity at 0.10C. The discharge capacity increase when 2.5% and 5% of RGO was used in the synthesis process. The high initial coulombic efficiency and the increase in the specific capacity with RGO content suggest that RGO particles contribute to electrochemical performance, through the capacitive phenomena storage in the LFP/RGO hybrid system.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Epa (V)</th>
<th>Ipa (mA)</th>
<th>OPC (V)</th>
<th>Epc (V)</th>
<th>Ipc (mA)</th>
<th>Discharge capacity (mAh/g) at 1C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP113STEGRGO5%</td>
<td>3.57</td>
<td>1</td>
<td>3.28</td>
<td>3.37</td>
<td>-0.9</td>
<td>122</td>
</tr>
<tr>
<td>LFP113STEGRGO2.5%</td>
<td>3.59</td>
<td>0.8</td>
<td>3.35</td>
<td>3.33</td>
<td>-0.6</td>
<td>116</td>
</tr>
<tr>
<td>LFP113STEGRGO1%</td>
<td>3.60</td>
<td>0.6</td>
<td>3.39</td>
<td>3.28</td>
<td>-0.6</td>
<td>95</td>
</tr>
</tbody>
</table>
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

Figure 5-8 (a) Cyclic Voltammetry at 1 mV/s (b) Rate capability (c) Discharge cycle stability at 1C (d) Charge-discharge curve at different c rates of RGO/LFP. (e) Rate capability of RGO/LFP (f) discharge capacity at 3 different c rate of samples with 5%, 2.5% and 1% of RGO.

5.3.4 Morphology of the LFP11REGRGO5%

Figure 5-9 gathers several photographs from various electron microscopy techniques. First, a TEM image of LFP11REGRGO5% hybrid shows the aspect of a layer of RGO supporting two nanoparticles of LiFePO4 (Figure 5-11a). RGO can be easily identified as...
a thin layer in the image; however the identification of LFP particles required a more
detailed study by STEM (Figure 5-11 b) and by EDS. Thus, the EDS analyses of the bright
spots observed in the STEM image unambiguously confirm that those two particles are
LFP.

High magnification HRTEM images were difficult to get because the sample was
frequently affected by the electron beam. However, Figure 5-11 c corresponds to one
such HRTEM image of the sample and allowed us to measure a \( d \) spacing (0.35 nm,
corresponding to 111) in agreement with the JCPDS card 83-2091. The SAED pattern for
this sample (Figure 5-11 d) shows diffuse rings that are characteristic of RGO, but well-
defined dots corresponding to an LFP crystal can also be detected. We conclude through
the analysis of the SAED image that the pattern observed correspond to 200 Miller
index. The information obtained by this technique is in agreement with the XRD data.

These images and results help us in understanding how the electrochemical
performance of LFP can be substantially improved by integration of RGO and LFP in a
single hybrid electrode, thanks to the close interaction between the active material (LFP)
and RGO. Furthermore, the confinement of this active material by the graphene
network could effectively suppress the excessive growth and aggregation of LFP crystals,
thus enhancing the rate capability and electrode stability against cycling.
Figure 5-9 (a) TEM (b) STEM (c) HRTEM (d) SAED images of LFP111REGRGO5% showing diffuse rings from RGO and weak but well-defined spots (200) corresponding to LFP. The bright spots observed in the STEM image (b) correspond to LFP particles grown onto RGO as shown in the TEM image (a).

5.3.5 LFP-RGO chemical composition and carbon characterization

The chemical composition of the hybrid was studied by Raman and XPS techniques, we also determined the amount of carbon in the hybrid by chemical analysis. The carbon amounts in the various LFP/RGO hybrid composites were 5%, 2.6% and 1.1%. This same analysis gives us the amount of H, N and S in these samples, which turned out to be less than 0.1% of each element in all cases.

As an example, we are going to discuss the Raman spectrum of sample LFP111REG5 %, Figure 5-10 (a). We have fitted the Raman intensity profile using four Gaussian lines, and have estimated intensity ratios I_D/I_G and I_sp2/I_sp3 = (I_{1350} + I_{1600}) / (I_{1220} + I_{1530}). For the LFP111REGRGOS5% sample, we found values for I_D/I_G ≈1.2 and I_sp2/I_sp3 ≈2.3. As we
mentioned in chapter 4 the amount of sp² carbon are characteristic of a carbon material with a good electronic conductivity. The same analysis of Raman intensity ratios conducted for pure RGO led to values of 1.0 for I_D/I_G in the reaction mixture.

XPS measurement allows differentiation of oxidation states of iron in LFP. The Fe core spectra shown in Figure 5-10 (b) Correspond to a typical Fe II, once again the RGO does not cause any negative influence on the LFP crystal formation, in good agreement with the literature.

![Figure 5-10](image)

**Figure 5-10 (a) Deconvolution of the G and D bands (b) Fe core spectra of LFP111REG5%**

### 5.3.6 Surface area and pore dimensions

The nitrogen adsorption-deadsorption analysis was carried out to investigate the porosity of LFP111REGREGO5%. The results of the corresponding BET analysis are shown in Figure 5-11 (a). The isotherm can be described as a type II with hysteresis loop, which indicates the slit-shaped pores in the hybrid. According to BET method, the surface area of this sample is 33.04 m²/g. The pore size distribution according BJH analysis, Figure 5-11 (b), indicates that the size of pores is mainly between 15 and 100 Å, with a pore volume of 0.21 cm³/g. The surface area of this sample is almost double of the sample reported in chapter 3 section 5 (Table 3-3), which can be correlated with its improved electrochemical performance.
5.4 Final Remarks

We successfully used a reflux synthetic method to produce LFP with an unusual morphology. This method was also employed to synthesize an LFP/RGO hybrid composite. LFP particles showed a novel thin plate morphology which we judged well-suited to prepare an LFP/RGO hybrid composite. It is important to notice here that this synthetic route produces almost 3.6 g of LFP without any impurity detectable by XRD. This can reduce the price of industrial LFP production and boost the LIB’s industry.

Unfortunately, the electrochemical performance of pristine and carbon-coated LFP111REG samples did not show an optimal electrochemical performance. Our first thought was that the thermal treatment did not work as we expected. However, we confirmed that the carbon coating formed on the LFP materials described in this chapter has a similar quality as that of the materials discussed in previous chapters. This led us to analyze in more detail the crystal faces of the platelets in order to correlate their indices with the paths of optimal diffusion of Li ions.

We indexed the platelet faces with electron diffraction and used Rietveld refinements to confirm these results by analysis of preferential orientation. In both cases the platelet faces correspond to the \textit{bc} plane which is detrimental for an optimal diffusion of Li, which is known to take place along the \textit{b} direction. In order to modify this crystal growth several approaches are possible, including the use of different capping agents, changing the order of aggregation of reagents or using specific surfactants\textsuperscript{25}.
As a matter of fact, we found out that also the use of RGO for the production of a hybrid LFP/RGO electrode leads to a different crystallization of LFP. In addition, it should be mentioned that EG can enhance the interaction between LFP crystals and graphene sheets by building up a robust hydrogen bond network between EG and RGO, which effectively helps in trapping the free ions during the crystallization of LFP.

Finally, in the case of the LFP111REGRGO hybrid composites, we found that 5% of RGO is the optimal amount of additive in order to get a good electrochemical performance. This sample shows an excellent coulombic efficiency and good rate capability, but also shows a relatively high charge-discharge polarization. This polarization seems to be correlated with the amount of RGO used in each of these hybrid composites. In the case of this sample no preferential orientation was found, confirming a different crystal growth process as a result of the nucleation sites provide by the use of RGO.
5.5 References


Towards LFP nanofluid
6.1 Overview

In all the previous chapters, we have presented our research and development of LFP based electrodes in solid form, which is the conventional way to prepare electrodes for state of the art batteries. In this chapter, we will present our most recent efforts to try to push the boundaries for the delivery of electroactive materials in energy storage devices. We will describe our preliminary work on LFP-based electroactive nanofluids made by dispersion of LFP nanoparticles in electrolytic base fluids.

Nanomaterial dispersions in liquids (nanofluids) constitute a new expanding area in nanotechnology, with applications in energy conversion and storage. The first reports on energy-related nanofluids were focused on their thermal properties for use as Heat Transfer Fluids (HTFs). The development of electroactive nanofluids which could be used for energy storage in flow cells is a much more recent research topic. On the other hand, most of the research on nanofluid conducted during the past decades focused on a single type of nanoparticle as the base for nanofluids. The advancement in nanomaterials has enabled the production of hybrid nanoparticles (nanocomposites) and recently, there is a growing number of researchers working on hybrid nanofluids. However, challenges such as hybrid nanofluids stability, selection of proper hybrid nanoparticles and its complex fabrication process for hybrid nanofluids need to be addressed first.

Our approach has been to use graphene instead of activated carbon as the material providing the electrical percolation effect on the solution. We have recently shown that even at low concentrations of nanocarbons particles, nanofluids can deliver effective charge transfer through the bulk. Thus, a stabilized dispersion of RGO in aqueous sulfuric acid solution can deliver energy storage capacities similar to those of solid electrode supercapacitors (169 F g⁻¹ (RGO)) but working up to much faster rates (from 1 mV s⁻¹ to the highest scan rate of 10 V s⁻¹) in nanofluids. Nanofluids based on RGO offer a method to integrate high energy density solid active materials into redox flow battery system.

RGO nanofluids have been prepared and reported as useful materials with independence of specific applications. Generally, dispersed RGO flakes tend to aggregate and precipitate because of flakes re-stacking. Currently, the chemical modification of graphene through covalent or non-covalent functionalization has been...
widely used to improve its dispersity. RGO must be properly dispersed in electrolytes to be used as a nanofluid. This has been attempted both in aqueous and organic solvents. For example, Xu et al. reported a successful production of stable high-concentration graphene dispersions in low-boiling-point, low-polarity conventional organic solvents by liquid-phase noncovalent exfoliation of graphite assisted using polyethylene (HDPE) as the stabilizer\(^6\). Other example of RGO dispersion, this time in water, is the report of an imidazolium-modified hexa-peri-hexabenzocoronene derivative (HBC-C\(_{11}\)-MIM[Cl]) designed and synthesized as a stabilizer to disperse RGO. The resulting RGO/HBC-C\(_{11}\)-MIM[Cl\(^-\)] hybrid can reach stable concentrations of 5.0 mg mL\(^{-1}\) (RGO) in water\(^7\).

The rechargeable nanofluid technology could become a transformational advancement of redox flow battery concepts, where energy is stored and released through a reversible electrochemical interaction between two different two redox species. Large-scale applications require energy storage systems to be economical, fast in response time and have a long cycle life. Redox flow batteries satisfy most of these requirements, besides having the advantages of being modular in design and tolerant to over-charge and over-discharge. Therefore, redox flow batteries (RFBs) constitute a promising energy storage technology for large-scale applications such as “green grid” and load balancing. However, conventionally RFBs suffer from low energy density due to the limited solubility of the active materials in the electrolyte. These problems could be solved by the semisolid flow batteries. Currently this technology uses surfactant and Ketjen black (and others carbons), which transform the solution into a slurry electrode to be used as an electrochemical flow capacitor (ECF)\(^8\). Solid redox electroactive particles cannot diffuse to the current collector, so a high amount of carbon is need in order to achieve a percolation effect. This large amount of carbon and the use of surfactant are responsible for a high viscosity in the solution which represents a drawback, when is compared with conventional RFBs. A significant increase in viscosity is highly undesirable because any improvement in functional properties could be diminished by increased pumping power penalties, which would reduce the efficiency of the device.

A redox flow lithium battery (RFLB) based on the redox-targeting concept has been reported that stores energy in Li-ion battery materials (LFP) using an approach proposed by Grätzel and collaborators by introducing the concept of shuttle redox molecular
solutions with suitable redox potentials, solubility, stability and kinetics to transfer the charge to solid particles stored in a separate reservoir. Other example based on this shuttle concept is a full flow cell design using suitable pairs of redox mediators (one for each active material) for LiFePO₄ and TiO₂ as part of the catholyte and the anolyte respectively in RFLB. These two examples use the conventional LiPF₆ electrolyte of LIBs.

With complete independence from these works, we conceived the development of a new form of electrode using the LFP materials discussed in the previous chapters. We chose four different LFP samples, namely, pristine LFP (either in the form of platelets or as small nanoparticles). These materials were added to suitable electrolytic base fluids (aqueous Li₂SO₄) and were developed with the intention to use them as part of a novel redox flow cell. Aqueous electrolytes (pH controlled) were selected for simplicity, with high-conductivity and eco-friendly advantages.

This chapter presents the formulation, optimization and electrochemical performance of these electroactive nanofluids as a preliminary step for their application as energy-storage materials in flow cells.

6.2 Experimental procedure

We will first describe the experimental setups and parameters which were common to all the nanofluid materials studied. The preparation and tests of each of them will be described below.

6.2.1 Cyclic Voltammetry

We used a three-electrode cell for these experiments. The electrodes used were Ag/AgCl (3.5 M KCl) as reference electrode and platinum sheet as working and counter electrode (with the counter electrode (1.5 cm²) featuring a larger area than the working electrode (1 cm²)). The experiments were carried out within the voltage range from -0.2 V to 1.2 V vs Ag/AgCl 3.5 M KCl. The samples were tested at different scan rates (5 mV/s to 25 mV/s).
6.2.2 Potentiostatic electrochemical impedance spectroscopy

Potentiostatic electrochemical impedance spectroscopy (PEIS) experiments were carried out over a frequency range of 5000 kHz and 100000 mHz. The voltage of the experiments was 0.1 V vs. Ag/AgCl or 0.9 V vs. Ag/AgCl with an amplitude of 10 mV. Measurements were taken after 10 minutes applying the potential for the PEIS experiment to get a constant current in the system.

6.2.3 Galvanostatic charge discharge tests

A commercial Electrolysis Cell (BASi Bulk), consisting of a 75 mL glass cell container with a porous glass frit of 4-6 μm pore diameter, was used for the charge and discharge tests. The electroactive nanofluid was placed inside the glass frit compartment. The counter electrode nanofluid was contained in the main body of the 75 mL glass cell, in contact with the reference electrode of Ag/AgCl KCl 3.5M. The cell was cycled between -0.2V to 1V vs. Ag/AgCl KCl 3.5M. The dispersion was stirred during the experiment. It is important to mention that we systematically balanced the charge of the working (positive) and counter-electrode volumes. Results for RGO/DABA nanofluid.

6.2.4 Nanofluids preparation

RGO nanofluids were prepared with the addition of diaminobenzoic acid (DABA), combining polar and aromatic moieties, as a stabilizing agent. As a benchmark for comparison with our nanofluids, we prepared also a dispersion of RGO with a more conventional surfactant (Triton-X 100) known to stabilize carbon materials. Finally, we also prepared and tested a more conventional formulation, including a different carbon (Super-P) stabilized with Triton-X 100. The preparation of RGO/DABA, RGO/Triton-X and CSP/Triton-X are described here.

6.2.4.1 Preparation of RGO nanofluid

1M Li$_2$SO$_4$·H$_2$O was used as an electrolyte and dissolve in water. 1 mL of Triton x-100 and different amounts of RGO were added (Table 6-3). Finally, we proceed to sonicate
the dispersion with a probe sonicator for 5 min (20% of maximum power), then this dispersion was sonicated for 30 minutes in an ultrasonicator.

### 6.2.4.2 Preparation of RGO/DABA nanofluids

1M Li₂SO₄·H₂O (3.1973 g dissolved in deionized water in a 25mL volumetric flask) was used as electrolyte. Diamino benzoic acid (DABA) was used as a stabilizer for the dispersion of RGO with different DABA/RGO mass ratios being used (Table 6-2). LiOH·H₂O (100 mg) was added to reduce the acidity of the solution, which ended up with a pH of 7. We sonicated the dispersion with a probe sonicator for 5 minutes (20%) and then in an ultrasonicator for 30 minutes.

### 6.2.4.3 Preparation of CSP/Triton X-100 nanofluid

25 mL of 1M aqueous Li₂SO₄·H₂O was used as electrolyte and 1 mL of Triton x-100 and 6.7 mg of Carbon Super-P (CSP) was added. Finally, we sonicated the dispersion with a probe sonicator for 5 min (20%) and then in an ultrasonicator for 30 minutes. The amount of CSP was chosen based on the optimal mass ratio obtained for the DABA/RGO nanofluid.

### 6.3 Results of the RGO nanofluids

#### 6.3.1 Stabilization

Our first step was to stabilize the RGO dispersions using DABA stabilizing agent. We decided to use diaminobenzoic acid (DABA) as stabilizer because of its aromatic nature and small organic functional groups.

DABA solubility has a strong dependence on pH, with lower solubility in acidic media (Table 6-1) due to the protonation of its carboxylic acid moiety. Therefore, LiOH·H₂O was used in order to adjust the pH at 7. We used lithium hydroxide in order to avoid the presence of other cations in solution. The control of pH is important because it can also affect LFP nanoparticles, which will be added to this electrolyte fluid. Guyomard and
collaborators reported that LFP has an initial pH near 7 in a water dispersion; they concluded that the stability and the electrochemical performance is better when this initial pH is not altered. Also Behera et al. have reported that reduced graphene oxide has a better dispersibility in a pH range of 7 to 11.

Table 6-1 DABA experimental solubility

<table>
<thead>
<tr>
<th>DABA concentration</th>
<th>LiOH.H₂O</th>
<th>pH</th>
<th>DABA Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 g/L</td>
<td>N/A</td>
<td>4</td>
<td>no</td>
</tr>
<tr>
<td>12 g/L</td>
<td>1.6 g/L</td>
<td>6</td>
<td>partially</td>
</tr>
<tr>
<td>12 g/L</td>
<td>2.8 g/L</td>
<td>7</td>
<td>yes</td>
</tr>
<tr>
<td>12 g/L</td>
<td>3.6 g/L</td>
<td>10</td>
<td>yes</td>
</tr>
</tbody>
</table>

Three different DABA/RGO mass ratios were tested: 20/1, 30/1 and 40/1. The details of the volume, pH and mass composition are detailed in Table 6-2. It was obvious that the most stable dispersion was the one with a mass ratio of 40/1 of DABA/RGO. The stabilization of RGO is achieved by a solvated aromatic molecule that holds RGO in suspension by π-π interactions with the ring while providing polarity by the introduction of functional groups. The stability of the 40/1 sample was remarkable remaining 5-6 days dispersed. We noted that a smooth, stirring was effective to prevent the precipitation in these cases.

For comparison, pure RGO was dispersed in the Li₂SO₄ aqueous electrolyte at a nominal concentration of 0.29 g/L. However, at this concentration RGO precipitates immediately, although a grey-colored dispersion was maintained. This means that, although some graphene flakes remain in solution thanks to the polar oxygen groups remaining in the structure of Reduced Graphene Oxide, in the absence of DABA, the solubility limit for RGO is much lower.

It should be noted that, in addition to DABA, we also tested the ability of a conventional surfactant like Triton-X 100 to stabilize our RGO (Table 6-2). However, we did not find an optimal mass ratio of Triton X-100 that could allow us to suitably stabilize the dispersion in order to perform proper electrochemical studies. The poor stability of
these samples might be due to the aliphatic tails of this surfactant preventing its aromatic ring to interact with RGO.

As a benchmark for comparison with our nanofluids just described, we used a nanofluid with a conventional formulation, including a different carbon (Super-P) stabilized with a surfactant (Triton X-100). As shown in Table 6.2, this nanofluid was less stable and began to precipitate just after 2 hours. It is possible that this dispersion has characteristics similar to an emulsion. But the purpose of the experiment was not the optimization of the nanofluids made of Triton X-100 and CSP, we only made a nanofluid of triton and CSP with a concentration equivalent to the nanofluid with optimal concentrations of DABA/RGO. In the cases where Triton X-100 was used the agitation did not prevent the sedimentation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (h)</th>
<th>Opacity/Color</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO (0.29 g/L)</td>
<td>N/A</td>
<td>Translucent grey</td>
<td>immediate</td>
</tr>
<tr>
<td>DABA / RGO (12g/L:0.6g/L) (20:1)</td>
<td>8</td>
<td>Opaque orange</td>
<td>begins at 4 h.</td>
</tr>
<tr>
<td>DABA / RGO (12g/L:0.4g/L) (30:1)</td>
<td>56</td>
<td>Opaque orange</td>
<td>begins at 27 h.</td>
</tr>
<tr>
<td>DABA / RGO (12g/L:0.3g/L) (40/1)</td>
<td>120</td>
<td>Translucent orange</td>
<td>begins at 97 h.</td>
</tr>
<tr>
<td>Triton X-100/RGO (0.100 mL) (1g/L RGO)</td>
<td>0.5</td>
<td>Black</td>
<td>immediate</td>
</tr>
<tr>
<td>Triton X-100/RGO (0.250mL) (1g/L RGO)</td>
<td>2</td>
<td>Black</td>
<td>immediate</td>
</tr>
<tr>
<td>TritonX-100 (0.300 mL) 0.28 g/L of SuperP</td>
<td>5</td>
<td>Black</td>
<td>begins at 2 h</td>
</tr>
</tbody>
</table>

6.3.2 Electrochemistry

The RGO/DABA nanofluid with the optimal DABA/RGO mass ratio (40/1) was selected for electrochemical studies by cyclic voltammetry which will be presented in this section. Pure RGO and pure DABA dispersions in the same Li2SO4 electrolyte were also analyzed for comparison.

Figure 6-1 shows cyclic voltammograms of those three samples together with that of the SuperP/Triton-X sample. The RGO/DABA nanofluid leads to a CV with a much greater current in comparison with DABA (12 g/L) or with pure RGO. As a matter of fact, the
later has been expanded in the inset in order to be able to appreciate its shape (note the different current scales). The RGO dispersion shows a capacitive behavior rather than a faradaic redox process. DABA did not show any clear electrochemical activity beyond two very poorly defined waves. However, when we add RGO the CV profile changes. The addition of RGO leads to the appearance of an oxidation wave at 0.4V vs Ag/AgCl. Thus, RGO seems to promote an irreversible oxidation process of DABA. This effect is associated with the strong interaction between DABA and RGO that enhances charge transfer between them. This strong interaction can increase the effective concentration of RGO in solution. On the other hand, the nanofluid containing carbon Super-P and Triton-X did not show any kind of electroactive signal.

![Graph showing CV of DABA, optimal DABA/RGO (40/1) nanofluid, and Super-P/Triton-X with a mass ratio of 1/40 at 5 mV/s. The inset is a CV of pure RGO nanofluid at 5 mV/s.](image)

Figure 6-1 CV of DABA, the optimal DABA/RGO (40/1) nanofluid and Super-P/Triton X-100 with a mass ratio of 1/40 at 5 mV/s. The inset is a CV of pure RGO nanofluid at 5 mV/s.

### 6.3.3 Rheology

The viscosity of the DABA/RGO (40/1) nanofluid was analysed. The value obtained for this sample at 20°C was 1.02 mPa·s, very close to the tabulated value for water at 20°C. This value means that the incorporation of RGO (0.3g/L) and DABA (12 g/L) does not increase the viscosity of the electrolyte substantially and therefore confirms that DABA/RGO can be used as easy-flowing fluids in flow cells.
6.4 DABA/LFP-RGO

The next section describes the attempts to develop nanofluids using LFP/RGO hybrids as starting solid components. Both LFP small nanoparticles (LFP113STEGRGO20%) as well as LFP nanoplatelets (LFP111REGRGO20%) were used to prepare two different nanofluids based on hybrid solids. The first question that pops up is whether a pre-formed hybrid of LFP and RGO (containing the optimal amount of RGO determined in the previous section) would perform as electroactive nanofluid. RGO was not added to the nanofluid in this new formulation. This section describes the physical-chemical and the electrochemical characterization of these nanofluids.

6.4.1 LFP/RGO synthesis and nanofluid formulation

6.4.1.1 Synthesis of LFP113STEHRGO20%

0.2769 g of RGO (prepared as detailed in appendix 1) was sonicated for 15 minutes in 140 mL of ethylene glycol. In a typical reaction 2.7537g (0.066 moles) of lithium hydroxide monohydrate (LiOH·H2O) was added to 70 mL of a preheated (70 °C) RGO/ethylene glycol suspension and stirred for 10 minutes. In parallel, 6.6714 g (0.0241 moles) of iron sulfate heptahydrate (FeSO4·7H2O) was dissolved in the other half of the RGO/ethylene glycol suspension (70 mL) and stirred for 2 minutes. Then we slowly added 1.65 mL (0.024 moles) 85% phosphoric acid (H3PO4) to the iron sulfate solution using a micropipette, and the resulting solution was stirred for 10 minutes. We then mixed the Li and Fe/PO4 solutions and stirred for 10 more minutes. Finally, the mixture was transferred to a 200 mL hydrothermal reactor (Teflon vessel sealed in a stainless-steel autoclave reactor) and the reactor put in the oven and heated up to 200 °C for 24 h. The solution was filtered-off and washed with deionized water twice and finally with ethanol. The sample was dried in vacuum oven at 80°C overnight. The final pH of this solution was 8 and we obtained 3.7222 g of powder which represents a 97 % yield. The XRD pattern, TEM images and the chemical composition of this sample are discussed in appendix 5.
6.4.1.2 Synthesis LFP111REGRGO20%

This RGO-LFP sample was prepared by the reflux method. As an example, 0.9164 g of RGO was sonicated in 70 mL of ethylene glycol for 15 minutes and heated at 70°C. Stoichiometric amounts (0.03 mol) of Li(CH$_3$COO)·H$_2$O (3.0920g), Fe(COO)$_2$·2H$_2$O (iron oxalate dihydrate) (5.3968) and 85% v/v H$_3$PO$_4$ (phosphoric acid) (2.01mL) were dissolved in 70 ml of RGO/ethylene glycol. The reaction mixture was placed in a round-bottom flask open only at the top. This flask was connected to a condenser and refluxed vigorously for 72 h at 200°C. After cooling down to room temperature, the resulting LFP pale green powder was filtered-off and washed with deionized water and ethanol before being dried at 80°C in a vacuum oven overnight. The final pH of this solution was 5 and we obtained 3.9214 g of powder which represent 98% yield. See appendix 5 for the discussion of the XRD pattern, TEM images and the chemical composition of this sample.

6.4.1.3 Nanofluid formulation

The nanofluid corresponding to this hybrid composition was prepared by dispersing 28 mg of the hybrid material in 1 M of Li$_2$SO$_4$ aqueous electrolyte and 12 g/L DABA. We add 100 mg to control the pH, the pH was around 7. The sonication procedure was described in section 6.2.4.1.

6.4.2 Stability of the nanofluids

The stability of these electroactive nanofluids was tested by a sedimentation method. Table 6-3, shows the permanence in the dispersion of the LFP hybrid of these electroactive nanofluids. The electroactive nanofluids with LFP111REGRGO20% and LFP113STEGRGO20% did show a good stability. These samples show better behavior that the nanofluids with pristine LFP platelets or nanoparticles, Table 6-4. This behavior is a result of a surface modification of the LFP with RGO. RGO is a direct link between LFP and DABA, stabilizing the composite.
Table 6-3 Stability of an electroactive nanofluid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sedimentation Time (h)</th>
<th>Opacity/Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>DABA 12 g/L / 1.4 g/L LFP111REGRGO20%</td>
<td>48</td>
<td>Black</td>
</tr>
<tr>
<td>DABA 12 g/L / 1.4 g/L LFP113STEGRGO20%</td>
<td>44</td>
<td>Black</td>
</tr>
</tbody>
</table>

6.4.3 Electrochemistry

Figure 6-2 (a) shows the CV of the electroactive nanofluid with LFP111REGRGO20% (solid hybrid based on LFP platelets) at different scan rates. At 1 mV/s scan rate, the oxidation wave at 0.37 V vs Ag/AgCl, previously assigned to DABA is very prominent. The intensity of the oxidation wave at 0.62 V vs. Ag/AgCl, assigned to LFP oxidation, is very low. The oxidation wave of DABA can be seen at all scan rates but when the scan rate increases the wave becomes a shoulder. The redox waves corresponding to LFP can be clearly seen at high scan rates. The oxidation peak of LFP can be observed between 0.62 and 0.73 V vs Ag/AgCl, at 1 mV/s and 25 mV/s respectively. The LFP reduction peak (at 25 mV/s) appeared at 0.2 V vs. Ag/AgCl and at 10 mV/s the peak can be seen at 0 V vs. Ag/AgCl. At low scan rates the reduction waves are very broad and is very difficult to identify the Eap.

Figure 6-2 (b) shows the CVs of the sample with LFP113STEGRGO20% (hybrid made from LFP small nanoparticles). In this case the oxidation peak of LFP appears at 0.7 V vs. Ag/AgCl (at low scan rates). The intensity of this LFP oxidation peak is small as compared to the oxidation peak of DABA (0.37V vs. Ag/AgCl). The intensity of the LFP reduction peak is very small and at fast scan rate is very broad. At slow scan rate (between 1 and 10 mV/s) the LFP reduction peak is well defined around 0.2 V vs. Ag/AgCl.

The preponderance of DABA at high scan rates and the low intensity recorded for the LFP waves, are not optimal characteristics for an LFP nanofluid. TEM images of the LFP composites (appendix 5) show that the LFP particles in both hybrid cases (LFP nanoparticles or platelets) are anchored to the RGO and therefore part of LFP active area is blocked by RGO. This, plus the fact that the free movement of LFP particles is limited in the fluid when preformed hybrids are dispersed are factors against the practical application of these pre-formed hybrid materials in nanofluids.
Alternative approaches for the fabrication of the electrodes based on LiFePO₄ as cathodes in LIBs

6.5 DABA/RGO/LFP nanofluid

6.5.1 Preparation of nanofluids

These nanofluids were made using the optimal composition of the base fluid with DABA/RGO (40/1). We proceeded to add different amounts of LFP113STEGRG-2 or LFP111REG to the base fluid to make a 25 mL of the new electroactive nanofluid. The mixture was sonicated with a probe sonicator for 5 min (20% of maximum power) and then with an ultrasonicator for 30 minutes (see Table 6-4 for details).

6.5.2 Stability

This section describes the stability of different nanofluids that contain either LFP platelets or LFP nanoparticles both dispersed in the DABA-RGO (40/1). The stability was tested by sedimentation of the samples with different concentrations of the LFP samples mentioned above.

Table 6-4 collects the results of sedimentation tests for the various nanofluids. Nanofluids with 0.4 g/L of LFP were the most stable both in the case of nanoparticles or platelets. Samples containing 1g/L and 1.4g/L mg of LFP exhibit a stability of ca. 24 h, that can be considered good enough to develop a nanofluid. Unfortunately, samples with 2g/L of LFP did not show a good stability. These observations are valid for both types of LFP particles. Depending on the LFP particle concentration the stability of the
sample is compromised. The addition of LFP eventually leads to the coprecipitation of LFP and RGO. We also observe during the experiments that stirring the dispersion prevents the precipitation in all cases. It can noted that the stability of the platelet nanofluid is a little bit higher than that of the nanoparticles nanofluid. This could be a consequence of the morphology and a better contact between the RGO and the platelets.
### Table 6-4 Results of sedimentation experiments for the nanofluids with pristine LFP (1M of Li$_2$SO$_4$H$_2$O, pH 7)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sedimentation Time (h)</th>
<th>Opacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>DABA / RGO (40:1)/ 0.4g/L LFP111REG</td>
<td>38</td>
<td>Brown color</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 1.0g/L LFP111REG</td>
<td>Around 24</td>
<td>Almost black</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 1.4g/L LFP111REG</td>
<td>Around 24</td>
<td>Almost black</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 2.0g/L LFP111REG</td>
<td>More than 12 less than 24</td>
<td>Black</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 0.4g/L LFP113STEG-2</td>
<td>36</td>
<td>Brown color</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 1.0g/L LFP113STEG-2</td>
<td>24</td>
<td>Almost black</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 1.4g/L LFPSTEG-2</td>
<td>24</td>
<td>Almost black</td>
</tr>
<tr>
<td>DABA / RGO (40:1)/ 2.0g/L LFP113STEG-2</td>
<td>More than 12 less than 24</td>
<td>Black</td>
</tr>
</tbody>
</table>
6.5.3 Rheology

The viscosity recorded for LFP113STEG-2 and LFP11REG nanofluids were 1.7 and 1.6 mPa·s respectively, at 20.1°C with a shear rate of 2880 s⁻¹. The viscosity of these materials is higher than that of water or the DABA/RGO base nanofluid (1.02mPa·s). The addition of the nanoparticles increases the viscosity of the nanofluid. But the viscosity of these samples is still low enough to be used as fluids in flow cells.

6.5.4 Electrochemistry

6.5.4.1 DABA/RGO/LFP111REG

Figure 6-3(a) shows the CVs of the four nanofluids prepared with different concentration of LFP 111REG. The sample with 0.4 g/L shows an irreversible oxidation wave at 0.37 V vs Ag/AgCl, associated to DABA. This nanofluid does not show any other waves, in particular no LFP waves were detected. Samples with 1g/L, 1.4 g/L, 2 g/L of LFP show two reversible peaks at 0.3 V and 0.65V vs. Ag/AgCl, which are the result of the well-known oxidation and reduction of Fe in LFP. The oxidation wave assigned to DABA was detected around 0.35 V vs. Ag/AgCl. Among these samples, the dispersion that contains 1.4g/L of LFP111REG shows the highest current intensity and better defined peaks. This is probably a result of the combination of high concentration and sufficient stability of the nanofluid. We proceeded therefore to explore in more detail the electrochemistry of nanofluids with and 1.4 g/L of LFP by measuring CVs at different scan rates and collecting and analyzing PEIS data.

Figure 6-3 (b) shows CVs of the sample with 1.4g/L of LFP111REG at different scan rates. The peak at 0.35 V vs. Ag/AgCl corresponding to DABA is most apparent at low scan rates but is barely detectable as a shoulder as the scan rate is increased up to 25 mV/s due to the increase of the waves corresponding to LFP. Indeed, the intensity of the waves between 0.7 V vs. Ag/AgCl (scan rate 25 mV/s) and 0.6 V vs. Ag/AgCl (scan rate 1 mV/s), assigned to LFP, increases as the scan rate is increased. These redox peaks associated with LFP have a symmetric current intensity. It should be noted that the order for recording these CVs was from fastest to slowest. Thus, the disappearance of the DABA signal cannot be due to full consumption of the chemical.
Our final electrochemical study of these samples was the PEIS, Figure 6-3 (c) (d). The impedance study of the system with 1.4 g/L LFP showed semicircles, related to charge transfer. PEIS spectra were recorded at two different potentials, namely 0.0 V and 0.9 V vs Ag/AgCl, corresponding to potentials with LFP reduced and oxidized, respectively. The spectrum at 0.9 showed a larger semicircle in the Nyquist plot (Figure 6-2 c), implying a larger charge transfer resistance. This means that the Li$^+$ de intercalation process (oxidation of LFP) presents a greater resistance than the corresponding intercalation process (reduction).

The inclined line in the low frequency represented the Warburg impedance ($Z_w$), which was associated with lithium-ion diffusion of the material. This process is associated with a mass transfer control.

The results fit with the Randles equivalent circuit (inset Figure 6-3 (d)) typical for a simple electrochemical process. In this equivalent circuit, there is a resistance associated with the electrolyte and the external circuit, which in the Nyquist plot correspond with the point in the real axes where the semicircle star. This point is the same for the oxidation and reduction process of the sample, the value of this resistance is negligible.

We also noted that the semicircles appear distorted due to the aleatory nature of the electrical contact between RGO layers providing charge to the LiFePO$_4$ nanosheets in the dispersion.
Figure 6-3 (a) CV at 5 mV/s of 0.4 g/L, 1 g/L, 1.4 g/L, 2 g/L of LFP (DABA-RGO (1:40)) (b) Cyclic Voltammetry at different scan rate, 1.4 g/L of LFP inset CV of 1g/L LFP in DABA/RGO (40/1) (C) PEIS of 1.4 g/L of LFP in DABA/RGO (40/1)

6.5.4.2 DABA/RGO/LFP113STEGRGO

Figure 6-4 (a) shows Cyclic Voltammograms of the nanofluids with different amounts of LFP113STEG-2 in a base fluid of DABA/RGO (40/1) prepared as described above. The
characteristic LFP waves at 0.61 V and 0.31 V vs Ag/AgCl are detected in all cases. On the other hand, the DABA oxidation peak (0.40V vs. Ag/AgCl) is only apparent and well defined when the concentration of LFP is 0.4 g/L, that is, the sample with the lowest LFP concentration. Samples that contain 1g/L, 1.4 g/L and 2g/L show a weak shoulder around 0.40 V vs. Ag/AgCl were the DABA wave should appear. The nanofluid with an LFP concentration of 1.4 g/L shows the highest current intensity. A more detailed analysis of the nanofluid with a concentration of 1.4 g/L of LFP113STEG-2 was carried out, by measuring CVs at different scan rates and PEIS. Figure 6-4 (b), shows the CVs of this sample at different scan rates. The CV recorded at 1 mV/s shows an oxidation peak at 0.37 V vs. Ag/AgCl that corresponds to DABA, the intensity of this wave is similar to the oxidation wave at 0.60 V vs. Ag/AgCl corresponding to LFP. There is a slight shift in the position of the redox waves from LFP. Thus, the oxidation waves appear at voltages between 0.7 V (25 mV/s) and 0.6 V (1mV/s) vs. Ag/AgCl, whereas reduction waves present maxima at 0.2 V (25mV/s) and 0.3 V vs. Ag/AgCl (1 mV/s). As it could be expected, both waves increase their intensity as the scan rate increases. In this case, the current intensities of the two redox waves are not symmetric. It should be noted that this series of measurements began at high scan rate and ended at 1 mV/s, to avoid DABA consumption.

Finally, Figure 6-4 (c) shows the Nyquist plot result of the PEIS experiments. These plots present a semicircle due to the charge transfer of the nanoparticles that are part of the electroactive nanofluid. As we discussed in section above, the de deintercalation process is less favorable that the intercalation and the starting point of the semicircle observed in the Nyquist is the same for the oxidation and reduction process. The
Chapter 6: Towards LFP nanofluid

The semicircle width for the de intercalation process has a larger width than the previous sample. The Li\textsuperscript{+} diffusion process in this sample is less favorable than in the nanofluid with LFP111REG, see Figure 6-3 (c). We also noted that the semicircles appear distorted due to the aleatory nature of the electrical contact between RGO layers providing charge to the LiFePO\textsubscript{4} nanosheets in the dispersion.

Figure 6-4 Cyclic Voltammetry (a) of a nanofluid with different amount of LFP113STEG-2 at 5 mV/s (b) of an electroactive nanofluid with 1.4 g/L of LFP113STEG-2 (c) PEIS of a nanofluid with 1.4 g/L of LFP113STEG-2.

### 6.5.5 Charge discharge of DABA/RGO/LFP nanofluids

Figure 6-5 (a) shows the discharge capacity behavior of a full cell, using DABA/RGO/LFP111REG as catholyte and DABA/RGO as anolyte. The maximum discharge capacity obtained for this sample was 145 mAh/g (LFP) at 2C, which is 85% of its theoretical capacity. The discharge capacity looks stable during the charge-discharge experiments. The efficiency of the cell increases, reaching 90% by the last cycle.

Figure 6-5 (b) shows the discharge capacity performance of a DABA/RGO/LFP113STEG-2 catholyte in a full cell device, also with DABA/RGO as anolyte. The maximum capacity obtained for this sample was 130 mAh/g at 2C. The efficiency also increases with cycling for this sample reaching 70% after 6 cycles.

The sample with LFP111REG shows a higher discharge capacity. This could be a result of a better interaction between the RGO layers and the LFP platelet particles. What is really impressive is that we obtained a relative high capacity using pristine particles of LFP, with no carbon coating, demonstrating that the dispersion of RGO in an LFP nanofluid can serve a similar function.
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

6.6 Final remarks

This chapter has described some preliminary work on the development and optimization of stable electroactive nanofluids using an aromatic molecule, DABA, to stabilize RGO in an aqueous Li$_2$SO$_4$ electrolyte. After the optimization of a base nanofluid composed of DABA/RGO in aqueous Li$_2$SO$_4$, we prepared LFP nanofluids by addition of pristine LFP either in the form of small nanoparticles (20nm) or nanoplatelets. In parallel we also prepared nanofluids based on hybrid LFP/RGO solids (previously prepared from the same LFP nanoparticles and nanoplatelets) dispersed in aqueous LiSO$_4$ containing the same amount of DABA.

We tested the stability of all nanofluids measuring the sedimentation time of their dispersed solid nanoparticles. First of all, we could conclude that DABA effectively stabilizes RGO in the dispersion. Thus, the optimal formulation with a concentration of 0.3g/L of RGO and 12 g/L DABA shows a stability of 120 hours. When pristine LFP was added to this base fluid these particles drastically decreased the time of sedimentation. The electroactive nanofluids (either LFP platelets or LFP nanoparticles) with a longer sedimentation time were those with a concentration of 0.4g/L of LFP. On the other hand the sample with 2g/L of LFP has a short sedimentation time. In any event, despite the decreased stability, it should be noted that sedimentation in LFP/RGO/DABA nanofluids is in all cases slow enough to allow for their use in flow cells. The two nanofluids with DABA and a hybrid LFP/RGO 20% (based on LFP nanoparticles and nanoplatelets)
presented a higher stability compared to the nanofluids containing pristine LFP. The stability of these nanofluids is probably the result of the surface modification of LFP with RGO and the subsequent interaction of RGO with DABA.

We tested the viscosity of LFP/RGO/DABA nanofluid samples made with pristine nanoparticles. The viscosities range from 1.6 to 1.7 mPa·s. This is a very relevant because the viscosity is similar to that of water and does not represent a problem to use these materials as truly flowing nanofluids in flow cells.

Concerning the electrochemical studies, we tested nanofluids made with preformed hybrid LFP/RGO solid particles and those prepared with pristine LFP added to RGO/DABA. The ratios between LFP RGO and DABA were kept identical in both cases. Unfortunately, the nanofluids with LFP/hybrids did not show an optimal electrochemical behavior according to the preponderance of the irreversible oxidation process of DABA with respect to LFP redox activity as detected in their CVs. Furthermore, in these nanofluids LFP particles might be partly blocked by RGO.

On the other hand nanofluids with free LFP and RGO worked more satisfactorily. The nanofluid with a 1.4 g/L of LFP shows the best electrochemical behavior, this could be related to a combination of the stability of the nanofluid and the high concentration of LFP. This observation was true for both LFP samples (nanoparticles and nanoplatelets). The DABA irreversible oxidation wave was not detected when the concentration of LFP was higher than 1.4g/L. The sample with LFP111REG (LFP nanoplatelets) shows a higher discharge capacity of 140 mAh/g at 2C. This could be a result of a better dynamic interaction between the RGO layers and the LFP platelet particles. What is really impressive is that we obtained a relatively high capacity using pristine particles of LFP, with no carbon coating. The RGO dispersed in the nanofluid seems to act as a (dynamic) equivalent to a conducting coating.
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

6.7 References


(9) Huang, Q.; Li, H.; Gratzel, M.; Wang, Q. PCCP 2013, 15, 1793.


7 Conclusions
This thesis was developed under the European Project SOMABAT and has successfully accomplished the tasks of contributing to the development of low-cost synthesis methods of LFP. These synthesis methods are simple and allow the control and tailoring of LFP nanoparticle morphologies and microstructural aggregates. Furthermore, a second important part of the thesis has dealt with the development of hybrid nanocomposites of LFP and conductive polymers or carbons. Finally, we have included in the Thesis the development of electroactive nanofluids based on LFP nanoparticles as a novel objective (not related to SOMABAT) in order to carry out preliminary studies of its use in novel flow cells for energy storage, trying to push the boundaries of the state of the art of LFP as an electrode.

Related to these three accomplishments we can extract the following conclusions:

1. The experiments discussed in Chapter 3 led to the development of a hydrothermal synthesis method (based on the use of aqueous PEI solutions) at low temperatures that allowed the production of nanoparticles with controlled fractal geometry, formed by primary nanoparticles grown into microspherical formations. This dual nano-micro structuration is important for keeping a high active surface area and a high tap density.

2. We applied a method to determine the diffusion coefficient of Li\(^+\) of these fractal LFP electrodes. The diffusion coefficient of this sample was \(1.83 \times 10^{-13} \, \text{cm}^2/\text{s}\) for a granular geometry with a fractal dimension, which is higher than other diffusion coefficients reported in the literature.

3. Chapter 4 described our efforts to reduce the particle size of LFP. We successfully decreased the size of LFP nanoparticles (ca. 60 nm) using only 5% of surfactant in solvothermal (EG) reactions, and found out that this sample showed a better electrochemical performance than the sample with a larger particle size (ca. 40 nm). As a matter of fact, this nanoparticulate sample showed the best performance as cathode in a lithium cell (vs. Li) 168 mAh/g.

4. Hybrid nanocomposites materials LFP/RGO and LFP/PPy were successfully prepared and were compared with the conventional carbon-coated LFP. We
found that with the addition of RGO to the synthesis mixture we obtained a material where LFP nanoparticles (ca. 20nm) are strongly anchored to the RGO sheets. We found that a 2.5% of RGO in the synthesis mixture is the optimal amount to develop a material with good properties. This strong interaction can enhance the electrochemical performance of the LFP, with very good results. Unfortunately, the hybrid composite of LFP/PPy did not show an optimal electrochemical behavior. This could be a result of a weak interaction between PPy added to the synthesis media and LFP. However, the results show that there is room for improvement in the development of the LFP/PPy hybrid composites.

5. In Chapter 5 we described the successful implementation of a reflux synthetic method to produce LFP with an unusual platelet morphology. This method was also employed to synthesize an LFP/RGO hybrid composite. This can reduce the price of industrial LFP production.

6. However, these platelet particles did not show an optimal electrochemical performance. This was explained by morphological studies which showed that the large faces of these crystals were parallel to the DDD plane and not to the ac plane as it would be the optimal case.

7. In the case of these LFP111REGRGO hybrid composites, we found that 5% of RGO is the optimal amount of additive in order to get a good electrochemical performance. This sample shows an excellent coulombic efficiency and good rate capability. In the case of this sample no preferred orientation was found, confirming a different crystal growth process as a result of the nucleation sites provided by the use of RGO.

8. Chapter 6 described our efforts to develop an electroactive nanofluid using LFP and RGO. The base fluid was made using DABA, which successfully stabilized RGO in the dispersion with an optimal ratio 40/1 DABA/RGO (stable without sedimentation for 120 hours).
9. We prepared LFP nanofluids made from preformed hybrid LFP/RGO solid particles and those prepared with pristine LFP added to RGO/DABA. The ratios between LFP RGO and DABA were kept identical in both cases. We established that RGO in solution has the positive effect to increase the conductivity of LFP.

10. The nanofluids with LFP/RGO hybrids did not show an optimal electrochemical behavior due to the preponderance of the irreversible oxidation process of DABA with respect to LFP redox activity as detected in their CVs. Furthermore, in these nanofluids LFP particles might be partly blocked by RGO.

11. On the other hand, nanofluids with free LFP (either nanoparticles or nanoplatelets) and RGO worked satisfactorily. The nanofluid with a 1.4 g/L of LFP showed the best electrochemical behavior, this could be related to a combination of the stability of the nanofluid and the high concentration of LFP. The DABA irreversible oxidation wave was not detected when the concentration of LFP was higher than 1.4g/L. The sample with LFP111REG (LFP nanoplatelets) showed a higher discharge capacity of 140 mAh/g at 2C.

12. It is remarkable that we obtained a relatively high capacity in an electroactive nanofluid made of pristine particles of LFP, with no carbon coating. The RGO dispersed in the nanofluid seems to act as a dynamic equivalent of a conducting coating.
8 Appendices
1 Appendix RGO characterization

Hummers Method

Graphene oxide was first prepared by Brodie\(^1\) in 1859 who treated graphitic powder with potassium chlorate in concentrated fuming nitric acid. This troublesome method was changed by Staudenmaier\(^2\) forty years later by using higher excess of the oxidizing agent and additive of concentrated sulfuric acid. This modification enabled to carry out continuous process without the necessity of nitric acid addition during the reaction.

But these two methods were still too long till Hummers\(^3\) proposed in 1958 graphite oxidation using potassium permanganate and sodium nitrate in concentrated sulfuric acid that shortened oxidation time to several hours. Although tremendous amount of papers concerning graphite oxide, the precise structure of graphite oxide is not known. Probably the reason is some discrepancies in graphite substrates used in synthesis, reaction conditions and analytical methods. Graphite chemical oxidation involves intercalation of the oxygen-containing groups in interlayer space. Embedded oxygen breaks van der Waals forces that hold layers together and an increase in the interlayer distance is observed. Carbon-oxygen bonds cause partial change of carbon atoms hybridization from sp\(^2\) to sp\(^3\).

Characterization

Raman scattering is one of the most widely used techniques to characterize the structural and electronic properties of carbon materials. We are going to compare the starting material (graphite), GO and RGO, Figure 8-1.

Graphite shows an intense G (1578 cm\(^{-1}\)) band and weak D (1350 cm\(^{-1}\)) band. The D band arises from a breathing mode of K-point phonons of A\(_{1g}\) symmetry, and the G band correspond to the first-order scattering of E\(_{2g}\) mode. In addition, 2D and D+D bands are present, the intensity of these bands is weak. The band corresponding to D+D (3230 cm\(^{-1}\)), are combination scattering peak \(^4,5\). The 2D band is a product of a second order overtone of a different in plane vibration (2729 cm\(^{-1}\))\(^5\).

GO exhibit the D band at 1361 cm\(^{-1}\) and a G band at 1591 cm\(^{-1}\). RGO bands D and G can be seen at 1355 cm\(^{-1}\) and 1600 cm\(^{-1}\). The D band is more intense that in graphite for both
samples. The D band is connected to the quantity of disorder and its intensity shows the level of edge chirality. Thus, the intensity ratio of D and G band (ID/IG) indicated the degree of the disorder; such defects can be related to several features: the presence of edges in small crystals, deviations from planarity, the presence of a certain number of carbon atoms in the sp³ hybridization state, etc.

Table 8-1 shows the intensities ratio of the D and the G bands of the samples mention above. As we can see the intensity of the D band increase as the initial material is transformed in RGO, thus the disorder is high in RGO.

The intensity ratios of sp² to sp³ type carbon vibrations is often used to evaluate the nature of the carbon using the deconvoluted Raman bands. As the Raman bands in D and G region of the spectra are broad the intensity profiles are often deconvoluted using four Gaussians or Gaussian-Lorentzian lines. The two additional bands needed to satisfactorily fit the intensity profiles, around 1205 and 1520 cm⁻¹ and are assigned to sp³ type carbon which are often observed in amorphous carbonaceous compounds. We have fitted the Raman intensity profiles using four Gaussian lines, see Figure 8-1, and have estimated intensity ratio of \( I_{\text{sp}^2} / I_{\text{sp}^3} = (I_{1340} + I_{1595}) / (I_{1205}+I_{1520}) \). For the RGO sample, we found a value of \( I_{\text{sp}^2} / I_{\text{sp}^3} = 5 \).

Figure 8-1 Raman spectra of Graphite, GO and RGO inset deconvolution of D and G band of RGO
Table 8-1 Intensities ratio of the D and G bands of graphite, Go and RGO

<table>
<thead>
<tr>
<th>Sample</th>
<th>D/G intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>0.15</td>
</tr>
<tr>
<td>GO</td>
<td>0.99</td>
</tr>
<tr>
<td>RGO</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Table 8-2 Chemical composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon %</th>
<th>Nitrogen %</th>
<th>Hydrogen %</th>
<th>Sulphur %</th>
<th>Oxygen %</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>52</td>
<td>0</td>
<td>0.7</td>
<td>0.3</td>
<td>48</td>
</tr>
<tr>
<td>RGO</td>
<td>61</td>
<td>0</td>
<td>0.7</td>
<td>0.3</td>
<td>37</td>
</tr>
</tbody>
</table>

Figure 8-2 shows the surface characterization of the RGO thought XPS and EDS. XPS was analyzed in detail specifically the C near spectra. Figure 8-2 (a) shows the RGO general XPS spectrum of RGO. The spectrum analysis shows the presence of oxygen and carbon if the RGO sample.

RGO is characterized by a C(1s) peak at 284.6 eV, Figure 8-2 (b). The peak at 284.6 eV arises from the non-oxygenated ring C (C-C bonds), where the peak at 286.7 eV arise from the C in C-O bonds of the hydroxyl group. At 288 eV we can identify the peak corresponding to a carbon oxygen double bond.

Figure 8-2 (c) shows the EDS. A small amount of impurities that does not affect the properties of RGO concerning to our applications were identified. These impurities are sulfur, Chloride, Potassium and Phosphorus. These impurities are a result of the aggressive conditions of the synthesis.
Figure 8-2 (a) EDS (b) XPS (C) near XPS C spectra of RGO

Figure 8-3 shows the SEM images of the RGO. Figure 8-3 (a) shows a wrinkle porous material with an unknown number of layers. Figure 8-3 (b) shows a close image of the pores in the sample. The pores in the RGO were formed by rapid gas evolution under the high vapor pressure generated upon treatment with the concentrated HCl (37wt%). The pores were formed by gas evolution, the pores were interconnected and extended from the inside to the surface of the materials.

Figure 8-3 SEM images of RGO (a) general view (b) pores close up

Figure 8-4 show the TEM in the RGOes and a SEAD image of RGO. Figure 8-4 (a) show that these sheets partially overlap with each other. Buckling of the sheets is evident, these images show the flakes and the wrinkles of the RGO, particularly in the overlapped regions.

Figure 8-4 (b) shows a HRTEM image of RGO. This image shows what appears to be a single layer with wrinkles. The SAED pattern from the dotted circle area (inset Figure 8-4 b) shows a typical hexagonal symmetry, which is representative for graphene layers.
Alternative approaches for the fabrication of the electrodes based on LiFePO$_4$ as cathodes in LIBs

Figure 8-4 (a) General TEM image (b) HRTEM inset SAED (the SAED image correspond to the layer in the HRTEM) of RGO


2 Appendix Polypyrrole characterization

Pyrrole polymerization

Some of the first examples of polypyrrole were reported in 1963 by Weiss and coworkers. These workers described the pyrolysis of tetraiodopyrrole to produce highly conductive materials. Most commonly PPy is prepared by oxidation of pyrrole, which can be achieved using ferric chloride in methanol:

\[ n \text{C}_4\text{H}_4\text{NH} + 2 \text{FeCl}_3 \rightarrow (\text{C}_4\text{H}_2\text{NH})_n + 2 \text{FeCl}_2 + 2 \text{HCl} \]  

**Reaction 8-1**

Polymerization is thought to occur via the formation of the \( \pi \)-radical cation \( \text{C}_4\text{H}_4\text{NH}^+ \). This electrophile attack the carbon- carbon bond of an unoxidized molecule of pyrrole to give a dimeric cation \( (\text{C}_4\text{H}_4\text{NH})_2^{++} \). The process repeats itself numerous times. Conductive forms of PPy are prepared by oxidation ("\( \pi \)-doping") of the polymer:

\[ (\text{C}_4\text{H}_2\text{NH})_n + \text{FeCl}_3 \rightarrow (\text{C}_4\text{H}_2\text{NH})_n\text{Cl}_x + \text{xFeCl}_2 \]  

**Reaction 8-2**

Characterization

Figure 8-5, shows the SEM images and EDS of PPy-NanoPipes (PPy-NPs). In the Figure 8-5 (a) PPy-NPs is notorious that the nanotubes are randomly spread with well-developed nanoscale pores. No aggregation and alignment of bundles of PPy-NTs has been observed. FeCl\(_3\) is considered to act as a flocculant which suppresses the electrostatic repulsions between MO aggregations and/or reacts with negatively charged aggregates of MO(SO\(_3\)) in solutions, then destabilize the charged particles and build an amorphous aggregate. Figure 8-5 (b) shows the image of one PPy-NPs with a diameter of 80 nm. The EDS analysis of PPy-NPs suggests the presence of C, N, O and Cl, confirming the formation Cl doped PPy nanostructure.
Alternative approaches for the fabrication of the electrodes based on LiFePO₄ as cathodes in LIBs

Raman spectra of PPy-NPs is show in Figure 8-6. The peaks at 1588 cm⁻¹ (G-band) and 1379 cm⁻¹ (D-band) are assigned to the stretching C=C backbone and antisymmetric stretching of C-N bond in PPy-NPs, respectively. In addition, the smaller intensity of D-band as compared to G-band (I_D/I_G=0.94) is related to the less defects present in PPy-NPs. Moreover, the peak at 1269 cm⁻¹ is assigned to the C-H in-plane and the ring stretching while the peaks at 978 and 1040 cm⁻¹ associated with polaron and peak at 1070 cm⁻¹ indicates the bipolaron structure. The ring deformation vibration is assigned by the peak at 919 cm⁻¹.

Figure 8-6 Raman Spectra of PPyNPipes

In order to get more insights about elements and oxidation states of the as-prepared PPy-NTs XPS analysis was performed and the corresponding results are presented in
Figure 8-7. Figure 8-7 (a) reveals the presence of characteristic peaks for C1s, N1s and O1s smalls peaks corresponding to Cl and S as result of the use of FeCl₃ as oxidizing agent and the employment of MO as template. The oxygen has probably originated from the surface oxidation of PPy-NPs. As the conducting polymers are nitrogen containing aromatic polymer materials, PPy-NPs possesses N1s peak. As shown in Figure 8-7 (b), the deconvolution of N 1s signals in the XPS spectrum gives three Gaussian components. The main N peak at 399.6 eV is attributed to the neutral N in the Py ring (–NH–). The high binding energy peak can be attributed to oxidized/protonated N. Comparing to the position of the main peak, the 0.9 eV higher binding energy (400.5 eV) peak is indicative of –NH•+– in the polaron charge carrier species. Figure 8-6 (c) shows the near XPS spectra of C. The deconvolution of the carbon spectra reveals a C-C bond (284.7 eV) and a C-O bond (288 eV). Figure 8-7 (d) shows the first derivate of the CKLL in order to get the D parameter. The d parameter of the PPy shows a value of 20 eV, which indicate that the sp² character is by far more dominant than the sp³.
Figure 8-8 shows the FT-IR spectra of PPyNPs. The characteristic PPy peaks are located at 1,547 and 1,446 cm$^{-1}$ due to the pyrrole ring stretching and the conjugated C–N stretching mode, respectively. The peaks at 1,315 and 1,029 cm$^{-1}$ are related to the in-plane vibrations of C–H, 1,163 cm$^{-1}$ is assigned to the C–N stretching mode $^5$. In addition, the peaks at 895, 694 cm$^{-1}$ corresponds to the stretching vibration of the SO$_3^-$ group, which indicates the MO entering the PPy-NPs as dopant $^6$.

PPy produced by oxidation, peaks were observed at 1588, 1062 and 981 cm$^{-1}$ confirming the presence of PPy which correspond to C-H stretching vibration, C=C stretching vibration, C-N in-plane deformation vibration and C-C out-of-plane asymmetric vibration, respectively. Is important to mention that this polymer does not show any sign of –OH, in the oxidized polymers (conductive), these bonds are completely obscure by one free-carrier absorption. Therefore, as OH bonds become more dominant, conductivity is expected to be low.

![Figure 8-8 FTIR Pyrrole and PPyNPs](image)


3 Appendix Triangulation method.

Is very similar to cube counting method and is also based directly on the box-counting fractal dimension definition. The method works as follows: a grid of unit dimension l is placed on the surface. This defines the location of the vertices of a number of triangles. When, for example, l=X/4, the surface is covered by 32 triangles of different areas inclined at various angles with respect to the xy plane. All areas of the triangles are calculated and summed to obtain an approximation of the surface area S(l) corresponding to l. The grid size is then decreased by successive factor of 2, as before, and the process continues until l corresponds to distance between two adjacent pixel points. The slope of a plot of log(S(l)) versus log(1/l) then corresponds to D_f–2.
4 Appendix Rietveld refinement

Rietveld refinement is termed as a structure refinement method, rather than a structure solution method, although it can be a great aid in the elucidation of crystal structures. The main idea is that high quality powder diffraction data which have been transformed into a diffraction pattern, are compared to an ideal simulated diffraction pattern. The X-ray diffraction pattern can be simulated using Rietveld refinement software like TOPAS, FullProof and High Score plus, and this simulation are then compared to the actual diffraction pattern. The software is then used to manipulate the simulated pattern by varying a number of parameters like site occupancies, atomic displacement parameters, unit cell coordinates, instrumental and experimental parameters and many others in order to match the experimental pattern as closely as possible often using a least squares minimization procedure.

The main point to keep in mind while doing such refinements the initial data must be of the best possible quality. Generally, for data to be used in a refinement, the step size should not be more than 0.02°/step, with at least five to ten steps across the top of each peak, with a longer time per step applied to maximize the intensities at the higher angles to compensate for the general decline of intensity at those higher angles. Care must be taken to ensure that a large enough 2θ range is used in the data collection, particularly at the higher angles, since the precision calculation of lattice parameters hinges strongly on the high 2θ peaks, as the bulk of the crystallographic structure information are contained in those higher angles.
5 Appendix Characterization of the materials discussed in chapter 6

![XRD pattern of samples LFP111REG20% and LFP113STEGGO20%](image)

Figure 8-9 XRD pattern of samples LFP111REG20% and LFP113STEGGO20%. These patterns do not show any sign of impurity in these samples. These patterns did not show any sign of RGO at 2\(\theta\) 2\(\theta\) was not detected by this method.

![TEM images](image)

Figure 8-10 TEM images of (a) LFP111REGGO20% and (b) LFP113STEGGO20%
Table 8-3 Results of the elemental analysis for samples LFF discuss in chapter 6

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon %</th>
<th>Nitrogen %</th>
<th>Hydrogen %</th>
<th>Sulphur %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP111REGRGO20%</td>
<td>21.0</td>
<td>&gt; 0.1</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>LFP113STEGRG020%</td>
<td>20.4</td>
<td>&gt; 0.1</td>
<td>0.7</td>
<td>0.9</td>
</tr>
</tbody>
</table>
6 Appendix List of publications


5. Synthesis and characterization of mesoporous FePO₄ as positive electrode materials for lithium batteries” by Amel Salamani, Abdallah Merrouche, Laid Telli, Pedro Gómez-Romero, Zahilia Caban Huertas. *Surface Engineering And Applied Electrochemistry*