SYNTHESIS AND MICROSTRUCTURAL CHARACTERIZATION OF PHOSPHATE CATHODE MATERIALS PREPARED BY A POLYMERIC STERIC ENTRAPMENT PRECURSOR ROUTE

BY

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THESIS

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ABSTRACT

Due to its high energy density and cycling performance Li-ion batteries play an important role as energy storage technology in the future human development. Lithium ion batteries are appealing for applications that include portable electronics such as cellular phones and laptop computers. However, larger scale Li-ion battery system for vehicles and grid load leveling as well as complementary energy storage for renewable energy resources, such as solar and wind power seems to be the next target for metal-ion battery technology.

In this work, a nanoscale and pure olivine structure LiFePO₄ (triphylite) was synthesized at low temperature (since 300 °C) using an organic–inorganic steric entrapment solution, from precursor chemicals of LiNO₃, Fe(NO₃)₃·9H₂O and (NH₄)₂HPO₄ stoichiometrically dissolved in distilled water. A long-chain polymer such as polyvinyl alcohol (–[CH₂–CHOH]–n or PVA) having a degree of polymerization corresponding to a molecular weight of 9,000 to 10,000 was used as the organic carrier for the precursors, which served for the physical entrapment of the metal ions in the dried network. Normally, when calcined and crystallized in air, this method leads to the synthesis of compounds where the cations are in their highest oxidation state. However, in this study we found a way to make compounds having lower oxidation states (e.g. Fe²⁺ versus Fe³⁺) which may have wider applications in the synthesis of other compounds having variable oxidation states, with potential applications in electronic ceramics of complex chemistry.

LiFePO₄ was selected as a model system to evaluate the influence of variables such as the amount of water, pH of the solution, drying procedure, HNO₃ addition, amount of polymer, calcination/crystallization atmosphere and temperature on the synthesis. Then the variables were tuned to produce NaFePO₄ and NaTi₂(PO₄)₃ based on the concepts learned from the model system. NaFePO₄ (maricite) was synthesized at low temperature (~ 300 °C) using PVA as a polymer carrier and dissolving stoichiometric amounts of NaNO₃, Fe(NO₃)₃·9H₂O and (NH₄)₂HPO₄ in water. For the NaTi₂(PO₄)₃ system, a hybrid synthesis method was used because some reagents (NaNO₃ and (NH₄)₂HPO₄ sources) dissolved in water, but not in alcohol. Moreover, another reagent such as titanium (IV) isopropoxide
(Ti[OCH(CH\textsubscript{3})\textsubscript{2}]\textsubscript{4}, also called “TISO”) decomposed in water (forming isopropyl alcohol and a hydrated form of titania) but dissolve and remained stable in alcohol. However, the decomposition to titania could be hindered by adding excess isopropyl alcohol, so as to drive the equilibrium to the titanium (IV) isopropoxide side instead of the titania side. The titanium isopropoxide was therefore dissolved in isopropyl alcohol. For this hybrid method, an ethylene glycol (EG) monomer (HOCH\textsubscript{2}CH\textsubscript{2}OH) was chosen as a polymeric carrier.

The resulting LiFePO\textsubscript{4} or (Li\textsubscript{2}O•2FeO•P\textsubscript{2}O\textsubscript{5}), NaFePO\textsubscript{4} or (Na\textsubscript{2}O•2FeO•P\textsubscript{2}O\textsubscript{5}) and NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (Na\textsubscript{2}O•2FeO•P\textsubscript{2}O\textsubscript{5}) powders were characterized by TG/DTA thermal analysis, X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) nitrogen absorption, inductively coupled plasma (ICP) emission spectroscopy and particle size analysis.

In this work, has been demonstrated that by drying the solution at low temperature, release of organic or nitrates was avoided, which meant full availability of these two components (fuel and oxidizer) for the next step (calcination/crystallization). Fuel and oxidizer generated a strong exothermic reaction which could be used for crystallization of the desired compound at a lower temperature.

In general, the morphology of the powders produced by the polymeric steric entrapment method was porous secondary particles formed from primary particles in the range of 20 nm – 10 microns, in the case of LiFePO\textsubscript{4}. These secondary particles were soft agglomerates that showed this particular microstructure, due to the violent exothermic decomposition reaction of organics reacting with nitrates. These porous structures have a higher specific surface area (40-50 m\textsuperscript{2}/g) compared to the reference commercial LiFePO\textsubscript{4} powder (17.92 m\textsuperscript{2}/g), which it is desirable for ion and electron diffusion in lithium ion batteries. For the case of pure crystalline NaFePO\textsubscript{4} phase, crystals of irregular shapes of about 100 nm - 200 nm were found in the powders crystallized at temperatures between 300 °C and 500 °C. Their specific surface area was around 28.92 m\textsuperscript{2}/g. Moreover, for NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, synthesized at 700 °C, the secondary particles were formed from primary crystals with no particular morphology in the range of 50 - 150 nm and showed specific
surface areas of the amorphous and crystalline powders of 82.97 m²/g and 40.93 m²/g, respectively.
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# TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION .................................................................................................................. 1

CHAPTER 2: LITHIUM BATTERY OVERVIEW ..................................................................................... 5
  2.1 General Aspects and Fundamentals of Electrochemical Energy Storage ...................................... 5
     2.1.1 Electrochemical Fundamentals ......................................................................................... 8
     2.1.2 Thermodynamic Principles ............................................................................................ 11
     2.1.3 Principles of Lithium Ion Batteries ................................................................................. 13
     2.1.4 Current Status of Lithium-Ion Battery Technology .......................................................... 21

CHAPTER 3: SYNTHESIS OF BATTERY MATERIALS .......................................................................... 37
  3.1 Overview .................................................................................................................................. 37
  3.2 Polymeric Steric Entrapment Precursor Route .......................................................................... 47
  3.3 Overview of LiFePO₄ .................................................................................................................. 50
  3.4 Overview of NaFePO₄ ................................................................................................................ 55
  3.5 Overview of NaTiₓ(PO₄)₃ ............................................................................................................ 61

CHAPTER 4: EXPERIMENTAL PROCEDURES .................................................................................... 65
  4.1 Chemical and Powder Processing ............................................................................................. 65
     4.1.1 The Polymeric Steric Entrapment Method to Produce Subvalent and Multicomponent Compounds (LiFePO₄ and NaFePO₄) for Energy Storage Applications ............................................. 65
     4.1.2 Hybrid Polymeric Steric Entrapment Method to Produce Maximum Valent and Multicomponent Compounds (NaTiₓ(PO₄)₃) for Energy Storage Applications ......................................................... 70
  4.2 Powder Characterization ......................................................................................................... 72
     4.2.1 Thermal Analysis .............................................................................................................. 72
     4.2.2 X-ray Diffraction Analysis .............................................................................................. 73
     4.2.3 Microstructure Characterization ..................................................................................... 73
     4.2.4 Chemical Analysis .......................................................................................................... 73
     4.2.5 Particle Size and Surface Area ........................................................................................ 73

CHAPTER 5: RESULTS AND DISCUSSION ....................................................................................... 75
  5.1 Model System LiFePO₄ ............................................................................................................... 75
     5.1.1 Characterization of Commercial LiFePO₄ ....................................................................... 75
     5.1.2 Calcination /Crystallization Atmosphere Effect ................................................................ 79
     5.1.3 Solution pH Effect .......................................................................................................... 82
     5.1.4 Solution Drying Effect .................................................................................................... 84
     5.1.5 Crystallization of LiFePO₄ ............................................................................................... 91
CHAPTER 1
INTRODUCTION

For many years, the only way to synthesize cathode materials was by thermal treatment at high temperatures from mixtures of reactants. Due to diffusional limitations and low reactivity of starting materials, this solid state method implied long reaction times, high temperatures and regrinding processes between subsequent firings. Due to the abovementioned drawbacks, the solid state reaction method is considered as a low-efficiency, energy and time consuming technology which in addition, produces a wide range of particle size distribution, which could prevent the preparation of high performance powder materials.

Ceramic processing is evolving in the direction of chemical synthesis of powders. In recent years, there has been considerable interest in the development of other techniques that allow the production of materials with various powder morphologies, bulk density, and stoichiometry. In this way, the use of polymers to synthesize mixed-oxide ceramic powders has been a recent development in concurrent work by several groups. For instance, the Pechini process, emulsion or emulsion drying method and sol-gel route. However, these methods consist of complicated preparation steps to obtain the correct stoichiometric compound and need further calcination and grinding of powders to obtain the high crystallinity. Also, the production rate for these techniques is very low. Therefore, the mentioned drawbacks should be overcome to make the preparation techniques more practical and suitable for effective industrial application.

The advancements in lithium-ion battery technology evolved with this new synthesis approach. Therefore, over the last few years, material scientists and chemists have explored the wet chemical methods including classical precipitation [1-5], hydrothermal [6-15], sol-gel [16-21], polyol, solvothermal [22], microwave-assisted solvothermal [23], Pechini process [24-26], spray pyrolysis [27-30] and ionothermal [31-33] synthesis to produce nanostructured electrode materials. In general these methods produce homodisperse powders with a well-defined shape and size at low temperatures via fine-tuned control of the reaction pH and precursor concentration. This is in contrast to ceramic methods, which
require high temperatures to ensure the diffusion of the reactants and the growth of the grains, usually leading to highly polydispersed powders. One interesting trend in cheaper electrode materials is that the electrochemical responses rely on the nanosized nature of the materials. Nanotechnologies have enabled new compounds to function as an electrode material, which was not possible at the micron level.

Some excellent results were obtained using wet chemical methods mentioned above. However, these techniques use very low concentrations of starting materials, which leads to a very low production rate. Thus, these processes are very difficult to be used for the commercial production of cathode materials. Therefore, it is crucial to develop a simple, easy to scale-up and cost-effective technique because in real-world applications elaborate chemical routes are often found to be less attractive.

A versatile technique has been developed by our group based on a polymeric steric entrapment precursor route [34-44]. The method uses long-chain polymers, such as poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG) that ensure a homogeneous distribution of the metal ions in their polymeric network structure, and it inhibits their segregation or precipitation from solution [35, 39, 41, 43]. In the solution involving a polymer and nitrate ions, a continuous long chain polymer prevents contact between the cations and it limits their phase separation and precipitation [36]. The chemistry of the precursor solution differs from other solution–polymerization techniques. The stabilization of the cations in the precursor is established not only through the chemical binding of cations with the functional groups, but also, in major part, through the physical entrapment of the metal ions in the network of the dried polymer carrier. An important criterion for the selection of the cation sources is the aqueous solubility of the corresponding metal salts; the more soluble the salts, the higher the yield of the new process [35]. In a water–soluble system, the PVA polymer can be used. However, the process can be extended to chemicals that decompose in water such as metal-alkoxide (titanium isopropoxide) by applying an ethylene glycol (EG) polymerizing agent. In particular, the ethylene glycol can act as an effective solvent for a wet chemical synthesis of a titanate powder because a water–soluble titanium salt is not commercially available [36, 39, 45, 46]. Furthermore, a linear polymer such a PVA has the ability to wrap around the cation precursor improving the cation
distribution due to attrition and/or repulsion forces. It has been also documented for this method that the decomposition of the polymer is similar to that of a fuel-oxidizer system. The fuel can be any polymer in which oxidation occurs easily. The oxidizer is usually an acid or in the specific case of this method, nitrates sources. It has been proposed that the ratio of oxidizer to fuel should be close to unity in order to release the maximum energy to induce ceramic conversion. Unless the chemistry behind this method is more elaborate, the factors which must be considered to produce particles with the desirable crystal structure, microstructure, particle size/size distribution, particle morphology, and high purity, are the size and valence of the cations, the degree of polymerization, the oxidizer/fuel ratio, type of solvent, calcination and crystallization temperature and time.

The polymeric steric entrapment precursor route has been successfully used to synthesize various monophase, fine (micro and nano), and pure mixed-oxide powders with high technological importance \[34-42, 45, 47-58\]. Although this solution polymerization route has been studied by the Kriven group for more than 15 years with remarkable advances (1 patent \[59\] and 30 papers), our aim in the project, is to use this synthesis route to produce these materials based on 3-d metal redox elements such as LiFePO\(_4\), NaFePO\(_4\) and NaTi\(_2\)(PO\(_4\))\(_3\). These complex compounds are composed by cations called “zwitterions” because of their special changeable characteristic of different oxidation states M\(^{+2}\)/M\(^{+3}\) that make them interesting for electronic applications. So far, the polymerized organic–inorganic entrapment route leads the synthesis reaction toward the maximum oxidation state, and there is a big challenge to find the way to control the different oxidation states through this synthesis route that can be useful to produce a wide range of technologically important compounds.

Among other methods to prepare oxide ceramics, the polymeric steric entrapment precursor route has been demonstrated to be a low temperature, simple, continuous, and easy to scale-up technique. This technique allows controlling powder composition and morphology as well as shortening production time. The prepared powders are homogeneous, both chemically and physically, and have a narrow particle size distribution in
the micro/nano sized range. All these factors allow outstandingly reduced product cost and decreasing the ecological impact of material production.

In this thesis, a broad overview of lithium battery technology is given in chapter II. It includes thermodynamic and kinetic fundamentals, as well as general aspects of battery components. A detailed discussion on synthesis methods of battery materials, including the polymeric steric entrapment precursor route, and the compositions that will be investigated in this work, are offered in chapter III. The experimental procedures and powder characterization techniques are explained in chapter IV. The results and discussion of the powders synthesized by the polymeric steric entrapment precursor route are presented in chapter V. Finally, conclusions are drawn in chapter VI.
2.1 General Aspects and Fundamentals of Electrochemical Energy Storage

Electrochemical power sources convert chemical energy into electrical energy (Figure 2.1). At least two reaction partners undergo a chemical process during this operation. The energy of this reaction is available as electric current at a defined voltage and time [60].

![Image of Electrochemical Energy Storage](image)

Figure 2.1 Electrochemical Energy Storage.

The simplest system consists of one electrochemical cell the so-called galvanic element [60]. This supplies a comparatively low cell voltage of 0.5–5 V. To obtain a higher voltage the cell can be connected in series with others, and for a higher capacity it is necessary to link them in parallel. In both cases the resulting ensemble is called a battery [61].

Depending on the principle of operation, cells are classified as follows:

1. Primary cells are nonrechargeable cells in which the electrochemical reaction is irreversible. They contain only a fixed amount of the reacting compounds and can be discharged only once. The reacting compounds are consumed by discharging, and the cell cannot be used again. A well-known example of a primary cell is the Daniell element (Figure 2.2), consisting of zinc and copper as the electrode materials.
Secondary cells are those that can be electrically recharged after use to their original pre-discharge condition, by passing current through the circuit in the opposite direction to the current during discharge. Only reversible electrochemical reactions offer such a possibility. After the cell is discharged, an externally applied electrical energy forces a reversal of the electrochemical process; as a consequence the reactants are restored to their original form, and the stored electrochemical energy can be used once again by a consumer. The process can be reversed hundreds or even thousands of times, so that the lifetime of the cell can be extended. This is a fundamental advantage, especially as the cost of a secondary cell is normally much higher than that of a primary cell.

Fuel cells: Fuel cells are similar to batteries except for the fact that all active materials are not an integral part of the device (as in a battery). In fuel cells, active materials are fed continuously into batteries (commonly hydrogen and oxygen) from an outside source. This type of cells is not a reversible system.

Typical fields of application for electrochemical energy storage systems are in portable systems such as cellular phones, notebooks, cordless power tools, SLI (starter-light-ignition), batteries for cars, and electrically powered vehicles. There are also a growing number of stationary applications such as devices for emergency current and energy storage systems for renewable energy sources (wind, solar). Particularly for portable applications the batteries should have a low weight and volume, a large storage capacity, and a high specific energy density. Most of the applications mentioned above could be covered by
primary batteries, but economical and ecological considerations lead to the use of secondary systems [61].

Developing high-performance primary and secondary batteries for different applications has been an extremely challenging task due to the need to meet simultaneously multiple battery performance requirements such as:

- High energy (watt-hours per unit battery mass or volume)
- High power (watts per unit battery mass or volume)
- Long life (5–10 years and some hundreds of charge-discharge cycles)
- Low cost (measured per unit battery capacity)
- Resistance to abuse and operating temperature extremes
- Safety
- Minimal environmental impact.

So far and despite years of intensive worldwide R&D, no battery can meet all of these goals. Table 2.1 shows a comparison between different battery systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Specific Energy (Theoretical) (Wh/Kg)</th>
<th>Specific Energy (Practical) (Wh/Kg)</th>
<th>Energy Density (Practical) (Wh/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (Zinc) - Manganese cell</td>
<td>336</td>
<td>50 – 80</td>
<td>120 -150</td>
</tr>
<tr>
<td>Silver - Zinc</td>
<td>150</td>
<td>105</td>
<td>180</td>
</tr>
<tr>
<td>Zinc - Carbon</td>
<td>358</td>
<td>60 – 90</td>
<td>140 - 200</td>
</tr>
<tr>
<td>Lead - Acid</td>
<td>170</td>
<td>35</td>
<td>90</td>
</tr>
<tr>
<td>Nickel - Cadmium</td>
<td>209</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>Nickel - Hydrogen</td>
<td>60</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>Nickel - Metal Hybrid</td>
<td>380</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>Lithium ion - Metal Oxide</td>
<td>500 – 550</td>
<td>150</td>
<td>220</td>
</tr>
</tbody>
</table>
2.1.1 Electrochemical Fundamentals

The characteristic feature of an electrochemical cell is that the electronic current, which is the movement of electrons in the external circuit, is generated by the electrochemical processes at the electrodes. In contrast to the electric current in the external system, the transportation of the charge between the positive and the negative electrode within the electrolyte is performed by ions. Generally the current in the electrolyte consists of the movement of negative and positive ions. The limiting factor for the electronic current flow is the transport of these ions. Therefore the electrolyte solution should have a low resistance.

From the chemical viewpoint, a galvanic cell is a current source in which a local separation of oxidation and reduction processes exists. A typical feature of a redox reaction is an exchange of electrons between at least two reaction partners. It is characterized by the fact that oxidation and reduction always occur at the same time. Both together form the corresponding redox pair:

\[
\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2
\]

For example: \(\text{CuSO}_4 + \text{Zn} \rightarrow \text{ZnSO}_4 + \text{Cu}\) (Daniell’s cell)

The electrode at which the oxidation dominates during discharge is named the anode (negative pole), and the other, where the reduction dominates, is the cathode (positive pole). This nomenclature is valid only for the discharging reaction; for the charging reaction the names are reversed [61].

In Galvanic cells it is only possible to determine the potential difference as a voltage between two half cells, but not the absolute potential of the single electrode. For the measurement of the potential difference it has to be ensured that an electrochemical equilibrium exists at the phase boundaries (electrode/electrolyte). At least it is required that there is no flux of current in the external and internal circuit. To compare the potentials of half cells a reference had to be defined. For this reason it was decided arbitrarily that the potential of the hydrogen electrode in a 1 M acidic solution should be equal to 0 V at a
temperature of 25°C and a pressure of 101.3 kPa. These conditions are called standard conditions [62].

The potentials of the metals in their 1 M salt solution are all related to the standard or normal hydrogen electrode (NHE). To measure the potential of such a system, the hydrogen half cell is combined with another half cell to form a Galvanic cell. The measured voltage is called the normal potential or standard electrode potential $E^0$ of the metal. If the metals are arranged in the order of their normal potentials, the resulting order is named the electrochemical series of the metals (Figure 2.3). Depending on their position in this potential series, they are called base ($E^0 < 0$) or noble ($E^0 > 0$) metals [61].

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrode reaction</th>
<th>$E^0/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$</td>
<td>+1.43</td>
</tr>
<tr>
<td>Ag</td>
<td>$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$</td>
<td>+0.80</td>
</tr>
<tr>
<td>Cu</td>
<td>$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>H</td>
<td>$\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}$</td>
<td>0</td>
</tr>
<tr>
<td>Pb</td>
<td>$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$</td>
<td>−0.13</td>
</tr>
<tr>
<td>Sn</td>
<td>$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$</td>
<td>−0.14</td>
</tr>
<tr>
<td>Ni</td>
<td>$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$</td>
<td>−0.25</td>
</tr>
<tr>
<td>Cd</td>
<td>$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}$</td>
<td>−0.40</td>
</tr>
<tr>
<td>Fe</td>
<td>$\text{Fe}^{3+} + 2\text{e}^- \rightleftharpoons \text{Fe}$</td>
<td>−0.44</td>
</tr>
<tr>
<td>Zn</td>
<td>$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$</td>
<td>−0.76</td>
</tr>
<tr>
<td>Ti Titanium</td>
<td>$\text{Ti}^{4+} + 2\text{e}^- \rightleftharpoons \text{Ti}$</td>
<td>−1.63</td>
</tr>
<tr>
<td>Al Aluminium</td>
<td>$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$</td>
<td>−1.66</td>
</tr>
<tr>
<td>Mg</td>
<td>$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$</td>
<td>−2.37</td>
</tr>
<tr>
<td>Na</td>
<td>$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$</td>
<td>−2.71</td>
</tr>
<tr>
<td>K</td>
<td>$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}$</td>
<td>−2.93</td>
</tr>
<tr>
<td>Li</td>
<td>$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$</td>
<td>−3.05</td>
</tr>
</tbody>
</table>

**Figure 2.3 Electrochemical Series of The Metals.**

For the arrangement of a galvanic cell for use as a power source the half cells are chosen such that their potentials $E^{0,\text{cathode}}$, $E^{0,\text{anode}}$ are as far apart as possible. Therefore, it is obvious why alkaline metals, especially lithium or sodium, are interesting as new materials for the negative electrode. As they have a strong negative standard potential and a comparatively low density, a high specific energy can be realized by combination with a positive electrode [61]. Moreover, a metallic lithium anode possesses many difficulties in
order to be used in commercial batteries. As an alkali metal, lithium is chemically reactive with the non-aqueous electrolytes, which results in the formation of a passivating film on the metallic lithium anode. Although the passivating film on the surface prevents the bulk from further corrosion, it leads to a non-uniform plating of lithium during charging. This results not only in a total cell failure due to dendritic short circuiting, but also in serious safety problems due to overheating [63]. That is why, nowadays lithium insertion compounds are preferred as an anode instead of metallic lithium.

During the discharge process, electrons are released at the anode from the electrochemically active material, which is oxidized. At the same time, cathodic substances are reduced by receiving electrons. The transport of the electrons occurs through an external circuit (the consumer). There is a relationship between the electronic current \( I \) and the mass \( m \) of the substance which donates electrons, and this is known as the Faraday’s first law [64]:

\[
m = \frac{M}{z \times F} \times I \times t
\]

\( m \) = active mass  
\( M \) = molar mass  
\( z \) = number of electrons exchanged  
\( F \) = Faraday constant: 96 485 C mol\(^{-1}\) = 26.8 Ah mol\(^{-1}\).  
\( t \) = time

As it was mentioned before, the charging process can only be applied to secondary cells, because, in contrast to primary cells, the electrochemical reactions are reversible. Attempting to charge primary cells may lead to electrochemical side reactions, for instance, the decomposition of the electrolyte solution with dangerous follow-up reactions leading to explosions.

While charging, ions are generally reduced at the negative electrode and an oxidation process takes place at the positive electrode. The voltage source must be at least equivalent
to the difference $\Delta E^0$ between the equilibrium potentials of the two half cells. Generally the charge voltage is higher [61].

### 2.1.2 Thermodynamic Principles

The first law of thermodynamics requires a conservation of energy. Thus, $\Delta U = \Delta Q + \Delta W$ (where $Q$ and $W$ are heat and work, respectively). With $W_e$ the electrical work done by an electrochemical cell, and $S$ and $V$ being the entropy and volume, we can express $\Delta U$ as [64]:

$$\Delta U = T\Delta S - P\Delta V + W_e \quad (2)$$

We can see that $W_e$ is directly related to the Gibbs free energy, $\Delta G$, since $\Delta G$ is the difference between the reaction enthalpy, $\Delta H = \Delta U + P\Delta V$ and the entropic term, $T\Delta S$:

$$W_e = \Delta U - T\Delta S + P\Delta V = \Delta H - T\Delta S = \Delta G \quad (3)$$

For the electrochemical cell reaction, the reaction free energy $\Delta G$ is the utilizable electric energy. The reaction enthalpy $\Delta H$ is the theoretical available energy, which is increased or reduced by $T \cdot \Delta S$. The product of the temperature and the entropy describes the reversible amount of heat consumed or released during the reaction [61].

The thermodynamic treatment requires that during one formula conversion the cell reaction is reversible. This means that all partial processes in a cell must remain in equilibrium. The current is kept infinitely small, so that the cell voltage $E$ and the equilibrium cell voltage $\Delta E^0$ are equal. Furthermore, inside the cell no concentration gradient should exist in the electrolyte. Under these conditions, the utilizable electric energy, $\Delta E^0 \times z \times F$ per mol, corresponds to the reaction free energy $\Delta G$ of the Galvanic cell, which is therefore given by:

$$\Delta G = -z \times F \times \Delta E^0 \quad (4)$$
The standard potential of a cell ($\Delta E^0$) is determined by the thermodynamics of the system through its relationship to $\Delta G$ [64]. It is established from chemical thermodynamics that the sum of the chemical potentials $\mu_i$ of the substances $v_i$ involved in the gross reaction is equal to the reaction free energy [61].

$$\Delta G = \sum v_i \times \mu_i$$

(5)

Here $v_i$ are the stoichiometric factors of the compounds used in the equation for the cell reaction, having a plus sign for the substances formed and a negative sign for the consumed compounds. Since,

$$-\frac{\Delta G}{z \times F} = \Delta E^0 = \frac{1}{z \times F} \sum v_i \times \mu_i$$

(6)

The chemical potential of one half cell depends on the concentrations $c_i$ of the compounds, which react at the electrode:

$$\mu_i = \mu_{i0} + R \times T \ln c_i$$

(7)

$R =$ universal gas constant: 8.3 Jmol$^{-1}$K$^{-1}$.

As a consequence, the equilibrium potential of the single half cell also depends on the concentrations of the compounds. The NERNST equation (Equation 8), which is one of the most important electrochemical relations, expresses this [65]. It results if Equation (7) is inserted into Equation (6) with regard to one half cell:

$$\Delta E = \Delta E^0 + \frac{R \times T}{z \times F} \sum v_i \ln c_i$$

(8)

For a metal-ion electrode the NERNST equation is:

$$\Delta E = \Delta E^0 + \frac{R \times T}{z \times F} \sum \ln \frac{c_{Me^{z+}}}{c_{Me}}$$

(9)
2.1.3 Principles of Lithium Ion Batteries

The lithium-ion battery is currently one of the most promising energy storage technologies and extensively used in portable electronics such as cellular phones and laptop computers. Li-ion cells have become a commercial reality after the initial announcement by SONY in the early 1990s because of an intense world-wide activity on lithium insertion compounds (electrode materials) during the past three decades [63]. The number of lithium-ion cells made worldwide has increased from 800 million in 2002 to 4.4 billion in 2012, according to the Portable Rechargeable Battery Association, a trade group of battery makers. According to a new IHS iSuppli Rechargeable Batteries Special Report [66] from information and analysis provider IHS, global lithium-ion battery revenue is expected to expand to $53.7 billion in 2020, up from $11.8 billion in 2010, as presented in the Figure 2.4. Revenue will rise to $31.4 billion in 2015, allowing lithium-ion to be the dominant rechargeable battery technology over the lead acid one. The main reason behind such rapid growth is its high energy density and cycling performance that no other energy storage devices can match. Recent demands on energy and environmental sustainability have further stimulated great interest in a larger scale lithium-ion battery system for vehicles and grid load leveling as well as complimentary energy storage for renewable energy resources, such as solar and wind power [67]. Lithium ion batteries are appealing for these applications as they provide higher energy density compared to the other rechargeable battery systems such as lead-acid, nickel-cadmium, and nickel-metal hybrid batteries as shown in Figure 2.5.

![Global Lithium-Ion Battery Market Revenue Forecast (Millions of U.S. Dollars)](image)

*Figure 2.4 Global Lithium-Ion Battery Revenue Forecast [66].*
LiCoO$_2$ was the cathode in the first lithium-ion battery reported in the literature. This cathode material is still the main cathode chemistry in the lithium battery industry and currently about 70% of the mobile electronics are powered by batteries with this cathode. Despite its electrochemical performance, LiCoO$_2$ suffers from the disadvantages of the toxicity of cobalt and its high cost. Therefore, there is extensive research for alternative cathode materials for lithium-ion batteries [67].

The energy storage mechanism of lithium-ion batteries is quite straightforward. Lithium-ion batteries store electrical energy in electrodes, commonly made of lithium-intercalation (or insertion) compounds, with simultaneous oxidation and reduction processes occurring at the two electrodes. A lithium-ion battery usually comprises a layered positive electrode (cathode), commonly LiCoO$_2$, a graphite negative electrode (anode) and, a nonaqueous liquid electrolyte, as shown in Figure 2.6 [67].
Figure 2.6 A Traditional Lithium-Ion Battery Cell in Which, During Discharge, Li\(^{+}\) Ions Migrate Through The Electrolyte and Electrons Flow Through The External Circuit, Both Moving from A Graphite Negative Electrode (Anode) To The Layered (LiCoO\(_2\)) Positive Electrode [69].

During charging, Li\(^{+}\) ions are extracted or deintercalated from the layered LiCoO\(_2\) cathode host, transferred through the electrolyte, and inserted or intercalated between the graphite layers in the anode. During discharge this process is reversed and the electrons pass around the external circuit to power various systems. The rechargeable lithium-ion battery started with the discovery of intercalation compounds, such as Li\(_x\)MO\(_2\) (M = cobalt or nickel) which were initially proposed by Goodenough and it is an ultimate representation of solid-state chemistry in action [70, 71]. The energy conversion in these systems also called rocking-chair cells is completed via the following reactions [67, 72, 73]:

\[
\text{Cathode: } \text{Li}_1x\text{CoO}_2 + x\text{Li}^+ + xe^- \xrightarrow{\text{discharge}} \text{LiCoO}_2 \\
\text{Anode: } \text{Li}_x\text{C}_6 \xrightarrow{\text{discharge}} x\text{Li}^+ + xe^- + \text{C}_6
\]

Full Cell Reaction:

\[
\text{LiC}_6 + \text{CoO}_2 \xrightarrow{\text{discharge}} \text{C}_6 + \text{LiCoO}_2 \quad E = 3.7 \text{ V at } 25 \text{ °C}
\]

Typical lithium-ion cells have a capacity about 150 Ah/kg, power over 200 Wh/kg and operate at 3.7 V. The great success of lithium-ion technology for mobile electronics has
been due to favorable electrochemical performance in energy/power densities, as well as advancements in system design and manufacturing.

Different types of structures are available as possible hosts for the lithium intercalation reaction, including but not limited to graphite, \( \text{V}_2\text{O}_5 \), and layered oxides. For successful application as an electrode in a lithium-ion battery, the host intercalation material should provide sufficient lithium-ion conductivity and retain its structural stability and mechanical integrity (low volume changes) upon repeated lithium insertion (lithiation) and extraction (delithiation). These characteristics assure prolonged cycling abilities of a cathode for rechargeable batteries but narrow the choices of the prospective intercalation cathodes. The intercalation structures could be divided into three major groups according to the lithium intercalation pathways: 1-D, 2-D, and 3-D structures (Figure 2.7). Along these directions the host structure is strongly bonded, and thus the lithiation and delithiation reactions do not affect the host structure, nevertheless, in the perpendicular directions there might be a tremendous expansion and shrinkage, which may lead to the structural exfoliation of the intercalated structure. The layered (2-D) materials are preferred over 1-D and 3-D counterparts due their relatively high stability of the host matrix and high selectivity concerning the dimensions of the intercalating species. Graphite and layered oxides such as \( \text{LiM} \text{O}_2 \) (\( \text{M} = \text{Co, Ni, Mn} \)) are the most important examples of the layered materials for lithium battery application [67].

![Figure 2.7 Schematics of Possible Lithium Intercalation Pathways (a) One-, (b) Two-, and (c) Three-Dimensional Structures [67].](image)

Although the concept is simple, there are some key requirements that the lithium insertion compound should satisfy to be a successful cathode material in a lithium ion battery [61, 63]:
The insertion compound Li$_x$M$_y$X$_z$ (X= anion) should have a high lithium chemical potential ($\mu_{\text{Li}}(c)$) to maximize the cell voltage. This implies that the transition metal ion M$^{n+}$ in Li$_x$M$_y$X$_z$ should have a high oxidation state in the cathode and a low oxidation state in the anode.

The intercalation compound Li$_x$M$_y$X$_z$ should allow an insertion/extraction of a large amount of lithium, x, per formula unit to maximize cell capacity. This depends on the number of available lithium sites and the accessibility of multiple valances for M in the insertion host. A combination of high capacity and cell voltage can maximize the energy density which is given by the product of the capacity and the voltage.

The lithium insertion/extraction reaction should be reversible, with minimal or no change in structure, leading to good cycle life. This implies that the insertion compound Li$_x$M$_y$X$_z$ should have good structural stability without breaking any M-X bonds.

The insertion compound should support mixed conduction. It should have a good electronic conductivity $\sigma_e$ and lithium-ion conductivity $\sigma_{\text{Li}}$ to minimize polarization losses during the discharge/charge process, thereby supporting fast charge–discharge rates, high current density and power density. This depends on the crystal structure, arrangement of MX$_n$ polyhedral geometry and interconnection of lithium sites, the nature and electronic configuration of the M$^{n+}$ ion, and the relative positions of the M$^{n+}$ and X$^{n-}$ energies.

The intercalation compound should be chemically stable without undergoing any reaction with the electrolyte over the entire range, x, of lithium insertion/extraction.

The redox energy of the cathode in the entire range, x, of lithium insertion/extraction should lie within the band gap of the electrolyte to prevent any unwanted oxidation or reduction of the electrolyte.

From a commercial point of view, the insertion compound should be inexpensive, environmentally benign, thermally and chemically stable and lightweight. This implies that the M$^{n+}$ ion should preferably be from the 3d transition series.
It is really important and useful for research and development of battery technology to understand the fundamental theory behind an electrochemical storage system. Figure 2.8 shows a schematic of the relative electron energies in the electrodes and the aqueous electrolyte of a battery cell at thermodynamic equilibrium. The energy gap, $E_g$, between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte defines the stability window of the electrolyte. Therefore, thermodynamic stability considerations require the redox energies of the cathode ($\mu_C$) and anode ($\mu_A$) to lie within the band gap $E_g$ of the electrolyte, as shown in Figure 2.8. Cathodes and anodes with chemical potentials lying outside the electrolyte gap will cause reduction or oxidation of the electrolyte unless a passivating solid electrolyte interface (SEI) layer will be formed to prevent such reactions [74].

Thus,

$$eV_{oc} = \mu_A - \mu_C \leq E_g$$

(13)

e: magnitude of the electron charge.

Figure 2.8 Schematic of The Relative Electron Energies in The Electrodes and The Aqueous Electrolyte of A Battery Cell at Thermodynamic Equilibrium [74].

However, the formation of an SEI layer can provide a kinetic stability to a larger $V_{oc}$, if $eV_{oc} - E_g$ is not too large. The energy density of a battery is given by $\Lambda \times V_{oc}$, where $\Lambda$ is the capacity of a reversible charge transfer per unit weight (Ah/g) between the anode and
cathode. The specific capacity of an electrode material can be calculated in mAh/g based on:

\[
\text{Specific Capacity (mAh}^{-1}) = n \times F \times 1000 / (MW \times 3600) \tag{14}
\]

\(n\): number of lithium used in moles
\(F\): Faraday constant (96,485 s A/mol)
\(MW\): molecular weight

While the capacity of a cell relies on the electrodes, the cell lifetimes are mainly governed by the electrode–electrolyte interface side reactions. Breaking the SEI layer can result in lithium dendrite growth and can short-circuit a cell with dangerous consequences.

For an aqueous electrolyte, \(E_g \approx 1.3\) eV limits the \(V_{oc}\). Consequently, to achieve higher \(V_{oc}\) and energy density \(\Lambda \times V_{oc}\) for a battery cell, an electrolyte with a larger \(E_g\) is required. Such \(E_g\) can be provided by a nonaqueous liquid or polymer electrolyte containing soluble lithium salts in which the limiting \(\mu_C\) of the cathode is determined by both the HOMO of the salt and that of the solvent. Lithium metal would be the ideal anode, but the \(\varepsilon F = \mu_A\) of lithium lies above the LUMO of practical known nonaqueous electrolytes. However, the formation of the SEI layer enables lithium metal to work as the anode in half cells where the \(\mu_A\) or \(\mu_C\) relative to the Li\(^+\)/Li can be measured [67, 74].

The range of voltages that are exhibited by some of the host structures is shown in Figure 2.9. The energy of a given \(\mu_A\) or \(\mu_C\) may correspond to the Fermi energy in an itinerant-electron band for carbon or the energy of a transition-metal redox couple determined by the formal valence state of the cation and the covalent component of its nearest-neighbor bonding. This is not only influenced by the placement and character of any counter cations, but also by the Madelung energy of the ionic component of the bonding relative to the crystal structure. The redox couple position relative to the bottom of a broad conduction band or to the top of an anion p band may determine the intrinsic voltage limit versus Li\(^+\)/Li of a given electrode material [74].
Figure 2.9 Schematic of Corresponding Energy Versus Density of States With Relative Positions of The Fermi Energy in An Itinerant-Electron Band for $\text{Li}_x\text{C}_6$, Redox Couple for $\text{Li}_x\text{TiS}_2$, $\text{Li}_x\text{CoO}_2$, and $\text{Li}_x\text{CoPO}_4$ [74].

The influence of structure on the energy of a transition-metal redox couple is depicted by the comparison in Figure 2.10 of the voltages from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in the olivine $\text{Li}_x\text{FePO}_4$, the NaSiCON structure of $\text{Li}_{3+x}\text{Fe}_2(\text{PO}_4)_3$, and some diphosphates.

Figure 2.10 Positions of The $\text{Fe}^{3+}/\text{Fe}^{2+}$ Redox Couples Relative To The Fermi Energy of Lithium in Different Phosphates [74].

The improvement of the energy density of the lithium-ion battery can be made through appropriate use of existing or new electrode materials. Besides the cathode and anode electrodes, the electrolyte, which commonly refers to a solution comprising the salts and solvents, constitutes the third key component of a battery. Although the role of the
electrolyte is often considered to be trivial, the choice of electrolyte is crucial in designing the actual lithium-ion battery. The criteria differ, depending on different types of electrolytes, which may be an organic liquid, a polymer, or an inorganic solid electrolyte. However, other than a large electrolyte window \( E_g \), which is preferred, there are additional requirements that need to be fulfilled such as (1) ionic conductivity and chemical stability over the temperature range of battery operation, (2) electronic conductivity, (3) transference number, (4) low toxicity, (5) low cost, (6) a passivating SEI layer being formed and retained during cycling, and (7) nonflammable and nonexplosive if short-circuited.

2.1.4 Current Status of Lithium-Ion Battery Technology

A battery made of \( \text{LiCoO}_2 \) and graphite at the cathode and anode electrodes was the first generation of lithium-ion battery technology. Li ion batteries can store more than twice the energy of nickel or lead batteries of the same size and mass. However, the current and the future demand of energy for electronic applications and vehicle industry require even better performance in terms of energy density, power, safety, price, and environmental impact. Therefore, continuous progress has been made in electrode materials other than \( \text{LiCoO}_2 \) [75-78] (Figure 2.11), such as \( \text{LiNiO}_2 \) [69, 79], \( \text{LiMn}_2\text{O}_4 \) [20, 25, 80, 81], \( \text{LiNi}_{1-x-y}\text{Mn}_y\text{Co}_2 \) [61, 69, 76, 82, 83], \( \text{LiFePO}_4 \) [1, 4, 9, 22, 84-89], and \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) [90-93], which have reached the market at different levels. Nonetheless, all these materials still have intrinsic limitations that are derived from the redox mechanism related to the crystal structural aspects of the material. The reversible intercalation of lithium ions is mostly limited by the changes in the host crystal structure and redox activity of the transition metals that handicap the energy density.

Breakthroughs will only come from discovering novel electrode materials with the right crystal structure to withstand repetitive cycling. Table 2.2 summarizes the various cathode and anode materials has been developed since the invention of the lithium-ion battery technology 20 years ago.
Figure 2.11 Voltage vs Capacity of Some Electrode Materials Relative to The E<sub>g</sub> of 1M LiPF<sub>6</sub> in EC/DEC [74].

Table 2.2 Various Cathode and Anode Materials for The Lithium-Ion Battery and Their Characteristics [63, 94, 95].

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemistry</th>
<th>Specific Capacity in mAh/g (theoretical/observed)</th>
<th>Potential vs. Li/Li</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>LiCoO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>273/160</td>
<td>3.9</td>
<td>First cathode, expensive</td>
</tr>
<tr>
<td></td>
<td>LiNi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>274/180</td>
<td>3.6</td>
<td>Cheaper than LiCoO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>LiNi&lt;sub&gt;1&lt;/sub&gt;Co&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;0.5&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>~270/150–180</td>
<td>3.8</td>
<td>Cheap and stable</td>
</tr>
<tr>
<td></td>
<td>LiNi&lt;sub&gt;1&lt;/sub&gt;Co&lt;sub&gt;0.5&lt;/sub&gt;Al&lt;sub&gt;0.5&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>~250/180</td>
<td>3.7</td>
<td>Stable</td>
</tr>
<tr>
<td></td>
<td>LiMn&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>148/130</td>
<td>4.1</td>
<td>Unstable cycling</td>
</tr>
<tr>
<td></td>
<td>LiMn&lt;sub&gt;1.5&lt;/sub&gt;Ni&lt;sub&gt;0.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>146/130</td>
<td>4.7</td>
<td>High voltage, cheap</td>
</tr>
<tr>
<td></td>
<td>LiFePO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>170/160</td>
<td>3.45</td>
<td>Low voltage, safe, cheap</td>
</tr>
<tr>
<td></td>
<td>LiMnPO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>171/80–150</td>
<td>4.1</td>
<td>Slow kinetics, cheap, high voltage</td>
</tr>
<tr>
<td></td>
<td>LiNiPO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>166/-</td>
<td>5.1</td>
<td>No suitable electrolyte</td>
</tr>
<tr>
<td></td>
<td>LiCoPO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>166/60–130</td>
<td>4.8</td>
<td>Expensive</td>
</tr>
<tr>
<td></td>
<td>LiFeSiO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>165/160</td>
<td>2.8</td>
<td>Cheap, low voltage</td>
</tr>
<tr>
<td></td>
<td>LiMnSiO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>166/140</td>
<td>~4.0</td>
<td>Cheap</td>
</tr>
<tr>
<td></td>
<td>LiV&lt;sub&gt;2&lt;/sub&gt;(PO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>131/130</td>
<td>4.1/3.6</td>
<td>Two voltage plateau</td>
</tr>
<tr>
<td></td>
<td>LiFeBO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>220/~150</td>
<td>2.7</td>
<td>Cheap, air sensitive</td>
</tr>
<tr>
<td></td>
<td>LiMnBO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>222/-</td>
<td>3.7</td>
<td>Cheap, difficult to make active</td>
</tr>
<tr>
<td></td>
<td>TiS&lt;sub&gt;2&lt;/sub&gt;</td>
<td>239/200</td>
<td>2.0</td>
<td>Low voltage, Li metal anode</td>
</tr>
<tr>
<td></td>
<td>V&lt;sub&gt;2&lt;/sub&gt;</td>
<td>233/210</td>
<td>2.2</td>
<td>Low voltage, Li metal anode</td>
</tr>
<tr>
<td>Anode</td>
<td>Graphite</td>
<td>372/330</td>
<td>0.1–0.2</td>
<td>Li&lt;sub&gt;C&lt;/sub&gt; vol. change: ~11%</td>
</tr>
<tr>
<td></td>
<td>Soft Carbon</td>
<td>~/.&lt;700</td>
<td>&lt;1</td>
<td>High capacity, sloping voltage profile</td>
</tr>
<tr>
<td></td>
<td>Hard Carbon</td>
<td>~/.600</td>
<td>&lt;1</td>
<td>High capacity, sloping voltage profile</td>
</tr>
<tr>
<td></td>
<td>Li&lt;sub&gt;2&lt;/sub&gt;TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>175/170</td>
<td>1.55</td>
<td>High voltage, no vol. change</td>
</tr>
<tr>
<td></td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; (anatase/rutile)</td>
<td>168/168</td>
<td>1.85</td>
<td>Cheap, vol. change: ~4%</td>
</tr>
<tr>
<td></td>
<td>SnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>782/780</td>
<td>&lt;0.5</td>
<td>Large initial irreversible loss</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>993/990</td>
<td>&lt;0.5</td>
<td>Poor cycling, vol. change: 257%</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>4198/3500</td>
<td>0.5–1</td>
<td>Poor cycling, vol. change: 297%</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>2235</td>
<td>&lt;0.3</td>
<td>Poor cycling, vol. change: 238%</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>385</td>
<td>&lt;0.8</td>
<td>Vol. change: 115%</td>
</tr>
</tbody>
</table>
2.1.4.1 Cathode Materials Overview

Numerous families of cathode materials have been developed for lithium batteries since the first research paper published on rechargeable lithium battery by Whittingham in 1976 [96]. The most common material from the commercial point of view remains LiCoO$_2$, which was first studied in Goodenough’s laboratory in 1980 [71]. Due to the high cost of cobalt, and also the instability of Li$_x$CoO$_2$ for $x < 0.5$, several other LiMO$_2$-type cathodes (where M = Co, Ni, Mn, or V) have also been developed [97]. Among them are layered compounds with hexagonal symmetry based on an $\alpha$-NaFeO$_2$ structure with a space group of R-3m, such as LiNiO$_2$, LiNi$_x$Co$_y$O$_2$, LiMn$_x$Co$_y$O$_2$, LiMn$_x$Ni$_y$O$_2$, LiNi$_x$Co$_x$Al$_2$O$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, and so on as shown in Figure 2.12 [72, 74, 94, 98-100]. Another mature alternative cathode is spinel-type LiMn$_2$O$_4$ (Figure 2.12b), originally proposed by Thackeray et al. [101], and its derivatives have a voltage of over 4.0 V versus lithium and a capacity about 10% less than that of LiCoO$_2$. The LiM$_2$O$_4$ (M = Ti, V, Mn) materials are normal spinels with the space group Fd3m in which the lithium ions occupy tetrahedral sites (8a), and the transition metal ions reside at octahedral sites (16d). Doped spinels LiMn$_{2-x}$M$_x$O$_4$ (M = nickel, iron, chromium, cobalt, copper, aluminum, or lithium) have shown promising results.

Among doped transition-metal spinels, LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO) with a potential plateau of 4.7 V where charge neutrality is maintained by oxidizing Ni$^{2+}$ to Ni$^{4+}$ is one of the most attractive compositions because of the decent specific capacity of 147 mAh/g with good cycling and rate capabilities at room temperature. However, the LMNO spinel demonstrates a significant capacity loss at an elevated temperature, which is critical for hybrid electric vehicle/electric vehicle (HEV/EV) applications [67].

Lithium iron phosphate (LiFePO$_4$), particularly in nanosize [102], is another promising positive electrode material shown in Figure 2.12 (c). Padhi et al. [103], proposed olivine structured LiFePO$_4$ with the space group Pnma, in the late 1990s, which exhibits a lower voltage (3.45 V vs. Li$^+$/Li) but a higher capacity of 170 mAh/g compared to LiCoO$_2$. This was the first cathode material using low cost, abundant, and environmentally benign elements, such as iron or manganese that could have a major impact on electrochemical energy storage. LiFePO$_4$ has a lithium-diffusion path along the (010) direction, due to its tunnel structure (as shown in Figure 2.12 (c)). Furthermore, this cathode material has a flat
potential of 3.45 V against Li/Li⁺ because of the two-phase LiFePO₄/FePO₄ transition. Nanostructured LiFePO₄ is the most recent cathode material that has gained commercial success in lithium-ion batteries [67]. Another phosphate material which could become more popular in the future is monoclinic Li₃V₂(PO₄)₅. Two moles per functional unit can be reversibly removed and inserted, giving a capacity of 130 mAh/g at an average voltage of 3.8 V vs. Li/Li⁺. The extraction of the last lithium takes place at 4.6 V, and it appears to be energetically unfavorable, exhibiting a large overvoltage. However, it is possible to remove all three Li atoms, giving 175 mAh/g. If the kinetics and cyclability of this reaction could be improved, this could be a promising cathode [97, 104].

In addition to the abovementioned cathode materials, there is a significant amount of ongoing research and development on advanced and thermally stable cathode materials of a higher capacity. Even with all the progress made in recent years, there are only a few compositions coming close to commercialization basically because the performance of cathode materials depends on many factors such as the arrangement of the active particles
with the carbon additive, polymeric binder, and current collector. This is critical because it must form an efficient pathway for electron and lithium-ion transportation within the electrode. The crystal structure, microstructure, and secondary phases on the active material surface (such as impurity phases or engineered coatings) will determine the lithium-ion and electron transport properties within the particles and the stability of the material towards the electrolyte. In any large-scale production process, major efforts are focused on controlling the crystal structure, microstructure, particles size/particle architecture, and impurities of the material.

In reality, an optimum cathode material is a good trade-off between many different requirements, such as capacity, rate capability, cycle life, processability, cost, and safety. In most cases, these requirements cannot be met simultaneously. This is because the numerous requirements can only be met with different crystal structures, microstructures, particle size/morphology, and material compositions (Figure 2.13). For instance, the high-rate capability in battery materials requires smaller (down to nanosize in the case of LiFePO₄ [105]) particles, because of the intrinsically low electronic and ionic conductivity of traditional cathode materials, whereas good processability and high active material loading

Figure 2.13 Schematic Drawing of The Overall Performance of The Cathode Materials for Lithium-Ion Batteries [67].
require large micron-sized particles. In an actual production process, cathode material composition, structure, particle size, and morphology are optimized for maximum electrochemical reactivity but minimum side reactions with electrolyte [67].

2.1.4.2 Anode Materials Overview

Lithium metal is very attractive anode material, since it can be more easily handled (though with care) than other alkali metals and more significantly, the lightest and the most electropositive among the alkali metal family. The low density of lithium metal (0.534 g/cm³) leads to the highest specific capacity value of 3860 mAh g⁻¹ [106]. However, lithium is chemically reactive with non-aqueous electrolytes making this metal not a safe choice for rechargeable lithium batteries [97]. On the other hand, since the first two reports of carbon-based anodes in 1989 by Kanno et al. [107] and Mohri et al.[108], carbonaceous materials have become the choice of anode for the lithium-ion battery [109]. Graphite in particular has gained considerable attention in the late 1980s as an alternative anode material to lithium metal because of its capability to reversibly intercalate/deintercalate lithium ions into/from the graphite lattice. As a result, in the commercial lithium-ion battery, graphite was the first anode material of choice and remains as the only anode material practically used because of its low redox potential and excellent structural stability during repetitive cycling.

Carbonaceous materials capable of reversibly intercalating lithium ions can be classified into graphitic or nongraphitic (disordered) carbon. Another common description is soft carbon (graphitic carbon) and hard carbon (glassy carbon). Graphitic carbons have a theoretical capacity of 372 mAh/g, which corresponds to an insertion of one lithium per 6 carbon atoms (x = 1 in LiₓC₆), and an observed capacity of 280–330 mAh/g, depending on the type. Graphite is available naturally or as a byproduct of petroleum, but the price varies, depending on the heat-treatment process. On the other hand, soft carbons (heat treated at 500°C–1000°C) give a reversible capacity of nearly 700 mAh/g with a characteristic plateau in discharge/charge properties at about 1.0 V; hard carbons (~1100°C) give a reversible capacity of 600 mAh/g, but with small irreversible capacity loss and polarization [110]. The hard carbons are typically obtained by a thermal decomposition of phenolic and epoxy resins and products from petroleum pitch. They have a significant amount of open pores, which
tend to become closed on heating at higher temperatures, and some of them consist of single graphene sheets. Hard carbons show higher capacities than does graphene [63].

Among many different types of carbonaceous electrodes, well-ordered graphite is currently the industrial standard because of its long plateau in the voltage profile and its low electrode potential relative to lithium metal. In commercial cells, well-ordered graphite, such as mesocarbon microbeads (MCMBs) heat treated at 3000°C, natural graphite, and non-graphitizing carbons (hard carbon) have mainly been used [67, 110].

A few oxides, nitrides, phosphides and intermetallic compounds have also been investigated as anode hosts. Metal nitrides and phosphides offer lower voltages versus lithium due to the covalent character and the stabilization of lower oxidation states [63]. A spinel material, Li$_4$Ti$_5$O$_{12}$ is under consideration for an anode in high-power cells, since its charging potential is around 1.55 V vs. lithium, so there is no danger of lithium metal deposition, which could happen when cycling graphitic anodes at high rates. However, use of this material as an anode would reduce the overall cell voltage, and the capacity of this material is only 160 mAh/g [111].

Other candidate anodes include lithium binary alloys (Li-Al, Li-Si, Li-Sn, Li-Ge), which all have higher specific capacities than graphite (Li-Si, at Li$_{22}$Si$_5$ has a capacity 4200 mAh/g and Li-Ge at Li$_{22}$Ge$_5$ has a capacity 1600 mAh/g). However, these compounds undergo crystallographic phase changes and also large volumetric expansion when alloyed with lithium. Therefore, only nanosized particles or films have been successfully used, and life cycles have been limited. Graetz et al. [112, 113] developed amorphous nanosized thin films, having 2000 mAh/g and 1700 mAh/g, for Si and Ge films, respectively, for over 50 cycles. However, extended cycling has not been studied sufficiently.

Rutile-type MoO$_2$ and WO$_2$, Fe$_2$O$_3$, MnP$_4$ and intermetallic compounds such as Cu$_6$Sn$_5$ having NiAs-Type structure have also been investigated. These anodes, including carbon, do not contain Li and they can be coupled only with cathodes such as LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$ that already contain lithium [63].
Composites of graphite and nano-Si can result in good cycle life, while also maintaining a relatively high capacity. For example, Holzapfel et al. [114] were able to cycle a 20% nanosilicon/80% graphite composite with little capacity fade and a capacity of around 1000 mAh/g for over 100 cycles. In such a composite, the graphite matrix serves as a structural support for the nano-Si. This may be a good compromise to increasing the anode capacity while still retaining good cycle life characteristics [97].

### 2.1.4.3 Electrolytes for Lithium-Ion Batteries

As it was discussed before, the electrolyte materials are key determinants of battery performance. The cell lifetimes are mainly governed by the electrode–electrolyte interface side reactions. The electrolyte can also have a significant impact (i.e., by reacting with the electrode active material to form an SEI, by limiting accessibility of ions to active material, etc.). The electrolyte and electrode/electrolyte interfaces, however, are also a central factor in battery power, cost, life, and safety.

![Diagram of electrolyte components and performance](image-url)

**Figure 2.14** Links Between Electrolyte Composition, Properties, and Battery Performance [67].
Historically there have been difficulties to identify an electrolyte composition which enabled the reversible cycling of the graphite anode and LiCoO$_2$ cathode. Although lithium graphite intercalation compounds were discovered in the 1950s, it took decades to develop the mixture of ethylene carbonate (EC, C$_3$H$_4$O$_4$), a linear carbonate such as diethyl carbonate (DEC, C$_5$H$_{10}$O$_3$) and lithium hexafluorophosphate (LiPF$_6$) which enabled the commercialization of Li-ion batteries by Sony in 1991. Current state-of-the-art electrolytes have a very similar composition: EC plus a linear carbonate, mixed with LiPF$_6$ and selected additives (Figure 2.14) to optimize the properties of the solid-electrolyte interface (SEI) [67].

In general, the electrolyte is specifically designed for a particular battery system. While the electrolyte can be a liquid, a gel, a solid polymer, or an inorganic solid, the majority of lithium-ion batteries use liquid electrolytes containing a lithium salt, such as LiPF$_6$, LiBF$_4$, LiClO$_4$, LiBC$_4$O$_8$ (LiBOB), or Li[PF$_6$(C$_2$F$_5$)$_3$] (LiFAP), dissolved in a mixture of organic alkyl carbonate solvents. There is a high risk when flammable organic electrolyte solvents are used due to the fact that they can generate heat, thermal runaway, and fire. An additional challenge is the high cost, which may not be critical to small portable electronic applications, but is very important for scaled-up applications. In addition, a variety of additives has been introduced, including vinylene carbonate (VC, C$_3$H$_2$O$_3$), to stabilize the electrolyte/electrode interfaces [67].

Two key challenges for the application of Li-ion batteries for plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) include battery cost and cycle/calendar life (in addition to the need for an improved operating temperature range and the noted safety requirement). One method to effectively reduce cost is to increase the energy density (capacity), thus reducing the size of the battery pack necessary. To access the higher capacity of so-called high-voltage electrodes requires new electrolytes which enable stable cycling outside the operating potential range of current state of the art electrolytes ($\geq$4.3 V or greater vs. Li/Li$^+$) [67].

2.1.4.4 Battery cell

The lithium-ion battery cell design varies with size and specific applications. Typical configurations of lithium-ion battery cells are coin, cylindrical, prismatic, and pouch forms as
shown in Figure 2.15, but the general components used are the same [115]. The cylindrical cell has an exterior stainless steel can as its package, and it is the most common form of lithium-ion cell package used today. The cylindrical cell package is also equipped with a resealable vent to release pressure under excessive charge. Typical applications of the cylindrical cells include wireless communications, biomedical instruments, power tools, and applications that do not demand an ultra-compact size. Moreover, the use of the prismatic cell design has also become widespread due to the increase of portable consumer electronics. The prismatic cell design supports thinner cell geometries, and its rectangular packaging can be custom designed for each application use. For instance, lithium polymer batteries exclusively use prismatic cell packaging. Whereas the cylindrical cell and the prismatic cell designs use expensive metallic enclosures, a heat-sealable, multilayer foil is used in the lithium-ion pouch cell design. The electrical contacts in the pouch cell consist of conductive foil tabs that are welded to the electrode and sealed to the pouch material. The pouch cell has the advantage of being lighter and cheaper, and it can make the most efficient use of the available space. This type of configuration is the most appropriate design for cell phones and portable consumer electronics that require ultra-thin enclosures. For vehicle and stationary applications, a lithium-ion battery pack consists of a number of prismatic cells with or without a cooling system [67].

Figure 2.15 Lithium Ion Battery Cell Configurations: a) Cylindrical, b) Coin, c) Prismatic, and d) Pouch [68].
In addition to the previously mentioned battery components, the current collectors for the cathode and the anode are aluminium and copper foil respectively. Electrodes operate orthopedically on a current collector sheet with binder (polyvinylidene fluoride (PVdF, \(-(C_2H_2F_2)_n\)), styrene-butadiene rubber (SBR, \(CH_2=CHC_6H_5\)), Teflon (polytetrafluoroethylene (PTFE, \(C_2F_4n\)), carboxymethyl cellulose (CMC, \(C_6H_7O_2(OH)2\)CH2COONa) and conductive additives (e.g., acetylene black, Ketjen black). In the electrode manufacturing process, a mixture of active materials with conductive additives and a binder dissolved in n-methyl-2-pyrrolidinone (NMP, \(C_5H_9NO\)) are made into a slurry or paste. The slurry is tape cast over both sides of the Al/Cu foil, dried, and roll-pressed. The manufacturing process consists of (1) mixing the active cathode and anode materials with binder and conductive additives, (2) tape casting on the current collector, (3) drying, and (4) pressing. The next step involves (1) assembly of electrodes and the simultaneous rolling-up with separator, (2) electrode insertion, (3) electrolyte injection into the battery case, and (4) sealing [67, 68, 115].

2.1.4.5 Material Challenges of Lithium-Ion Batteries

Currently, lithium-ion batteries are widely used as rechargeable power sources for consumer electronics such as cell phones, laptop computers, digital cameras, and power tools because they are light-weight and efficient. Moreover, there is a requirement of lithium-ion batteries with high power and energy densities for future energy storage devices for HEVs, plug-in hybrid vehicles (PHEV) and EVs. Although the lithium-ion battery can store more energy than any other storage system, a higher charge/discharge rate of more than one order of magnitude is required to meet the future demands of HEVs. Limits exist because of the intrinsic diffusivity of the lithium ion in the solid state (<10\(^{-8}\) cm\(^2\)s\(^{-1}\)), and the resistance of the electrolyte inevitably limits the power density [67].

The primary challenges facing the development of batteries for electric vehicles are cell energy density (voltage x capacity), rate of charge/discharge, cost, safety, and service life. Material selection, optimization of the synthesis methods, automation of manufacturing, and service life are the keys to lower costs [74]. Long service life requires elimination of side chemical reactions between the electrodes and the electrolyte as well as
Some target requirements for the development of an energy storage device for an electric drive train has been placed by the U.S. Department of Energy. They are a 15-year lifespan at 300 Wh, a discharge power of 25 kW, and a cost of $20/kW. To develop a PHEV battery that enables a 40-mile, all-electric range and costs $3400 by 2014, there are still technical barriers that need to be overcome. Despite the new breakthroughs brought by recent nanotechnology, the present lithium-ion technology still falls short of meeting all of the requirements. The current cost of the most promising lithium-ion-based battery chemistry is approximately a factor of three to five too high on a kWh basis for PHEVs and approximately a factor of two too high on a kW basis for HEVs. The main expenses are the high costs of raw materials as well as materials processing and cell and module packaging.

As depicted in the Figure 2.16, the cost mainly depends on the material-synthesis process, its abundance and renewability. Therefore, electrodes based on sustainable 3d transition metal redox elements, such as manganese (LiMn$_2$O$_4$, LiMnPO$_4$), iron (LiFePO$_4$, Li$_2$FeSiO$_4$), and titanium (TiO$_2$, Li$_4$Ti$_5$O$_12$), which are made via low temperature processes, are of great interest with respect to limited cobalt- or nickel-based electrodes requiring high-temperature synthesis. Electrode materials with higher energy densities are needed to meet the volume and weight requirements, especially for the PHEV system. Also, the number of cells in the battery needs to be reduced, thus reducing the system cost. Many lithium-ion batteries are not intrinsically tolerant to abusive conditions, such as short-circuit, overcharge, crushing, or exposure to fire and/or other high-temperature environments. Also, there are enormous efforts involved to prove a 15-year lifespan with 300,000 cycles for an HEV or 5,000 cycles for an EV and to increase the energy of a battery (180 Wh/kg) by a factor of 15 to match a liter of gasoline (3000 Wh/L). Since the energy density of batteries has only increased by a factor of 5 over the last two centuries, the chances of having a 10-fold increase over the next few years without unexpected breakthroughs are very slim. Fortunately, a more realistic goal of doubling the present lithium-ion battery energy density
in the next 10 years for EVs to approach 500 km at single charge has been set by the auto industry [67].

On the other hand, the requirements for stationary energy storage for renewable power are quite different. There is a broad spectrum of discharging times, from a few kWh to MWh, and, more importantly, there needs to be a capability for long duration (hours) of storage. For stationary applications, volume and weight are less constrained as portable/vehicle applications, but cost, efficiency, cycle life, calendar life, low operation and maintenance costs, and safety must be emphasized over energy and power density [67].

Nanotechnology has become one of the most promising technologies to meet the abovementioned requirements for lithium ion batteries [117]. Reports on the processing, properties, and applications of nanomaterials are rapidly increasing. Different methods of synthesis have been reported for obtaining nanostructured electrodes such as solution-based, soft-chemistry routes, such as sol-gel, hydrothermal, template, and reverse micelle. These methods allow tailoring the size and morphology of the nanostructures with remarkable reliability, efficiency, selectivity, and variety. There have been numerous electrode materials that have benefitted from nanotechnology; for instance, nanostructured LiFePO$_4$ cathode materials made by Padhi et al [103]. It is clear that nanostructured electrodes offer improved energy storage capacity and kinetics as well as better cyclic
stabilities owing to their huge surface area for Faradaic reaction, the short distance for mass and charge diffusion, as well as the added freedom for volume change that accompanies Li\(^+\) ion insertion/extraction. However, nanomaterials are certainly not a whole solution. There are some associated problems with their huge surface area and nanometer size. The reactivity of the active particles will increase the electrode solubility and instability due to side reactions. Therefore, a smart design is required, and nanotechnology should only be applied when it is necessary. Many reports on nanomaterials for those materials without any intrinsic material limitation should be carefully evaluated and applied. The advantages and disadvantages of nanostructured electrodes for lithium-ion battery materials are summarized in Table 2.3 [67].

Thinking in the future, there is a growing concern over lithium resources for the next decades with the increasing lithium demands dictated by transportation and grid-related applications. Lithium sources are extracted from brines, mainly located in Chile and Bolivia.

Alternatively, unlimited quantities of lithium can be found in seawater, but recovery is more expensive and tricky than extracting it from brines via a concentrating step using only solar energy. That is why; new chemistries based on a sodium alternative instead of lithium are envisioned because sodium resources are unlimited and easy to recuperate. Sodium has already been successfully implemented in high-temperature Na/S cells for MW-level storage or Na/NiCl\(_2\) ZEBRA-type systems for EVs, both of which take advantage of highly conducting Na-\(\beta\)-alumina ceramics. Nowadays, developing a room-temperature, sodium-ion cell appears feasible because highly oxidizing positive sodium-electrode materials such as Na\(_{0.44}\)Mn\(_2\)O\(_4\) or Na\(_2\)FePO\(_4\)F do exist [118]. In contrast, a material capable of inserting sodium at a low potential must still be investigated. A sodium-ion battery will always fall short of meeting the energy densities of the lithium-ion counterparts because sodium is heavier than lithium and is less reducing. However, for larger scale applications, such drawbacks will be compensated for by the lower cost of unlimited Na resources [67].
Table 2.3 Advantages and Disadvantages of Nanomaterials for Lithium-Ion Batteries [67].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron and ion transport within the particles is enhanced by reduced dimensions. Shorter distances increase the rate of the charge/discharge process significantly. The characteristic time constant for diffusion is given by $\tau_{eq} = L^2/D$, where $L$ is the diffusion length and $D$ is the diffusion constant. The time $\tau_{eq}$ for intercalation decreases with the square of the particle size.</td>
<td>Nanomaterials may be more difficult and costly to synthesize, and dimensions may be more difficult to control on a large scale.</td>
</tr>
<tr>
<td>Electrode redox reactions that cannot take place in micrometer-sized particles are enabled.</td>
<td>The chemical potential change $\mu_0(r) = \mu_0\left(r = \infty\right) + 2(\gamma/r) V$ is due to the surface contribution where $\gamma$ is the surface tension, $V$ is the partial molar volume, and $r$ is the effective grain radius.</td>
</tr>
<tr>
<td>A high surface area permits a high contact area with the electrolyte and hence increased ion fluxes across the interface.</td>
<td>A high electrolyte/electrode surface area may lead to more significant SEI side reactions with the electrolyte, and there could be more difficulty in maintaining interparticle contact.</td>
</tr>
<tr>
<td>The chemical potentials for lithium ions and electrons are modified, resulting in a change of electrode potential.</td>
<td>The densities of nanomaterials are generally lower than that of micrometer-sized particles. The volume of the electrode increases for the same mass of material, thus reducing the volumetric energy density.</td>
</tr>
<tr>
<td>The range of composition of solid solutions that exist is often more extensive for nanoparticles.</td>
<td>Nanomaterials with high surface energy tend to form agglomerates. This makes it difficult to disperse and mix them with carbon and binder.</td>
</tr>
<tr>
<td>More strain associated with lithium-ion insertion/ extraction can be accommodated.</td>
<td></td>
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</tbody>
</table>
Finally, after reviewing the battery history (around for more than 200 years), and understanding the future energy demand, some researchers dare to share their point view of the battery landscape for the next decades (Figure 2.17). These predictions include new raw abundant elements for electrode active materials made via eco-efficient processes or obeying the renewable concept with zero carbon footprints. Achieving these challenges for the next generation of storage technologies will require interdisciplinary approaches, and the success will depend on how good we are in setting cross-fertilization between these different disciplines [119].

**Figure 2.17 Battery Technology Landscape for The Next Decades** [119].
CHAPTER 3
SYNTHESIS OF BATTERY MATERIALS

3.1 Overview

The cathode and the anode are two key components for lithium-ion batteries. Many different compositions have been identified as possible cathode or anode materials for rechargeable lithium-ion batteries, however, just a few have been mass produced and commercialized, such as the layer structured metal oxides (LiCoO$_2$, LiNi$_{1-x-y}$Mn$_x$Co$_y$O$_2$, LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$), a spinel structured oxide (LiMn$_2$O$_4$), and an olivine structured phosphate (LiFePO$_4$) for cathode materials and various carbon materials for the anode.

For commercial applications, active cathode or anode materials should have high electrochemical performance such as high reversible lithium storage capacity, high rate of lithium insertion/de-insertion, high stability toward storage in electrolyte and electrochemical cycling, as well as low cost, high-quality consistency and safety. The electrochemical properties of the cathode materials are determined by the crystal structure, particle size/morphology, and stoichiometry of the active materials, and these are directly influenced by the chosen synthesis or production method. Very little fluctuation in their performance between production batches is required for high-volume and automated lithium battery production. Thus, the production process of active materials has to be simple and reproducible with low toxicity and environmental impact. Despite the fact that numerous synthetic processes that are used in the research laboratory provide very interesting advantages, some of them cannot be used for mass production because of the processing costs or the cost of precursors [67]. However, many battery materials are metastable phases, and therefore non-traditional synthesis methods must be devised to allow kinetics to over-ride thermodynamics. Consequently, many soft chemistry techniques have been strongly studied such as hydrothermal [6, 8-10, 12, 15], ion-exchange, intercalation, sol-gel [16-20], co-precipitation [1-4], spray-drying synthesis with heat treatment, combustion synthesis [17, 120-124], emulsion method, ultrasonic spray pyrolysis [27-30], molten salt synthesis [125], complex formation method [126], supercritical hydrothermal synthesis, microwave synthesis, etc. [63].
The traditional cathode materials for lithium-ion batteries (LiCoO$_2$, LiMn$_2$O$_4$, and LiFePO$_4$) have very different crystal structures from one to another. In each case, the lithium-ions are located in different chemical environments within the crystal lattice, and therefore, the energy level, transport pathways, and kinetics for lithium-ion insertion/de-insertion are different. The electrochemical properties of each compound such as the voltage plateau, capacity, and kinetics are determined by the crystal structure and local chemical environment of the lithium-ions. The crystal structure obtained during the synthesis process depends on numerous aspects including, the activities of precursors, the stoichiometry, any doping or substitution, the processing route, the reaction temperature/atmospheres, and the cooling rate. During synthesis, imperfect crystal structures may form creating anti-site defects, vacancies, dislocations, stacking faults, and grain boundaries. These defects can have a great effect on the lithium-ion diffusion and storage mechanism within these materials. For instance, lattice distortions change the energy level for lithium storage sites, and so the lithium storage capacity and the voltage plateau of the material. This has been proven in amorphous cathode materials that tend to give a charge–discharge plateau with a distinct slope compared to the crystalline material.

Other imperfections, such as anti-site defects, may lead to the blockage of lithium-ion diffusion paths and therefore slow down lithium-ion diffusion in the lattice and reduce the rate capability of the material. It has been demonstrated in LiFePO$_4$ where the Li-ion transport is one dimensional, and when an iron ion resides on a lithium site, there is a severe reduction in the lithium-ion mobility and thus the rate capability of the material [67].

The synthesis of cathode materials from precursor materials in the gas, liquid, or solid state involves the nucleation and growth of crystals. For the case of solid-sate reactions, a very fine mixture of reactants is a prerequisite for generating numerous nuclei of cathode material particles during reaction. To avoid the coarsening or growth of particles a low reaction temperature is required, especially to avoid abnormal growth of particles. Controlling the size and morphology of the particles in solid-state reactions is more difficult because of the
coalescence and sintering of particles when they are in direct contact with each other. Other parameters such as the reaction atmosphere and the activity of the precursors also affect the nucleation and growth process for the solid-state synthesis of cathode materials. A good example is the effect of the partial pressure of CO\textsubscript{2} and O\textsubscript{2} within the calcination atmosphere on the formation of pure single phase of LiFePO\textsubscript{4} and on the particle size of LiCoO\textsubscript{2}. In solid-state reactions, the reaction kinetics, the phase purity, and the particle sintering of the product are highly dependent on the treatment of the precursor and reaction conditions. The process of grinding precursor particles is often used during the production of cathode materials to reduce particle size and to increase the reactivity of the precursor particles by generating defects and surfaces.

For many years, the only way to synthesize cathode materials was by thermal treatment at high temperatures of mixtures of reactants. Due to diffusion limitations and low reactivity of starting materials, this solid state method implies long reaction times, high temperatures and regrinding between subsequent firings. For instance, attempts to synthesize materials with complex compositions such as Li(Ni\textsubscript{x}Co\textsubscript{y}Mn\textsubscript{1-x-y})O\textsubscript{2} using solid state reactions have resulted in an inhomogeneous or impure product. Also, a prolonged annealing at high temperature causes inevitable coarsening of the powder and evaporation of lithium, which significantly affects the electrochemical performance of the cathode material. Due to the abovementioned drawbacks, the solid state reaction method is considered to be a low-efficient, energy- and time-consuming technology which in addition, produces a wide range of particle size distribution, which could prevent the preparation of a high-performance cathode.

The synthesis of an intermediate compound as a precursor for use in a final calcination process has been a common strategy for the production of cathode materials having a complex composition. For instance, a (Ni\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3})(OH)\textsubscript{2} hydroxide intermediate is prepared initially by coprecipitation to finally synthesize Li(Ni\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3})O\textsubscript{2} [5, 127]. The multi-element hydroxide is then mixed with Li\textsubscript{2}CO\textsubscript{3} or LiOH.H\textsubscript{2}O and calcined to make the final cathode material. The same approach can be used for all layered, spinel, or olivine cathode materials.
In the case of LiFePO₄, an intermediate precursor of FePO₄.2H₂O can be made by a coprecipitation reaction of an iron salt with H₃PO₄ as well as a base. Further on, FePO₄.2H₂O can be mixed with Li₂CO₃ and reacted under reducing conditions to form LiFePO₄ [128].

Moreover, having a homogeneously mixed solution or intermediate compound may not lead to the desired homogeneous product. Sometimes, when removing the solvent, the salt is segregated, forming various precipitates. The coprecipitation method is not suitable for elements with vastly different chemical properties. For instance, the coprecipitation of alkali or nontransition metals with transition metal ions is difficult because they tend to precipitate separately; thus, it is difficult to achieve a good homogeneity of precipitates by this method [67].

In all wet precipitation techniques, some ionic species in wastewater can be an environmental problem such as SO₄²⁻ ions and ammonium ions. If so, the wastewater requires treatment before it can be released from the production plant which can increase the cost of the process. Another issue that should be taken into account when precursors are produced via the coprecipitation method is that in some compounds such as (Mn,Ni,Co)(OH)₂ mixed hydroxide, manganese is highly susceptible to oxidation and is readily oxidized to a trivalent manganese ion by a trace amount of oxygen dissolved within the aqueous solution. The trivalent manganese forms MnOOH which has a different crystalline structure from Ni(OH)₂, Co(OH)₂, or Mn(OH)₂ leading to a nonhomogenous distribution within the precipitate. To avoid this problem, bubbling an inert gas such as nitrogen or argon into the aqueous precipitating solution or ascorbic acid as reducing agents can be used. However, any of these solutions can complicate the synthesis process and increase the production costs [67].

Another method, widely studied in the last years to process ceramic materials or cathode materials, is the so-called, mechanochemical reaction method (developed in Russia at the Institute for Solid State Chemistry and Mechanochemistry). Although most scientists were initially skeptical about this novel approach to synthesize new materials, it has now gained
complete credibility [63, 129, 130]. Ball milling, a mixture of Fe$_3$(PO$_4$)$_2$·8H$_2$O and Li$_3$PO$_4$, can increase the reaction interface and promote mixing. This leads to the formation of LiFePO$_4$ at lower heat treatment temperatures (HTTs), giving rise to a product with finer particles [131, 132]. When milling Fe$_3$(PO$_4$)$_2$·8H$_2$O and Li$_3$PO$_4$ in a high-energy ball mill, the repeated impact of the powder mixtures results in a composite of powders consisting of both reactants at submicrometer or nanometer scale. The subsequent nucleation of LiFePO$_4$ occurs upon heat treatment at the numerous interfaces of the reactant mixture and thus LiFePO$_4$ with fine primary particles can be achieved [133]. Some anode materials have been synthesized by this technique, and carbon has been effectively coated onto LiFePO$_4$. Furthermore, many intermetallic compounds such Cu$_6$Sn$_5$, SnFe$_2$, and Sn$_2$Mn have been proposed as anode materials using this synthesis method [63].

In this method, each precursor can be mixed and ground in a high-energy mill, using either a dry or wet process. For instance, lithium or iron salts are easy to mill, but Fe, Ni, or Co metal and metal oxides are much more difficult to mill and require additional milling time. The right selection of the precursors is important to reduce milling time, milling energy, and contamination. Mechanochemical treatment has not been widely used to produce commercial cathode materials because of concerns with contamination and difficulties in controlling the size of secondary particles [67].

As has been mention earlier, better mixing of the precursor is desired to produce homogeneous products at both lower temperatures and less time. The sol-gel process has the advantage of mixing the metal ions at the atomic scale and thereby providing a homogeneous composition throughout the particle. Furthermore, the sol-gel process allows a high degree of control over the physicochemical characteristics of the products, typically provides high purity, homogeneity, a narrow particle size distribution and a highly reactive powder that requires a lower crystallization/annealing temperature than a conventional solid-state reaction.
In general, the sol-gel process consists of the following steps: (a) the preparation of a homogeneous solution either by the dissolution of inorganic salts in water or by the dissolution of metal organic precursors in an organic solvent that is miscible with water; (b) conversion of the homogeneous solution to a sol by treatment with a suitable reagent (pure water or water with HCl, NH₄OH), (c) aging, which involves changes of the sol into a gel by self-polymerization, and d) calcination at low temperature [21, 67].

Typically, the sol-gel method requires a large amount of complexing agent such as ethylene glycol. Therefore, a long time is required for the dehydration polymerization, decreasing the production rate. Also, a viscous gel is formed which increases the complexity of handling for a commercial operation. The abovementioned drawbacks as well as expensive precursors and various gaseous reaction products make the sol-gel solution–based process inefficient in the context of costs for large-scale synthesis. In addition, homogeneity is not a given within the sol-gel process, as problems may be encountered when removing the solvent from the composite complex leading to segregation.

In the case of making electrode compounds by hydrothermal or solvothermal reactions, the nucleation and the growth of the cathode material particles are within the liquid media and therefore can be controlled by numerous parameters, such as concentration, reaction temperature, and organic additives. A hydrothermal or solvothermal process generates cathode materials within the liquid phase and under pressure at a mild temperature. Numerous publications have shown the feasibility and advantages of making submicron or nano-sized cathode material particles using hydrothermal, microwave-assisted hydrothermal, ultrasound-assisted hydrothermal, or solvothermal processes. The advantage of the hydrothermal method is to make fine and homogeneous particles, whereas disadvantages include the high capital investment of the process and the excess lithium within the solution that requires treatment [6-12, 15, 22, 134].
For layered LiCoO$_2$ or spinel LiMn$_2$O$_4$, micron-sized materials have shown satisfactory capacity for many low or medium rate applications, so that submicron or nano-sized particles have not been pursued by hydrothermal reaction. Conversely, for LiFePO$_4$, fine particles are the prerequisite to achieve good high-rate performance. The hydrothermal reaction has shown advantages in controlling particle size homogeneity and suppressing the aggregation of particles. It has also been proven to be a cost-effective process for making LiFePO$_4$ on a large volume production scale. In the hydrothermal process, the reaction temperature, concentration, and ion mobility in the reacting solvent has a great effect on the nucleation and growth of cathode material. In addition, the studies of vanadium oxides showed the critical role that pH plays in determining the desired structure [63]. Temperatures above the super-critical point of water (solvent) increase the solubility of the precursors and enhance the kinetics of the reactions. Therefore, the formation reaction will use a short residence time and the process can be made continuous.

The classic solvothermal reaction consists of reacting the corresponding metal/nonmetal based soluble salt precursors, in a liquid medium; with the proper bases at a temperature sufficient enough to promote the precipitation and growth of the desired phase via Ostwald ripening [23].

The solvothermal process has not been used in any commercial production of cathode materials, although it may provide certain advantages for particle morphology and material crystallinity control compared with the hydrothermal method [23]. The high cost of the solvothermal method limits its practical application toward large-scale production [67]. Both hydrothermal and solvothermal methods suffer from some disadvantages such as the need to conduct the synthesis under reflux and controlled environment (e.g., the solvothermal process) and with the mandatory use of investment intensive autoclaves for hydrothermal processes. However, ionothermal synthesis seems to overcome some of the abovementioned drawbacks. This method uses Ionic liquids, which are room temperature molten salts and provide some advantages such as: first, like water, ionic liquids resulting from compatible cationic/anionic
pairs having excellent solvent properties which enable low temperature processes; and second, the synthesis can be performed outside of an autoclave because ionic liquids possess high thermal stability and negligible volatility. In addition, practically an unlimited number of ionic liquids can be made because they are formed using organic cation-anion pairs which provide different physical-chemical properties (i.e., hydrophobicity, melting point, viscosity, and solvating properties). In contrast, the number of inorganic molten salts is relatively limited [23]. Different cathode materials have been produce by this method at low temperatures (<250) with reaction times between 24 and 48 h [31-33, 119, 135].

On the other hand, the spray pyrolysis method has attracted attention as an effective, easy scale-up and continuous technology with a short production time to prepare spherical solid particles having a homogenous chemical composition and one-step production method. The particle size distribution of the product is narrow and controllable from micrometer to submicrometer, compared with the particles obtained from solid state-reaction. For these reasons this method has been widely used to produce TiO$_2$, SnO$_2$, ZrO$_2$, or superconducting fine particles [67]. Spray pyrolysis is the aerosol process that atomizes a solution and heats the droplets to produce solid particles. This synthesis method includes processes such as atomization, evaporation of a solvent, precipitation of solute, drying, thermal decomposition or pyrolysis and sintering within a laminar flow aerosol reactor.

As was mentioned before, the electrochemical performance of the cathode material is strongly affected by the powder particle size and morphology, the specific surface area, the crystallinity, and the composition of the material. It has been shown that materials composed of spherical particles have higher tap density than that of irregular particles [78], which is a very important factor to produce high energy density and power batteries. Therefore, spray pyrolysis could be considered as a good technique to prepare cathode materials for the high power lithium-ion batteries [67].
A method that was originally developed to prepare metal oxide powders such as titanates and niobates for capacitors is called the Pechini method. More recently it has been used to synthesize a wide variety of other electroceramic compositions including superconductive fibers. In the Pechini process the following three basic reactions occur, (a) formation of metal chelates, (b) esterification, and (c) polymerization during the formation of the polymeric precursor. The process is based on the ability of certain weak acids to form polybasic acid chelates with various cations. These chelates can undergo polyesterification when heated in a polyhydroxyl alcohol to form a solid polymeric resin, throughout which the cations are uniformly distributed. Thus the resin retains homogeneity on the atomic scale and may be calcined at low temperature to yield fine particulate oxides. Commonly, citric acid and ethylene glycol are used as the monomers for the formation of the polymeric matrix [24, 25]. The main drawback of this synthetic method is that a large organic/metal cation ratio has to be used to assure chelation, which makes the process a low production rate method.

One interesting trend in cheaper electrode materials is that the electrochemical responses rely on the nanosized nature of the materials. Nanotechnologies have enabled new compounds to function as an electrode material, which was not possible at the micron level. The advancements in lithium-ion battery technology evolved with this new synthesis approach. Therefore, over the last few years, material scientists and chemists have explored the wet chemical methods including classical precipitation [1-5], hydrothermal [6-15], sol-gel [16-21], polyol, solvothermal [22], microwave-assisted solvothermal [23], Pechini process [24-26], spray pyrolysis [27-30] and ionothermal [31-33] synthesis, in order to produce nanostructured electrode materials. In general these methods produce homodisperse powders with a well-defined shape and size at low temperatures, via fine-tuned control of the reaction pH and precursor concentration. This is in contrast to ceramic methods, which require high temperatures to ensure the diffusion of the reactants and the growth of the grains, usually leading to highly polydispersed powders.
Additionally, crystallinity is as important as particle size for high-potential cathode materials, but it is widely recognized that low-temperature routes are designed in order to avoid grain growth and agglomeration and generally result in less-ordered crystal structure that block the diffusion path of lithium ions, especially when lithium diffusion occurs in 1D as in olivine structures, thereby limiting the electrochemical activity. In addition, high-potential cathode materials require a higher sintering temperature to form a more thermodynamically stable phase. For instance, temperatures above 600°C are required to fully oxidize Ni$^{2+}$ to Ni$^{3+}$ and increase the material crystallinity. However, the high vapor pressure of lithium oxide at high temperatures results in the lithium volatilization and content decrease. For instance, lithium evaporation starts at 950°C and accelerates at 1050°C [94]. Another example is when LiFePO$_4$ is produced. The chosen synthetic method may also lead to secondary phases or the segregation of some doping elements into the grain or grain boundaries phases depending on reaction conditions. Fe$_2$P phase may form at temperatures higher than 700°C under reducing conditions and other secondary phases such as Li$_3$PO$_4$, Li$_4$P$_2$O$_7$, Li$_3$Fe$_2$(PO$_4$)$_3$, LiFeP$_2$O$_7$, iron pyrophosphate, or even iron oxide and metallic iron can be observed under various reaction conditions [67].

In any large-scale production process, proper measures have to be taken to avoid inhomogeneous mixing, severe lithium loss, segregation, or separation of reactants. Even when using wet chemical methods it is not always possible to maintain a homogeneous reactant distribution during heating and some undesirable phases may form at the beginning of calcination.

As it was shown above, several techniques were adopted to prepare nanostructured cathode materials having a narrow particle size distribution [136-140]. Some excellent results were obtained using sol-gel, hydrothermal, solvothermal, ionothermal and coprecipitation routes. However, these techniques use very low concentrations of starting materials, which leads to very low production rates. Thus, these processes are very difficult to be used for the commercial production of cathode materials. Therefore, it is crucial to develop a simple, easy
to scale-up and cost-effective technique, because in real-world applications, elaborate chemical routes are often found to be less attractive [141].

We have reviewed the different synthesis methods to produce cathode materials for lithium-ion batteries and their relationship with structure-properties. The introduction of new high capacity cathode and anode materials for lithium-ion batteries is highly dependent on the successful development of an economical processing technology, which can provide reproducible production of the desirable crystal structure, microstructure, particle size/size distribution, particle morphology, and phases with high purity within these materials.

3.2 Polymeric Steric Entrapment Precursor Route

Ceramic processing is evolving in the direction of chemical synthesis of powders. In recent years, there has been considerable interest in the development of other techniques that allow the production of materials with various powder morphologies, bulk density, and stoichiometry. In this way, the use of polymers to synthesize mixed-oxide ceramic powders has been a recent development in concurrent work by several groups, for example, the Pechini process, emulsion or emulsion drying method, sol-gel route, and the others mentioned in the previous section. However, these methods consist of complicated preparation steps to obtain the correct stoichiometric compound and need further calcinations and grinding of powders to obtain the high crystallinity. Also, the production rate for these techniques is very low. Therefore, the mentioned drawbacks should be overcome to make the mentioned preparation techniques more practical and suitable for effective industrial application.

A versatile technique has been developed by our group, based on a polymeric steric entrapment precursor route [34, 37, 38, 41, 46, 55, 58, 59, 142-144]. To achieve a really good intimate mixing, metal salts are dissolved in water or alcohol to form a solution where the metal sources are mixed in their ionic states, so that a very homogeneous mixing is achieved within the solution. The method uses long-chain polymers, such as poly(vinyl alcohol) (PVA, [-CH$_2$CHOH-]$_n$) and poly(ethylene glycol) (PEG, H(OCH$_2$CH$_2$)$_n$OH) that ensure a homogeneous
distribution of the metal ions in their polymeric network structure, and it inhibits their segregation or precipitation from solution [35, 39, 41, 43]. In the solution involving a polymer and nitrate ions, a continuous long chain polymer prevents selective phase separation of cations and limits their agglomeration and precipitation [36]. The chemistry of the precursor solution differs from other solution–polymerization techniques. The stabilization of the cations in the precursor is established not only through the chemical binding of cations with the functional groups, but also, in a major part, through the physical entrapment of the metal ions in the network of the dried polymer carrier. An important criterion for the selection of the cation sources is the aqueous solubility of the corresponding metal salts; the more soluble the salts, the higher the yield of the new process [35]. In a water–soluble system, the PVA polymer can be used. However, the process can be extended to chemicals that decompose or do not dissolve in water such as metal-alkoxide (titanium isopropoxide) by applying an ethylene glycol (EG) polymerizing agent. In particular, the ethylene glycol can act as an effective solvent for a wet chemical synthesis of a titanate powder because the water–soluble titanium salt is not commercially available [36, 39, 45, 46].

Furthermore, a linear polymer such a PVA has the ability to wrap around the cation precursor improving the cation distribution due to attrition and/or repulsion forces. It has been also documented for this method that the decomposition of the polymer is similar to that of a fuel-oxidizer system. The fuel can be any polymer in which oxidation occurs easily. The oxidizer is usually an acid or in the specific case of this method, a nitrate source. It has been proposed that the ratio of oxidizer to fuel should be close to unity in order to release the maximum amount of energy to induce ceramic conversion. Unless the chemistry behind this method is more elaborate, the factors which must be considered to produce particles with the desirable crystal structure, microstructure, particle size/size distribution, particle morphology, and high purity, are the size and valance of the cations, the degree of polymerization, the oxidizer/fuel ratio, type of solvent, calcination and crystallization temperature and time. For instance in systems where not enough polymer is used, agglomeration may occur causing segregation of cation, multiphase product, and a large particles size in the end products [142].
The polymeric steric entrapment precursor route has been successfully used to synthesize various monophase, fine (micro and nano), and pure mixed-oxide powders with high technological importance (Table 3.1) [34-42, 45, 47-58].

Table 3.1 Summary of Oxides Powders Prepared The Polymeric Steric Entrapment Precursor Route [37].
(Polymeric Carrier: Poly Vinyl Alchol (PVA), Poly Ethylene Glycol (PEG), Ethylene Glycol (EG))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heating temperature (°C)</th>
<th>Specific surface area (m²/g)</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Amorphous</td>
<td>Crystalline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>as-calcined</td>
<td>attrition-milled</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>800</td>
<td>83</td>
<td>6.2</td>
</tr>
<tr>
<td>β-Cristobalite (SiO₂)</td>
<td>800</td>
<td>188</td>
<td>3</td>
</tr>
<tr>
<td>Mullite (Al₂Si₂O₅)</td>
<td>800</td>
<td>157</td>
<td>0.1</td>
</tr>
<tr>
<td>Zircon (ZrSiO₄)</td>
<td>800</td>
<td>81</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>Wollastonite (CaSiO₃)</td>
<td>800</td>
<td>18</td>
<td>0.7</td>
</tr>
<tr>
<td>Calcium aluminate (CaAl₂O₄)</td>
<td>650</td>
<td>12</td>
<td>60 nm (hard aggl.)</td>
</tr>
<tr>
<td>Belite (β-Ca₂SiO₄ or Ca₂Si)</td>
<td>700</td>
<td>22.1</td>
<td>0.3-0.4</td>
</tr>
<tr>
<td>Alite (Ca₃SiO₅ or Ca₃Si)</td>
<td>700</td>
<td>0.9†</td>
<td>3.0-5.0</td>
</tr>
<tr>
<td>Cordierite (Mg₂Al₂Si₅O₁₄)</td>
<td>800</td>
<td>181 (attrition milled)</td>
<td>0.2-0.4†</td>
</tr>
<tr>
<td>Barium titanate (BaTiO₃)</td>
<td>700</td>
<td>5.6</td>
<td>50 nm (hard aggl.)</td>
</tr>
<tr>
<td>Barium orthotitanate (Ba₂TiO₄)</td>
<td>700</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Dysprosium titanate (Dy₂TiO₅)</td>
<td>800</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Yttrium titanate (Y₂TiO₅)</td>
<td>850</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Alumina-Zirconia composite (Al₂O₃•ZrO₂)</td>
<td>700</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Nickel aluminate (NiAl₂O₄)</td>
<td>800</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Calcium phosphate (Ca₃P₂O₇)</td>
<td>700</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>Xenotime (YPO₄)</td>
<td>500</td>
<td>12</td>
<td>70 nm (hard aggl.)</td>
</tr>
<tr>
<td>Aluminium phosphate (AlPO₄)</td>
<td>800</td>
<td>136</td>
<td>0.9†</td>
</tr>
<tr>
<td>Lithium phosphate (LiPO₄)</td>
<td>700</td>
<td>800</td>
<td></td>
</tr>
</tbody>
</table>

† after attrition milling for 1h: 50 m²/g
¥ after attrition milling for 1h: 55 m²/g
usaha form
Although this solution polymerization route has been studied by the Dr. Kriven’s group for more than 15 years with remarkable advances (1 patent [59] and 30 papers), our aim in the project, is use this synthesis route to produce these materials based on 3-d metal redox elements such as LiFePO$_4$, NaFePO$_4$ and NaTi$_2$(PO$_4$)$_3$. These complex compounds are composed by cations called “zwitterions” because of their special changeable characteristic of different oxidation states M$^{+2}$/M$^{+3}$ that make them interesting for electronic applications. So far, the polymerized organic–inorganic entrapment route leads the synthesis reaction toward the maximum oxidation state, and there is a big challenge to find the way to control the different oxidation states through this synthesis route that can be useful to produce a wide range of fascinating compounds.

Among other methods to prepare oxide ceramics, the polymeric steric entrapment precursor route has demonstrated to be a low temperature, simple, continuous, and easy scale-up technique. This technique itself allows the control of powder composition and morphology and shortened production time. The prepared powders are homogeneous, both chemically and physically, and have a narrow particle size distribution in the micro/nano sized range. All of these factors allow an outstanding reduction of the product cost and decrease the ecological impact of material production.

**3.3 Overview of LiFePO$_4$**

In 1997, Goodenough’s group identified LiFePO$_4$ olivine (Figure 3.1) as a cathode for rechargeable lithium batteries [103]. Olivine structured transition metal phosphates LiMPO$_4$ (M = Co, Ni, Fe, Mn) have attracted tremendous attention from worldwide researchers as lithium insertion/extraction hosts, due to the low-cost, nontoxic (for Fe and Mn), and environmentally friendly nature of these materials. In addition, these materials can easily be combined with a carbon anode in lithium-ion cells. For these reasons, nowadays, the LiFePO$_4$ cathode has become one of the main commercial cathode materials for lithium-ion [63].
LiFePO$_4$ operates at a very flat voltage of about 3.4 V versus Li$^+$/Li, yielding a theoretical capacity of 170 mAh g$^{-1}$. The triphylite mineral LiFePO$_4$ belongs to the olivine structured lithium ortho-phosphates having the space group Pnma. In phospho-olivines, all of the oxygen ions form strong covalent bonds with P$^{4+}$ to form PO$_4^{3-}$ tetrahedral polyanions, which allow for greater stabilization of the structure compared to layered oxides, (for example, LiCoO$_2$) where the oxide layers are more weakly bound. In the LiFePO$_4$ structure (Figure 3.1), the oxide ions form a hexagonal close packing (hcp) arrangement [74, 103, 145, 146]. The iron ions form zigzag chains of octahedra in alternate basal planes bridged by the tetrahedral phosphate groups (PO$_4$). Each FeO$_6$ octahedron shares corners with six PO$_4$ tetrahedra, and each PO$_4$ tetrahedron, in turn, shares its corners with four FeO$_6$ octahedra, thus forming a 3-D framework. This framework provides improved stability and extreme safety under abusive conditions. For instance, LiFePO$_4$ is stable up to 400°C, while LiCoO$_2$ starts to decompose at 250°C. The lithium atoms occupy octahedral sites, located in the remaining basal planes.

**Figure 3.1 Crystal Structure of Olivine LiFePO$_4$ [61, 74].**

Due to the strongly bonded oxygen atoms with both Fe and P mentioned above, this structure limits the electrochemical reaction kinetics in phospho-olivines. This is due to the insulation effect of the polyanions, leading to a very low Li-ion diffusivity and a very low electronic conductivity of $\sim 10^{-9}$ S cm$^{-1}$ at room temperature. The lithium diffusion pathway in
LiFePO$_4$ is 1-D along the $b$-axis. Both electronic conduction and ion diffusion problems lead to a poor performance of LiFePO$_4$ cathode in lithium-ion batteries [67].

In the initial work, Padhi and Goodenough, reported that just 0.7 lithium ions were extracted per formula unit of LiFePO$_4$ even at very low current densities, which corresponds to a reversible capacity of $<120$ mAh$^{-1}$ [103, 145]. As the lithium is extracted from LiFePO$_4$ (triphylite), a new phase FePO$_4$ (heterosite) is formed. Both phases are isostructural (space group $Pnma$) with a slight difference in the unit cell parameters ($<$7%). Padhi et al. suggested that the lithium extraction/insertion occurred via a two-phase mechanism with LiFePO$_4$ and FePO$_4$ as end members, without much solid solubility. The two-phase character of the reaction seems to provoke a low rate capability of this compound due to the hindered lithium diffusion through the LiFePO$_4$/FePO$_4$ interface, and there is a miscibility gap between these two phases at the temperatures below 60°C except for close to the end-composition. In fact the solid solution Li$_x$FePO$_4$ does not exist under “normal” conditions in particles that are large enough so that size effects are negligible [61, 67].

Despite the limited reversible capacity and low rate capability of LiFePO$_4$, this material has attracted immense interest as a potential cathode because Fe is abundant, inexpensive, and environmentally benign. However, recognizing that its weaknesses may be linked to the poor electronic conductivity, researchers have investigated the possibility of improving the electronic conductivity by different alternatives such as coating the LiFePO$_4$ powder with conductive carbon [88, 147-154], particle size minimization and doping the material with supervalent cations like Ti$^{4+}$, Zr$^{4+}$, Nb$^{5+}$ [17, 86, 155-157]. Improvements in reversible capacity with values such as 160 mAhg$^{-1}$ and electronic conductivity by a factor of $10^8$ have been made. The last one has been attributed to the formation of a percolating nano-network of metallic iron phosphides [61].

Awareness of the importance of both the decrease in particle size as well as the improvement in electronic conductivity has increased the activity in investigations on solution-
based synthesis of LiFePO$_4$ in order to minimize the particle size (as was shown in the previous sections) and to coat the LiFePO$_4$ particles with conductive species such as carbon and conducting polymers. Examples can be mentioned, such as the production of nanorod-like morphologies with excellent crystallinity by microwave-assisted hydrothermal and solvothermal approaches, the addition of conducting polymers and the formation of nano-networking with multi-walled carbon nanotubes (MWCNTs). While decreasing the particle size to the nanometer level has been successful in reducing the diffusion length of lithium-ions and overcoming the lithium-ion transport limitations in LiFePO$_4$, the LiFePO$_4$/MWCNT nanocomposites exhibit higher capacity at a given C-rate than do the pristine LiFePO$_4$ due to the enhancement in electronic conductivity [61].

Even though the initial work by Goodenough’s group revealed a two-phase reaction mechanism with LiFePO$_4$ and FePO$_4$ as end members, further investigations have indicated that the miscibility gap between the two phases decreases with both increasing temperature and decreasing particle size. The occurrence of a single-phase solid solution Li$_x$FePO$_4$ with $0 \leq x \leq 1$ has been reported at 450 °C and in about 40 nm size crystals. Consequently, what was originally found to be a two-phase reaction mechanism with micrometer-sized particles has now turned into a single-phase reaction mechanism with nano-sized particles [61]. This is a clear demonstration of how nanoparticles can behave entirely differently from their micrometer-sized counterparts. In addition, it has been reported that defects caused by the existence of cationic vacancies in the samples prepared at low temperatures contribute to the unique behavior of the nano-sized particles. In general, nanosized particles of LiFePO$_4$ provide short lithium diffusion paths within the cathode. The preparation of LiFePO$_4$/C nanocomposites remarkably increases the cathode conductivity leading to cycle life, discharge capacity, and rate capability enhancement [4, 16, 63, 81, 158-164].

The addition of carbon coating prevents the LiFePO$_4$ particle agglomeration as well as the reaction of LiFePO$_4$ with carbon at high annealing temperatures leading to the reduction of the neighboring Fe and P ions in the lattice and the formation of conductive Fe$_2$P and/or Fe$_3$P in
LiFePO₄ materials [165]. It has been shown that a LiFePO₄/Fe₂P composite allowed enhanced of electronic conductivity, thereby improving the electrochemical performance [67].

The combination of particle size reduction and carbon coating approaches could be the most effective way to overcome the drawbacks of olivine materials. Carbon-coated LiFePO₄ particles by a combination of spray pyrolysis with dry ball-milling followed by heat treatment at 500°C have been reported by Konarova and Taniguchi [166]. This cathode material exhibited first-discharge capacities of 158 mAh g⁻¹ at 0.1 C and 114 mAh g⁻¹ at 5 C with excellent cycle performances at 25°C. The cell tested at 60°C delivered the theoretical capacity (170 mAh g⁻¹) at 0.1 C or 78% (133 mAh g⁻¹) of its theoretical capacity at 5 C, respectively. The electrochemical properties of LiFePO₄ nanoparticles were strongly affected by the formation of Fe₂P, Fe₃P and α-Fe₂O₃ at higher charge–discharge rates [67].

For the synthesis of LiFePO₄, a reducing condition is required to either convert Fe³⁺ in the precursors to Fe²⁺ or to prevent oxidization of Fe²⁺ in LiFePO₄ to an Fe³⁺ containing impurity phase. Usually, particulate carbon has been used during the solid-state reaction to convert Fe³⁺ precursors to Fe²⁺ at a temperature higher than 650 ⁰C. Alternatively, a reducing atmosphere during the synthesis of LiFePO₄ can be generated via an in situ decomposition of different organic materials such as ascorbic acid, citric acid, PVA, and so forth, or by feeding the reaction chamber with CO, H₂, NH₃, or other reducing gases, that provide a much lower temperature for the reduction of Fe³⁺ [67].

At high temperatures (>700°C), LiFePO₄ is not the most thermodynamically stable state for this composition, and thus it can be further reduced to Fe₂P or even metallic Fe under very high reducing conditions [165]. Under less reducing conditions, Fe³⁺-containing impurity phases (from an incomplete reduction) in the form of Li₃Fe₂(PO₄)₃, Fe₂O₃, Fe₃O₄, and LiFeP₂O₇ may remain and lead to a loss in capacity and cycle life for the electrode [67].

On the other hand, it is important to mention that unless the most studied material in the [100, 167] phospho-olivine family is LiFePO₄, there other interesting compounds in this
family where everything we have discussed so far may apply and better electrochemical behavior can be reached. Replacing the transition-metal ion Fe$^{2+}$ by Mn$^{2+}$, Co$^{2+}$, and Ni$^{2+}$ increases the redox potential significantly from 3.45 V in LiFePO$_4$ to 4.1, 4.8 and 5.1 V, respectively, in LiMnPO$_4$, LiCoPO$_4$, and LiNiPO$_4$ because of the changes in the positions of the various redox couples. As we have seen earlier, the electronegativity of X and the strength of the X–O bond play a role in controlling the redox energies of metal ions in polyanion-containing samples [61].

LiMnPO$_4$ is of particular interest because of the environmentally benign manganese and the favorable position of the Mn$^{2+/3+}$ redox couple at 4.1 V vs Li/Li$^+$, which is compatible with most of the electrolytes [32, 141]. However, it has been shown to offer low practical capacity even at low currents due to the wide band gap of $\sim$2 eV and low electronic conductivity of $\sim$10$^{-14}$ S cm$^{-1}$ compared to LiFePO$_4$, which has an electronic conductivity of $\sim$10$^{-9}$ S cm$^{-1}$ and a band gap of $\sim$0.3 eV. Nevertheless, optimizing the synthesis process and carbon coating has recently shown promising electrochemical performances for LiMnPO$_4$ nanoparticles [61].

Finally, the mixed transition-metal ion systems have recently attracted considerable interest. Among these, the LiFe$_{1-y}$Mn$_y$PO$_4$, LiMn$_{1-y}$Co$_y$PO$_4$ and LiFe$_{1-y}$Co$_y$PO$_4$ solid solution systems has attracted particular attention because they exhibit higher energy density, high operating voltages and improved redox kinetics due to improved electronic conductivity and the high-voltage Co$^{2+/3+}$ redox couples. It is important to keep in mind that enhancement in energy density will require high-voltage electrolytes [61].

### 3.4 Overview of NaFePO$_4$

Considering the massive production of Li-ion batteries in the future and the limited and unevenly distributed lithium source which is mainly in remote and politically sensitive areas in South America, the cost of lithium will become one of the critical issues for future Li-ion batteries [168, 169]. Current estimates demonstrate that, at the present rate of consumption, the world lithium reserve will be depleted in less than 150 years [170]. Nowadays, lithium is mostly used for Li-ion batteries. Therefore, with the increasing demand for Li-ion batteries in
electric vehicles and portable consumer electronic devices, this demand can only be expected to further increase. In the coming years, finding a suitable substitute for Li-ion batteries in various targeted applications will become increasingly critical.

Sodium is a possible natural substitute for lithium in battery technology because Na is similar to lithium, sodium is an alkali metal with low ionization potential making it a possible suitable candidate for rechargeable battery electrode materials. However, sodium is a larger ion than lithium, with an ionic radius of 1.2 Å as compared to 0.90 Å for lithium. It is also almost three times heavier than lithium, with an atomic weight of 22.99 g mol⁻¹, compared to only 6.941 g mol⁻¹ for that of Li. These differences in size and weight slows down significantly the charge transfer in Na-ion batteries compared to Li-ion batteries, due to the increased difficulty of ionic insertion and extraction into the cathode, respectively. This slower charge transfer ends in lower capacity of the cell due to Na⁺ transport limitations in the electrodes, which correspondingly results in lower energy and lower power densities.

Regardless of these disadvantages, sodium-ion (Na-ion) batteries are potentially cheaper due to the low cost (Table 3.2) and abundance of sodium in the earth, which makes Na-ion batteries suitable for replacement of Li-ion batteries in several applications, particularly where weight and size are not important, such as large scale energy storage devices, stationary land-based power applications, non-portable systems and electrical grid stabilization. Using energy storage devices in the electric grid can help store electricity when it is being produced in excess of demand and release it during periods of higher demand. This type of application has motivated the scientific community because non-lithium based cost effective battery cathodes with long cycle life can have a lot of advantages over lead acid batteries for land based energy storage system application [169, 171, 172].
Table 3.2 Main Characteristics of Na and Li Materials [168].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Na</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price (for carbonates)</td>
<td>0.07-0.37a € kg⁻¹</td>
<td>4.11-4.49b € kg⁻¹</td>
</tr>
<tr>
<td>Capacity density</td>
<td>1.16 A h g⁻¹</td>
<td>3.86 A h g⁻¹</td>
</tr>
<tr>
<td>Voltage vs. S.H.E.c</td>
<td>-2.7 V</td>
<td>-3.0 V</td>
</tr>
<tr>
<td>Ionic radius</td>
<td>0.98 Å</td>
<td>0.69 Å</td>
</tr>
<tr>
<td>Melting point</td>
<td>97.7 °C</td>
<td>180.5 °C</td>
</tr>
</tbody>
</table>

aPurity: 98.8-99.2% min. bBattery grade: 99.9%. cS.H.E.: Standard Hydrogen Electrode.

Na metal has already been successfully used in Na/S and Na/NiCl₂ Zebra cells. It must be declared that electrochemical Na-ion cells will always fall short of meeting energy densities compared to Li-ion batteries. Basically, because the equivalent weight of Na is higher than Li, and because there are two competing factors regarding the formation of sodium-based intercalation compounds commonly employed as anode materials in “rocking chair” type batteries: one is the ionization potential and the other is the size of the alkali metal. The ionization potential increases from 3.893 eV to 5.390 eV as we go from Cs to Li in the series of alkali metal elements in the periodic table. The lower the ionization potential, the more easily the electron transfers from the alkali metals to graphite for example, which is used as a standard anode material. Consequently, the energy gain upon the charge transfer becomes smaller in the order of Cs > Rb > K > Na > Li. Therefore, Na-based cells will have difficulties in competing with Li based cells in terms of energy density. However, they can be considered for use in applications where the weight and footprint requirement is less drastic, such as storage of off-peak and essentially fluctuating renewable energies, such as wind and solar farms [168].

Figure 3.2 shows the most important cathodic and anodic materials for sodium-ion batteries, indicating their specific capacity and operating voltage. As it can be seen, many materials have been proposed as possible cathodes for Na-ion batteries, whereas only some carbon-based anodes have been pointed out for this storage technology.
Over the last past decade and due to the success of LiFePO$_4$ as a cathode material for Li-ion batteries, the scientific community has been inspired to investigate the analogous NaFePO$_4$ as a cathode material for Na-ion batteries and Na$^+$/Li$^+$ mixed-ion batteries. It is important to mention that although LiFePO$_4$ is often addressed in the literature as “olivine” it should be more accurately described as “triphylite”, since “maricite” is also derived from the olivine structure type [171].

Unlike LiFePO$_4$, the NaFePO$_4$ analogue exists in two distinct polymorphs (triphylite and maricite). Initially it has been said that unless the maricite structure is thermodynamically more stable, it is electrochemically inactive due to the edge-sharing FeO$_6$ octahedra which generate no Na diffusion channels [173]. However, the triphylite NaFePO$_4$ polymorph is isostructural with LiFePO$_4$ and offers one dimensional channels delivering a reversible discharge capacity exceeding 120 mAh/g with a Fe$^{3+}$/Fe$^{2+}$ redox activity at around 3 V [174].
Figure 3.3 Crystallographic Structure Comparison Between (a) Maricite NaFePO₄, (b) Olivine LiFePO₄ and (c) Olivine NaFePO₄ [168].

In olivine LiFePO₄ the Li⁺ and Fe²⁺ ions occupy 4(a) and 4(c) sites, respectively, while in maricite, Na⁺ cations occupy the 4(c) Wyckoff sites and the Fe²⁺ species are situated in 4(a) sites. This is probably due to the larger ionic radius of Na⁺ compared to that of Li⁺. Thus, maricite presents one-dimensional, edge sharing FeO₆ octahedra and no cationic channels, thus hindering cation exchange. Fig. 3.3 shows the crystallographic structure of the three compounds.

Direct preparation of triphylite NaFePO₄ is really complicated because this polymorph is less favored thermodynamically than is the maricite structure. Some attempts to produce triphylite NaFePO₄ have led to the following preparation process steps: first, preparation of
LiFePO$_4$ by different methods such as solid state or soft chemical methods; second, chemical oxidation of LiFePO$_4$ to heterosite FePO$_4$ by using NO$_2$BF$_4$ in acetonitrile or bromine dissolved in water, and third, electrochemical Na insertion by using FePO$_4$ as the positive electrode and metallic Na foil as an anode. An electrochemically synthesized NaFePO$_4$ has been obtained by Zaghib et al [175]. They have shown a 147 mAhg$^{-1}$ specific capacity in the first discharge at 60 °C and C/24 rate), nevertheless poor reversibility has been achieved so far (50.6 mAhg$^{-1}$ in the second cycle). Moreover, Moreau et al. [176] could cycle reversibly 0.9 Na in the first charge/discharge cycle (139 mAhg$^{-1}$), but the cycle life of the material produced was not investigated.

Table 3.3 Main Phosphate Phases and Their Specific Capacity [168].

<table>
<thead>
<tr>
<th>Compound</th>
<th>e$^-$ transfer</th>
<th>Theoretical capacity/mA h g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaFePO$_4$(olivine)</td>
<td>1</td>
<td>154</td>
</tr>
<tr>
<td>NaVPO$_4$F</td>
<td>1</td>
<td>143</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_2$F$_3$</td>
<td>2</td>
<td>128</td>
</tr>
<tr>
<td>Na$_{1.5}$VOPO$<em>4$F$</em>{0.5}$</td>
<td>1</td>
<td>130</td>
</tr>
<tr>
<td>Na$_2$FePO$_4$F</td>
<td>1</td>
<td>124</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$</td>
<td>2</td>
<td>118</td>
</tr>
<tr>
<td>NaFe$_2$Mn(PO$_4$)$_3$</td>
<td>2</td>
<td>108</td>
</tr>
</tbody>
</table>

Among all cathode materials for Na-ion batteries, phosphate polyanion based cathode materials seem to be the most promising candidates due to the relatively high operating potentials and thermal stability. Among phosphate polyanion cathode materials (NaFePO$_4$, NaVPO$_4$F, Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and Na$_2$FePO$_4$F, etc., as it shown in table 3.3), olivine NaFePO$_4$ has the highest theoretical specific capacity (154 mAhg$^{-1}$), which makes it an attractive cathode material for Na-ion batteries [169].

Much more work has to be performed to develop a high capacity Na-based cathodic material. The research on olivine structured materials for Na-ion batteries has been extended
to Na[Mn_{1-x}M_x]PO_4 (M = Fe, Ca, Mg) by Nazar et al [171]. Preliminary galvanostatic tests at low cycling rate in Na cells indicated that electrochemical reaction takes place in a single-phase, with a sloping voltage profile. However, this point must be confirmed, because kinetic limitations could induce the sloping voltage curve.

Although the capacities observed and the corresponding energy densities are lower compared with Li ion chemistries, the long term stability appears to be good. Even though further study is required, these materials could be of interest for large scale energy storage systems and/or for smart grid applications. Identification of various processes to tailor the architecture of the cathode nanostructures, identification of suitable sodium electrolytes, and separator materials to further improve the Na mobility will likely lead to improved performance of this system [172].

### 3.5 Overview of NaTi_2(PO_4)_3

As it is known, the demand of rechargeable batteries with large energy density has increased due to the electric vehicle (EV) growing trend in the global automotive industry. Lithium-ion batteries have been extensively studied as an attractive alternative to metal-based batteries which have insufficient energy density and poor cyclability. Standard lithium-ion batteries can store twice the energy of the nickel metal hydride cells and have better cyclability. However, they are relatively expensive.

In addition, as it was mentioned before, although the resource of lithium is not so scarce now, the Li resources are not sufficient to replace cars of the world with EVs. Moreover, the price of raw material in rechargeable batteries could still be reduced by turning to other candidates for large-scale power storage systems such as the promising sodium-ion battery. The main issue with the commercial Li and proposed Na ion batteries concerning EVs applications is in severe safety problems due to flammable organic electrolytes in the cells. For large cells, it is more difficult to remain stable under conditions of overcharging or overheating which can cause gas evolution or even explosion of a battery. In addition, both the use of
organic electrolytes and strict humidity control of the assembling environment make lithium and sodium-ion batteries fairly expensive. A key factor of research in alternative chemistries that may lead to considerably cheaper and/or longer lasting batteries would be the discovery of a safer substitute for flammable electrolytes.

One novel approach to overcome the limitations of the conventional organic solvents including their low conductivity would be to use an aqueous electrolyte. Several common cathode and anode compounds that have been used in this new type of lithium-ion battery system are capable of operating with an aqueous electrolyte. Aqueous electrolyte systems possess three big advantages against non-aqueous systems. They are nonflammable and will be able to reduce the material and process cost, significantly.

The high ionic conductivity results in low internal resistance; therefore, an aqueous rechargeable battery is one of the promising candidates for large scale energy storage that emphasizes safety and cost.

The most important consideration is the proper selection of cathode and anode active materials due to the electrochemical decomposition of water. So far, NaSiCON-type LiTi$_2$(PO$_4$)$_3$ has been investigated as an anode in aqueous electrolyte. However, just a few reports of anode active materials such as NaTi$_2$(PO$_4$)$_3$ have been reported for aqueous sodium-ion battery [171, 177-181]. NaSiCON-type phase LiTi$_2$(PO$_4$)$_3$ anode material can be combined with LiMn$_2$O$_4$ cathode material in a neutral pH aqueous electrolyte. These devices have been able to work as an aqueous electrolyte lithium-ion battery with reasonably good performance in terms of cycling stability, energy and power density. NaTi$_2$(PO$_4$)$_3$, as its analog, has the similar open-frame structure with two types of interstitial sites that allow Na-ions to diffuse rapidly. This material reversibly intercalates two sodium atoms and the intercalants occupy the M1 position of the NaSiCON matrix. It was found that a lattice parameter of the NaSiCON structure was reversibly increased on sodium insertion, due to the larger Ti$^{3+}$ ions in Na$_3$Ti$_2$(PO$_4$)$_3$ [178]. Delmas et al. [177], were the first to analyze the electrochemical properties of phase-pure
NaTi$_2$(PO$_4$)$_3$, and reported that the low electronic conductivity of this type of material inhibits its potential in battery applications. However, other studies performed using carbon-coated NaTi$_2$(PO$_4$)$_3$ synthesized by the Pechini method proved its feasibility for battery applications with relatively good cycling stability and rate capability in an aqueous electrolyte [180].

In general, NaTi$_2$(PO$_4$)$_3$ belongs to the NaSiICON-type compounds with the R-3c group. Figure 3.4 shows the crystal structure of NaTi$_2$(PO$_4$)$_3$, which exhibits an open three-dimensional structure with two types of interstitial spaces (M1, M2) where conductor cations are distributed. The matrix can be broken down into fundamental groups of 2 MO$_6$ octahedra separated by 3 XO$_4$ tetrahedra, with which they share common corner oxygens. There are no shared edges or shared faces in the matrix, so all of the large sodium sites are connected to one another. Although the corner-sharing matrix of NaSiICON should be suitable for Na diffusion, the poor electronic conductivity restrains Na intercalation.

Figure 3.4 Crystal Structure of NaTi$_2$(PO$_4$)$_3$ [180].

Sodium titanium phosphate has been recently reported as a good anode material to be used in aqueous Na-ion batteries. Its theoretical specific capacity of 130 mAhg$^{-1}$ and the
specific capacities of 120 and 123 mAhg$^{-1}$ in nonaqueous and aqueous electrolytes, respectively, makes it an interesting anode material. In aqueous electrochemical cells, it shows much lower polarization, better cyclability and rate capability, which makes it a promising anode for water-based cells, in spite of the limited voltage range [168]. Moreover, NaTi$_2$(PO$_4$)$_3$ synthesized by the Pechini method shows a reversible discharge capacity 130 mAhg$^{-1}$, which is enough to operate as an anode with a long cycle life in an aqueous sodium-ion battery. Also, it was confirmed that by using an aqueous electrolyte with high conductivity and low viscosity, the insulative nature of NaTi$_2$(PO$_4$)$_3$ could be overcome [178].

Finally, apart from carbonaceous materials, anodic compounds compatible with water-based electrolytes should be researched. As a future prospect of anode materials for Na ion technology, Palacin et al., describes the use of titanates as possible anodes for a room temperature Na-ion cell [182]. They prepared Na$_2$Ti$_3$O$_7$ and tested versus a sodium anode. This compound allows the intercalation of two sodium ions in a plateau at around 0.3 V vs. Na/Na$^+$, which corresponds to a 200 mAhg$^{-1}$ specific capacity. In this sense, other titanate compounds that have been tested in Li ion cells, such as Na$_2$Ti$_6$O$_{13}$ or Na$_4$Ti$_5$O$_{12}$, could be applied to sodium ion technology. This way, a new family of compounds has joined the quest for an anode material for Na-ion cells.
CHAPTER 4
EXPERIMENTAL PROCEDURES

4.1 Chemical and Powder Processing

4.1.1 The Polymeric Steric Entrapment Method to Produce Subvalent and Multicomponent Compounds (LiFePO$_4$ and NaFePO$_4$) for Energy Storage Applications

The synthesis procedure described in this section was adapted from the original polymeric steric entrapment method developed to produce ceramic oxide powders. In general binary compounds, where the cations always reach their maximum oxidation state (maximum valent state) [34, 35, 37, 38, 41, 43]. It is important to mention that this is the first time that this synthesis method has been adapted to produce multicomponent (three or more cations) compounds where the cations (transition metals) have multiple valence states (zwitter ions) and reach a lower oxidation state (or subvalent). This is the case for Fe in LiFePO$_4$ (triphylite), where its valence is 2+ instead of 3+. This redox couple (3+/2+) characteristic makes LiFePO$_4$ a suitable material for energy storage applications.

LiFePO$_4$ was selected as a model compound because it has been widely studied due to its technological importance, and there is a lot of background and technical information, that would help us to understand the system, synthesis, processing, and more importantly we could have access to standard and commercial materials to compare our results. Variables such as the amount of water, pH of the solution, drying procedure, HNO$_3$ addition, amount of polymer, calcination /crystallization atmosphere and temperature were tested in the model system and then the variables were tuned to produce NaFePO$_4$ based on the concepts learned from the model system.

Polyvinyl alcohol (PVA) was selected as a polymer to perform the steric entrapment because all of the cations and PVA are soluble in water. Due to the fact that the amount of water in the system affects some synthesis variables such as pH and some processing variables such as drying time (further explained later), a 20 weight % solution of polyvinyl alcohol (PVA) in de-ionized (DI) water was prepared using a 80% hydrolyzed PVA (M.W. 9.000 – 10.000, Sigma
Aldrich Corporation, USA). The polymer was dissolved by adding small quantities to DI water (to reduce mixing time) and stirring on a hot plate at room temperature overnight.

The cation sources for LiFePO₄ preparation were lithium nitrate (LiNO₃, Reagent Plus®, Sigma Aldrich Co, St Louis, MO), iron(III) nitrate nonahydrate (FeN₃O₉ • 9H₂O, ACS Reagent ≥ 98%, Sigma Aldrich Co, St Louis, MO) and ammonium phosphate dibasic ((NH₄)₂HPO₄, Reagent Grade, ≥ 98%, Sigma Aldrich Co, St Louis, MO).

Table 4.1 pH of Each Cation Solution, Each Mixing Step and The Final Solution pH to Produce LiFePO₄

<table>
<thead>
<tr>
<th>Source</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>8.69</td>
</tr>
<tr>
<td>Fe</td>
<td>≈ 0</td>
</tr>
<tr>
<td>P</td>
<td>7.88</td>
</tr>
<tr>
<td>Li+Fe</td>
<td>0.40</td>
</tr>
<tr>
<td>Final</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Stoichiometric amounts of the Li, Fe and P sources were dissolved independently in 40 ml of DI water and stirred during 1 hour to assure complete dissolution and homogeneity. Then the cation solutions were mixed in specific order to avoid agglomeration or gelation. First, Li and Fe nitrates solutions were mixed, and then the P source was added dropwise. Table 4.1 shows the pH of each cation solution, each mixing step and the final solution pH. It was noticed that when the P source was added to the Li and Fe mixture, the pH started to rise and formed agglomerates, which could be re-dissolved as soon as the pH solution could be kept below 0.5.

That is why in principle, addition of HNO₃ was necessary to form a clear solution. Unless the mixing conditions (order of addition, pH, amount of water) mentioned above assured the formation of a multi-cation clear solution, an extra time of mixing on the hot plate at room temperature (for at least 4 hours) was given to the solution before the addition of the PVA solution. The amount of PVA solution added to the system was calculated based on the ratio of total (+) valences of the cation to the (-) valences of the OH- functional groups in the PVA. For
the model system, different rations were evaluated, 2:1, 4:1 and 6:1. The final solution (cation + PVA) was allowed to mix overnight to assure a very good mixing of all components.

Tree different ways to dry the solution were tested:

a) Drying the solution on a hot plate at a temperature of 350 °C inside a fume hood, where water vapor, orange and white gases were observed. The dried powder was reddish and it was ground with a mortar and pestle. The ground powder was thermally treated in two different ways:

   I. Calcined in air for 2 hours at 250 °C (10 °C/min) and then crystallized at different temperatures (300 °C – 800 °C, 10 °C/min) for 2 hours in a calcining furnace (Carbolite CWF 12/13, Carbolite Inc.).

   II. Calcined in air for 2 hours (10 °C/min) in a calcining furnace (Carbolite CWF 12/13, Carbolite Inc.), and then crystallized in reducing atmosphere (forming gas, 95 % N₂ and 5 % H₂) at different temperatures (300 °C – 800 °C, 5 °C/min) for 2 hours in a controlled atmosphere alumina tube furnace (Lindberg, Asheville, NC).

b) Drying the solution on a hot plate at a temperature of 70 °C inside a fume hood, to form a viscous solution and then finishing the drying in an oven at 110 °C, where the smell of nitrate decomposition was noticed. The dried powder was pale yellowish and it was ground with a mortar and pestle. The ground powder was calcined and crystallized in a single step in reducing atmosphere (forming gas consisting of 95 % N₂ and 5 % H₂) at different temperatures (300 °C – 800 °C, 5 °C/min) for 2 hours in the controlled atmosphere alumina tube furnace (Lindberg, Asheville, NC). A pale yellowish gas release was detected at temperatures between 280 °C and 290 °C. The colors of the final powder varied between different tones of orange, red and brown depending on the maximum temperature.

c) Drying the solution in a hot plate at temperature at 70 °C to form a viscous solution and then finishing the drying in a vacuum oven (Fisher Scientific, Model 282 A, Pittsburgh, PA) at 60 °C. The dried gel was pale yellowish and it was more or less sticky depending on the
amount of PVA used. The ground powder was calcined and crystallized in a single step in a reducing atmosphere (forming gas, 95 \% \text{N}_2 and 5 \% \text{H}_2) at different temperatures (300 °C – 800 °C, 5 °C/min) for 2 hours in a controlled atmosphere alumina tube furnace (Lindberg, Asheville, NC). A red-yellowish gas release, bubbled through water, was detected at temperatures between 240 °C and 290 °C. The temperature, color and how long the gas was released were dependent of the nitrate/PVA ratio. The colors of the final powder varied between different tones of orange, brown, gray and black, depending on the maximum temperature and nitrate/PVA ratio.

A flowchart of the polymeric steric entrapment method and the variables tested in this study to produce LiFePO$_4$ is shown in the Figure 4.1.
For the case of the production of NaFePO₄, where we wanted to probe the concept of the production of subvalent and multicomponent compounds using the organic steric entrapment method, the cation sources for NaFePO₄ preparation were sodium nitrite (NaNO₂, Reagent Plus®, Sigma Aldrich Co, St Louis, MO), iron(III) nitrate nonahydrate (FeN₃O₉ • 9H₂O, ACS Reagent ≥ 98%, Sigma Aldrich Co, St Louis, MO) and ammonium phosphate dibasic ((NH₄)₂HPO₄, Reagent Grade, ≥ 98.0%, Sigma Aldrich Co, St Louis, MO). In addition, this system will show us how viable is substitute cations in the synthesis and produce different compounds. As NaFePO₄ was a proof of concept, just some variables were tuned based on what we learned in the model system, in order to produce a single phase. HNO₃ was added to keep the pH below 0.5 as was done in the model system.

Figure 4.2 Shows The Flowchart and Tuned Conditions to Prepare NaFePO₄ by The Polymeric Steric Entrapment Method Using Polyvinyl Alcohol.

![Flowchart](image)

**Figure 4.2 Flowchart of The Polymeric Steric Entrapment Method and The Variables Tested to Produce NaFePO₄**
4.1.2 Hybrid Polymeric Steric Entrapment Method to Produce Maximum Valent and Multicomponent Compounds (NaTi$_2$PO$_4$) for Energy Storage Applications.

The cation sources for NaTi$_2$(PO$_4$)$_3$ preparation were sodium nitrite (NaNO$_2$, Reagent Plus®, Sigma Aldrich Co, St Louis, MO), titanium(IV) isopropoxide (Ti[OCH(CH$_3$)$_2$]$_4$, ≥ 97.0%, Sigma Aldrich Co, St Louis, MO) and ammonium phosphate dibasic ((NH$_4$)$_2$HPO$_4$, Reagent Grade, ≥ 98.0%, Sigma Aldrich Co, St Louis, MO). For this synthesis a hybrid method should be used because some reagents (Na and P sources) dissolved in water, but not in alcohol, while another reagent such as titanium(IV) isopropoxide (also called “TISO”) decomposed in water (forming isopropyl alcohol and a hydrated form of titania) but dissolve and remained stable in alcohol. However, the decomposition to titania could be hindered by adding excess isopropyl alcohol, so as to drive the equilibrium to the left. The titanium isopropoxide was therefore dissolved in isopropyl alcohol.

As a polymer carrier, ethylene glycol (EG) monomer (HOCH$_2$CH$_2$OH, Fisher BioReagents, ≥99%, Fair Lawn, NJ) was chosen, because it is a linear polymer that does not decompose in isopropyl alcohol and it can help to prevent titanium isopropoxide decomposing right away when it is mixed with the other cation sources dissolved in water.

The dissolution of the reagents was made in following way:

- Stoichiometric amounts of Na and P sources were dissolved in 40 ml of DI water, independently.

- A stoichiometric amount of TISO was dissolved in 50 ml of isopropyl alcohol.

- The EG was dissolved in 50 ml of isopropyl alcohol. The amount of EG added to the system was calculated based on the ratio of total (+) valences of the cation to the (-) valences of the OH$^-$ functional groups in the EG.
After all the reagents were dissolved in their proper solvent, they were stirred for 4 h on a hot plate at room temperature to ensure complete dissolution. Then, Na and P solutions were mixed and TISO and EG solution were mixed separately. At this point no segregation or decomposition of any reagent was noticed. Finally, the solution containing Na and P sources was added dropwise to the solution containing TISO and EG. If this mixing procedure is made slowly and in the proper order of mixing, no acid addition (HNO₃) or more isopropyl alcohol is needed, and the final solution is white (milky) but no precipitates or agglomerates are formed. If the last mixing is performed too fast or the reagents are mixed in different order, some agglomerates, precipitates or even a gel formation can be seen. If soft agglomerates were formed, addition of HNO₃ and isopropyl alcohol could help to dissolve them and obtain a white (milky) suspension without precipitates. The final solution (cation + EG) was allowed to mix overnight to assure a very good mixing of all components.

The drying process was carried out on a hot plate at temperature ≈ 350 °C inside a fume hood. Upon heating, with the evaporation of water and isopropyl alcohol an exothermic reaction took place and the dried powder exploded like popcorn. During drying a pale yellowish gel was formed but after the powder started to explode the powder turned white. The dried powder was ground with a mortar and pestle. The ground powder was calcined in air for 2 hours at 250 °C (10 °C/min) and then crystallized at different temperatures (500 °C – 700 °C, 10 °C/min) for 2 hours in a laboratory furnace (Carbolite CWF 12/13, Carbolite Inc., Hope Valley, England).

Figure 4.3 shows the flowchart to prepare NaTi₂(PO₄)₃ by the hybrid polymeric steric entrapment method using ethylene glycol.
Figure 4.3 Flowchart of The Hybrid Polymeric Steric Entrapment Method to Produce NaTi$_2$(PO$_4$)$_3$

4.2 Powder Characterization

4.2.1 Thermal Analysis

A simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) (Model STA 409, Netzsch GmbH, Selb, Germany) was used to evaluate endothermic and exothermic processes such as pyrolysis, decomposition and crystallization of precursors in the model system. The samples used for this analysis were the LiFePO$_4$ precursors with different amounts of polymer dried in the combination of hot plate and vacuum oven (see section IV.1.1). The analyses were performed at a heating rate of 5°C/min in the temperature range of 25 °C – 850 °C under N$_2$ atmosphere.
4.2.2 X-ray Diffraction Analysis

The evolution of crystalline phases as a function of heating temperature was studied using a diffractometer (Seimens-Bruker D5000, Bruker AXS Inc., Madison, WI), with Cu Kα radiation (\(\lambda = 1.540598 \text{ Å}\)). The operating conditions of the diffractometer were 40 kV, 30 mA, 10 ° to 70 °2θ, at a step size of 0.02° 2θ, and a measurement time of 0.5 s per step. X’pert HighScore Plus software (PANalytical) was used to identify the phases in the samples.

4.2.3 Microstructure Characterization

The morphologies and crystal sizes of all samples were examined by scanning electron microscopy (SEM) (JSM-6060LV, JEOL USA, Inc., Peabody, MA). Prior to imaging, the samples were Au–Pd sputter-coated to avoid surface charging. To confirm the production of nanoparticles, transmission electron microscopy (TEM) was performed of the best sample in this study using a JEOL-2010 (LaB₆ thermionic emission source) electron microscope with an acceleration voltage of 200 KeV. For TEM sample preparation a planetary mill (Planetary Micro Mill PULVERISETTE 7 classic line, Fritsch) was used to break up the soft agglomerate produced in the calcination/crystallization process. The grinding process was performed at 350 rpm for 10 min. Drops of the slurry were placed on top of carbon coated 200 mesh copper grids.

4.2.4 Chemical Analysis

A PerkinElmer 2400 Series II CHNS/O Elemental Analyzer (2400 Series II) was used to determine the residual carbon, hydrogen and nitrogen contents in the final powders. The chemical composition was analyzed using inductively coupled plasma (ICP) emission spectroscopy (PerkinElmer 2000DV ICP-OES, Norwalk, CT). All work was done at the School of Chemical Sciences at the University of Illinois at Urbana-Champaign.

4.2.5 Particle Size and Surface Area

The particle size and particle size distributions (PSD) of calcined powders were evaluated using a laser scattering particle size analyzer (Partica LA-950V2, Horiba, Kyoto, Japan). The
specific surface area (SSA) was measured using seven-point BET analyses by nitrogen gas adsorption (Model ASAP 2020, Micromeritics, Norcross, GA). To perform PSD and SSA the samples were ground in the same way as for TEM sample preparation (see section IV.2.3).
CHAPTER 5
RESULTS AND DISCUSSION

5.1 Model System LiFePO₄

As it was reviewed in the past chapter, LiFePO₄ was selected as a model system due to its technological importance and the vast information available that will help us to understand and compare our results. In this chapter, we will see how variables such as the amount of water, pH of the solution, drying procedure, HNO₃ addition, amount of polymer, calcination/crystallization atmosphere and temperature affects the model system. Finally, we hope to use the knowledge developed in this system to synthesize other interesting compounds.

5.1.1 Characterization of Commercial LiFePO₄

Commercial LiFePO₄ produced by MTI Corporation (Richmond, CA) was used as a commercial standard in this study. Table 5.1 shows powder specifications provided from the company.

Table 5.1 LiFePO₄ Specifications Provided by MTI Corporation

<table>
<thead>
<tr>
<th>Item</th>
<th>standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td></td>
</tr>
<tr>
<td>D10(μm)</td>
<td>0.67</td>
</tr>
<tr>
<td>D50(μm)</td>
<td>1.86</td>
</tr>
<tr>
<td>D90(μm)</td>
<td>21</td>
</tr>
<tr>
<td>Dmax(μm)</td>
<td>&lt;25</td>
</tr>
<tr>
<td>Tap density (g/ml)</td>
<td>&gt;0.98</td>
</tr>
<tr>
<td>Specific Area (m²/g)</td>
<td>&lt;16</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>Chemical Composition</td>
<td></td>
</tr>
<tr>
<td>Fe(%)</td>
<td>32.5-34.5</td>
</tr>
<tr>
<td>Li(%)</td>
<td>4.0-4.5</td>
</tr>
<tr>
<td>pH</td>
<td>8.0-11.0</td>
</tr>
<tr>
<td>Fe(%)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>K(%)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na(%)</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Ca(%)</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>SO₄(%)</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Electric-chemical Properties</td>
<td></td>
</tr>
<tr>
<td>Capacity at 0.5C discharging</td>
<td>&gt;150.2 mAh/g</td>
</tr>
<tr>
<td>Coulomb rate at first cycle</td>
<td>96.1%</td>
</tr>
<tr>
<td>Capacity at 1C discharging cycle</td>
<td>131.1 mAh/g</td>
</tr>
<tr>
<td>Rate of CC Charging at first cycle</td>
<td>96.2%</td>
</tr>
</tbody>
</table>
Figure 5.1 X-ray Diffraction (XRD) Pattern for MTI LiFePO$_4$ and The Indexed ICDD Card 00-040-1499 for Triphylite.
In order to have more detailed information and have the same conditions for the characterization of the reference and our samples, the MTI powder was characterized by X-ray diffraction (XRD), electron microscopy (SEM), chemical analysis by inductive coupled plasma (ICP), particle size (PSD) and specific surface area (SSA).

As is depicted in Figure 5.1, only a LiFePO$_4$ phase was found in the powder. Also, it was noticed that the noise/peak ratio was high. This can be explained by the fact that when a Cu (K$_\alpha$) X-ray source is used to analyze materials containing Fe, there is fluorescence effect which increases the noise of the spectrum.

![Figure 5.2 SEM Micrographs of Commercial MTI LiFePO$_4$ Powder.](image)

Figure 5.2 SEM Micrographs of Commercial MTI LiFePO$_4$ Powder.
Figure 5.2 shows SEM micrographs of commercial MTI LiFePO\textsubscript{4} powder. It can be noticed that some crystals have a platelet shape, but in general they exhibit irregular shapes. Crystallite sizes are in the range of 0.25 μm to 1 μm. The powder appears to have a low degree of necking and high porosity which suggests a high surface area (17.92 m\textsuperscript{2}/g).

Table 5.2 Chemical Analysis (ICP), Particle Size (PSD) and Specific Surface Area (SSA) Characterization of MTI LiFePO\textsubscript{4}

<table>
<thead>
<tr>
<th>Item</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td></td>
</tr>
<tr>
<td>D10(μm)</td>
<td>1.81</td>
</tr>
<tr>
<td>D50(μm)</td>
<td>5.87</td>
</tr>
<tr>
<td>D90(μm)</td>
<td>7.23</td>
</tr>
<tr>
<td>Dmax(μm)</td>
<td>7.69</td>
</tr>
<tr>
<td>Specific Area BET (m\textsuperscript{2}/g)</td>
<td>17.92</td>
</tr>
<tr>
<td>Chemical Composition (wt,%)</td>
<td></td>
</tr>
<tr>
<td>Fe(%)</td>
<td>31.40</td>
</tr>
<tr>
<td>Li(%)</td>
<td>4.20</td>
</tr>
<tr>
<td>P(%)</td>
<td>18.02</td>
</tr>
<tr>
<td>C(%)</td>
<td>1.87</td>
</tr>
<tr>
<td>N(%)</td>
<td>0.00</td>
</tr>
<tr>
<td>H(%)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The characterization results obtained for MTI LiFePO\textsubscript{4} powder are shown in Table 5.2. It can be seen that the PSD analysis gave different results compared to those reported in the technical data sheet provided by the producer. It is important to mention that PSD analysis really measures the aggregated particles and not the crystal sizes. Agglomeration can occur due to electrostatic forces between small particles or simply because primary particles agglomerate during the synthesis process due to intermolecular forces. Surface area values agree with the values reported by the producer. Chemical analysis shows carbon content around 1.5 wt\% and amounts of Fe and Li close to the values reported by the producer.
5.1.2 Calcination/Crystallization Atmosphere Effect

To evaluate and have a sense of how the atmosphere affects the formation of subvalent multicomponent compounds, two different atmospheres (air and forming gas) were tested in the model system LiFePO$_4$. Samples were prepared using the standard procedures for the production of ceramic powders by the organic steric entrapment method [34, 35, 37, 38, 41, 43]. This process can be summarized as follows: the hot plate was set to $\approx 350 \, ^\circ C$, then the dried powder was calcined in air for 2 hours at 250 $^\circ C$ at 10 $^\circ C$/min, and finally, calcined powders were heated (crystallized) at 10 $^\circ C$/min in air or forming gas at different temperatures of 700$^\circ C$ and 800$^\circ C$, and held for 2 hours. The atmosphere effect was tested for samples with two different cation/organic ratios of 4:1 and 2:1.

Figures 5.3 and 5.4 are X-ray diffractograms for the samples made in air and forming gas at 700 $^\circ C$ and 800 $^\circ C$ using cation/organic ratios of 4:1 and 2:1, respectively. The black spectrum in both figures is the LiFePO$_4$ reference from MTI corp. These figures clearly show that by working in air it is not possible to obtain the single phase; rather a powder with more than five phases, including binary and ternary compounds, is obtained. However, by working in forming gas, powders with less than three phases mostly consisting of LiFePO$_4$ can be obtained. These results demonstrate that unless working with polymers such as PVA and nitrates which generate a reducing atmosphere when they are decomposing, a more reduced atmosphere is required to avoid formation of oxidized secondary and ternary phases. If oxidized binary or ternary species are formed during any step of the synthesis process, it is very difficult to get rid of them in subsequent stages of the synthesis, because usually they are thermodynamically more stable. It would take high energy (time, temperature and multiple grinding steps) to transform all of those phases to the desired LiFePO$_4$ single phase.

Based on these results, forming gas (95 % N$_2$ and 5 % H$_2$) was selected as a calcination/crystallization atmosphere and as a standard condition to evaluate the other variables in the model system.
Figure 5.3 X-ray Diffraction (XRD) Patterns for Samples Made With A Cation/Organic Ratio 4:1 in Air and Forming Gas at 700 °C and 800 °C.
Figure 5.4 X-ray Diffraction (XRD) Patterns for Samples Made With A Cation/Organic Ratio 2:1 in Air and Forming Gas at 700 °C and 800 °C.
5.1.3 Solution pH Effect

The advantage of producing materials using a wet chemical process is the ability to form a solution which has all the components very well dissolved, and homogeneously distributed in the entire volume. In other words, it is to have an atomic mixing between all the components. When all elements in the mixture dissolve, it is called a solution and it is clear; however, when the elements do not dissolve, the mixture is called a dispersion and it is cloudy or milky. The best scenario is when a clear solution is formed because an atomic mixing of elements and homogeneity in the entire volume can be reached. When agglomerates, floculates or precipitates are formed, segregation of the components, heterogeneities and multiphases in the final product can be expected. The ionic characteristics of each component and the pH of the solution can cause gelation, agglomeration, flocculation or precipitation. As it was shown in the Table 4.1., the pH of the Fe source is really low (Fe nitrate, pH \( \approx 0 \)) and for the P source is close to neutral (pH = 7.88); this big difference can cause gelation.

When solutions containing Fe and Li sources were mixed, a clear solution can be formed. However, when the solution containing the P source was added to the former solution an agglomeration of components was observed. Figure 5.5 shows how the solution appears when all of the components were mixed.

After agglomeration, additional stirring homogenizes the solution, but a clear solution is never reached. Instead, a cloudy and milky dispersion is formed. As it was mention before, a clear solution where an atomic mixing is guaranteed is crucial for single phase formation. Therefore, nitric acid (HNO\(_3\)) was added dropwise while the solution containing P source was added to the solution containing Li and Fe sources. HNO\(_3\) was selected because it will not affect the stoichiometry of the system and it would burn out during the calcination process. It was noticed that by keeping the pH of the solution below 0.5 the agglomerates could be dissolved and a clear solution formed (Figure 5.6), while by having the pH above 0.5, the agglomeration was irreversible, and a cloudy dispersion formed (Figure 5.7).
Figure 5.5 Agglomeration of Components When A Solution Containing P Source Was Added To A Solution Containing Li and Fe Sources.

Figure 5.6 Formation of A Clear Solution by Keeping the pH Below 0.5.
Based on these results, addition of HNO₃ was established as a standard condition to produce a clear solution which guaranteed the atomic mixing of all components in the system. It is important to mention that the amount of water in the system modified the pH of the solution. Therefore, the amount of acid was dependent on variables such as the amount of nitrates, as well as the type and amount of solvent.

5.1.4 Solution Drying Effect

After many unsuccessful trials to synthesize single phase LiFePO₄, the effect of the drying process was studied. Basically, three different conditions (section IV.1.1) of drying and calcination/crystallization were tested during the whole study:

a)

1. 
   (i). The sample was initially dried on a hot plate set at ≈ 350 °C.
   (ii). The sample was calcined in air for 2 hours at 250 °C (10 °C/min).
   (iii). The sample was heated for crystallization 10 °C/min in air to 700 °C- 800 °C and held for 2 hours.
2.

(i). The sample was initially dried on a hot plate set at ≈ 350 °C.
(ii). The sample was calcined in air for 2 hours at 250 °C (10 °C/min).
(iii). The sample was heated for crystallization 10 °C/min in forming gas to 700 °C-800 °C and held for 2 hours.

b)

(i). The sample was initially dried on a hot plate set at ≈ 70 °C.
(ii). The sample was further dried in an oven in air at 110 °C.
(iii). The sample was calcined and crystallized in a single step at 5 °C/min in forming gas to 300 °C-800 °C and held for 2 hours.

c)

(i). Sample was initially dried on a hot plate set at ≈ 70 °C.
(ii). Sample was further dried in a vacuum oven at 60 °C.
(iii). Sample was calcined and crystallized in a single step at 5 °C/min in forming gas to 300 °C-800 °C and held for 2 hours.

Two different types of dried samples (d and e) were tested in a simultaneous DSC/TGA apparatus to evaluate endothermic and exothermic processes such as pyrolysis, decomposition and crystallization of precursors. These two extreme conditions were selected because in (d), organic and nitrates released during drying were abundant and this procedure has been the standard procedure taken, so far, in the production of ceramic powders by the organic steric entrapment method. Sample (d) had the (a) drying conditions shown in section IV.1.1. In the shown other condition (e), the release of organic or nitrates were barely detected, which meant the full availability of these two components (fuel and oxidizer) for the next step (calcination/crystallization). Sample (e) had the (c) drying conditions shown in section IV.1.1.

Figures 5.8 and 5.9 show a thermal analysis (DSC/TGA) of the sample type (d) made with the cation/organic ratios 4:1 and 2:1, respectively. These thermal analyses showed that this type of samples had an exothermic peak at a temperature around 350 °C. This peak could be
associated with the initiation of the crystallization process. The total weight percent loss was about 11% and 26% for the 4:1 and 2:1 samples, respectively. These values agreed with differences in the amount of organics in both samples. It is also important to notice that these weight losses were relatively low because the amount of organics was low with respect to other synthesis methods. Furthermore, the samples were dried on a hot plate at ≈ 350 °C and then calcined in air for 2 hours at 250 °C (10 °C/min). Orange and white gases were observed during drying and a reddish dried powder was obtained.

![Thermal Analysis Graph](image)

**Figure 5.8 Thermal Analyses (DSC/TGA) of The Sample Type (d) Made with The Cation/Organic Ratio 4:1.**

Figures 5.10, 5.11, and 5.12, are from thermal analyses (DSC/TGA) of the sample type (e) made with the cation/organic ratios 2:1, 4:1 and 6:1, respectively. It can be noticed that the total weight loss percentage in sample type (e) was bigger as compared with that of sample type (d).
Figure 5.9 Thermal Analyses (DSC/TGA) of The Sample Type (d) Made with The Cation/Organic Ratio 2:1.

The total weight percent lost was about 78%, 83% and 40% for 2:1, 4:1 and 6:1 samples, respectively. These total weight loss percentages were larger because the samples were dried at a low temperature, in order to remove water content. All the organics and nitrates remained in the sample and they could be used in subsequent steps in the synthesis. In addition, the maximum weight loss could be observed at the same temperature were the large exothermic peak in the DSC curve was observed. These large weight losses can be attributed not only to the release of organics and nitrates gases, but also, to some sample losses from the sample container, due to the explosive reaction taking place during the analysis. These explosive reactions were observed not only during the thermal analysis, but also, during the powder production in the laboratory. In addition, the TGA curves indicated that full calcination occurred at low temperature, especially for samples 4:1 and 6:1, viz., at 150 °C and 250 °C, respectively.
Differential scanning calorimetric curves revealed exothermic peaks between 150 °C and 300 °C. For the sample with ratio 2:1 (Figure 5.10) two peaks are observed at 175 °C and 225 °C. These two peaks could be attributed to organics and nitrates decomposing at different temperatures. The decomposition reaction of this sample in the tube furnace was strong, long and the released gases were yellow/whitewish.

![THERMAL ANALYSIS](image)

**Figure 5.10 Thermal Analysis (DSC/TGA) of The Sample Type (e) Made With The Cation/Organic Ratio 2:1.**

In the case of the sample with ratio 4:1 (Figure 5.11), a single large exothermic peak was sensed in the DSC analysis at 150 °C, which meant that not only did the organics and nitrates decomposition reactions occur at the same time, but also, the crystallization started such as really low temperature. All the energy available from these decomposition reactions was released at the same time and could be used to induce crystallization. This exothermic peak perfectly matched the large weight loss observed in the TGA curve. This decomposition
reaction was also observed in the tube furnace and it was really violent, long and released gases were red/yellowish.

Figure 5.11 Thermal Analysis (DSC/TGA) of The Sample Type (e) Made With The Cation/Organic Ratio 4:1.

Figure 5.12 indicates that for sample with ratio 6:1 the decomposition reaction also took place at two different temperatures, 220 °C and 275 °C for organics and nitrates, respectively. In the tube furnace, this decomposition reaction was also observed and it was short, not strong as the previous ones and the released gases were mostly whitewish.
In the Figure 5.13, it can be seen that there was an optimum ratio between organics and nitrates to produce a strong and single exothermic decomposition reaction. For this model system, the optimum ratio was 4:1. This was the best scenario to generate the maximum amount of energy in the system, which could be used to induce crystallization. Furthermore, the optimum ratio coincides with when the decomposition reaction and crystallization took place at lower temperature. Movements (to a higher or lower ratio) from this optimum ratio shifted the decomposition reaction towards higher temperatures. Decomposition reactions of organics and nitrates that took place at different and higher temperatures could generate the formation of multiphase products because in a specific system thermodynamic stable phases could be different at different temperatures. Moreover, metastable phases could be formed by taking advantage of the single decomposition reaction, because in fast and exothermic reactions, thermodynamic mechanisms are no longer the controlling mechanism of the phase formation; instead, it is the kinetic mechanism.
5.1.5 Crystallization of LiFePO$_4$

So far, the effects of drying conditions have been observed in terms of energy released. Now, the effect of these variables in the crystallization process will be depicted. Working with standard conditions (defined earlier in this chapter) of amounts of acid, water, furnace atmosphere and with the conditions (section IV.1.1) of drying and calcination/crystallization type (a), a single phase of triphylite (LiFePO$_4$) could be produced.
Figure 5.14 Pure LiFePO$_4$ Formed Using Drying and Calcination/Crystallization Type (a) and Standard Conditions of HNO$_3$, Water and Furnace Atmosphere.
Figure 5.14 shows that at 700 °C small amounts of secondary phases were still present in the sample. However, upon increasing the temperature to 800 °C those secondary phases recombined through a solid state reaction to form a single phase. It is important to mention here that unless an atomic mixing was guaranteed and sufficient amount of polymer was added to the system to ensure steric entrapment and avoid segregation, formation of single phase at low temperature was unsuccessful. High temperature (800 °C) and solid diffusion would be required to form pure LiFePO$_4$ phase.

In contrast, by taking advantage of the strong, energetic and violent decomposition reactions observed in the dried samples of type (e), unexpected and interesting results were obtained. As it was seen in the thermal analysis (section V.1.4.) the temperature, magnitude and characteristics of the decomposition reaction were dependent on the ratio of organics/nitrates (i.e., fuel/oxidizer). The following Figures 5.15, 5.16, and 5.17, show the phase evolution when temperature was increased (300 °C to 800 °C) for the dried samples type (e) with different cation/organic ratios of 2:1, 4:1 and 6:1.

Figure 5.15 indicates that formation of a single phase LiFePO$_4$ was possible at 500 °C using a 2:1 cation/organic ratio. All samples were compared not only with the ICDD cards but also, with commercial LiFePO$_4$ from the MTI Corporation. Samples below 500 °C evidenced formation of small amounts of crystalline phases, but an amorphous phase was still predominant. No secondary phases were detected in samples treated above 500 °C, which means that atomic mixing and steric entrapment were successful. Here in this group of samples, the effect of the exothermic decomposition reaction on the crystallization process was evident. The energy released during the decomposition of organics and nitrates helped to induce crystallization of the single phase LiFePO$_4$ at lower temperatures, as compared to other synthesis methods and also with the methodology implemented for dried samples type (d).
Figure 5.15 X-ray Diffractograms of Dried Samples Type (e) with 2:1 Cation/Organic Ratio in The Range 300 °C - 800 °C.
Figure 5.16 X-ray Diffractograms of Dried Samples Type (e) with 4:1 Cation/Organic Ratio in The Range 300 °C to 800 °C.
For samples containing a 4:1 cation/organic ratio the results were even more exciting. As can be seen in Figure 5.16, formation of a pure crystalline LiFePO$_4$ phase at 300 °C was successful. At 300 °C peak broadening and less intense peaks than the reference sample suggests the formation of nanoparticles. At 800 °C some extra peaks were detected, which could correspond (as was found in the literature), to a more reduced phases such as FeP. These results agreed with the information obtained from the thermal analysis where a single strong exothermic peak was detected at 150 °C. Moreover, in the tube furnace, the decomposition reaction was detected at around 240 °C and it seems that the energy released was enough to induce crystallization of the single phase. As no secondary phases were detected in the samples below 800 °C, the atomic mixing, amount of organics and nitrates were in the right proportion to produce the steric entrapment, avoid segregation and generate an exothermic decomposition reaction strong enough to crystallize olivine-type LiFePO$_4$ at low temperatures.

The behavior of samples containing a 6:1 cation/organic ratio is depicted in Figure 5.17. Below 500 °C only amorphous powder was produced, however, it can be seen that crystallization started at temperatures around 500 °C. Secondary phases, especially binaries and oxidized species such as Fe$_2$O$_3$ were detected. With an increasing of temperature and under reducing atmospheres those secondary phases recombined through solid state reaction to form a more pure powder. These results confirmed the information obtained in the thermal analysis where the exothermic peaks were detected at higher temperatures of 220 °C and 275 °C. This was observed in the tube furnace at around 290 °C. The fact that the decomposition of organics and nitrates took place at different temperatures led to the exothermic reaction being less strong, which means that the energy released was not enough to induce crystallization at a low temperature. The finding of secondary phases suggests that unless there was atomic mixing, the amount of organics were not sufficiently sterically entrapping the cations so as to avoid segregation.
Figure 5.17 X-ray Diffractograms of Dried Samples Type (e) with 6:1 Cation/Organic Ratio in The Range 300 °C to 800 °C.
To summarize these results, it has been demonstrated that there is an optimum ratio (4:1) of organics/nitrates, not only to effect the polymeric steric entrapment, but also, to generate a single strong exothermic decomposition reaction, which provides enough energy to induce crystallization of the desired phase at temperatures lower than those involved in conventional methods. Shifts from the optimum ratio provoke delays in the starting of the decomposition reaction because extra energy was required to decompose the extra amount of organics and also because the amount of nitrates was not enough to react with the total amount of organics. This was the case for 2:1 ratios. For 6:1 ratios, there is also an imbalance of fuel/oxidizer which made the exothermic reaction of organic and nitrates occur at different temperatures and also produce a less energetic reaction. Furthermore and more importantly, the amount of organics was not enough to make an optimum steric entrapment which produced segregation of the components in the system and allowed formation of multiphase materials. Finally, it is important to mention that the addition of HNO₃ not only helps in the dissolution of all reagents and formation of a clear solution, but also, it helped to balance the ratio of fuel/oxidizer which in the end, was a crucial condition to generate a single strong exothermic decomposition reaction which could induce crystallization of a single phase at low temperatures.

5.1.6 Microstructure Characterization

The microstructure of LiFePO₄ produced from the dried sample type (a) at 800 °C is shown in the Figure 5.18. Platelet-like crystals in the range between 0.5 to 10 μm were found in the samples. Evidence of crystal growth and necking (sintering) was found in this sample which means that high temperature promotes mass diffusion toward the particle interfaces. This also proves that solid state diffusion took place and so that secondary phases recombined and disappeared at higher temperatures.

Unless this sample was pure LiFePO₄ and the microstructure resembled the microstructure reported in the literature for triphylite, 800 °C was a high processing temperature which was not only uneconomically for an industrial process, but also, it produced
large crystals and sintered powders which affected the surface area, and thus the electrochemical properties. For these reasons, more effort to optimize the method using dried samples of type (c) was expended. The effect of other variables such as the amount of polymer in the system and a broad range of temperatures were tested. Furthermore, a complete characterization was carried out on this optimized process.

![Figure 5.18 SEM Micrographs of Pure LiFePO₄ Formed Using Drying and Calcination/Crystallization Type (a) and Standard Conditions of HNO₃, Water and Furnace Atmosphere.](image)

In general, the morphology of the powders produced by the polymeric steric entrapment method, and specially using dried sample type (c), was porous secondary particles (soft agglomerates) formed from primary particles in the range of 20 nm – 10 microns, see Figure 5.19. These secondary particles or soft agglomerates resulted in this particular microstructure due to the violent exothermic decomposition reaction of organics and nitrates.
These porous structures had a high specific surface area which was desirable for ion and electron diffusion in lithium ion batteries, specifically for LiFePO₄.

A comparison between the morphologies of amorphous and crystalline powder obtained using optimized conditions and cation/organic ratio of 2:1 are shown in the Figure 5.20. Samples treated at temperatures between 300 °C and 400 °C (Figure 5.20 (a) and (b)) did not show any particular morphology, and an amorphous mass was observed instead. This amorphous mass was composed of all of the precursors of LiFePO₄ and polymer chains coming from PVA. At temperatures between 500 °C and 600 °C ((c) and (d), Figure 5.20) crystallization had already taken place. Nanocrystals with platelet-like shapes and with a narrow distribution of sizes in the range of 50 nm – 150 nm could be observed. At higher temperatures (700 °C to
800 °C), crystals of about 1 μm in size with platelet-like shapes and a narrow size distribution were produced. Additionally, crystal growth and necking between particles was noticed, which meant that solid state diffusion started and pre-sintering took place.

Figure 5.20 SEM Micrographs of LiFePO₄ Powder Produced Using Optimized Conditions and Cation/Organic Ratio 2:1.
Figure 5.21 exhibits a pure crystalline LiFePO$_4$ powder obtained using optimized conditions and cation/organic ratio of 4:1 at temperatures in the range 300 °C to 800 °C. At 300 °C nanoparticles of roughly less than 100 nm were formed. These nanoparticle sizes were narrowly distributed and had a platelet-like shape. It can be seen that at 600 °C and 800 °C crystals still had sizes in the nanoscale range of about 100 nm. These results were very
interesting because after increasing the furnace temperature up to 800 °C there was not too much crystal growth or pre-sintering. This effect was very important because it means that small particle size and high surface area can be kept even while working at high temperatures. It is believed that this behavior occurred because of the organic steric entrapment. The remnant carbon covered and coated the nanoparticles, thereby avoiding solid state diffusion, and hence, crystal growth and sintering. It is important to mention that pure LiFePO₄ produced at low temperatures (300 °C) by the polymeric steric entrapment method was comparable with the LiFePO₄ produced by other wet chemical synthesis methods such as the sol-gel, hydrothermal and Pechini methods. However, expensive reagents (alkoxides), high pressure or special sealed containers and large amounts of polymers were not used.

The nanoparticle microstructures revealed in the Figure 5.21 agreed totally with the information obtained from the XRD analysis where peak broadening suggested the formation of nanocrystals. Taking these pictures of nanoparticles using a SEM machine was pushing the resolution limit of this technique. If further microstructure analysis of these nanoparticles were desired, a transmission electron microscopy (TEM) would be required.

Unless it was shown (using XRD analysis) that samples prepared using optimized conditions and cation/organic ratio 6:1 produced multiphase compounds, it is important to know how their microstructure appeared. At temperatures below 500 °C (Figure 5.22 (a) and (b)), particles without any particular shape were found because of the lack of crystallization. After 500 °C, particles with platelet-like shapes were seen in all samples which agreed with the morphologies of LiFePO₄ as shown in the literature. Particles about 1 μm with narrow size distribution were found up to 600 °C. At higher temperatures (700 °C – 800 °C), crystal growth and onset of sintering was noticed due to solid state diffusion. It would be interesting to know if there was any difference in the chemical composition of the particles and correlate them with the X-ray data, but EDS or WDS could not be performed because lithium is a very light element which cannot be detected by these techniques.
Figure 5.22 SEM Micrographs of LiFePO$_4$ Powder Produced Using Optimized Conditions and Cation/Organic Ratio 6:1.
So far, the most interesting sample in this study was the powder obtained using the optimized conditions and a cation/organic ratio of 4:1 at 300 °C, because it was pure crystalline
LiFePO₄ produced at really low temperature, with particle sizes about less than 100 nm. The production conditions and the characteristics described suggested a material with high surface area, carbon coating and small diffusion paths for ions and electrons, which makes this a promising material for energy storage applications. That is why this sample is considered to be the best sample resulting from this study.

The best sample was characterized by TEM in order to clearly see the crystallite sizes and their morphology (Figure 5.23). Agglomerates of about 1µm were formed by platelet-like nanoparticles of 20 nm. The agglomerates formed by the polymeric steric entrapment method were soft agglomerates due to the effect of the polymer network which hindered solid state diffusion and sintering. A diffraction pattern of the selected region in the micrograph (e) is shown in the micrograph (f), where clear periodic rings which correspond to a polycrystalline sample can be seen.

Table 5.3 Physical Properties of The Best Samples of Pure LiFePO₄ Produced by The Polymeric Steric Entrapment Method

<table>
<thead>
<tr>
<th>Item</th>
<th>2:1 400°C</th>
<th>2:1 500°C</th>
<th>4:1 300°C</th>
<th>MTI</th>
</tr>
</thead>
<tbody>
<tr>
<td>D10(µm)</td>
<td>1.86</td>
<td>2.17</td>
<td>3.97</td>
<td>1.81</td>
</tr>
<tr>
<td>D50(µm)</td>
<td>2.23</td>
<td>2.56</td>
<td>4.24</td>
<td>5.87</td>
</tr>
<tr>
<td>D90(µm)</td>
<td>2.53</td>
<td>2.92</td>
<td>4.74</td>
<td>7.23</td>
</tr>
<tr>
<td>Dmax(µm)</td>
<td>2.97</td>
<td>3.41</td>
<td>5.15</td>
<td>8.82</td>
</tr>
<tr>
<td>Specific Surface Area (m²/g)</td>
<td>44.24</td>
<td>54.39</td>
<td>48.25</td>
<td>17.92</td>
</tr>
</tbody>
</table>

To conclude the characterization of the model system and compare it with the reference, a particle size analysis, specific surface area and chemical analysis were carried out under the same conditions. Table 5.3 summarizes the physical properties of the best samples of pure LiFePO₄ obtained in this work. Samples made at cation/organic ratio 2:1 at 400 °C are included because it was an amorphous precursor to produce pure LiFePO₄ using the polymeric steric entrapment method.
It can be noticed that the values of the particle size analysis were very far away from the crystal sizes observed in the SEM and TEM micrographs. These results indicate that the particle size measured by a laser scattering particle size analyzer (Partica LA-950V2, Horiba, Kyoto, Japan), really measured the agglomerates, which were also observed in the low magnification SEM and TEM micrographs. What is important, however, is the fact that comparing our results with the commercial references, both the crystal sizes and the agglomerated particles produced in this work were smaller than the reference powders.

The specific surface areas values indicated in table 5.3, that all powder produced in this study had the twice specific surface area compared with the MTI reference powder. These results were expected because of both the crystallite sizes (nanocrystals) and the sponge-like microstructure of the agglomerates observed in the SEM and TEM micrographs. It is important to have powders with high surface area because it can improve the ionic and electronic conduction.

Table 5.4 Chemical Compositions of LiFePO$_4$ Selected Samples

<table>
<thead>
<tr>
<th>Item</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
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<td>Chemical Composition</td>
<td>Fe(%)</td>
</tr>
<tr>
<td>2:1 300°C</td>
<td>26.6</td>
</tr>
<tr>
<td>2:1 500°C</td>
<td>42.03</td>
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<tr>
<td>2:1 800°C</td>
<td>31.86</td>
</tr>
<tr>
<td>4:1 300°C</td>
<td>27.00</td>
</tr>
<tr>
<td>4:1 500°C</td>
<td>30.9</td>
</tr>
<tr>
<td>4:1 800°C</td>
<td>34.2</td>
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<tr>
<td>6:1 300°C</td>
<td>20.64</td>
</tr>
<tr>
<td>6:1 500°C</td>
<td>30.47</td>
</tr>
<tr>
<td>6:1 800°C</td>
<td>32.2</td>
</tr>
<tr>
<td>MTI</td>
<td>31.4</td>
</tr>
</tbody>
</table>

Chemical compositions of selected samples are shown in Table 5.4. These samples were chosen in order to see how the carbon content changed with temperature and cation/organic ratio. It was important to take into account that the nature of the exothermic reaction also affected the carbon and nitrogen content, because both fuel and oxidizer were consumed during the reaction. The ICP chemical analysis had the disadvantage that the values were expressed in terms of weight percent (wt%) which takes into account the whole mass of the
powder. Large variation could be expected in all elements measured because they were relative to the amount of other elements such as C, N, H and O, which were consumed or added during the synthesis process. For instance, multiphase samples containing oxidized phases had more oxygen in the whole mass, which affected the relative amount of other cations in the system.

Nevertheless, there was a tendency to have about 10 wt% and 1.5-2 wt% of carbon and nitrogen respectively, in samples calcined/crystallized at low temperatures using cation/organic ratios of 2:1 and 4:1. Furthermore, the amounts of carbon and nitrogen decreased with increasing temperature. For Li ion battery applications, it has been demonstrated that carbon coating improves the electrical conductivity of the active particles improving electrochemical performance. Therefore, the fact that in this work LiFePO$_4$/C composites have been produced generates hopeful expectations for energy storage applications. Samples calcined/crystallized using cation/organic ratio 6:1 show low contents of C and N. These results agree with the low amount of organic (PVA) added during the synthesis.

Finally, we have demonstrated in this section, that the polymeric steric entrapment synthesis can be used to produce compounds with complex chemistry (more than two cations) and with changeable oxidation states (Fe$^{2+}$/Fe$^{3+}$). Furthermore, it has been shown that variables such as the type of solvent, pH of the solution, type of drying, amount of organic (PVA) and amount of nitrates, strongly affected the synthesis process. Pure nanocrystals with the correct chemistry were produced at a low temperature (300 °C), making this process competitive with other wet chemical synthesis methods and more efficient than the traditional solid state reaction method. To prove the generality of the methodology developed in this work, other compounds with high interest in energy storage applications such as NaFePO$_4$ and NaTi$_2$(PO$_3$)$_4$ were therefore developed.
5.2 NaFePO₄ System

NaFePO₄ was selected as a proof of concept compound because of the fact that, at the present rate of consumption, the world lithium reserve will be depleted in less than 150 years [4–7]. Sodium is a possible natural substitute for lithium in battery technology because Na is similar to lithium. However, Na ion batteries have a lower energy and lower power densities. Nevertheless, sodium-ion (Na-ion) batteries are potentially cheaper due to the low cost (Table 2.2) and abundance of sodium in the earth, which makes Na-ion batteries suitable for replacement of Li-ion batteries in several applications, particularly where weight and size are not important such as large scale energy storage devices, stationary land-based power applications, non-portable systems and electrical grid stabilization.

Due the absence of commercial NaFePO₄, information from the literature and ICDD pattern data base were used to compare our results. Concepts learned from the model system were applied to produce pure NaFePO₄. Processing parameters such as the calcination/crystallization atmosphere (forming gas), the amount of water, HNO₃ addition and drying processes were taken directly from the model system. Cation/organic ratio and temperature were modified in order to have the right proportions of polymer entrapper, fuel/oxidizer ratio and exothermic decomposition temperature.

Figure 5.24 present the X-ray diffractograms for the NaFePO₄ samples made in forming gas at 500 – 700 °C using a cation/organic ratio of 4:1. The bottom lines show the peak list of the samples and the peak position of the NaFePO₄ reference corresponding to a Maricite 01-089-2052 ICDD reference card. It can be seen that at 500 °C a multiphase compound was formed. This compound was composed not only of NaFePO₄, but also, of secondary and ternary compounds. At 600 °C and 700 °C the synthesized compounds were almost single phase but contained small amounts of other phases. During the synthesis process a strong and long exothermic decomposition was detected at around 270 °C. Reddish and yellowish gases were expelled during the decomposition reaction. The presence of secondary and ternary phases suggested segregation and lack of entrapment during the synthesis step. Therefore, the
amount of polymer was increased to the 2:1 ratio. Figure 5.25 are X-ray diffractograms for the NaFePO₄ samples made in forming gas at 300 °C – 800 °C using a cation/organic ratio of 2:1.

For samples containing a 2:1 cation/organic ratio the results were what we expected when the amount of organic carrier was increased. As can be seen in Figure 5.25, the formation of a pure crystalline NaFePO₄ phase at 300 °C was successful. At 300 °C, peak broadening and less intense peaks suggested the formation of nanoparticles. As soon as the temperature was increased, sharp and more intense peaks appeared in the diffractograms. These results, as well as a single, strong, exothermic decomposition reaction observed in the tube furnace at 270 °C, resembled the behavior observed in the model system. Again, it seems that the energy released was enough to induce crystallization of the single phase at low temperatures. As no secondary phases were detected in the samples at all temperatures, the atomic mixing, amount of organics and nitrates were in the right proportions to achieve the steric entrapment, avoid segregation and generate an exothermic decomposition reaction strong enough to crystallize NaFePO₄ at low temperatures.

The microstructure and morphology of the NaFePO₄ produced using the polymeric steric entrapment method and cation organic ratio 2:1 are shown in Figure 5.26. In general, the morphology of the powders consisted of porous secondary particles (agglomerates) formed by primary particles in the range of hundreds of nanometers to a few microns, see Figure 5.26 (a) and (b). Crystals of irregular shapes in the range of 100 nm - 200 nm were found in the powders crystallized at temperatures between 300 °C and 500 °C. When the temperature was increased, crystal growth and necking could be seen. At 600 °C, crystals in the range of 300 nm - 500 nm were observed. As was seen in the model system, crystal growth and sintering was retarded. This effect can be attributed to the effect of the polymeric entrapment, which avoided contact and mass diffusion between particles. This behavior is depicted in micrographs (g) and (h), where crystals in the range of 700 nm - 900 nm were found. 700 °C and 800 °C were high temperatures where large and sintered crystals formed.
Figure 5.24 X-ray Diffractograms for the NaFePO$_4$ Samples Made in Forming Gas at 500-700 °C Using A Cation/Organic Ratio of 4:1.
Figure 5.25 X-ray Diffracograms for the NaFePO₄ Samples Made in Forming Gas at 300-800 °C Using A Cation/Organic Ratio of 2:1.
Figure 5.26 SEM Micrographs of NaFePO₄ Powder Produced Using Cation/Organic Ratio of 2:1.
Particle size distribution and specific surface area analysis results are shown in Table 5.5. In this case there was no commercial reference, however, as in the model system, the values of particle sizes corresponded to the agglomerates (secondary particles). The crystal sizes (primary particles) should be measured using SEM or TEM.

Table 5.5 Physical Properties of Pure NaFePO$_4$ Produced by The Polymeric Steric Entrapment Method at 300 °C Using 2:1 Cation/Organic Ratio

<table>
<thead>
<tr>
<th>Item</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>D10(μm)</td>
<td>2.62</td>
</tr>
<tr>
<td>D50(μm)</td>
<td>3.01</td>
</tr>
<tr>
<td>D90(μm)</td>
<td>3.38</td>
</tr>
<tr>
<td>Dmax(μm)</td>
<td>3.90</td>
</tr>
<tr>
<td>Specific Area BET (m$^2$/g)</td>
<td>28.92</td>
</tr>
</tbody>
</table>

The specific surface area was even higher than for the LiFePO$_4$ reference and lower than the LiFePO$_4$ prepared by the polymeric steric entrapment method. These values of particle size and surface area agreed with the microstructure and morphology observed by SEM, as well as with the peak broadening observed in XRD spectra.

Table 5.6 Chemical Compositions of NaFePO$_4$ Selected Samples

<table>
<thead>
<tr>
<th>Item</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Composition</td>
<td>2:1 300°C</td>
</tr>
<tr>
<td>Fe(wt%)</td>
<td>24.32</td>
</tr>
<tr>
<td>Na(wt%)</td>
<td>9.72</td>
</tr>
<tr>
<td>P(wt%)</td>
<td>13.58</td>
</tr>
<tr>
<td>Na/Fe</td>
<td>0.40</td>
</tr>
<tr>
<td>Na/P</td>
<td>0.72</td>
</tr>
<tr>
<td>P/Fe</td>
<td>0.56</td>
</tr>
<tr>
<td>C(wt%)</td>
<td>11.76</td>
</tr>
<tr>
<td>H(wt%)</td>
<td>0.46</td>
</tr>
<tr>
<td>N(wt%)</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Chemical compositions of NaFePO$_4$ selected samples are shown in Table 5.6. These samples were chosen in order to see how the carbon content changed with temperature.
Disadvantages of the ICP method explained before have to be taken into account to interpret this data. Nevertheless, there was a tendency to retain about 12 wt% and 2 wt% of carbon and nitrogen, respectively, in samples calcined/crystallized at low temperatures using cation/organic ratio 2:1. At higher temperatures (800 °C) the amount of carbon was very low (about 1.8 wt%) and nitrogen and hydrogen were not detected. Knowing the amount of carbon and having the knowledge to control the amount of carbon in the synthetic powder is very important, because it is known that for Li ion battery applications a carbon coating improves the electrical conductivity of the active particles improving electrochemical performance.

To conclude, we have been demonstrated the generality of the polymeric steric entrapment synthesis to produce compounds with complex chemistry (more than two cations) and with changeable oxidation states (Fe$^{2+}$/Fe$^{3+}$). Managing variables such as type of solvent, pH of the solution, type of drying, amount of organic (PVA) and amount of nitrates, enable pure synthetic multicomponent compounds to be produced. Again, pure nanocrystals with the correct chemistry (NaFePO$_4$) were produced at low temperatures (300 °C), making this process competitive with other wet chemical synthesis methods and more efficient than the traditional solid state reaction method.

5.3 NaTi$_2$(PO$_4$)$_3$ System

The NaTi$_2$(PO$_4$)$_3$ was selected not only because of its technological importance as an active anode material for sodium aqueous batteries, but also, because its synthesis required a modification in the synthesis method because the titanium source decomposed in water. A single solvent could not be used to dissolve all reagents, so that complete dissolution (atomic mixing) was a challenge. NaTi$_2$(PO$_4$)$_3$ provided a probe of concept in the replacement not only of the diffusing ion, but also, the intermetallic cation framework.

Due to there being no commercial NaTi$_2$(PO$_4$)$_3$ powder available, information from the literature and ICDD patterns were used to compare with our results. Concepts learned from the model system were applied to produce pure NaTi$_2$(PO$_4$)$_3$. The amount of water and HNO$_3$
addition were taken directly from the model system. Traditional drying on a hot plate was used because a reduced Ti oxidation state was not required in the final system. Air as the calcination/crystallization atmosphere, a 4:1 cation/organic ratio and temperatures in the range of 500 °C-700 °C were used in order to maintain the correct proportions of polymer entrapper, fuel/oxidizer ratio and exothermic decomposition temperature.

Figure 5.27 are the X-ray diffractograms for the NaTi$_2$(PO$_4$)$_3$ samples made in air at 500 °C – 700 °C using a cation/organic (EG) ratio of 4:1. The bottom lines show the peak list of the samples and the peak positions of the NaTi$_2$(PO$_4$)$_3$ reference, corresponding to a sodium titanium phosphate 01-033-1296 ICDD reference card. It was seen that at 500 °C and 600 °C an amorphous compound was formed. At 700 °C the synthesized compound was single phase and sharp and intense peaks were in the correct positions compared with the pattern. As no secondary phases were detected in the sample at 700 °C, the atomic mixing, amount of organics and nitrates were in the right proportions to make the steric entrapment, avoid segregation and promote crystallization of pure NaTi$_2$(PO$_4$)$_3$ directly from the amorphous phase without forming any binary or ternary stable phases. These facts are very important, because it means that decomposition of titanium isopropoxide to titania was hindered, and dissolution of all components (atomic mixing) was achieved.

During drying on the hot plate exothermic reactions were observed. Water, isopropyl alcohol and nitrates evaporated and decomposed. The wet powder started to pop out all over the Corningware pot until it was totally dried. A white and soft powder was collected for subsequent steps.
Figure 5.27 X-ray Diffractograms for the NaTi$_2$(PO$_4$)$_3$ Samples Made in Air at 500 - 700°C Using A Cation/Organic Ratio of 4:1.
Particle size distribution and specific surface area analyses results are shown in Table 5.7. In this case there was no commercial reference, however, as in the model system; the values of particle size analysis corresponded to the agglomerates (secondary particles). The specific surface area was far higher than for the LiFePO₄ reference and comparable with the LiFePO₄ prepared by the polymeric steric entrapment method. It was noticed that the surface area of the amorphous powder was twice (82.97 m²/g) that of the crystalline powder (40.93 m²/g). Such information could be really useful for some applications. These values of particle size and surface area agreed with the microstructure and morphology observed by SEM, where porous secondary particles consisting of nanoparticles were seen.

The microstructure and morphology of the NaTi₂(PO₄)₃ produced using the polymeric steric entrapment method and cation to organic ratio of 4:1 is shown in Figure 5.28. In general, the morphology of the powders consisted of porous secondary particles (agglomerates) formed by primary crystals with no particular shape in the range of 50 - 150 nm, see Figure 5.28. No differences were found in the morphology or microstructure between amorphous (a)-(b) and crystalline (c)-(d) powders. Again, crystal growth and sintering seemed to be hindered by organic entrapment.

Table 5.7 Physical Properties of Pure NaTi₂(PO₄)₃ Produced by The Polymeric Steric Entrapment Method at Using A 4:1 Cation/Organic Ratio

<table>
<thead>
<tr>
<th>Item</th>
<th>Sample 600°C</th>
<th>Sample 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>D10(μm)</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>D50(μm)</td>
<td>2.39</td>
<td>0.11</td>
</tr>
<tr>
<td>D90(μm)</td>
<td>15.70</td>
<td>4.73</td>
</tr>
<tr>
<td>Specific Area BET (m²/g)</td>
<td>82.97</td>
<td>40.93</td>
</tr>
</tbody>
</table>
Figure 5.28 SEM Micrographs of NaTi₂(PO₄)₃ Powder Produced Using A Cation/Organic Ratio of 4:1. (a)-(b) Amorphous Powder, (c)-(d) Crystalline Powder.

<table>
<thead>
<tr>
<th>Item</th>
<th>4:1 600°C</th>
<th>4:1 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(%)</td>
<td>19.30</td>
<td>20.71</td>
</tr>
<tr>
<td>Na(%)</td>
<td>4.70</td>
<td>3.01</td>
</tr>
<tr>
<td>P(%)</td>
<td>22.78</td>
<td>23.40</td>
</tr>
<tr>
<td>Na/Ti</td>
<td>0.24</td>
<td>0.14</td>
</tr>
<tr>
<td>Na/P</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>P/Ti</td>
<td>1.18</td>
<td>1.13</td>
</tr>
<tr>
<td>C(%)</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>H(%)</td>
<td>0.23</td>
<td>0.01</td>
</tr>
<tr>
<td>N(%)</td>
<td>0.00</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Chemical compositions of selected NaTi₂(PO₄)₃ samples are shown in Table 5.8. These samples were chosen in order to see how the carbon content changed with temperature. The
disadvantages of the ICP method explained before need to be taken into account to interpret this data. Nevertheless, there was a tendency for the composition to contain small amounts of carbon, nitrogen and hydrogen. Working in air favored the oxidation of carbon and nitrogen to form CO\textsubscript{x} and NO\textsubscript{x}, which was why almost all of the C and N content coming from organics and nitrates were consumed during the calcination and crystallization process.

To conclude, we have demonstrated that the polymeric steric entrapment synthesis can be used to produce materials where its raw materials do not dissolve in the same solvent. Furthermore, we proved that by using ethylene glycol (EG), decomposition of titanium isopropoxide can be prevented and have avoided the formation of stable binary phases such as titania (TiO\textsubscript{2}). This compound allowed us to learn how to manage variables such as type of solvent, type of drying and type of organic carrier to produce materials using different raw materials.

Finally, in this chapter we have shown how variables such as the amount of water, pH of the solution, drying procedure, HNO\textsubscript{3} addition, amount of polymer, calcination/crystallization atmosphere and temperature affect the synthesis of compounds with complex chemistry (more than two cations) and with changeable oxidation states.
CHAPTER 6
CONCLUSIONS

In this thesis, we have shown how to synthesize multicomponent complex compounds based on 3d metal redox elements such as LiFePO$_4$, NaFePO$_4$ and NaTi$_2$(PO$_4$)$_3$, using the polymeric steric entrapment precursor route. These compounds were composed of cations called “zwitterions” because of their special changeable characteristic of different oxidation states $M^{+2}/M^{+3}$ that makes them interesting for electronic applications, specifically for energy storage applications. We shed light over how variables such as the amount of water, pH of the solution, drying procedures, HNO$_3$ addition, amount of polymer, calcination /crystallization atmosphere and temperature affect the synthesis process. Due to its technological importance and the technical information availability, LiFePO$_4$ was selected as a model compound, whereas NaFePO$_4$ and NaTi$_2$(PO$_4$)$_3$ were used to probe concept compositions.

Synthesis of LiFePO$_4$

It have been demonstrated that unless working with polymers such as PVA and nitrates which generate a reducing atmosphere when they are decomposing, a more reduced atmosphere was required to avoid formation of oxidized secondary and ternary phases. Working in air was not possible to obtain LiFePO$_4$ single phase; rather a powder with more than five phases including binary and ternary compounds was obtained. However, by working in forming gas, single phase powders consisting of LiFePO$_4$ could be obtained.

The formation of a clear solution indicating atomic mixing of element is a fundamental requirement to produce homogeneous and single phase products. When all elements in the mixture dissolve, it is called a solution and it is clear. However, when the elements do not dissolve, the mixture is called a suspension or dispersion and it is cloudy or milky. When agglomerates, flocculates or precipitates are formed, segregation of the components, heterogeneities and multiphases in the final product can be expected. The ionic characteristics of each component and the pH of the solution can cause gelation, agglomeration, flocculation or precipitation. It was shown that by keeping the pH of the solution below 0.5 the
agglomerates could be dissolved and formed a clear solution, while having the pH above 0.5 the agglomeration was irreversible, so that a cloudy dispersion was formed. The amount of water in the system modified the pH of the solution. Therefore, the amount of acid was dependent on variables such as the amount of nitrates and type and amount of solvent. HNO₃ acid not only acted as a pH modifier, but also, as an oxidizer. It was demonstrated that an optimum fuel/oxidizer ratio was required to generate a strong and single exothermic decomposition reaction which induced crystallization at low temperatures.

The drying method combined with the fuel/oxidizer ratio was a fundamental criterion that must be taken into account during the synthesis. By drying the solution in a standard procedure using a hot plate, organic and nitrate release during drying was abundant and it was the standard procedure taken, so far, in the production of ceramic powders by the polymeric steric entrapment method. Using this procedure, advantage of the decomposition reaction could not be taken. Moreover, drying the solution at low temperature using a vacuum oven 70 °C, release of organic or nitrates were barely detected, which meant full availability of these two components (fuel and oxidizer) for the next step (calcination/crystallization). Fuel and oxidizer generated a strong exothermic reaction which could be used for crystallization.

It was demonstrated using thermal analysis that the temperature, magnitude and characteristics of the decomposition reaction were dependent on the ratio of organics/nitrates (i.e. fuel/oxidizer). It has been proven that there was an optimum ratio (4:1) of organics/nitrates, not only to make the polymeric steric entrapment, but also, to generate a single strong exothermic decomposition reaction, which provided enough energy to induce crystallization of the desired phase at lower temperatures than in conventional methods. The single large exothermic peak was sensed in the DSC analysis at 150 °C, which meant that not only did the organic and nitrate decomposition reactions took place at the same time, but also, the crystallization started at that really low temperature.
All the energy available from these decomposition reactions was released at the same time and could be used to induce crystallization. In the laboratory process, formation of a pure crystalline LiFePO$_4$ phase at 300 °C was successful. At 300 °C peak broadening and lower intensity peaks than the reference were hints of formation of nanoparticles. At 800 °C some extra peaks were detected, which could correspond (according to findings in literature), to more reduced phases such as FeP. Shifts from the optimum organics/nitrates ratio provoked delays of the starting of the decomposition reaction because extra energy was required to decompose the extra amount of organics and also because the amount of nitrates was not enough to react with the whole amount of organics. This was the case in the 2:1 ratio samples. For the 6:1 ratio, there was also an imbalance of fuel/oxidizer, which made the exothermic reaction of organic and nitrates take place at different temperatures and also produced a less energetic reaction. Furthermore and more importantly, the amount of organics was not enough to enable sufficient steric entrapment, instead producing segregation of the components in the system and allowing formation of a multiphase material. Decomposition reactions of organics and nitrates that occurred at different and higher temperatures could generate the formation of multiphase products because in a specific system different thermodynamically stable phases could be stable at different temperatures. Moreover, metastable phases could be formed, taking advantage of the single decomposition reaction. This was due to the fact that in fast and exothermic reactions, thermodynamic mechanisms were no longer the controlling mechanism of the phase formation, but instead, it was the kinetic mechanism.

In general, the morphology of the powders produced by the polymeric steric entrapment method, and specially using samples dried in a hot plate at ≈ 70 °C and then in a vacuum oven at 60 °C, is porous secondary particles formed by primary particles in the range of 20 nm – 10 microns. These secondary particles are soft agglomerates that show this particular microstructure due to the violent exothermic decomposition reaction of organics and nitrates. These porous structures have a higher specific surface area (40-50 m$^2$/g) compared to the reference powder (17.92 m$^2$/g), which it is desirable for ion and electron diffusion in lithium ion
batteries, specifically for LiFePO₄. These results were expected because both the crystal sizes (nanocrystals) and the sponge-like microstructure of the agglomerates observed in the SEM and TEM micrographs. The particle size measure by a laser scattering particle size analyzer (Partica LA-950V2, Horiba, Kyoto, Japan), really measured the agglomerates, which was also observed in the low magnification SEM and TEM micrographs. What is important, though, is the fact that on comparing our results with the commercial references, both the crystal sizes and the agglomerated particles produced in this work were smaller than the reference powders.

The pure crystalline LiFePO₄ powder obtained using optimized conditions and a cation/organic ratio of 4:1 at 300 °C consisted of nanoparticles of about 20 nm in size. These nanoparticles were narrowly distributed and had a platelet-like shape. It was shown that at 600 °C and 800 °C crystals still had sizes in the nanoscale range, i.e., 100 nm. These results were very interesting because after increasing the furnace temperature up to 800°C there were not too much crystal growth or sintering. This effect was very important because it meant that small particle sizes and high surface areas could be retained even on working at high temperatures. It is believed that this behavior occurred because of the polymeric steric entrapment. The polymer covered and coated the nanoparticles avoiding solid state diffusion, and hence, crystal growth and sintering. It is important to mention that the pure LiFePO₄ produced at low temperatures (300 °C) by the polymeric steric entrapment method is comparable with the LiFePO₄ produce by other wet chemical synthesis method such as sol-gel, hydrothermal and Pechini although without using expensive reagents (alkoxides), high pressure or special sealed containers and large amounts of polymers. The nanoparticulate microstructures revealed in the SEM and TEM micrographs totally agreed with the information obtained from XRD analysis where peak broadening suggested the formation of nanocrystals.

The chemical analysis performed by ICP had the disadvantage that the values were expressed in terms of weight percent (wt %) which took into account the whole mass of the powder. Large variation was found in all elements measured because they were given relative to the amount of other elements such as C, N, H and O, which were consumed or added during
the synthesis process. For instance, multiphase samples containing oxidized phases had more oxygen in the whole mass, which affected the relative amount of other cations in the system. Furthermore, it is important to also take into account that the nature of the exothermic reaction affects the carbon and nitrogen contents because both fuel and oxidizer are consumed during the reaction.

Nevertheless, there was a tendency to have about 10 wt% and 1.5-2 wt% of carbon and nitrogen respectively, in samples calcined/crystallized at low temperature using cation valence/organic functional group ratios of 2:1 and 4:1. Furthermore, the amount of carbon and nitrogen decreased with increasing of temperature. For Li ion battery applications it has been demonstrated that a carbon coating improves the electrical conductivity of the active particles, thereby improving electrochemical performance. Therefore, the fact that in this work LiFePO₄/C composites can be produced generates high expectations for energy storage applications. Samples calcined/crystallized using a cation/organic ratio of 6:1 showed low contents of C and N. These results agreed with the low amount of organic (PVA) added during the synthesis.

Using the model system LiFePO₄, we have demonstrated, that the polymeric steric entrapment synthesis can be used to produce compounds with complex chemistry (more than two cations) and having changeable oxidation states (Fe²⁺/Fe³⁺). Furthermore, it has been shown that variables such as the type of solvent, pH of the solution, type of drying, amount of organic (PVA) and amount of nitrates, strongly affect the synthesis process. Pure nanocrystals with the correct chemistry were produced at low temperature (300 °C), making this process competitive with other wet chemical synthesis methods and more efficient that the traditional solid state reaction method.

The generality of the methodology developed in this work has been proven in other compounds of high interest in energy storage applications such as NaFePO₄ and NaTi₂(PO₃)₄. Na-ion batteries are suitable for replacement of Li-ion batteries in several applications,
particularly where weight and size are not important, for example as large scale energy storage devices, stationary land-based power applications, non-portable systems and electrical grid stabilization.

**Synthesis of NaFePO₄**

Pure crystalline NaFePO₄ phase was successfully produced at 300 °C. Concepts learned from the model system were applied for the synthesis. Forming gas as the calcination/crystallization atmosphere, amount of water, HNO₃ addition, drying process were taken directly from the model system. Cation/organic ratio and temperature were modified in order to give the correct proportions of polymer entrapper, fuel/oxidizer ratio and exothermic decomposition temperature. As in the model system, at 300 °C peak broadening and less intense peaks suggested the formation of nanoparticles. As soon as the temperature was increased, sharp and more intense peaks were formed. These results, as well as a single strong exothermic decomposition reaction observed at 270 °C, resembled the behavior seen in the model system. Again, it seems that the energy released was enough to induce crystallization of the single phase at low temperature. As no secondary phases were detected in the samples at all temperatures, the atomic mixing, amount of organics and nitrates were in the correct proportions to achieve steric entrapment, avoid segregation and generate an exothermic decomposition reaction strong enough to crystallize NaFePO₄ at low temperature.

In general, the microstructure and morphology of the NaFePO₄ produced using the polymeric steric entrapment method and cation organic ratio of 2:1 consisted of porous secondary particles (agglomerates) formed by primary particles in the range of hundreds of nanometers and a few microns. Crystals of irregular shapes in the range of 100 nm - 200 nm were found in the powders crystallized at temperatures between 300 °C and 500 °C. When the temperature was increased, crystal growth and necking could be seen. At 600 °C, crystals in the range of 300 nm - 500 nm were observed. As was seen in the model system, crystal growth and sintering was retarded. This effect can be attributed to the effect of the residual carbon coating, which avoided contact and mass diffusion between particles.
The specific surface area of NaFePO₄ (28.92 m²/g) was even higher than the LiFePO₄ reference and lower than the LiFePO₄ prepared by the polymeric steric entrapment method. The values of particle size and surface area agreed with the microstructure and morphology observed by SEM, furthermore, with the peak broadening observed in the XRD spectra.

**Synthesis of NaTi₂(PO₄)₃**

NaTi₂(PO₄)₃ was selected not only because of its technological importance as an active anode material for sodium aqueous batteries, but also, because its synthesis required a modification in the synthesis method because the titanium source decomposed in water. A single solvent could not be used to dissolve all reagents. Thus, assuring complete dissolution (atomic mixing) was a challenge.

Pure NaTi₂(PO₄)₃ was synthesized at 700 °C in air using a 4:1 cation/organic ratio. The amounts of water and HNO₃ addition were taken directly from the model system. Traditional drying on a hot plate was used because a reduced oxidation state Ti was not required in the final system. As no secondary phases were detected in the sample at 700 °C, the atomic mixing, amount of organics and nitrates were in the correct proportions to achieve steric entrapment, avoid segregation and promote crystallization of pure NaTi₂(PO₄)₃ directly from the amorphous phase without falling into any binary of ternary stable phases. These facts are very important, because it means that decomposition of titanium isopropoxide to titania was hindered, and dissolution of all components (atomic mixing) was achieved. Below 700 °C an amorphous compound was formed, a fact that can be important for some applications were amorphous material with appropriate chemistry is required.

The microstructure and morphology of the NaTi₂(PO₄)₃ produced using the polymeric steric entrapment method and a cation organic ratio 4:1 was mainly composed of porous secondary particles (agglomerates). These secondary particles were formed by primary crystals with no particular shapes in the range of 50 - 150 nm. No differences were found in the
morphology or microstructure between amorphous and crystalline powders. Again, crystal growth and sintering seemed to be hindered by the organic entrapment.

The specific surface area of NaTi$_2$(PO$_4$)$_3$ was far higher than that of the LiFePO$_4$ reference powder and comparable with the LiFePO$_4$ prepared by the polymeric steric entrapment method. It can be noticed that the surface area of the amorphous powder was twice (82.97 m$^2$/g) that of the crystalline powder (40.93 m$^2$/g). These values of particle size and surface area agreed with the microstructure and morphology observed by SEM, where porous secondary particles formed by nanoparticles were observed. For this composition, working in air favored the oxidation of carbon and nitrogen to form CO$_x$ and NO$_x$, which was why most of the C and N content from organics and nitrates were consumed during the calcination and crystallization process.

We have used a hybrid organic steric entrapment synthesis method that is useful to produce materials where its raw materials do not dissolve in the same solvent. This hybrid method prevented and avoided decomposition of titanium isopropoxide into stable binary phases such as titania (TiO$_2$). This compound allowed us to learn how to manage variables such as type of solvent, type of drying and type of organic carrier to produce materials using different raw materials.

Finally, during this work we have shown how variables such as the amount of water, pH of the solution, type of solvent, drying procedure, HNO$_3$ addition, type and amount of polymer carrier, calcination/crystallization atmosphere and temperature affects the synthesis of compounds with complex chemistry (more than two cations) and with changeable oxidation states, that make them desirable for electronic applications, specifically for energy storage application.
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