MATERIALS DEVELOPMENT FOR MULTICOMPONENT SYSTEMS WITH VARIABLE OXIDATION STATES

BY

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DISSERTATION

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ABSTRACT

In this work, the synthesis by the polymeric steric entrapment method of materials that belong to the $M_1MnO_x$ and $M_1Ti_2(PO_3)_4$ ($M_1= Li, Na, K,$) families was evaluated. Furthermore, the influence on the physico-chemical characteristics of the powders by processing variables such as the dissolution conditions, pH of the solution, mixing conditions, drying procedures, HNO$_3$ addition, amount of polymer (cation:organic ratio), characteristics of the exothermic reaction ($C/N$ ratio), calcination/crystallization atmosphere and temperature, were investigated. Additionally, the electrochemical performance of the LiMn$_2$O$_4$ (LMO4) composition was evaluated and compared against commercial LiMn$_2$O$_4$ powders. Moreover, for powders in the $M_1Ti_2(PO_3)_4$ ($M_1= Li, Na, K,$) family, their thermal expansion behavior were studied by means of high resolution (synchrotron radiation) in-situ high temperature X-ray diffraction, Rietveld refinement and the coefficient of thermal expansion analysis suite (CTEAS) software developed at UIUC.

Specifically, powders in the family $M_1MnO_x$ ($LiMn^{3+}O_2$, $LiMn_2^{3+/4+}O_4$, $Li_2Mn^{4+}O_3$) could be synthesized at low temperature ($\sim 300^\circ C$) in a single step by taking advantage of the highly exothermic reaction produce by the nitrate and organic decompositions. In order to fully take advantage of the exothermic reactions and control the oxidation state, the precursor solutions had to be dried at low temperature ($\sim 70^\circ C\ -\ 80^\circ C$) to avoid early nitrate/organic decompositions and the micro and macro atmospheres in the process had to be controlled. The micro atmosphere was controlled by the cation:organic ratio which additionally controlled the steric entrapment and the exothermic reaction. Moreover, the macro atmosphere was controlled by the furnace atmosphere. It was found that LiMn$^{3+}O_2$ can be produced at 700$^\circ $C in flowing forming gas and using cation:organic ratio 6 to 1, whereas LiMn$_2^{3+/4+}O_4$ and Li$_2$Mn$^{4+}O_3$ were produced in air, calcined at 300$^\circ $C, and using a cation:organic ratio of 4:1. When powders were synthesized at low temperature ($300^\circ$C – $500^\circ$C) high surface areas ($14.6$ m$^2$/g for LMO4 at $300^\circ$C) and porous secondary particles composed by nanocrystals were produced, while at higher temperature ($600^\circ$C – $800^\circ$C) crystals grew (micron range) and showed necking. This suggested the onset of the sintering
process and exhibited a reduction of specific surface area (6.4 m$^2$/g for LMO4 at 700°C). On the other hand, LMO4 produced in this work, exhibited similar or even better electrochemical performance than did LMO4 commercial powders (99.8 mAh/g and 90.1 mAh/g at C/10 and C/5, respectively). In contrast, 93.3 mAh/g, 110 mAh/g 131.8 mAh/g were the specific capacities obtained at C/10 for LMO4 synthesized at 300°C, 500°C and 700°C, respectively. Likewise, the specific capacities obtained at C/5 for LMO4 produced at 300°C, 500°C and 700°C were 88.9 mAh/g, 107 mAh/g and 128.3 mAh/g, respectively.

The compounds LiTi$_2$(PO$_4$)$_3$ (LTP), Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (LATP), NaTi$_2$(PO$_4$)$_3$ (NTP) and KTi$_2$(PO$_4$)$_3$ (KTP) were produced by the polymeric steric entrapment method in air and using cation:organic ratio 4:1. It was found that the proper dissolution and mixing of the reagents was even more important than the cation:organic ratio. A pH modification (below 4.4) during the synthesis of LTP and LATP was necessary in order to keep Li + P and Li + Al + P solutions clear and stable. Furthermore, it was found that mechanical re-dispersion of the gel (formed after water soluble solutions (nitrates and P source) and alcohol soluble solutions (TISO + EG)), as well as HNO$_3$ addition and excess of isopropyl alcohol enabled the production of single phase powders. In all cases for powders in the $M_1$Ti(PO$_4$)$_3$ family, single phase powders were obtained at a calcining temperature of 700°C in one step without falling into any undesirable intermediate phase. In general, powders at low calcining temperatures were in the nano range with high specific surface area (500°C–700°C) with rapid crystal growth. However, reduction in the specific surface area as well as pre-sintering were notice at high temperature (1000°C).

The thermal expansion behavior of LTP, LATP, NTP and KTP were measured by in situ, high temperature, synchrotron powder diffraction. It was demonstrated that the CTEs were neither constant nor linear. LTP and LATP exhibited a positive but decreasing thermal expansion along the a-axis in the 25°C - 1000°C range, NTP displayed a negative but increasing thermal expansion in the 25°C - 1200°C range. KTP revealed a negative but increasing behavior up to ~500°C which then became positive and increasing up to ~1300°C.
In conclusion, this research work has shed light on how to use the polymeric steric entrapment method to produce materials that contain intermetallic elements which can adopt different oxidation states. Additionally, it has demonstrated a method on how to deal with compositions where their starting reagents do not dissolve or decompose in a specific solvent. Furthermore, it has been demonstrated that in some compositions, advantage of the highly exothermic reaction can be taken in order to synthesize materials at temperatures as low as 300°C which provides a technological advantage for future industrialization. Finally, the electrochemical performance and thermal expansion behavior of some of the produced powders were evaluated in order to verify that the synthesis method was effective.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

For many years, the only way to synthesize advanced ceramic materials was by thermal treatment at high temperatures from mixtures of components. 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 above mentioned drawbacks, the solid state reaction method is considered to be a low-efficiency, energy and time consuming technology, which in addition, usually produces multiphase powders having a wide range of particle size distributions, large crystals and low surface area which could prevent the preparation of high performance powder materials. Furthermore, many advanced ceramic materials are metastable phases, and therefore non-traditional synthesis methods must be devised to allow kinetics to override thermodynamics. Consequently, several soft chemistry techniques have been intensively studied such as hydrothermal [1-4], sol-gel [5-9], co-precipitation [10], combustion synthesis [11], spray pyrolysis [12-14], molten salt synthesis [15], complex formation methods [16], classical precipitation [17-21], solvothermal [22], microwave-assisted solvothermal [23], Pechini process [24-26], and ionothermal syntheses [27-29]. Despite the fact that these synthetic processes have yielded very interesting advantages when produced in the research laboratory, some of them cannot be used for mass production because they require complicated preparation steps to obtain the correct stoichiometric compound and need further calcination and grinding of powders to obtain high crystallinity. Additionally, these techniques use very low concentrations of starting materials, which leads to a very low production rate. Therefore, it is crucial to develop a simple, scalable, high-yield, cost-effective technique to be suitable for industrial processing.
In our research group, a versatile technique called the inorganic-organic steric entrapment method has been developed to produce multicomponent ceramic powders [30-66]. So far, the method always leads the synthesis reaction toward the maximum oxidation state, and it is a considerable challenge to find a way to control the different oxidation states through this synthesis route, which could be useful to produce a wide range of technologically important compounds. Previous unsuccessful attempts have been made to produce materials based on intermetallic elements having 3d electrons, which are able to exist in different oxidation states other than their maximum oxidation states. Another challenge is when a water–soluble metal salt is not commercially available such as for Ti or Si, an alkoxide source can be used. The problem is that these metal sources decompose in water and form undesirable binary compounds.

In this thesis, a detailed review about the different synthetic methods available (including the polymeric steric entrapment method) to produce materials with complex chemistries and containing intermetallic elements is provided in Chapter 2. Additionally, general aspects about thermal analysis (differential scanning calorimetry, DSC), electrochemical energy storage (lithium ion batteries) and thermal expansion studies are presented in Chapter 2.

Chapter 3 describes in detail the experimental procedures and characterization techniques employed to produce and evaluate the different materials and their physico-chemical characteristics. The results and discussion of the synthesis, microstructural, physico-chemical and electrochemical characterization of the powders that belong to the $M_1MnO_x$ family are presented in Chapter 4. Moreover, the results and discussion of the synthesis, microstructural, physico-chemical characterization and the thermal expansion behavior of the powders that belong to the $M_1Ti_2(PO_3)_4$ family are presented in Chapter 5. Finally, conclusions and suggestions for future work are drawn in Chapter 6 and Chapter 7, respectively.
1.2 Objectives and Scope of Research

This work aims to provide an alternative synthesis method, as well as a systematic study of which, and how the synthesis variables affect the chemistry, microstructure and crystal structure of materials on the following families: $M_1Ti_2(PO_3)_4$ and $M_1MnO_x$ ($M_1=$ Li, Na, K). Materials in these families are suitable for applications such as low/negative/near zero thermal expansion materials; insertion/extraction materials; fuel cells/SOFC; nuclear waste disposal; catalyst supports; gas sensors; ion selective electrodes; ultraviolet shielding and luminescence applications. The main questions originally posed were:

1. Can the inorganic-organic steric entrapment method be used to synthesize materials that contain cations in different oxidation states other than their maximum oxidation states, such as $Mn^{2+}$, $Mn^{3+}$, $Mn^{3/4+}$?
2. Which and how do the synthesis variables affect the chemistry, microstructure and crystal structure?
3. How versatile is this method to produce compounds with different cations (Li$^+$, Na$^+$ and K$^+$) for different applications?
4. Can the exothermic reaction generated during the synthesis be used to produce these materials at lower temperature? How can this reaction be characterized?
5. Is it possible to stabilize the Ti source (alkoxide) and avoid its decomposition in water to form secondary phases ($TiO_2$)?
6. How do the materials produced by this method compare with the materials made by other methods?

In a broader scope, this work opens the door to the use of the polymeric steric entrapment method to produce materials with complex stoichiometries and with different oxidation states that are very attractive in the energy field. The fine control of the chemistry, homogeneity, purity, particle size and surface area makes the synthesis method attractive from the scientific point of view. The ability to produce materials at low temperature, in a one step process and short processing time, attracts the attention for scaling up and industrialization of this synthetic method.
CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

The compound families we are interested in are $M_1\text{Ti}_2(\text{PO}_3)_4$ and $M_1\text{MnO}_x$ ($M_1=$ Li, Na, K). While our interest in materials that belong to these families is for their use in insertion/extraction and low/negative/near zero thermal expansion applications, they have also been found to be attractive for other high technology applications such as fuel cells/SOFC [13], nuclear waste disposal [67], catalyst supports [68-70], gas sensors [71, 72], ion selective electrodes [73], ultraviolet shielding and luminescence [74].

The cathode and the anode are two key components of Li/Na-ion batteries. Many different compositions have been identified as possible cathode or anode materials for rechargeable Li/Na-ion batteries (as seen in Figure 2.1), but just a few have been mass produced and commercialized. Such compounds are:

- Layered metal oxides ($\text{LiCoO}_2$, $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$, $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$).
- Spinel structured oxide ($\text{LiMn}_2\text{O}_4$).
- Olivine structured phosphate ($\text{LiFePO}_4$).
- Various materials for the anode ($\text{LiTi}_2(\text{PO}_4)_3$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and C).

Traditionally, these electrode materials have been synthesized by thermal treatment at high temperatures from mixtures of reactants (e.g. carbonates, metal salts, hydroxides, oxides, etc.). The low diffusion and reactivity of starting materials implies long reaction times, high temperatures and regrinding processes between subsequent firings. Due to the above-mentioned drawbacks, the solid state reaction method is considered to be a low-efficiency, high energy and time consuming technology.

The electrochemical properties of the electrode materials are determined by crystal structure, particle size, morphology, and stoichiometry of the active materials, and these are directly influenced by the chosen synthesis or production routes. Very little fluctuation in their performance between production batches is required for high-volume and automated metal-ion 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 [46]. 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 intensively studied.

![Diagram of Voltage vs Capacity of some electrode materials relative to the $E_g$ of 1M LiPF$_6$ in ethyl carbonate/diethyl carbonate (EC/DEC) organic solvent [75].]

2.2 Synthesis Methods

The advancements in synthesis of advanced ceramic materials are evolving in the direction of chemical synthesis of powders. Therefore, over the last few years, material scientists and chemists have explored wet chemical methods including classical precipitation [10, 17-20], hydrothermal [1-4], sol-gel [5-9], solvothermal [22], microwave-assisted solvothermal [23], Pechini process [24-26], spray pyrolysis [12-14, 76] and
ionothermal [27-29] syntheses to produce micro- and nano-materials. In general, these methods produce mono-dispersed powders with a well-defined chemistry, shape and size at low temperatures via fine-tuned control of the reaction pH and precursor concentration. This is in contrast to the traditional ceramic method (solid-state), which requires high temperatures to ensure the diffusion of the reactants and the growth of the grains, usually leading to highly poly-dispersed powders.

Attempts to synthesize materials with complex compositions such as Li(Ni_{x}Co_{y}Mn_{1-x-y})O_{2} using solid state reactions have resulted in an inhomogeneous or impure product. Furthermore, 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.

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_{1/3}Co_{1/3}Mn_{1/3})(OH)_{2} hydroxide intermediate is prepared initially by co-precipitation to finally synthesize Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_{2} [20, 21]. The multi-element hydroxide is then mixed with Li_{2}CO_{3} or LiOH.H_{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 LiFePO_{4}, an intermediate precursor of FePO_{4}•2H_{2}O can be made by a co-precipitation reaction of an iron salt with H_{3}PO_{4} as well as a base. FePO_{4}•2H_{2}O can be mixed with Li_{2}CO_{3} and reacted under reducing conditions to form LiFePO_{4} [77]. However, 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 co-precipitation method is not suitable for elements with vastly different chemical properties. For instance, the co-precipitation of alkali or non-transition metals with transition metal ions is difficult because they tend to precipitate separately. Thus, it is difficult to achieve good homogeneity of precipitates by this method [78].

In wet precipitation techniques, some ionic species in wastewater can be an environmental problem, such as SO_{4}^{2-} 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 co-precipitation method is that in some compounds such as (Mn,Ni,Co)(OH)\textsubscript{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)\textsubscript{2}, Co(OH)\textsubscript{2}, or Mn(OH)\textsubscript{2} leading to a non-homogenous 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 [78].

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 in Novosibirsk). Although most scientists were initially skeptical about this novel approach to synthesizing new materials, it has now gained complete credibility [79-81]. Ball milling a mixture of Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}•8H\textsubscript{2}O and Li\textsubscript{3}PO\textsubscript{4}, can increase the reaction interface and promote mixing. This leads to the formation of LiFePO\textsubscript{4} at lower heat treatment temperatures (HTTs), giving rise to a product with finer particles than those obtained by solid state reaction [82, 83]. When milling Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}•8H\textsubscript{2}O and Li\textsubscript{3}PO\textsubscript{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 sub-micrometer or nanometer scales. The subsequent nucleation of LiFePO\textsubscript{4} occurs upon heat treatment at the numerous interfaces of the reactant mixture and thus LiFePO\textsubscript{4} with fine primary particles can be achieved [84]. Some anode materials have been synthesized by this technique, and carbon has been effectively coated onto LiFePO\textsubscript{4}. Many intermetallic compounds such as Cu\textsubscript{6}Sn\textsubscript{5}, SnFe\textsubscript{2} and Sn\textsubscript{2}Mn have been proposed as anode materials using this synthesis method [80]. 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 [78].

As has been mentioned 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 ionic scale and thereby providing a homogeneous composition throughout the particle. The sol-gel process allows a high degree of control over the physicochemical characteristics of the products, and typically provides high purity, homogeneity, a narrow particle size distribution. It results in 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 [9, 80]. 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. In addition, 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 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 [1-4, 22].

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 reactions. 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 have a great effect on the nucleation and growth of cathode material. Studies of vanadium oxides exemplified the critical role that pH plays in determining the desired structure [80]. Temperatures above the supercritical point of water (solvent) increase the solubility of the precursors and enhance the kinetics of the reactions. Therefore, the formation reaction uses 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. The appropriate bases are at a temperature sufficiently high to promote the precipitation and growth of the desired phase via Ostwald ripening [23]. This method 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 [78]. Both hydrothermal and solvothermal methods suffer from some disadvantages. These are the need to conduct the synthesis under reflux and controlled
environments (e.g., the solvothermal process) and the mandatory use of investment-intensive autoclaves for hydrothermal processes.

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: firstly, like water, ionic liquids resulting from compatible cationic/anionic pairs having excellent solvent properties which enable low temperature processing; and secondly, 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 produced by this method at low temperatures (<250°C) with reaction times between 24 h and 48 h [27-29, 85, 86].

The spray pyrolysis method has attracted attention as an effective, easily scaled-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 sub-micrometer, 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 [78]. 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. The limitation to produce the desired particle size resides in the ability to produce small droplets and control the drying and calcination steps where the nucleation and growth of the particles occur.

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 [24, 25]. 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 poly-esterification 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 metal organic:cation ratio has to be used to assure chelation, which makes the process a low production rate method.

Some excellent results were obtained using the wet chemical methods mentioned above. However, these techniques have disadvantages that make them very difficult to be used for commercial production of electrode materials. Complicated preparation steps, low concentration of starting materials, calcination and grinding of powders to obtain the high crystallinity, make these methods less attractive for industrial applications. Consequently, it is crucial to develop a simple, easy to scale-up and cost-effective technique that can be used in large-scale industrial production.

2.3 Polymeric Steric Entrapment Method

The advanced ceramic materials technology evolved with the new synthesis methods. Therefore, over the last few years, material scientists and chemists have explored the wet chemical methods that allow one to produce controlled materials with the correct chemistry, crystal structure, shape and particle size distribution at lower temperature and less time.

A versatile technique has been developed by our group is based on a polymeric steric entrapment precursor route [30-66]. 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 inhibit their segregation or precipitation from solution [35, 38, 41, 87]. 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 [49]. 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 [87].

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-alkoxides (e.g. 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 [34, 38, 49]. However, a linear polymer such as PVA has the ability to physically entrap the cation precursor, thereby improving the cation distribution due to attrition and/or repulsive forces. For instance in systems where not enough polymer is used, agglomeration may occur causing segregation of cations, the formation of a multiphase product, and a large particle size in the end products [88]. 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, as well as high purity, are the size and
balance 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 of high technological importance (see Table 2.1) [30-66]. This solution polymerization route has been studied by the Kriven group for more than 15 years with remarkable advances (1 patent [64] and 35 papers). In general, 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 which is important to produce complex compounds for a wide range of energy applications. These complex compounds consist of cations called “zwitterions” because of their special characteristic of possessing changeable oxidation states e.g. $\text{M}^{2+}/\text{M}^{3+}$ that make them interesting for electronic applications. Previous unsuccessful attempts have been made to produce manganate-based materials such as $\text{Pr}_{0.46}\text{Ca}_{0.54}\text{MnO}_3$ using this polymeric steric entrapment method. This failure forced the use of other methods such as the acetate route [89]. This failure and the interest to produce advanced materials for applications such as energy storage motivated the work we are proposing here. Recently, the first successful attempts to produce materials based on 3-d metal redox elements ($\text{LiFePO}_4$ and $\text{NaFePO}_4$) using the polymeric steric entrapment method were made by Ribero et al. [59, 60].

For the $\text{LiFePO}_4$ model system via the polymeric steric entrapment precursor route, synthesis variables such as type of solvent, solution pH, drying procedure, cation:organic ratio, calcination/crystallization atmosphere, and temperature, were studied to understand their influence in the chemistry, microstructure and crystal structure. An ionic mixing of all elements in the system (clear solution) in water was achieved by keeping the pH of the solution below 0.5. This was the first step to avoid agglomeration, flocculation or precipitation that could lead to heterogeneities or multiphase formation in the final products. The best drying conditions for this system was found to be at low temperature on the hotplate (70°C) and vacuum oven (70°C and 20 psi). Then, the calcination and the crystallization of the dried precursor were performed in a single step in a tube furnace under
flowing forming gas (95% N₂, 5% H₂) atmosphere. Using the above conditions as well as a cation:organic ratio of 4:1, a highly exothermic reaction at low temperature was generated. It turned out that this energy was enough to start the crystallization of single phase LiFePO₄ at temperatures as low as 300°C (see Figure 2.2).

![Figure 2.2. X-ray diffractograms of low temperature dried samples with 4:1 cation:organic ratio in the range 300°C - 800°C. Single phase lifepo₄ was obtained under all conditions.](image)

The LiFePO₄ powder produced by the polymeric steric entrapment method was in the form of micron-sized porous secondary particles (soft agglomerates) formed from primary particles in the range of 20 nm –100 nm. These secondary particles or soft agglomerates resulted in this particular microstructure due to the intense exothermic decomposition reaction of organics and nitrates. These porous structures had a high specific surface area (48.25 m²/g) which may have been helpful for ion and electron diffusion in lithium ion batteries.
Table 2.1. Summary of Oxide Powders Prepared the Polymeric Steric Entrapment Precursor Route [42]. (Polymeric Carrier: Poly-Vinyl Alcohol (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>Calcination</td>
<td>Crystallization</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>800</td>
<td>1150</td>
<td>83</td>
</tr>
<tr>
<td>β-Cristobalite (SiO₂)</td>
<td>800</td>
<td>1100</td>
<td>188</td>
</tr>
<tr>
<td>Mullite (Al₆Si₂O₁₃)</td>
<td>800</td>
<td>1300</td>
<td>157</td>
</tr>
<tr>
<td>Zircon (ZrSiO₄)</td>
<td>800</td>
<td>1100</td>
<td>81</td>
</tr>
<tr>
<td>Wollastonite (CaSiO₃)</td>
<td>800</td>
<td>800</td>
<td>18</td>
</tr>
<tr>
<td>Calcium aluminate (Ca₁Al₁O₄)</td>
<td>650</td>
<td>900</td>
<td>12</td>
</tr>
<tr>
<td>Belite (β-Ca₂SiO₅ or C₂S)</td>
<td>700</td>
<td>800</td>
<td>22.1</td>
</tr>
<tr>
<td>Alite (Ca₃SiO₅ or C₃S)</td>
<td>700</td>
<td>1400</td>
<td>0.9</td>
</tr>
<tr>
<td>C₃A (Ca₃Al₂O₆)</td>
<td>700</td>
<td>1000</td>
<td>4.2</td>
</tr>
<tr>
<td>C₄AF (Ca₄Al₂Fe₂O₁₀)</td>
<td>700</td>
<td>700</td>
<td>17.1</td>
</tr>
<tr>
<td>YAG (Y₃Al₅O₁₂)</td>
<td>600</td>
<td>900</td>
<td>56</td>
</tr>
<tr>
<td>Leucite (KAlSi₂O₆)</td>
<td>750</td>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td>Hexacelsian (BaAl₂Si₂O₆)</td>
<td>800</td>
<td>1100</td>
<td>79</td>
</tr>
<tr>
<td>Cordierite (Mg₂Al₄Si₅O₁₈)</td>
<td>800</td>
<td>1200</td>
<td>181 (attrition milled)</td>
</tr>
<tr>
<td>Barium titanate (BaTiO₃)</td>
<td>700</td>
<td>700</td>
<td>5.6</td>
</tr>
<tr>
<td>Barium orthotitanate (Ba₂TiO₄)</td>
<td>700</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>Dysprosium titanate (Dy₂TiO₅)</td>
<td>800</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>Yttrium titanate (Y₂TiO₃)</td>
<td>850</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>Alumina-Zirconia composite (Al₂O₃•ZrO₂)</td>
<td>700</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td>Nickel aluminate (NiAl₂O₄)</td>
<td>800</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>Calcium phosphate (Ca₃P₂O₆)</td>
<td>700</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>Xenotime (YO₄)</td>
<td>500</td>
<td>830</td>
<td>12</td>
</tr>
<tr>
<td>Aluminium phosphate (AlPO₄)</td>
<td>800</td>
<td>800</td>
<td>136</td>
</tr>
<tr>
<td>Lithium phosphate (LiPO₄)</td>
<td>700</td>
<td>800</td>
<td></td>
</tr>
</tbody>
</table>

³ after attrition milling for 1h: 50 m²/g
¥ after attrition milling for 1h: 55 m²/g
⁴ crystalline form
Among other methods to prepare oxide ceramics, the inorganic-organic steric entrapment precursor route has been demonstrated to be a low temperature, simple, continuous, and easy to scale-up technique. It allows the control of powder composition and morphology as well as shortened production time. The prepared powders are homogeneous, both chemically and physically, and have a narrow particle size distribution in the submicron/nano-sized range. All these factors allow outstandingly reduced production cost and decrease of the ecological impact for material production.

2.4 Thermal Analysis (Differential Scanning Calorimetry, DSC)

Differential scanning calorimetry (DSC) monitors heat changes associated with phase transitions or chemical reactions as a function of temperature. In a single heating chamber, “heat-flux” DSC, an amplified differential thermocouple voltage signal is converted to energy per unit time, by means of a calibration constant obtained through the use of standard materials. Unlike structural or microscopic methods of materials characterization, DSC can provide information of how a substance evolves during thermal processing. The temperatures of the transformations as well as the thermodynamics and kinetics of a process may be determined using DSC [90].

Thermodynamic constants such as the heat released or absorbed in a phase transformation (latent heat), may be determined. In a DSC plot of \( \frac{dQ}{dt} \) versus time, the heat released or absorbed in a reaction is simply the area under the peak.

\[
Q = \int_{-\infty}^{\infty} \left( \frac{dQ}{dt} \right) dt [1]
\]

Using the first law of thermodynamics we have:

\[
dU = dQ - dW [2]
\]

\[
dU = dQ - pdV [3]
\]
When the experiment is performed using a sealed container, the volume is constant, so that

\[ dU = dQ \text{ or } \Delta U = Q \tag{4} \]

However, when the experiment allows gas to be released from the container (open crucibles), the volume is no longer constant and the enthalpy function should be used.

\[ H = U + pV \tag{5} \]

Deriving and using Eq. 3,

\[ dH = dQ + Vdp \tag{6} \]

Under constant pressure in the DSC chamber,

\[ dH = dQ \text{ or } \Delta H = Q \tag{7} \]

Some challenges or experimental concerns need to be addressed when violent decomposition reactions and reactions with gases occur. The partial pressure of some gases (e.g. CO, CO₂, NOₓ, etc) can modify the decomposition reaction itself and change the temperature and magnitude of the reactions. The sample packing, mass, size and type of container (sealed or open) can modify the reactions involving gases as well as the diffusion of gaseous species in or out of the reaction zones. Finally, the heating rate is also known to modify the onset and termination of the reaction, as well as to broaden the characteristic peaks in the DSC analysis [90].
2.5 Electrochemical Energy Storage (Lithium Ion Batteries)

In general, electrochemical power sources convert electrochemical energy into electrical energy, a process that could be irreversible (primary batteries) or reversible (secondary batteries). In an electrochemical cell at least two reactions have to occur, reduction in the cathode and oxidation in the anode. The principle of operation of a lithium ion battery is presented in Figure 2.3. Li ions are extracted from the cathode during the charging process and moved through the electrolyte (typically organic) to be inserted into the anode. Meanwhile, electrons move throughout the external circuit for charge compensation. The discharge occurs as the reverse process where Li ions are de-intercalated from the anode (typically graphite) and re-inserted into the cathode.

![Figure 2.3. Schematic representation of a lithium-ion battery [91].](image)
It is important to mention that the current and future energy demands require electrochemical cell (batteries) that simultaneously meet several performance requirements such as:

- High gravimetric and volumetric energy density (Wh/kg or Wh/l)
- High power (watts per unit of mass or volume)
- Good cyclability, capacity retention and longevity (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 of all the intensive research done in the energy storage field, there is no battery that can meet all the above requirements. Some compositions target high capacity applications, but, unfortunately, they operate at the limit of the electrolyte voltage stability window. That is why, multiple batteries which self-ignited (exploded or caught on fire) have been reported recently. Moreover, working inside the electrolyte stability window limits the operating power and voltage. This fact also restricts the scope of applications that some chemistries can target.

Multiple processing variables may affect the reproducibility, stability and performance of the electrochemical cell. Marks et al. presented the battery conditions that should be taken into account in order to produce similar electrodes to those used in the industry [92], as well as a detailed description of the processing variables that can affect the battery performance. Additionally, they found that the electrode composition (active material, conductive carbon and binder), mixing of the components (slurry preparation), density of the electrode (compressed or calendered) and thickness of the electrode, play an important role over the battery performance. That is why it is important to mention that batteries are assembled using several components as well as in different architectures (Figure 2.4) that may affect their performance (e.g. specific capacity, mAh/g).
Figure 2.4. Lithium ion battery cell configurations: a) cylindrical, b) coin, c) prismatic, and d) pouch [93].

On the other hand, typical characterization techniques are applied to electrochemical cells in order to evaluate their performance. These include and are not limited to galvanostatic cyclability (for capacity, rate capability and longevity determination), cyclic voltammetry, and electrochemical impedance. Figure 2.5 (a) shows the galvanostatic measurements where the plateaus can be noticed where Li is inserted and extracted (redox reactions) from the cathode and the anode. Additionally, it can be seen (in Figure 2.5 (a) and (b)) that the capacity is reduced when the charge/discharge rate is increased. This measurement allows the determination of the cell capacity, operational voltage, rate capability and longevity. Figure 2.5 (c) depicts an example of potentiodynamic (voltammetry or voltage vs current measurements), where not only the voltage at which the redox reactions occur can be observed, but also, the reversibility of the reactions can be visualized. Electrochemical Impedance measurements (EIS) are shown in Figure 2.5 (d) in the form of Nyquist plots. This type of measurement is able to distinguish the contributions of different cell elements to the electrochemical phenomena. In general, the EIS technique measures the current over a range of frequencies as a voltage is applied, or
vice versa. As shown in Figure 2.6, the Nyquist plot shows both the semicircle and straight line regions corresponding to the kinetic control and mass-transfer control reaction regions, respectively. In the impedance spectra, the intercept at the $Z_{\text{real}}$ axis in the high frequency region, corresponds to the ohmic resistance ($R_s$) while the semicircle also at the high frequency region correlates closely with the Li-ion migration resistance ($R_f$) through the multilayer surface films (not shown in the figure). The semicircle in the middle frequency range is related to the charge transfer resistance ($R_{\text{ct}}$), and the inclined line at the low frequency region represents the Warburg impedance ($Z_{\omega}$) which is associated with lithium-ion diffusion in the LiMn$_2$O$_4$ particles [94-98].

![Graphs](image)

Figure 2.5. Typical characterization techniques (a) galvanostatic cyclability [99] (b) rate capability [98] (c) cyclic voltammetry [96] (d) electrochemical impedance [96].

The determining feature is the charge-transfer resistance ($R_{\text{ct}}$), and its relation to the Warburg impedance ($Z_{\omega}$). If the system is kinetically sluggish, it will show a large $R_{\text{ct}}$, and may display only a very limited-frequency region where mass transfer is a significant
factor. At the other extreme, $R_{ct}$ might be very small by comparison to the ohmic resistance and the Warburg impedance. Then the system is so kinetically facile that mass transfer always plays a role, and the semicircular region is not well defined. These two extreme conditions are represented in Figure 2.6 as the kinetic control and mass-transfer regions [94].

Figure 2.6. Nyquist plot demonstrating the kinetic control and mass transfer regions [94].

2.6 Thermal Expansion Studies

Another application we are interested in is the unusual property of low, negative or near zero thermal expansion behavior of the compounds ($M_1$Ti$_2$(PO$_4$)$_3$ ($M_1$ = Li, Na, K)). Our first attempt to synthesize and characterize members of this family was with NaTi$_2$(PO$_4$)$_3$ (NTP) [60]. These materials have attracted considerable attention [100-107] and they belong to the NASICON-type (sodium super-ionic conductor) structures which are based on the NaZr$_2$(PO$_4$)$_3$ (NZP) family. Additionally, they possess anisotropic coefficients of thermal expansion (CTE), with expansion in two axial directions but a contraction in the third. Several compounds such as mixed metal oxides ZrP$_{2-x}$V$_x$O$_7$ [108], ZrW$_2$O$_8$ [109], zeolites (faujasite) [110], aluminum phosphates (AlPO-17) [111], metallo-organic structures as well as the siliceous zeolites ITQ-1, ITQ-3, ITQ-4 and SSZ-23 [112,
have been reported to possess similar behavior. However, NASICON-type structures have been the most studied.

Due to its structure and physicochemical properties, it has been shown and predicted that NASICON structures may be useful as low thermal expansion materials, insertion/extraction materials, fuel cells, nuclear waste disposal materials, catalyst supports, gas sensors (CO₂, SO₂, NO, NO₂, NH₃, and H₂S gases), ion selective electrodes, ultraviolet shielding and for luminescence.

Figure 2.7 depicts the crystal structure of NaTi₂(PO₄)₃, which crystallizes in the rhombohedral space group R₃c (167). This structure is an open, three-dimensional lattice, consisting of corner-shared TiO₆ and PO₄ polyhedra, with the large Na cation occupying interstitial, trigonal prismatic (M1) sites spaced at intervals along the c-axis. The structure has a rigid, but deformable framework, that not only offers a variety of ionic substitution at different lattice sites, but also, may be a contributing factor to the anomalous thermal expansion behavior. Traditionally, the thermal expansion behavior of these materials (of rhombohedral space group) has been reported, for convenience, in the hexagonal coordinate system.

Single crystals of NTP were synthesized by Hagman and Kierkegaard in 1968, by heating NaPO₃ and TiO₂ at 1100°C for several weeks. Recently, different methods such as solid state reaction, a hydrothermal method, microwave-assisted synthesis, a sol-gel method and others, have been used to prepare polycrystalline powders of NTP. As discussed earlier, all of these synthetic methods possess some disadvantages including high processing temperatures, long processing times, multiple and complicated preparation steps, and low concentrations of starting materials. It is been pointed out that the final properties of materials are very dependent on the processing method, at least in materials like this one, where the flexibility of its structural skeleton allows hysteresis and distortions induced by microstructural stresses.
Traditionally, the coefficient of thermal expansion (CTE) has been expressed in different ways such as linear, average, bulk and volumetric CTE, or by a polynomial equation describing the change in the lattice parameter as a function of temperature along each crystallographic axis. Largely due to the fact that the thermal expansion tensor is a second-rank, symmetric tensor relating strain to temperature, it is becoming increasingly popular to describe the thermal expansion of a material in terms of the following matrix [62, 129], where $\varepsilon_{ij}$ and $\alpha_{ij}$ are the strain and the coefficient of thermal expansion in the $ij$ direction, respectively.

\[
d\varepsilon_{ij} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix} dT
\]

At any time the number of matrix components can be reduced to six independent parameters due to the inversion symmetry of the thermal expansion tensor. These six
components can be further simplified depending on the crystallographic symmetry of the cell. For low-symmetry crystal systems, it would be necessary to have six and five components of the thermal expansion tensor for triclinic and monoclinic cells, respectively. In high-symmetry cells, such as cubic, the number of matrix components can be reduced to a single component. In crystal systems with orthonormal axes (i.e., cubic, tetragonal, and orthorhombic) the thermal expansion calculation can become quite trivial as the thermal expansion tensor components match their respective crystallographic axes (i.e. \( \alpha_a = \alpha_{11} \)).

For low-symmetry cells, however, such as cells with non-orthonormal axes (i.e., hexagonal, trigonal (rhombohedral), monoclinic, triclinic), the calculation becomes more complex. The hexagonal crystal system only requires two components of the thermal expansion tensor to be fully described (\( \alpha_{11} \) and \( \alpha_{33} \)). Therefore, the reduced thermal expansion tensors for the hexagonal cell is shown below. A more detailed description of thermal expansion of solids is given by Taylor [129].

\[
d\varepsilon_{ij} = \begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix} dT
\]

In addition, the program Coefficient of Thermal Expansion Analysis Suite (CTEAS) developed at UIUC can be used to calculate the coefficient of thermal expansion tensor from in-situ, high-temperature XRD data sets collected using the quadruple lamp furnace (QLF) and synchrotron radiation. Based on each \( hkl \) reflection and corresponding \( d \)-spacing, CTEAS will perform a least-squares polynomial fit as a function of temperature. The expansion information from each reflection is then recombined and evaluated to fully describe the thermal expansion behavior in a more complete manner, as opposed to that by conventional methods adopted to calculate thermal expansion coefficients [61, 62, 130, 131].
CHAPTER 3
EXPERIMENTAL PROCEDURES

3.1 Powder Synthesis

3.1.1 The Polymeric Steric Entrapment Method to Produce Manganate-Based Compounds ($M_1M_nO_y$, $M_1=Li, Na$)

The synthesis procedures described in this section were modified from the original polymeric steric entrapment method developed to produce ceramic oxide powders, where the cations always reach their maximum oxidation state (maximum valent state) [30-58, 61-66]. Recently, Ribero and Kriven [59, 60] adapted the synthesis method to produce compounds where the cations (transition metals) have multiple valence states (zwitier ions) and reach their lower oxidation state (or are 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 of Fe makes LiFePO$_4$ a suitable material for energy storage applications.

Based on the literature review of the synthesis methods and previous work done in the polymeric-steric entrapment method, it is well known that variables such as the type of reagents, solvents, pH, drying conditions, cation:organic ratio, atmosphere and temperature play an important role in the number of phases, crystal structure, purity, microstructure and properties of the synthesized compounds.

The $M_1M_nO_y$ system was selected because it imposes an interesting challenge since the Mn ion can adopt multiple oxidations states (+2 to +7), being one of the transition metals that has a larger number of possible oxidation states. The three common compounds explored for energy storage applications were LiMn$^{3+}$O$_2$, LiMn$_2$$^{3+/4+}$O$_4$ and Li$_2$Mn$^{4+}$O$_3$, where LiMn$_2$$^{3+/4+}$O$_4$ is the only one that has successfully reached commercial applications (electric vehicles). The cation sources for the three compounds in the $M_1M_nO_y$ system were lithium nitrate (LiNO$_3$, Reagent Plus®, Sigma Aldrich Co, St Louis, MO), manganese(II) nitrate tetrahydrate (Mn(NO$_3$)$_2$ ● 4H$_2$O, ≥ 97.0%, Sigma Aldrich Co, St Louis, MO), 80% hydrolyzed polyvinyl alcohol (PVA) (M.W. 9.000 – 10.000, Sigma Aldrich Corporation, USA). PVA was selected as the polymer to perform the steric
entrapment, since all of the cations sources were also soluble in water. In order to accelerate the mixing of the cations and polymer entrapper, PVA was added to the system as a 20 weight % solution (PVA) in de-ionized (DI) water.

Stoichiometric amounts of the Li and Mn 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 together and kept mixing for at least 4 h. No agglomeration or precipitation was observed at any stage of the mixing procedure, a problem which has been encountered in other compositions such as LiFePO₄.

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. Different ratios were evaluated, viz., 2:1, 4:1, 6:1 and 8:1. The final solution (cation + PVA) was allowed to mix overnight to assure very good mixing of all components.

All solutions were dried in a hot plate at a temperature of 70°C to form a viscous solution and then finishing the drying in a vacuum oven (Fisher Scientific, Model 282 A, Pittsburgh, PA) at 80°C. The dried gel was brownish and it was more or less sticky depending on the amount of PVA used. Different calcination, crystallization and atmosphere conditions were tested, in order to achieve single phase formation of the desired compound at the minimum possible temperature. For LiMn³⁺O₂, which has Mn in the lowest evaluated oxidation state, argon, forming gas (95 % N₂ and 5 % H₂), nitrogen and air atmosphere were used. In the case of LiMn₂³⁺/⁴⁺O₄, and Li₂Mn⁴⁺O₃, which have Mn in the mixed/intermediate and highest evaluated oxidation states, respectively, air atmosphere was utilized.

In all cases, violent exothermic reactions were detected in the 200 ± 10°C temperature range. The duration, strength and amount of gas released was dependent on the nitrate/PVA ratio. As the exothermic reactions for LiMn₂³⁺/⁴⁺O₄, and Li₂Mn⁴⁺O₃ occurred at low temperature (~200°C) and the desired crystal structures with the required oxidation states could be obtained in air, exothermic reaction process could be done on a hot plate (set temperature = 350°C). After the reactions occurred on the hot plate, the powders were placed inside a Carbolite furnace (Carbolite CWF 12/13, Carbolite Inc., Hope Valley,
England) heated at 10°C/min up to 200°C and annealed for 2 h. In all cases, the phase evolution was evaluated in the temperature range 300°C – 800°C. When air was the working gas, the Carbolite furnace operated at 10°C/min and 2 h annealing time was employed. Moreover, when argon, forming gas or nitrogen gases were used, a controlled atmosphere mullite tube furnace (Lindberg, Asheville, NC) working at 5°C/min and 2 h annealing time was utilized.

Equations 8 through 10 show the stoichiometric equations to produce each compound in the $M_1Mn_xO_y$ system.

\[
LiNO_3 + Mn(NO_3)_2 \cdot 4H_2O + (CH_2CH(OH))_n \rightarrow LiMnO_2 + WNO_x \uparrow + XCO_x \uparrow + YNH_3 \uparrow + ZH_2O \uparrow \quad [8]
\]

\[
LiNO_3 + Mn(NO_3)_2 \cdot 4H_2O + (CH_2CH(OH))_n \rightarrow LiMnO_4 + WNO_x \uparrow + XCO_x \uparrow + YNH_3 \uparrow + ZH_2O \uparrow \quad [9]
\]

\[
2LiNO_3 + Mn(NO_3)_2 \cdot 4H_2O + (CH_2CH(OH))_n \rightarrow Li_2MnO_3 + WNO_x \uparrow + XCO_x \uparrow + YNH_3 \uparrow + ZH_2O \uparrow \quad [10]
\]

A summary flowchart of the polymeric steric entrapment method and the variables investigated in this study to produce compounds in the $M_1Mn_xO_y$ system is shown in the Figure 3.1.
3.1.2 The Polymeric Steric Entrapment Method to Produce Titanium Phosphate-Based Compounds (M$_1$Ti$_2$(PO$_3$)$_4$, M$_1$=Li, Na, K)

The cation sources for the different compounds in the M$_1$Ti$_2$(PO$_3$)$_4$ system were lithium nitrate (LiNO$_3$, Reagent Plus®, Sigma Aldrich Co, St Louis, MO), sodium nitrite (NaNO$_2$, Reagent Plus®, Sigma Aldrich Co, St Louis, MO), potassium nitrate (KNO$_3$, Reagent Plus®, ≥ 99.0%, Sigma Aldrich Co, St Louis, MO), aluminum nitrate nonahydrate (Al(NO$_3$)$_3$ • 9H$_2$O, ≥ 98.0%, 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). The
stoichiometric amounts of each reagents were calculated based on the following chemical reactions:

\[
3(\text{NH}_4)_2\text{HPO}_4(s) + \text{LiNO}_3(s) + 2\text{Ti}([\text{OCH(CH}_3]_2)_4(l) + 3\text{HOCH}_2\text{CH}_2\text{OH}(l) + \\
Y_1\text{H}_2\text{O}(l) \rightarrow \text{LiTi}_2(\text{PO}_4)_3(s) + \text{WNO}_X(g) + X_2\text{CO}_X(g) + Y_2\text{NH}_3(g) \quad [11]
\]

\[
3(\text{NH}_4)_2\text{HPO}_4(s) + \text{NaNO}_2(s) + 2\text{Ti}([\text{OCH(CH}_3]_2)_4(l) + 3\text{HOCH}_2\text{CH}_2\text{OH}(l) + \\
Y_1\text{H}_2\text{O}(l) \rightarrow \text{NaTi}_2(\text{PO}_4)_3(s) + \text{WNO}_X(g) + X_2\text{CO}_X(g) + Y_2\text{NH}_3(g) \quad [12]
\]

\[
3(\text{NH}_4)_2\text{HPO}_4(s) + \text{KNO}_3(s) + 2\text{Ti}([\text{OCH(CH}_3]_2)_4(l) + 3\text{HOCH}_2\text{CH}_2\text{OH}(l) + \\
Y_1\text{H}_2\text{O}(l) \rightarrow \text{KTi}_2(\text{PO}_4)_3(s) + \text{WNO}_X(g) + X_2\text{CO}_X(g) + Y_2\text{NH}_3(g) \quad [13]
\]

\[
3(\text{NH}_4)_2\text{HPO}_4(s) + 1.3\text{LiNO}_3(s) + 0.3\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}(s) + 1.7\text{Ti}([\text{OCH(CH}_3]_2)_4(l) + \\
3\text{HOCH}_2\text{CH}_2\text{OH}(l) + Y_1\text{H}_2\text{O}(l) \rightarrow \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3(s) + \text{WNO}_X(g) + X_2\text{CO}_X(g) + \\
Y_2\text{NH}_3(g) \quad [14]
\]

For the synthesis of compounds such as LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (LTP), KTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (KTP), NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (NTP) and Li\textsubscript{1.3}Al\textsubscript{0.3}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{3} (LATP), a hybrid method was used because some of the reagents (Li, Na, K and P sources) dissolved easily in water, but not in alcohol, while the titanium source (titanium isopropoxide - “TISO”) decomposed in water (forming isopropyl alcohol and a hydrated form of titania) but dissolved and remained stable in alcohol. The decomposition to titania could be hindered or at least slowed down by adding excess isopropyl alcohol, so as to favor the equilibrium of the reaction [15] to the left.
(reactants). In this case, ethylene glycol (EG) monomer (HOCH₂CH₂OH) was chosen as a polymeric carrier, because it is a linear polymer that does not decompose in isopropyl alcohol. The amount of EG added to the system was calculated based on the molar ratio of total (+) valences of the cation to the (-) valences of the OH⁻ functional groups in the EG. 2:1, 4:1 and 6:1 cation:organic ratios were evaluated for all compositions.

$$\text{Ti[OCH(CH}_3\text{)]}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_7\text{OH}$$

[15]

Water soluble reagents were dissolved independently in 40 ml of DI water, while EG and Ti[OCH(CH₃)]₄ or “TISO” were diluted independently in 80 ml of isopropyl alcohol (“IPA”). Once all reagents were dissolved in their appropriate solvent and then were stirred for 4 hours on a hot plate at room temperature to ensure complete dissolution. Subsequently, water-based and alcohol-based solutions were pre-mixed separately. At this point no segregation or decomposition or hydrolysis of any reagent was noticed. However, after some time (~30 min) the water soluble solutions (containing LiNO₃) started turning white and showing some precipitate formation. This precipitation was found to be reversible upon a pH modification (HNO₃ addition) by keeping the pH below 4.4. Finally, both water and alcohol-based solutions were mixed together forming a thick white gel. This thick white gel was broken down using a spatula and turned back into a white dispersion. It has been found that mechanical stirring or high shear mixing not only helped to break down flocs and improved the homogeneity of products, but also simplified the process [58, 60] eluding the usage of HNO₃ and large amounts of isopropyl alcohol. The final colloidal suspension (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. The dried powder was ground with a mortar and pestle and then calcined in air for 2 hours at 200°C (10°C/min). Finally, the calcined powder was then crystallized at different temperatures (500°C – 1100°C, 10°C/min) for 1 hour in a laboratory box furnace (Carbolite CWF 12/13, Carbolite Inc., Derbyshire, UK).
A flowchart to prepare compounds in the $\text{M}_1\text{Ti}_2(\text{PO}_4)_3$ system by the polymeric steric entrapment method is shown in Figure 3.2.

![Flowchart](image)

**Figure 3.2.** Flowchart of the polymeric steric entrapment method and the variables tested to produce $\text{M}_1\text{Ti}_2(\text{PO}_4)_3$ powders.

3.2 Powder Characterization

3.2.1 Thermal Analysis

Either simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) (Model STA 409, Netzsch GmbH, Selb, Germany) or 2920 DSC TA instruments (TA instruments, New Castle, Delaware, USA) were used to evaluate
endothermic and exothermic processes such as pyrolysis, decomposition and crystallization of precursors in the model systems. Two different setups were used:

(a) When samples were highly exothermic (in the \( \text{M}_1\text{Mn}_x\text{O}_y \) family), aluminum pans and the TA instrument heated up to 600°C were used. The samples used for these analyses having different amounts of polymer were dried (70°C - 80°C) in the combination of hot plate and vacuum oven (see section 3.1.1). Heating rates (5°C - 20°C/min), atmosphere (Air, \( \text{N}_2 \) and \( \text{Ar} \)), sample mass (5 - 18 mg) and pre-testing drying conditions were evaluated.

(b) When the decompositions of nitrates and organics were not highly exothermic and violent (in the \( \text{M}_1\text{Ti}_2(\text{PO}_3)_4 \) family), alumina pans and lids along with simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) (Model STA 409, Netzsch GmbH, Selb, Germany) were used. These analyses were performed on samples containing 4:1 cation:organic ratio and dried using a combination of hot plate and box furnace (see section 3.1.2). A heating rate of 10°C/min, air atmosphere and 25°C - 1200°C temperature range were used as the analysis conditions for all samples in this family.

3.2.2 Phases Evolution by 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, USA), with Cu Kα radiation (\( \lambda = 1.540598 \text{ Å} \)). The operating conditions of the diffractometer were 40 kV, 30 mA, 10° to 70° 2\( \theta \), at a step size of 0.02° 2\( \theta \). In order to improve data quality due to X-ray absorption and fluorescence effects in some samples, two different measurement times per step conditions were utilized. 1.0 s per step for samples in the \( \text{M}_1\text{Ti}_2(\text{PO}_3)_4 \) family and 0.5 s per step for samples in the \( \text{M}_1\text{Mn}_x\text{O}_y \) family were used. Phase identification was performed using X’pert HighScore Plus software (version: 3.0.5, PANalytical B.V., Almelo, the Netherlands) coupled with the International Center for Diffraction Data PDF-4+ database (ICDD v. 2014, International Center for Diffraction Data, Newton Square, PA, USA).
3.2.3 Microstructure Characterization

The morphologies and crystal sizes of all samples were examined by scanning electron microscopy (SEM) (Hitachi S-4700 high resolution SEM, Hitachi High Technologies, Schaumburg, IL, USA). Prior to imaging, the samples were Au–Pd sputter-coated to avoid surface charging. To confirm the synthesis of nanoparticles, scanning transmission electron microscopy ((S)TEM) was performed on the low temperature samples using a JEOL-2010F (field-emission source) electron microscope at an accelerating 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.

3.2.4 Chemical Analysis

An Exeter Analytical analyzer (Exeter Analytical, Inc., model CE 440 CHN Analyzer, Coventry, U.K.) was used to determine the residual carbon, hydrogen and nitrogen contents in the final powders. In this technique the samples undergo a combustion in pure oxygen at 1800°C. Then, the resulting combustion products pass through specialized reagents to produce CO₂, H₂O, N₂ and NOₓ which are measured through a series of high-precision, thermal conductivity detectors. All work was done in the School of Chemical Sciences at the University of Illinois at Urbana-Champaign.

3.2.5 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 (0.01 to 3500 µm range Malvern Mastersizer 3500, Worcestershire, UK). Mie theory, a 1.6 refractive index (RI) for the particles, a 0.1 index of absorption, and 1.33 RI for the dispersion medium (water) were used for the M₁M₉O₃ materials. For the M₁Ti₂(PO₄)₃ powders, a 1.8 refractive index (RI) for the particles and 0.01 index of absorption were utilized. The specific surface area (SSA)
was measured using seven-point BET analyses by nitrogen gas adsorption (0.1 to 300 m$^2$/g range, Gemini, Micromeritics, Norcross, GA, USA). To perform particle size distribution (PSD) and specific surface area (SSA) the samples were ground in the same way as for TEM sample preparation (see section 3.2.3).

3.2.6 Thermal Expansion Behavior

The thermal expansion behavior of the different members in the $\text{M}_1\text{Ti}_2(\text{PO}_3)_4$ family in all \{hkl\} pole directions was determined by *in situ* high temperature X-ray diffraction using synchrotron radiation. The fully crystallized powders annealed at 1200°C for 4 hours were mixed with fully crystallized Pt powder (annealed at 800°C for 2 hours) and then loosely packed into either a quartz (for LTP, LATP and NTP) or sapphire capillaries (for KTP) that were then mounted in a longer alumina tube (Figure 3.3. (a)). Each sample was heated in air from room temperature to a maximum of 1200°C, in approximately 100°C steps, using a quadrupole lamp furnace (Figure 3.3. (b)) mounted at the synchrotron beamline [132]. Over the development of this project, three synchrotron facilities were used.

(a) Beamline X14-A of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton, NY (Figure 3.3. (c)). The characteristic energy of operation of NSLS was 2.8 GeV with a ring circumference of 170 m. The XRD patterns were collected at each temperature with a linear Si strip position-sensitive detector located at 1432 mm away from the center of the diffractometer. Patterns were acquired over the range of 5° to 35° 2θ. The X-ray beam was focused to 0.75 x 0.5 mm onto the sample. NaTi$_2$(PO$_3$)$_4$ data was collected under this experimental.

(b) Beamline 33BM-C of The Advanced Photon Source (APS) located at Argonne National Laboratory in Lemont, IL (Figure 3.3. (e)). The characteristic energy of operation of APS was 7.0 GeV with a ring circumference of 1104 m. The X-ray radiation was collected with a Pilatus 100k detector located approximately 1040 mm away from the center of the diffractometer. Patterns
were acquired over the range of 5° to 35° 2θ, while the X-ray beam was focused to 0.5 X 0.5 mm on to the sample. LiTi2(PO₃)₄, Li₁.₃Al₀.₃Ti₁.₇(PO₃)₄, and KTi₂(PO₃)₄ data were collected under this experimental configuration.

(c) X-ray powder beamline (XPD) 28 of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory in Upton, NY (Figure 3.3. (d)). The characteristic energy of operation of NSLS was 3.0 GeV with a ring circumference of 792 m. The XRD patterns were collected at each temperature with a 2D image plate detector located at 1295 mm away from the center of the diffractometer. Patterns were acquired over the range of 2° to 12.5° 2θ. The X-ray beam was focused to 0.5 x 0.5 mm onto the sample. Li₁.₃Al₀.₃Ti₁.₇(PO₃)₄ data was collected under this experimental configuration.

In all cases, the wavelength was calibrated with a LaB₆ standard (SRM 660a; National Institute of Standards and Technology, Gaithersburg, MD) and was found to be 0.77877 Å for NSLS, 0.563890 Å for APS and 0.237362 Å for NSLS-II setups, respectively.

The resulting X-ray diffraction patterns were refined by the Rietveld method with the General Structure Analysis System (GSAS) and EXPGUI programs [133, 134]. The background, lattice constants, scale factors, atomic positions, and profile functions were refined for each phase. The well characterized thermal expansion of platinum was employed to accurately calculate the temperature of each dataset. The resulting variable temperature M₁Ti₂(PO₄)₃ d₃h listings were then analyzed through the Coefficient of Thermal Expansion Analysis Suite (CTEAS) program developed at UIUC to determine the components of the second-rank thermal expansion tensor [130].
3.2.7 Electrochemical Characterization

3.2.7.1 Electrode Preparation

LiMn$_{2/3}$O$_4$ (“LMO4”) composition was selected as a model compound to test the electrochemical properties of the powders obtained by the polymeric steric entrapment method. This compound has been proven to be electrochemically active and can be compared with commercially available powders. Additionally, this composition is attractive because it’s low-cost, nontoxicity, and environmentally friendliness.
LMO4 commercial powders for comparison were purchased from Sigma-Aldrich (electrochemical grade, Sigma Aldrich Co, St. Louis, MO). Cathode electrodes (“8:1:1”) composed of 80 wt% of active material (LMO4), 10 wt% poly(vinylidene) fluoride (PVDF) binder ((-CH$_2$CF$_2$)$_n$, Alfa Aesar, Ward Hill, MA, USA) and 10 wt% conductive carbon black (Timcal Graphite & Super P®, MTI Corporation, Richmond, CA, USA), were prepared. A 3:1 n-methyl pyrrolidone (NMP) solvent (MTI Corporation, 99.5 %, Richmond, CA, USA) to powder ratio was used to finally form the slurries. A schematic description of the slurry, electrode and battery preparation is summarized in Figure 3.4. Powder and solvent systems were mixed and degassed in a Thinky ARE-250 planetary conditioning mixer (Intertronics, Kidlington, Oxfordshire, England). The Thinky mixer is a planetary mixer which rotates samples about a central axis (much like a centrifuge), while simultaneously rotating the sample in the opposite direction about the axis of the sample holder (Figure 3.4 (b)). Slurries were mixed for 10 min at 1600 rpm and degassed for 2 min at 1200 rpm in the Thinky mixer over five repetitions. Eight zirconia beads 5.1 mm were added to the mixing container in order to ensure uniform dispersal of the solvent, binder, active material, and conductive carbon (Figure 3.4 (a)). Slurries were spread using a doctor blade with a blade gap of 0.12 mm on to a 0.015 mm thick aluminum foil current collector (Figure 3.4 (c) - (d)). Electrodes were dried in air overnight at 120°C in a gravity-flow convection oven (Fisher Scientific Isotemp oven, 637G Model, Dubuque, IO, USA). Electrodes and Celgard® (25µm trilayer polypropylene-polyethylene-polypropylene membrane, MTI Corporation, Richmond, CA, USA) separators were cut into 12.7 mm (1/2 in) diameter disks prior to battery assembly (Figure 3.4 (e)).

Batteries were assembled using a Swagelok® cell configuration (Figure 3.4 (f) – (g)) in an argon-filled glove box with controlled water and oxygen concentrations being kept below 2 ppm. Lithium metal (lithium ribbon, 99.9%, Sigma Aldrich Co, St. Louis, MO) was utilized as a negative electrode (anode). 1 mol/L LiPF$_6$ salt in ethylene carbonate/dimethyl carbonate/diethylene carbonate (EC+DMC+DEC; 4:3:3 in volume, MTI Corporation, Richmond, CA, USA) solvent was use as a liquid organic electrolyte.
3.2.7.2 Galvanostatic Cycling

Swagelok® half cells made of LMO4 powder produced at 300°C x 2 h, 300°C x 20 h, 500°C x 2 h, 700°C x 2 h and LMO4 commercial powder were cycled (charge/discharged) by applying a constant current and monitoring the cell voltage. The current applied was calculated in each case based on the mass of the active material and the LMO4 theoretical specific capacity (148 mAh/g). Li metal was used as an anode, so that all voltages were based on the Li/Li⁺ electrochemical couple. Galvanostatic cycling measurements revealed the battery capacity and charge/discharge profiles. In order to test the ability of the battery
to operate at difference charge/discharge rates, multiple cycling rates or C-rates (C/10, C/5, C/2 and 1C) were evaluated using a 15 channel BioLogic VMP3 potentiostat system (VMP3, Bio-Logic SAS, Seyssinet-Pariset, France). C-rate (I = C/n, current (I), cell capacity (C) and hours (n)) is a common term used in the energy storage field, which express the current at which the battery is cycled. For instance, for a 10 mAh battery to be discharge in 1 h (1C), the discharge current must be 10 mA, while for discharging it at C/10 (10 h), the discharge current should be 1 mA. All measurements were performed at a room temperature of about 25°C.

3.2.7.3 Cyclic Voltammetry (CV)

Cyclic voltammetry measurements were performed in the same instrument described above used for galvanostatic cycling measurements. Cells were cycled at 0.1 mV/s over the 3 – 5 V range. CV analyses were carried out on the pristine electrodes as well as after the 1st, 2nd, 5th and 10th charging/discharging cycle. CV curves typically indicate at which voltage the redox (insertion/extraction) reactions occur and their reversibility.

3.2.7.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) measurements were performed on batteries charged up to 4.2 V by applying an AC potential (single sinusoidal signal of 10 mV amplitude) in the frequency range of 5 mHz – 1 MHz and then measuring the current through the cell. This measurement gives an idea of how an electrochemical cell or battery resist the flow of electrical current and can be compared with an “equivalent circuit” composed by different electrical circuit elements. EIS measurements are typically represented by a Nyquist plot, where the X-axis is the real part of the impedance while the Y-axis is the imaginary counterpart. From this analysis, different reaction behaviors such as kinetic control or mass transfer control reactions can be identified. Additionally, information such as double layer capacitance, electron transfer resistance and electrolyte resistance (ionic mobility) may be obtained from this type of measurement.
CHAPTER 4
POLYMERIC STERIC ENTRAPMENT METHOD TO PRODUCE
MANGANATE-BASED COMPOUNDS (M\textsubscript{1}Mn\textsubscript{x}O\textsubscript{y}, M\textsubscript{1}=Li, Na)
RESULTS AND DISCUSSION

4.1 Introduction

As mentioned earlier, M\textsubscript{1}Mn\textsubscript{x}O\textsubscript{y} was selected as a model system for several reasons: First, it provided an opportunity to evaluate how the polymeric steric entrapment method could be used to produce compounds having intermetallic cations which can adopt different oxidation states. Second, there was vast information available that helped us to understand and compare our results, and last but not least, compounds in this family such as LiMn\textsubscript{2}O\textsubscript{4} were commercially available and possess a current technological importance for EV and consumer electronics.

In this chapter, we will see how some synthesis variables such as, drying procedure, amount of polymer, calcination/crystallization atmosphere and temperature allow the production of compounds at low temperature with different oxidation states. Finally, for LiMn\textsubscript{2}O\textsubscript{4}, we will relate the synthesis variables with the physico-chemical characteristics of the powders and their electrochemical performance.

4.2 Dissolution of the Reagents to Produce Powders in the M\textsubscript{1}Mn\textsubscript{x}O\textsubscript{y} Family

The first, and one of the most important conditions to be tested in order to synthesize materials using the polymeric steric entrapment method is the solubility of the reagents (raw materials), hopefully, in a common solvent. In this system, fortunately and contrary to the M\textsubscript{1}Ti(PO\textsubscript{4})\textsubscript{3} family, all the reagents dissolved perfectly and quickly in water, thus forming clear solutions in all cases as shown in Figure 4.1. Additionally, when individual solutions containing water were mixed together, no precipitation, flocculation or agglomeration was encountered, as opposed to the behavior of the LiFePO\textsubscript{4} system [59, 60], where well dissolved reagents in water, flocculated when mixed together. In that case (the LiFePO\textsubscript{4} system), pH modification was needed to form a stable solution. As a guide,
Table 4.1 provides the concentration and pH of both individual and mixed solutions to produce LiMn$_2$O$_4$. NaNO$_2$ and Na + Mn solutions are included in the table because Na-based manganate compounds (e.g. Na$_{0.44}$MnO$_2$) are interesting compounds that follow the same synthesis procedure described for the Li-based manganate materials.

![Figure 4.1](image)

Figure 4.1. Clear solutions of (a) LiNO$_3$, (b) Mn(NO$_3$)$_2$, and (c) LiNO$_3$ + Mn(NO$_3$)$_2$.

Table 4.1. pH of each Cation Solution, each Mixing Step and the Final Solution pH to Produce LiMn$_2$O$_4$

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molarity (Mol/L)</th>
<th>pH</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>2.77</td>
<td>9.0</td>
<td>Clear</td>
</tr>
<tr>
<td>Mn(NO$_3$)$_2$ ● 4H$_2$O</td>
<td>5.53</td>
<td>2.0</td>
<td>Clear</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>2.29</td>
<td>8.8</td>
<td>Clear</td>
</tr>
<tr>
<td>Li + Mn</td>
<td>-</td>
<td>4.9</td>
<td>Clear</td>
</tr>
<tr>
<td>Na + Mn</td>
<td>-</td>
<td>4.1</td>
<td>Clear</td>
</tr>
</tbody>
</table>

As explained in the Experimental Section (section 3.1.1), stoichiometric solutions to produce LiMn$^{3+}$O$_2$, LiMn$_2$$^{3+/4+}$O$_4$ and Li$_2$Mn$^{4+}$O$_3$ were prepared and mixed overnight with different amounts of PVA solutions to assure organic cation ratios of 2:1, 4:1, 6:1 and 8:1.
It has been found that there were exothermic reactions occurring at low temperature (~200°C). These reactions, which came from the decomposition of nitrates and organics, were fast, violent, and highly energetic. The reaction temperature, duration, and energy depended mainly on the cation:organic ratio. Additionally, it has been observed that these exothermic reactions can promote crystallization at low temperatures (as low as ~200°C). Figure 4.2 shows some examples of how strong and violent were the exothermic reactions and how difficult it was to contained powders inside pots and crucibles. As a reference, the maximum amount of powder produced inside the pots was 10 g, while the maximum amount of sample calcined inside the crucibles was 1 g.

![Figure 4.2. Examples of the exothermic reactions of compounds in the M$_1$Mn$_x$O$_y$ system.](image)

In order to take full advantage of these exothermic reactions and crystalize materials at low temperature, early evaporation and decomposition of nitrates and organics have to be avoided. Furthermore, it is been identified that water in the systems not only acts a coolant (less energetic reactions) but also upon heating, the energy applied to the system in the 100°C - 300°C temperature range was consumed in major part by water evaporation (drying process). Therefore, by the time most of the water has been evaporated, a portion
of the nitrates and organics have already decomposed or evaporated, limiting and changing the exothermic reaction conditions. The exothermic reaction conditions determine the crystalline phase formation as well as the oxidation state. For these reasons, solutions were dried at low temperatures (70°C – 80°C) in a combination of the hot plate and vacuum oven in order to only evaporate water. Using these procedures, the nitrates:organic ratios remained constant (as calculated), and the exothermic reactions could be carried out under the desired environment conditions.

4.3 Synthesis of the LiMnO₂ Compound

4.3.1 Phase Evolution of the LiMnO₂ Compound

The LiMn³⁺O₂ compound has the lowest oxidation state of the compositions studied in this project. Different cation:organic ratios (2:1, 4:1, 6:1 and 8:1) and atmospheres (argon, forming gas and air) were evaluated in order to control the oxidation state. Figures 4.3 through 4.6 show the effect of the cation:organic ratio in the crystallization behavior under reducing atmosphere (forming gas).

Figure 4.3. X-ray diffractograms of the LiMnO₂ synthesized in forming gas using 2:1 cation:organic ratio in the range 300°C - 800°C.
Figure 4.4. X-ray diffractograms of the LiMnO$_2$ synthesized in forming gas using 4:1 cation:organic ratio in the range 300°C - 800°C.

Figure 4.5. X-ray diffractograms of the LiMnO$_2$ synthesized in forming gas using 6:1 cation:organic ratio in the range 300°C - 800°C.
Figure 4.6. X-ray diffractograms of the LiMnO$_2$ synthesized in forming gas using 8:1 cation:organic ratio in the range 300°C - 800°C.

At high cation to organic ratio (2:1) the reducing conditions were so extreme that only Mn$^{2+}$O and Li$_2$CO$_3$ were formed in the entire temperature range. At intermediate cation:organic ratio (4:1) less reduced phases such as LiMn$_2$O$_4$ appeared at low temperatures (300°C - 400°C), while at intermediate temperatures (500°C - 600°C) the desired phase LiMnO$_2$ appeared. At high temperatures (>700°C) the predominant phases were MnO and Li$_2$CO$_3$.

Working with a cation:organic ratio of 6:1 and 8:1 (Figures 4.5 and 4.6) and forming gas at intermediate temperatures (600°C - 700°C and 500°C – 600 °C, respectively) were determined to be conditions under which LiMnO$_2$ can be formed as the main phase. Nevertheless, small amounts of Li$_2$CO$_3$ and MnO could still be detected as secondary phases. These suggested that the cation:organic ratio may not have been the optimum and the reducing conditions during the heat treatment were still strong.

In order to evaluate the crystallization behavior for LiMnO$_2$ under different atmospheric conditions, samples containing cation:organic ratio 6:1 were allowed to react
under argon, and air atmospheres. Temperatures between 500°C – 700°C were chosen because within this range LiMnO₂ was formed as the main phase when working with forming gas as the atmosphere. Figure 4.7 shows the X-ray patterns of samples calcined and crystallized under air and argon in the range of to 500°C to 700°C for 2 h. It can be seen that in all cases, polycrystalline powders were produced. The synthesized powders contained crystalline phases having different oxidation states such LiMn₂O₄, Li₂MnO₃, LiMnO₂ and Mn₃O₄, phases where the Mn ion adopted oxidation states such +2, +3, +4 and their mixtures. Regarding the LiMnO₂ phase, which was the target, it could not be obtained as the main phase. These results demonstrated that argon and air atmospheres were not suitable for the formation of compounds with lower oxidation states, and in this particular case, for compounds containing Mn in an oxidation state lower than +4. Furthermore, the content of organic and nitrates in the precursors did not produce a strong-enough reducing atmosphere to form the desired LiMnO₂ phase.

![X-ray diffractograms](image)

Figure 4.7. X-ray diffractograms of the LiMnO₂ synthesized in argon and air using 6:1 cation:organic ratio in the range 500°C - 700°C.
The synthesis of the compound (LiMnO\textsubscript{2}) demonstrated how, in order to form the desired phase with the correct oxidation state, variables such as the amount of organics, nitrates and type of atmosphere had to be controlled. For the formation of LiMnO\textsubscript{2} phase, there was a very narrow condition where many variables were interdependent. The cation:organic ratio not only serves for the entrapment of the cations but also and very importantly to control the exothermic reaction and the micro-atmosphere around the particles. The gases released during the exothermic reaction depend on the cation:organic ratio and influence the oxidation state of the intermetallic cation.

4.3.2 Physico-chemical Characterization of the LiMnO\textsubscript{2} Compound

As discussed in the previous section, LiMnO\textsubscript{2} synthesized at 700°C in forming gas and using cation:organic ratio 6 to 1, was the purest compound produced. For this reason just this powder was selected for further microstructural and chemical characterization. Figure 4.8 (a) through (d) are SEM images of the LiMnO\textsubscript{2} powders at different magnifications. It can be seen in Figure 4.8 (a) that secondary particles in the micron range (1 µm - 20 µm) were constituted of smaller crystals of up to 1 micron. Figures 4.8 (b) through (d) revealed a diversity of crystal sizes and shapes in the range of 0.1 µm to 2 µm. Especially in Figure 4.8 (c) and (d) some crystals having a plate-like shape with thickness of about 0.1 µm can be observed. The size of the crystals agreed with the maximum heat treatment temperature (700°C) which allowed good crystallization and crystal growth. No necking between crystals was evident, which suggested a low degree of sintering. It is expected that this synthesis method produced porous secondary particles composed of small primary crystals due to the violent exothermic reactions and gas evolution during the synthesis.

As this compound was produced under reducing atmosphere and the precursors contained carbon and nitrogen, it became useful to know how much the content of these two elements was in the final product. Additionally, these measurements could be an indication of how well balanced was the exothermic reaction because these two elements should be consumed during the reaction. Table 4.2 lists the C, N and H contents of the LiMnO\textsubscript{2} powder processed at 700°C and annealed for 2 h in forming gas. The carbon
content in the sample was 1.86 wt% while the amount of nitrogen and hydrogen were zero. These results indicated that residual carbon was present in the sample and suggested that there was excess of carbon during the exothermic reaction because it was not totally consumed and furthermore, that it was incapable of reacting with O₂ in the atmosphere to form CO₂. The latter was understandable because the working atmosphere was forming gas (reducing).

Figure 4.8. SEM Micrographs at different magnifications of the LiMnO₂ powder produced at 700°C using a cation:organic ratio of 6:1.
Table 4.2. Chemical Composition of the LiMnO\(_2\) Powder Produced at 700°C Using a Cation:Organic Ratio of 6:1

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt%)</td>
<td>1.86</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>0.00</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

4.4 Synthesis of the Li\(_2\)MnO\(_3\) Compound

4.4.1 Phase Evolution of the Li\(_2\)MnO\(_3\) Compound

Figures 4.9 to 4.12 follow the phase evolution of Li\(_2\)Mn\(^{4+}\)O\(_3\) (which is the compound with the highest oxidation state in this study) upon increase in temperature, and using air as the atmosphere with different cation to organic functional group ratios (2:1, 4:1, 6:1 and 8:1).

From the figures below, it can be seen that in all cases, the crystallization process started below 300°C, which matched very well with the exothermic reactions observed during the drying/calcining process on the hot plate. The strength of the reaction and crystalline phases formed depended on the cation:organic ratio and the micro atmosphere generated by the nitrates and organics in the precursors. For instance, using cation:organic ratios of 2:1 and 4:1 (Figure 4.9 and Figure 4.10), Li\(_2\)CO\(_3\) was formed as a secondary phase at low temperature, while using cation:organic ratios of 6:1 and 8:1 (Figure 4.11 and Figure 4.12), respectively, LiNO\(_3\), Mn\(_2\)O\(_3\) and MnO\(_2\) phases were formed. These results (for the 6:1 and 8:1 ratios) demonstrated firstly, that the entrapment was not fully reached, so Li and Mn phases were formed independently. Secondly, they demonstrated that there was an imbalance of the nitrates:organic ratio to create a high enough exothermic reaction to transform all of the reactants (LiNO\(_3\)) into products. In the case of Li\(_2\)CO\(_3\) formation for cation:organic ratios of 2:1 and 4:1, it is believed that the entrapment was correct, and that the exothermic reaction was sufficiently balanced to transform the reactants into products.
However, the reduction power of the mixture of nitrates and organics was not totally balanced by the atmosphere (air), allowing the formation of Li$_2$CO$_3$. Qualitatively, it was found that with the increase in cation:organic ratio, a higher amount of Li$_2$CO$_3$ phase was formed, so that higher temperatures and longer times were needed to remove it. It is important to remember that these processes were carried out in a box furnace were the air was not flowing and the reducing gases released during the exothermic reaction could stay in contact with the particles for a prolonged time.

Figure 4.9. X-ray diffractograms of the Li$_2$MnO$_3$ Synthesized in Air Using 2:1 cation:organic ratio in the range 300°C - 800°C.
Figure 4.10. X-ray diffractograms of the Li$_2$MnO$_3$ synthesized in air using 4:1 cation:organic ratio in the range 300°C - 800°C.

Figure 4.11. X-ray diffractograms of the Li$_2$MnO$_3$ synthesized in air using 6:1 cation:organic ratio in the range 300°C - 800°C.
In all cases, Li$_2$MnO$_3$ phases was formed as a single phase at temperatures higher than 500°C and with the increased temperature, sharper and well defined peaks where formed, suggesting an increase in crystallinity and crystal growth. At temperatures between 300°C and 400°C, less intense and broad peaks were observed. These facts suggested formation of nanocrystals and furthermore, it made differentiation between Li$_2$MnO$_3$ and LiMn$_2$O$_4$ phases more difficult due to superposition of many of their diffraction peaks.

Based on our knowledge about the synthesis method and the phase evolution of the Li$_2$MnO$_3$ under different conditions discussed above, it is believed that the best condition, in order to have a good steric entrapment and take advantage of the exothermic reaction as well as to produce the desired phase at lower temperature is to use the cation:organic ratio 4:1.
4.4.2 Physico-chemical Characterization of the Li$_2$MnO$_3$ Compound

Powders of Li$_2$MnO$_3$ produced using a cation:organic ratio of 4:1 were selected for further characterization. Figure 4.13 (a) through (f) are images taken at different magnifications of powders produced in the range of 300°C – 500°C. At 300°C (Figure 4.13 (a) and (b)) secondary particles (soft agglomerates) formed by primary particles of 15 nm - 35 nm could be observed. Moreover, at 400°C and 500°C (Figure 4.13 ((c) through (f)) crystals grew, but still were in the nano size range (16 nm – 51 nm). These observations correlated with the peak broadening and less intense peaks observed in the XRD measurements. In all cases, no necking or sintering between particles were obvious which coupled with the small crystal sizes suggested that the powders have high specific surface area.

Figure 4.14 (a) through (f) depict SEM images for Li$_2$MnO$_3$ synthesized at temperatures between 600°C and 800°C. Still at 600°C and 700°C primary crystals were in the nano range (15 nm – 60 nm and 21 nm – 100 nm, respectively) and revealed a low degree of sintering. However, upon increased temperature, crystals continued to grow, resulting in at 800°C, crystals with sizes in the range of 84 nm – 270 nm. Furthermore, necks between particles suggested the reduction of specific surface area and that the pre-sintering process took place. At all temperatures, the crystals did not display any particular crystal shape or habit.
Figure 4.13. SEM micrographs of the Li$_2$MnO$_3$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 300°C, (c) - (d) 400°C and (e) - (f) 500°C.
Chemical analysis (for C, N and H) performed on samples of Li$_2$MnO$_3$ synthesized at 300°C, 500°C, 700°C and 800°C are seen in Figure 4.15. It was expected to find a lower amount of these elements than in samples of LiMnO$_2$ because in this case the atmosphere (air) was richer in oxygen. Even though the C and N content present in the samples were not considerably high, it can be noticed that the lower the temperature, the higher the C and N amounts. The maximum amount of carbon (2.02 wt%) was found in the sample treated at 300°C, which was very close to the reaction temperature. As the temperature and total processing time (under air atmosphere) increased, C and N contents were reduced, most likely due to formation of CO$_x$ and NO$_x$ compounds up to virtually zero at 800°C. These results led to the conclusion that although the reaction was highly exothermic and the energy released was enough to induce crystallization of the single phase at low temperatures, there were unreacted C and N during the process. These unreacted components could be responsible for the formation of the small amounts of secondary phases such as Li$_2$CO$_3$, MnO$_2$ and Mn$_2$O$_3$ at low temperatures. In case of a specific requirement of C and N amounts in the final products, these measurements provided a guide for determining the annealing time and temperature to fully remove these elements from the powders.
Figure 4.14. SEM micrographs of the Li$_2$MnO$_3$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 600°C, (c) - (d) 700°C and (e) - (f) 800°C.
Figure 4.15. Chemical analysis - carbon and nitrogen contents (wt%) of the Li$_2$MnO$_3$ powders produced at 300°C, 500°C, 700°C and 800°C using cation:organic ratio of 4:1.

4.5 Synthesis of the LiMn$_2$O$_4$ (“LMO4”) Compound

4.5.1 Characterization of the Commercial LiMn$_2$O$_4$

Commercial LiMnO$_4$ powder purchased from Sigma-Aldrich (electrochemical grade, Sigma Aldrich Co, St Louis, MO) was used as a commercial standard in this study. Table 4.3 presents the powder specifications provided by the company. It can be noticed that the particle size was inferred from the nitrogen absorption of the surface measurement (BET) which is not a direct particle or crystal size measurement. This measurement could be affected by surface roughness, microporosity, shape and size of the pores and particles. The specific surface area (SSA) which is usually measured by BET and a previous requirement in order to calculate the particle size by this method was not reported by the company.

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Table 4.3. Commercial LiMn$_2$O$_4$ Specifications

<table>
<thead>
<tr>
<th>Item</th>
<th>Standard</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Mn</td>
<td>59.8% - 61.7%</td>
<td>Titration by KMnO$_4$</td>
</tr>
<tr>
<td>Particle Size</td>
<td>≤ 5.00 microns</td>
<td>By BET</td>
</tr>
<tr>
<td>Purity</td>
<td>≥ 99%</td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Spinel, Cubic, Fd-3m</td>
<td>XRD</td>
</tr>
<tr>
<td>Density</td>
<td>4.1 g/cm$^3$</td>
<td>at 25°C</td>
</tr>
</tbody>
</table>

Both LMO4 commercial (reference) and our synthesized powders were characterized under the same conditions in order to make an unbiased comparison. X-ray diffraction (XRD), electron microscopy (SEM), chemical analysis, particle size (PSD), specific surface area (SSA) and electrochemical performance results for the LMO4 reference powder are shown below.

The X-ray diffraction pattern for the commercial LMO4 powder is seen in Figure 4.16. Only the cubic LiMn$_2$O$_4$ (spinel) phase (Fd-3m space group) was found in the powder, which agreed with what was reported by the supplier. Peaks were well defined and narrow which implied well crystallized samples having crystals in the micron size range.

Figure 4.17 are SEM micrographs of the commercial LMO4 reference powder at different magnifications. It can be seen that in general, crystals exhibited irregular shapes, although, some adopted a platelet shape. Crystallite sizes were in the range of 0.45 μm to 5 μm. The powder appeared to have some degree of necking (Figure 4.15 (b) and (c)) and low porosity, which suggested low specific surface area (0.7 m$^2$/g). The microstructural characterization (XRD, SEM and SSA) of this commercial powder allowed us to infer that the powder was produced at high temperature and prolonged times (typical for solid state reaction syntheses) which promote single phase formation, crystallinity and crystal growth.
Table 4.1 summarizes the PSD, SSA and chemical analysis measured for LiMn$_2$O$_4$ commercial powder. It is important to mention that the PSD analysis performed in this study really measured the aggregated or sintered particles and not the crystallite sizes. Agglomeration could have occurred due to electrostatic forces between small particles, or simply because primary particles agglomerated during the synthesis process due to intermolecular attractive forces. These values will be compared in the subsequent sections with powders produced by the polymeric steric entrapment method.

Carbon (C), nitrogen (N) and hydrogen (H) amounts present in the LMO4 commercial powder were measured and are presented in Table 4.4. It can be seen that the commercial powders were free of carbon, nitrogen and hydrogen, a fact that also suggested high temperatures, long processing time and oxygen containing synthesis conditions.
Figure 4.17. SEM micrographs of the commercial LiMn$_2$O$_4$ powder.

Table 4.4. Chemical Analysis, Particle Size (PSD) and Specific Surface Area (SSA) Characterization of the Commercial LiMn$_2$O$_4$ Powder

<table>
<thead>
<tr>
<th>Item</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td></td>
</tr>
<tr>
<td>Dv10 (μm)</td>
<td>4.12</td>
</tr>
<tr>
<td>Dv50 (μm)</td>
<td>9.85</td>
</tr>
<tr>
<td>Dv90 (μm)</td>
<td>22.10</td>
</tr>
<tr>
<td>Dvmax (μm)</td>
<td>40.10</td>
</tr>
<tr>
<td>Specific Area BET (m$^2$/g)</td>
<td>0.7</td>
</tr>
<tr>
<td>Chemical Composition (wt%)</td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>0.00</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.00</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>0.00</td>
</tr>
<tr>
<td>Structure</td>
<td>Spinel, Cubic, Fd-3m</td>
</tr>
</tbody>
</table>
As described in the Experimental Section (section 3.2.7), Swagelok cells were assembled using a positive electrode (cathode) which contained 80 wt% of active material (commercial LMO4). The electrochemical performance is shown in Figure 4.18. Typical specify capacity vs voltage or charge/discharge profiles at two different current rates (C-rates of C/10 and C/5) within a potential range of 3.0 - 4.3 V are depicted in Figure 4.18 (a). The discharge capacities at C/10 and C/5 were 99.8 mAh/g and 90.1 mAh/g, respectively. Both the current vs voltage (CV) and charge/discharge profiles (Figure 4.18 (a) and (c)) clearly show two consecutive slowly increasing (for charge) and decreasing (for discharge) plateaus, viz., one at 3.8/4.0 V and the other one at 4.1/4.15 V. These two galvanostatic platforms corresponded to a two-step redox reaction where half of the lithium is inserted or extracted at each step. Sharp and well-defined peaks in the CV curve suggested high crystallinity of the LMO4 powder in the electrode and good kinetics for lithium ion transport within it bulk. After the first cycle, all CV profiles were well-overlapped suggesting good reversibility of the electrochemical lithium intercalation and de-intercalation.

The rate performance of the batteries made using commercial LMO4 powder is shown in Figure 4.18 (b). A total of 60 full cycles using different C-rates such as C/10, C/5, C/2, 1C and over five repetitions were tested. It can be seen how the capacity decreased with an increase in the C-rate and number of cycles. However the battery showed good rate capability and cycle stability, which meant that after cycling the battery at C/5, C/2 and 1C for 3 cycles each, the battery recovered its capacity at C/10. Furthermore, after 48 cycles for instance, the battery capacity was 72.2 mAh/g at C/10, which corresponded to 82% of the initial capacity (87.9 mAh/g).

The electrochemical impedance spectroscopy (EIS) performed on the batteries made with the commercial LMO4 is presented in the form of Nyquist plots in the Figure 4.18 (d). Before the EIS measurement, the battery was charged at C/5 up to 4.2 V and held for 1 h at the same voltage. The Nyquist plot show both the semicircle and straight line regions corresponding to the kinetic control and mass-transfer control reactions, respectively. From this measurement and using an equivalent circuit information about the charge
transfer resistance, the solution resistance could be obtained. In this case, and based on the equivalent circuit shown in the inset in the Figure 4.18 (d), the solution resistance and the charge transfer resistance were determined to be 5.8 Ω and 75.0 Ω, respectively.

Figure 4.18. Electrochemical characterization of the commercial LiMn$_2$O$_4$ powder.

4.5.2 Phase Evolution of the LiMn$_2$O$_4$ Compound

The phase evolution of the LiMn$_2$O$_4$ phase in air at different temperatures and cation:organic ratios are shown in Figures 4.19 to 4.21. The LiMn$_2$O$_4$ compound has a mixed (intermediate) oxidation state +3/+4, and it is a compound that has shown sufficient electrochemical performance to be attractive for industrial production and commercialization.
In all cases a highly exothermic reactions were noticed during the synthesis processes on the hot plate. The amount of gases and strengths of the exothermic reactions were directly dependent on the cation:organic ratios, being the 6:1 ratio the less violent while 4:1 and 2:1 were highly exothermic but non-differentiable between them. LiMn$_2$O$_4$ phase was found as the main phase when working with cation:organic ratio of 2:1 and 6:1 (Figure 4.19. and Figure 4.21.), but a small amount of Mn$_2$O$_3$ phase was also found in some samples. Since in this secondary phase the Mn was +3, it was believed that working with these ratios there were an imbalance of the nitrate:organic ratios during the exothermic reactions, which led to an excess of carbon or nitrates contributing to an excessive reduction of some Mn$^{+4}$ to Mn$^{3+}$. Again, these reactions were carried out in a pot on the hot plate followed by treatment inside a box furnace where air was not flowing, so the micro-atmosphere generated by the CO$_x$ and NO$_x$ gases played an important role on the oxidation state of the powders produced.

Figure 4.19. X-ray diffractograms of the LiMn$_2$O$_4$ synthesized in air using a 2:1 cation:organic ratio in the range 300°C - 800°C.
The cation:organic ratio of 4:1 was found to be the best condition to produce pure LiMn$_2$O$_4$ phase at all temperatures starting right after the exothermic reaction. In this condition, the cation:organic ratio was well-balanced which provided a good steric entrapment (avoid component segregation) and generated a highly exothermic reaction to induced crystallization of the single phase without forming any intermediate or secondary phase. At 300°C diffracted peaks were broad and less intense suggesting formation on nanoparticles.

Figure 4.20. X-ray diffractograms of the LiMn$_2$O$_4$ synthesized in air using a 4:1 cation:organic ratio in the range 300°C - 800°C.
4.5.3 Physico-chemical Characterization of the LiMn₂O₄ compound

The microstructure of the LMO₄ powders produced in air and in the range of 300°C to 800°C using a cation:organic ratio of 4:1 is depicted in Figure 4.22. At low temperatures, 300°C – 400°C (Figure 4.22 (a) to (d)), porous secondary particles could be observed. These secondary particles were soft agglomerates, easy to break by hand, and fluffy. These characteristics were attributed to the violent exothermic reaction as well as the release of gases during the reaction. Secondary particles at 300°C and 400°C were composed of primary nanoparticles in the range of 10 nm – 50 nm. At 500°C (Figure 4.22 (e) and (f)), crystals grew and the onset of the sintering process (necking) could be observed. At this temperature crystals of about 80 nm were found.

Upon increased temperatures (600°C – 800°C), crystals grew and sintering of the primary particles become more pronounced. Figure 4.23 (a) through (d) are SEM images of powders made at 600°C and 700°C, where crystals between 80 nm and 120 nm were
imaged. Moreover, at 800°C (Figure 4.23 (e) - (f)), primary crystals of 100 nm – 500 nm appeared to be pre-sintered. A noticeable reduction in porosity and surface area were evident in the images and along with the increased crystal sizes, this agreed with the sharp and intense peaks observed in the XRD analysis.

A transmission electron microscopy (TEM) analysis was performed on the samples synthesized at 300°C, 400°C and 500°C (Figure 4.24) with the aim to clearly see and measure the sizes of the nanocrystals. Furthermore, selected area diffraction patterns (SAD) were also taken in order to confirm the crystallinity of the powders and the LiMn$_2$O$_4$ phase. Figure 4.24 image nanocrystals in the range of 10 nm to 60 nm for the LMO4 powder produced at temperatures between 300°C and 500°C. Figure 4.24 (b) and (f) are the indexed SAD patterns for the LMO4 crystallized at 300°C and 500°C, respectively. It can be observed that the seven first rings corresponded to the seven first hkl diffraction peaks (111, 220, 311, 222, 404, 331, 511) observed in the XRD data for the cubic LMO4 phase.

In order to correlate the previous findings, specific surface area (BET) and particle size analysis measurements were carried out. Figure 4.25 depicts and compares the specific surface area (SSA) of the LMO4 powders produced in this study (at 300°C, 500°C) and 700°C with the commercial LMO4 powder. As it was suggested by the XRD and SEM images, that the lower the heat treatment temperature, the smaller the particles and less sintered materials could be obtained. At 300°C, the highest surface area for LMO4 powders was obtained (14.6 m$^2$/g). At 500°C and 700°C the surface areas were 12.3 m$^2$/g and 6.4 m$^2$/g, respectively. It can be seen that at 500°C the surface area was not considerable sacrificed, a reduction of 16% was detected. On the contrary, the specific surface area of the powder treated at 700°C was reduced 56%. These results reassures the nano-dimension and high surface area characteristics of the powders suggested by SEM and XRD results. Thus, in all cases, LMO4 powders produced by the polymeric steric entrapment method exhibited smaller crystal sizes and higher surface areas (300°C - 21 times, 700°C – 9 times) than the commercial LMO4 powders.
Figure 4.22. SEM micrographs of the LiMn$_2$O$_4$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 300°C, (c) - (d) 400°C and (e) - (f) 500°C.
Figure 4.23. SEM micrographs at of the LiMn$_2$O$_4$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 600°C, (c) - (d) 700°C and (e) - (f) 800°C.
Figure 4.24. TEM images and selected area diffraction (sad) patterns of the LiMn$_2$O$_4$ powders produced using a cation:organic ratio of 4:1, (a) - (b) 300°C, (c) - (d) 400°C and (e) - (f) 500°C.
Figure 4.25. Specific surface area (SSA) of the LiMn$_2$O$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1 and compared with the commercial LiMn$_2$O$_4$.

The particle size analysis of the LMO4 powders is presented in Figure 4.26. For the particle size distribution analysis, it is often convenient to report parameters based upon the maximum particle size for a given percentage volume of the sample. Percentiles are defined as XyZ (e.g. D$_{v50}$, median particle size) where X usually is D (mean diameter), y is the distribution weighting (e.g. n for number, v for volume, i for intensity) and Z is the percentage of sample below this particle size (e.g. 50%, sometimes written as a decimal fraction 0.5). It can be seen that all curves are similar and characteristic of a mono-modal distribution. In the inset table, particular percentiles (10%, 50% and 90%) are specified for all materials. From these results, it is clear that these measurements referred to the sizes of the agglomerates or secondary particles. Multiple unsuccessful attempts were made in
order be able to measure primary crystals. These included: diluted dispersions, use of dispersants, different levels of ultrasound and stirring speeds.

In general, the median agglomerate size for all materials was in the range of 5 – 7 microns. As proven by these measurements, this type of particle size analysis cannot be used to determine the nano-character of the powders and differentiate between powders with different physico-chemical characteristics. Instead we are reporting the agglomerate size distributions.

As it has been discussed in this section, the amount of C and N in the final powders can vary depending on the initial cation:organic ratio, treatment temperature, atmosphere, processing time and how well balanced was the exothermic reaction. Figure 4.27 illustrate the C (a) and N (b) contents of the precursors using different cation:organic ratio (dried at 70°C) and the products treated at different temperatures. In first place, it can be noticed that the trend of the amount of C present in the precursor correlated with the trend of the amount of PVA entrapper added to the nitrate solutions. With respect to the 2:1 ratio (13.62 wt%), 4:1 was close to half the carbon amount (6.27 wt%), while 6:1 had almost one third of the amount of carbon. In the case of the nitrates, these values (amount in the precursors and products) were controlled by the stoichiometry and the ratio with the other components such as organics and water. That is why N contents should be of the same order as it is shown in Figure 4.27 (b). Another important proportion is the C:N ratio, because this was ultimately what controlled the exothermic reaction. Here was where drying at low temperature played an important role, because it was the way to guarantee that organics and nitrates did not decompose or evaporate before the exothermic reaction. The C:N ratios of the precursors dried at 70°C were 1.4, 0.88 and 0.4 for the 2:1, 4:1 and 6:1 cation:organic ratios, respectively. From our experience, 2:1 and 4:1 ratios produced a more violent and exothermic reaction than did the 6:1 ratio. Based on the LMO4 phase evolution discussed previously in this section, having a C:N ratio around 1 promoted the crystallization of LMO4 single phase at low temperatures (~300°C)
Figure 4.26. Particle size distribution (PSD) of the LiMn$_2$O$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1 and compared with the commercial LiMn$_2$O$_4$.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>300°C</th>
<th>500°C</th>
<th>700°C</th>
<th>Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Dv10(μm)</td>
<td>2.42</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Dv50(μm)</td>
<td>6.49</td>
<td>5.19</td>
<td>5.81</td>
</tr>
<tr>
<td></td>
<td>Dv90(μm)</td>
<td>22.60</td>
<td>17.10</td>
<td>17.50</td>
</tr>
</tbody>
</table>

Figure 4.27. Chemical analysis - carbon and nitrogen content (wt%) of the LiMn$_2$O$_4$ powders produced at 70°C, 300°C, 500°C, 700°C and 800°C using cation:organic ratio of 4:1.
Once the exothermic reactions had occurred (200°C - 300°C), the amount of carbon and nitrogen in the LMO4 powders were below 0.16 wt%. These values, especially the ones at 300°C indicated how balanced in terms of fuel and oxidizer were the reactions. Basically, all the C and N available were consumed during the combustion reactions and the energy released was effectively used to crystallize LMO4. Additionally, these analyses also suggested that the 2:1 ratio was better balanced than 6:1 and 4:1 ratios because at 300°C the carbon and nitrogen amounts were virtually zero. Furthermore, the higher the treatment temperature and processing time, the lower the amount of C and N in the final powders, a fact that can be used to design the thermal process and further improve the powders. This information could be helpful because in some applications C and N remnants can be detrimental to some properties. Here, it is important to mention that for the case of LiMnO₂, the amount of C of the sample using cation:organic ratio 6:1 treated at 700°C was 1.86 wt%, which reflects the influence of the exothermic reaction as well as the working atmosphere.

The results shown above are useful because being able to produce, in a single step, pure crystalline materials in both the nano and micron range and with high surface area using a low consumption energy method could be valuable and is quite challenging.

4.5.4 Thermal analysis (DSC) of the precursors to produce the LiMn₂O₄

As it have been elucidated in the previous sections, the characteristics of the exothermic reactions play an essential role in the synthesis (at low temperature) of materials that contained cations which can adopt multiple oxidation states. In this matter, our aim was to try to quantitatively measure the energy released by the exothermic reaction and to be able to correlate the C:N ratios with the energy required for crystallization. Unfortunately, the exothermic reactions were so violent and there were many overlapping exothermic peaks (corresponding to exothermic reactions) that it was impossible to measure the energy released during the process. Multiple attempts were carried out in order to contain the powders inside the DSC crucibles, using small amounts of samples,
sealed or crimped pans and different heating rates. Figure 4.28 summarizes the differential scanning calorimetry (DSC) results for the LMO4 dried precursor using a cation:organic ratio 4:1, which produced the LMO4 single phase.

Figure 4.28 (a) shows the effect of the sample amount on the DSC measurement. The higher the amount of sample, the more violent was the reaction and the more powder was expelled from the crucible, even when it was sealed. Additionally, with higher the amount of sample the more the crucible moved from the thermocouple placed holder which made the measurement less reliable. It was found that using less than 10 mg of sample, the measurements were at least repeatable. That is why, 5 mg of sample was selected for the next measurements.

Moreover, when the heating rate was too fast (> 10°C/min), the measurement started to show unresolved peaks and pronounced endothermic peaks right before the exothermic reactions started (Figure 4.28 (b)). Stable condition were found by working at 5°C/min and 10°C/min. As the heating rate used to synthesize LMO4 was 10°C/min, this one was the rate selected as a heating rate for the DSC measurements.

During the multiple experiments, the hygroscopic nature of the dried precursor was experienced. This fact also was noticed in the DSC curves, showing an endothermic hump between 100°C and 150°C which additionally, mitigated the exothermic reactions. Due to this effect, different pre-test drying conditions were evaluated (70°C, 150°C and no drying). It is important to clarify that the precursors were dried at 70°C to remove water as much as possible, however these pre-test dryings were additional processes to account for hygroscopic effects during storage and sample manipulation. In Figure 4.28 (c) it can be observed that drying the sample before the DSC measurements substantially removed the endothermic peak and better resolved the exothermic peaks.
Finally, the influence of the atmosphere over the exothermic reaction was evaluated (Figure 4.28 (d)). Air, nitrogen and a sealed pan were utilized even though LMO4 was produced in air. The aim of this was to try to contained the powder inside the crucible using crimped (sealed aluminum pans) and also, to identify if by working under reducing atmosphere, the strength of the exothermic reaction could be reduced. As it can be seen in Figure 4.28 (d), there were no appreciable differences between working in air versus nitrogen atmospheres. However, when working with sealed pans the intensity of the exothermic peaks were slightly reduced. This effect could be attributed to the build-up pressure inside the crucible, which could interfere with the measurement. Working with
sealed pans or pierced pans did not guarantee the containment of the powder inside the crucible.

Despite of all the difficulties with the DSC measurements, and the incapability to quantitatively measure the energy released during the exothermic reaction, some qualitative information could be extracted. For instance, the DSC measurements supported the concept of drying the precursor solution at low temperature to have full availability of the organic and nitrates to generate highly exothermic reactions by reacting together. Additionally, it showed that in all cases, the onset of the exothermic reactions was around 150°C and finished around 270°C. Furthermore, DSC curves would show that the water evaporation (endothermic humps) in the system, occurred right before the onset of the exothermic reaction, a fact that could hinder or diminish the strength of the exothermic reaction. Moreover, multiple exothermic peaks could represent different reactions, different temperature distributions through the sample and/or differences in the contact between reacting particles and the bottom of the crucibles, which is the place where the sensing thermocouples were located.

Finally, as it could be inferred from this section, that the thermal analysis measurement (to be accurate) of this type of precursors was very challenging and required possibly different equipment, techniques and special care.

4.5.5 Electrochemical Analysis of the LiMn$_2$O$_4$ Produced by the Polymeric Steric Entrapment Method

In order to evaluate the quality of the powders, electrochemical analyses were performed in batteries (Swagelok cells) made using LMO4 active powders in the cathode (positive electrode) and lithium metal as the negative electrode (anode). As many different components affect the battery performance, as well as the electrode preparation and battery assemble process, it was preferred to compare the performance of the batteries against batteries made using commercial LMO4 and the same elaboration process and components (describe in the Experimental Section 3.2.7).
Figures 4.29 to 4.32 summarize the electrochemical performance of the half cells (batteries) made using LMO4 synthesized by the polymeric steric entrapment method at 300°C x 2 h, 300°C x 20 h, 500°C x 2 h and 700°C x 2 h. The electrochemical performance of the powder made at the lowest temperature and shortest processing time (300°C 2 h) is seen in Figure 4.29. Typical charge/discharge curves at two different C-rates (C/10 and C/5) within a potential range of 3.0 - 4.3 are presented in Figure 4.29 (a). It can be noticed that the discharge capacities at C/10 and C/5 were 93.3 mAh/g and 88.9 mAh/g, respectively, and that the two typical plateaus for LMO4 were located at 3.9/4.1 V and 4.1/4.2 V. This behavior was also supported by the CV profiles (Figure 4.29 (c)) where the two peaks (broader than the commercial powder) corresponding to the redox couple can be observed. It can be seen that the first step redox reaction was shifted towards higher voltage (upon charging) and caused overlap between the two-step redox reactions. After the first cycle, all CV profiles were almost overlapping, suggesting good reversibility and stability of the electrochemical lithium intercalation and de-intercalation.

The rate and cycle stability (longevity) performances were evaluated (over 26 (284 h) cycles and different C-rates (C/10, C/5, and C/2)) and are presented in Figure 4.29 (b). As usual, the capacity decreased with increased in C-rate. However, the battery showed good recovery (rate capability) after charging/discharging at C/2. For instance, in the 4th cycle (C/5) the specific capacity was 89.4 mAh/g, while the capacity in the cycle 26th (at C/5) was 80.2 mAh/g (90%).

Figure 4.29 (d) depicts the typical EIS measurement of the cell when it was charged at C/5 up to 4.2 V and held there for 1 h at the same voltage. The plot reveals the characteristic semicircle and straight line regions corresponding to the kinetic control and mass-transfer control reactions, respectively. As for case of the commercial LMO4, the inset equivalent electric circuit model was used to calculate the solution resistance and the charge transfer resistance (9.7 Ω and 940.5 Ω, respectively).

A battery using the LMO4 synthesized at 300°C x 20 h was tested in order to evaluate the effect of the annealing temperature on the electrochemical performance. This annealing time could take the reactions up to full completion and improved the crystallinity of the
powder. Furthermore, it could reduce the remnant carbon and nitrogen contents in the powders, which may not be electrochemically active and could reduce the specific capacity.

Figure 4.29. Electrochemical characterization of the LiMn₂O₄ powder produced at 300°C x 2 h using cation:organic ratio of 4:1.

Figure 4.30 presents the electrochemical characterization of the 300°C x 2h cell in the same fashion that for the LMO4 commercial powder. It can be observed that the charge/discharge and CV curves for the 300°C x 20 h cells were very similar to the corresponding curves for the 300°C x 2 h batteries. The specific capacity at C/10 and C/5 (Figure 4.30 (a)) were 92.3 mAh/g and 89.1 mAh/g, respectively. Rate capability and cycle
stability (longevity) performances (Figure 4.30 (b)) were evaluated over 30 (584 h) cycles and the C-rates were C/10, C/5, and C/2. No significant differences were found in the charge/discharge profiles, cyclability and rate performance between powders produced at 300°C and annealed for 2 or 20 h. However, a difference was encountered in the EIS measurements (Figure 4.30 (d)). A lower charge transfer resistance (242.9 Ω) when the powder was annealed for 20 h was found, in contrast to a 940.5 Ω calculated for the charge transfer resistance in the cell made using powder annealed for 2 h. This could be attributed to a better organization of the atoms in the crystal structure (crystallinity) which reduced the resistance of the electron movements in the bulk.

Figure 4.30. Electrochemical characterization of the LiMn$_2$O$_4$ powder produced at 300°C x 20 h using cation:organic ratio of 4:1.
In order to see the effect of the synthesis conditions on the electrochemical performance, batteries using powder produced at 500°C x 2 h (Figure 4.31) and 700°C x 2 h (Figure 4.32) were made. Upon increase in synthesis temperature, the two-step redox reaction plateaus on the charge/discharge profiles were found to be more defined and flattened. This fact can also be observed in the CV curves, where sharper and less overlapped peaks were obtained. In all cases the CV curves at different cycles overlapped suggesting again the good reversibility of the redox reactions. For the case of 500°C, the specific capacity at C/10 and C/5 (Figure 4.31 (a)) were 110 mAh/g and 107 mAh/g, respectively. In comparison, for the 700°C cell, the specific capacities at C/10 and C/5 (Figure 4.32 (a)) were 131.8 mAh/g and 128.3 mAh/g, respectively. It is important to remember that the theoretical specific capacity for LMO4 is 148 mAh/g. In both cases (500°C and 700°C) the batteries were charged and discharged at C/10, C/5, C/2 and 1C. Both batteries showed good rate capability (capacity retention) and cycle life. 500°C and 700°C cells were cycled for a total of 38 (342 h) and 60 (540 h) cycles, respectively. The EIS measurements were similar to the curves presented for the previous conditions shown above and the same equivalent electric circuit was used. The solution resistance and the charge transfer resistance for the 500°C cell were 9.2 Ω and 411.7 Ω, respectively, while for the 700°C battery they were 10.19 Ω and 348.38 Ω, respectively.
Figure 4.31. Electrochemical characterization of the LiMn$_2$O$_4$ powder produced at 500°C x 2 h using cation:organic ratio of 4:1.

It is important to mention that the specific capacity measurement was dependent on the mass of the active material and in the Swagelok cell configuration, the electrode contained just about 0.0020 grams of active powder (80 wt% of the cathode material)), while the weight of the current collector (Al foil) was about 0.0054 g. This situation, along with the preparation of 2 grams of slurry per batch for the electrode preparation, resulted in the fact that the specific capacity measurement was highly variable.
Figure 4.32. Electrochemical characterization of the LiMn$_2$O$_4$ powder produced at 700°C x 2 h using cation:organic ratio of 4:1.

4.6 Summary

This chapter presented different synthesis conditions for producing Mn-based compounds and how the synthesis variables controlled the exothermic reactions, crystallization temperature, phase evolution and oxidation states. It has been shown how some physico-chemical characteristics such as, crystal sizes, surface area, and C and N content in the final products could be tuned during the synthesis process.

The first important condition that has to be controlled when using the polymeric steric entrapment method is the proper dissolution and intimate mixing of the reagents (at atomic or ionic level). This can be achieved by finding the proper dissolution medium (water or alcohol), order of addition and pH. For the specific case of the M$_1$Mn$_x$O$_y$ compounds
studied in this work, water and no pH modification was utilized in order to achieve full dissolution of the nitrates.

Moreover, it has been found that in order to control the oxidation state of the intermetallic cation (Mn in this case) not only the working atmosphere has to be controlled, but also, the cation:organic ratio play an important role. This latter can generate a micro-atmosphere that can modify the reduction or oxidation process. It was found that 700°C in forming gas and using cation:organic ratio 6:1 was the best condition to produce LiMn$^{3+}$O$_2$. For the case of LiMn$_2^{3+/4+}$O$_4$ it was found that the phase pure powder can be produced as low as 300°C using cation:organic ratio 4:1 and air as working atmosphere. Furthermore, the LMO4 phase was found to be stable at all temperatures in the evaluated range (300°C – 800°C). Moreover, it has been demonstrated that the best conditions to produce the Li$_2$Mn$^{4+}$O$_3$ phase were working in air and using cation:organic ratio 4:1 and air as working atmosphere. For this compound, pure phase was produced at temperatures higher than 500°C, and it is believe that the Li$_2$CO$_3$ secondary phase, found at temperature below 500°C, could be removed if flowing gas (air) and a better interaction between gas and reacting powder can be used.

It is important to remark that the crystalline phases in the M$_1$Mn$_x$O$_y$ family could be obtained at low temperatures (~300°C) by taking advantage of the highly exothermic reactions produce by the decomposition of nitrates and organics. This could be done by carefully remove the solvent (water) by drying at low temperature (70°C – 80°C), which guaranteed control of the nitrate:organic ratio.

Finally, it has been shown that the crystal sizes (nano to micron range) and specific surface areas can be tuned by modifying the calcining and annealing temperature. Moreover, the electrochemical performance determined by the specific capacity of the powders made at 300°C was found to be at least of the same order as that of the commercial LMO4 powders. Furthermore, for the powders produced at 500°C and 700°C, the specific capacities were always higher than the commercial powders. CV behavior, C-rate and cycle life of batteries made in this project were all similar, comparable and even superior to the batteries made using commercial LMO4.
CHAPTER 5
SYNTHESIS AND CHARACTERIZATION OF THE TITANIUM
PHOSPHATE-BASED COMPOUNDS (M\textsubscript{1}Ti\textsubscript{2}(PO\textsubscript{3})\textsubscript{4}, M\textsubscript{1}=Li, Na, K)

RESULTS AND DISCUSSION

5.1 Introduction

As it was pointed out before, M\textsubscript{1}Ti\textsubscript{2}(PO\textsubscript{3})\textsubscript{4} model system was selected because it gave us the opportunity to explore synthesis variables in order to solve different problems encountered with some reagents such as Ti source (titanium isopropanoxide – TISO which is insoluble in water). The synthesis behavior discussed in the previous section for the M\textsubscript{1}Mn\textsubscript{x}O\textsubscript{y}, differs in the sense that for the M\textsubscript{1}Ti\textsubscript{2}(PO\textsubscript{3})\textsubscript{4} system, the reagent is an alkoxide which decomposes very quickly when mixed with water. In this case, a single solvent (water) could not be used to dissolve all reagents, thus to complete full dissolution (atomic mixing) was the great challenge. Fast and isolated decomposition of the Ti source promoted phase segregation and formation of unwanted secondary phases, obstructing the formation of the desired single phase.

Moreover, this system provided the opportunity to explore the synthesis conditions to produce materials with compositions that are attractive and possess high technological importance. For instance, M\textsubscript{1}Ti\textsubscript{2}(PO\textsubscript{3})\textsubscript{4} compounds belong to the NASICON-type (sodium super-ionic conductor) compounds [100-107] which are based on the NaZr\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (NZP) family. Lately, LiTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (LTP), Li\textsubscript{1.3}Al\textsubscript{0.3}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{3} (LATP) and NaTi\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (NTP) have been investigated as electrolyte due to their fast ionic conduction property [135-139]. These materials have been typically produced by solid stated reaction and glass-ceramic methods where high temperatures and prolonged processing time favored Li evaporation, which made the phase and composition control more difficult. Additionally, large amount of glassy phase was formed, deteriorating the properties of the compounds.

Furthermore, these materials have attracted considerable attention for displaying the unusual property of negative, or very low, thermal expansion [100-106]. Additionally, they exhibited anisotropic coefficients of thermal expansion (CTE), with expansion in two
axial directions but a contraction in the third one. Also, materials from the $M_1Ti_2(PO_3)_4$ family such as $NaTi_2(PO_3)_4$ and $LiTi_2(PO_3)_4$, have been proposed as anodes for both lithium and sodium ion batteries.

In the following sections, we will see that even though the titanium isopropoxide decomposes when it is mixed with the water-soluble reagents, actions such as having an excess of isopropyl alcohol, $HNO_3$ addition, flocs disintegration by mechanical stress and specific order of addition of the reagents, slowed down the Ti decomposition and favored the formation of single phases. The physico-chemical properties for LTP, LATP, NTP and KTP powders will be presented as well as their thermal expansion behavior.

5.2 Dissolution of the Reagents to Produce Powders in the $M_1Ti_2(PO_3)_4$ Family

In general for the $M_1Ti_2(PO_3)_4$ system, the Ti cation adopted the +4 oxidation state (highest one) which allowed us to work in an oxidative atmosphere. For this family, air was selected as a working atmosphere. For all compositions, initially all the cation reagents, but especially the Ti source, dissolved easily in water. Titanium isopropoxide dissolved and stayed stable in isopropyl alcohol. Detailed information about the reagents, their dissolutions and mixing procedure were presented in the Experimental Section 3.1.2. The pH of the different solutions are presented in Table 5.1.

For the case of LTP and LATP a precipitation situation was encountered a couple of minutes (depending on the pH) after Li, P and Al solutions were mixed together. Applying knowledge from other systems such as the $LiFePO_4$ family [59, 60], a pH modification was employed. A clear solution could be obtained and kept stable in all cases for LTP and LATP when $HNO_3$ was added to the solution in order to preserve the pH below 4.4. Figure 5.1 shows how the precipitation condition of the solution was reversible upon change in pH by adding $HNO_3$.  

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Table 5.1. pH of each Cation Solution and each Mixing Step to Produce M$_1$Ti$_2$(PO$_3$)$_4$ Compounds

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Molarity (Mol/L)</th>
<th>pH</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO$_3$</td>
<td>1.85</td>
<td>8.7</td>
<td>Clear</td>
</tr>
<tr>
<td>NaNO$_2$</td>
<td>2.29</td>
<td>8.8</td>
<td>Clear</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>0.59</td>
<td>7.7</td>
<td>Clear</td>
</tr>
<tr>
<td>Al(NO$_3$)$_3$ ● 9H$_2$O</td>
<td>0.52</td>
<td>2.0</td>
<td>Clear</td>
</tr>
<tr>
<td>Ti[OCH(CH$_3$)$_2$]$_4$</td>
<td>1.98</td>
<td>6.9</td>
<td>Clear</td>
</tr>
<tr>
<td>((NH$_4$)$_2$HPO$_4$</td>
<td>3.13</td>
<td>8.0</td>
<td>Clear</td>
</tr>
<tr>
<td>Li + Al</td>
<td>-</td>
<td>2.4</td>
<td>Clear</td>
</tr>
<tr>
<td>Li + P</td>
<td>-</td>
<td>7.2</td>
<td>White</td>
</tr>
<tr>
<td>Na + P</td>
<td>-</td>
<td>7.8</td>
<td>Clear</td>
</tr>
<tr>
<td>K + P</td>
<td></td>
<td>7.8</td>
<td>Clear</td>
</tr>
<tr>
<td>Li + P + HNO$_3$</td>
<td>-</td>
<td>&lt; 4.4</td>
<td>Clear</td>
</tr>
<tr>
<td>Li + Al + P</td>
<td>-</td>
<td>6.7</td>
<td>White</td>
</tr>
<tr>
<td>Li + Al + P + HNO$_3$</td>
<td>-</td>
<td>&lt; 4.4</td>
<td>Clear</td>
</tr>
</tbody>
</table>

As mentioned in the Experimental Section 3.1.2, Ti containing solution remained stable (no decomposition) until mixed with the all–containing, water soluble, cation solution. From our experience, vastly alcoholic diluted systems (massive excess of alcohol and small amounts of water) or very acidic (high amount of HNO$_3$) helped to slow down the decomposition of the Ti source and to break down the precipitates, respectively. Unless these conditions were found to be helpful for the formation of the single phases, they were not practical for scaling up and industrialization, and they turned out to be expensive and inconvenient. In contrast, using a mechanical force to break down the gel (formed after the mixing of the water soluble solution with the Ti and EG containing solution) was found to be a preferable and a practical process to produce the desired phases in a more efficient manner. This process helped to avoid the use of acid and large amounts of alcohol.
Figure 5.1. Solution precipitation reversibility upon change in pH by HNO₃, (a) reagent clear solutions, (b) precipitation when Li and P solutions were mixed and (c) clear solution after adding HNO₃ to change the pH below 4.4.

5.3 Synthesis of the LiTi₂(PO₃)₄ Compound

5.3.1 Phase Evolution of the LiTi₂(PO₃)₄ Compound

In this system, as well as in the case of the MₓMₙOᵧ family, exothermic reactions were also noticed during the drying and calcining process. However they were not energetic enough to induce crystallization as low a temperature as in the MₓMₙOᵧ family. Apparently, some exothermic reactions such as decomposition and combustion of the alcohols, nitrates and organics occurred at low temperature but they were not coupled and occurred at different temperatures. This fact along with a possible higher crystallization activation energy for materials in this family, prevented the crystallization of the compound at lower temperatures. However, using the polymeric steric entrapment method, the mixing of the regents was carried out at the ionic level and long-range diffusion of the cations was not required. Therefore, the desired compounds where crystallized at lower temperatures than the temperatures required by other methods such as solid stated reaction and glass-ceramic methods. Additionally, the oxidative powders of the nitrates and the organics were not reducing enough to decrease the oxidation state of the Ti cation. Therefore, in this system the cation:organic ratio played only the role of steric entrapper required to avoid
segregation or agglomeration of the cations which prevented the formation of secondary phases.

For the synthesis of LiTi$_2$(PO$_3$)$_4$ which is the compound containing the smallest alkali metal cation (Li), three different cation:organic ratios were evaluated. Figures 5.2 through 5.4 show the phase evolution of the LiTi$_2$(PO$_3$)$_4$ in the 500°C – 1100°C temperature range. Different cation:organic ratios (2:1, 4:1 and 6:1) and air as atmosphere were tested. At all cation:organic ratios, it can be seen that at 500°C the powders were amorphous. Broad and less intense peaks were found at 600°C which suggested that the crystallization process started somewhere between 500°C and 600°C. It is important to mention that in all cases the comparison or indexing of the XRD patterns were made using the ICDD database because there were no commercial powders for any of the compositions in this family. In all figures containing X-ray diffraction data, the bottom XRD pattern correspond to ICDD reference.

It can be noted that by working with cation:organic 2:1 (Figure 5.2) and 600°C, a more intense and sharper peaks than when working at 500°C were found. However some very little unidentified peaks around 24° 2θ were noticed. During the peak search and match indexing process some C and N containing compounds contained these unidentified peaks, however the evidence was not conclusive. On the other hand, these secondary phases where not found in the powders made using cation:organic ratios 4:1 and 6:1 (Figures 5.3 and 5.4, respectively). In the 4:1 and 6:1 cases, the XRD patterns looked broad and less intense suggesting formation of either nanoparticles or powders with some amorphous content.

On the other hand, in some cases when the mechanical breakage of the gel (or agglomerates) was not satisfactory, some secondary phases such as TiO$_2$, Ti$_2$PO$_7$ were found in the powders at temperatures between 800°C – 900°C. Usually, if the amount of secondary phases was small, at temperature above 900°C, they recombined due to diffusional processes and formed single phases.
Figure 5.2. X-ray diffractograms of the LiTi$_2$(PO$_3$)$_4$ synthesized in air using 2:1 cation:organic ratio in the range 500°C - 1100°C.

Figure 5.3. X-ray diffractograms of the LiTi$_2$(PO$_3$)$_4$ synthesized in air using 4:1 cation:organic ratio in the range 500°C - 1100°C.
The cation:organic ratio 4:1 (Figure 5.3) was selected as the safer condition for the entrapment of the cations and formation of pure LiTi₂(PO₃)₄. This precursor was analyzed by a simultaneous differential scanning calorimeter (DSC)/thermogravimetric (TG) analyzer in order to see at which temperature some thermal process (such as combustion and crystallization) occurred. Figure 5.5 depicts the DSC/TG analyses from room temperature up to 1200°C for the LTP precursor. It is important to remember that this precursor was pre-calcined at 200°C x 2 h in air. Three exothermic peaks could be clearly observed in the figure. The two first exothermic peaks (200°C - 320°C and 350°C - 630°C) could be associated with the reaction between nitrates and organics as in the case of the Mn₃O₇. Moreover, the third exothermic peak (690°C - 750°C) could represent the onset of the crystallization process, which is closed to the crystallization temperature observed by the XRD studies.
Figure 5.5. DSC/TGA curves of the LiTi$_2$(PO$_4$)$_3$ (LTP) precursor powders made by the polymeric steric entrapment method.

Figure 5.5 also shows a total mass loss of 42.54 wt%. The mass loss occurred in a three-step process, the first between 20°C and 230°C, resulting in a 5.62 wt% loss; the second between 230°C and 280°C with a weight loss of 31.94 wt% loss, and the final step from 280°C to 500°C which resulted in a loss of 4.98 wt%. The first small weight loss could be attributed to water and alcohol removal, while the second large weight loss stage could be related to the removal of nitrates and organics through the combustion reaction. The third and final stage could be associated to the removal of the unreacted or remnant carbon and nitrates.

The powders produced using this condition were further analyzed in order to understand the effect of the temperature on the microstructure, chemical composition, surface area and particles size.
5.3.2 Physico-chemical Characterization of the LiTi$_2$(PO$_3$)$_4$

Figure 5.6 shows the SEM images of the powders calcined at 500°C ((a) - (b)) and 600°C ((c) - (d)), temperature range where the transition from the amorphous phase to the crystalline phase occurred. Nanoparticles with no specific shape can be observed forming larger micron-sized secondary particles or agglomerates (Figure 5.6 (a)). At 500°C amorphous nanoparticles in the range of 10 nm – 20 nm were found while at 600°C crystalline nanoparticles of about 40 nm were observed. No necking between crystals and porous secondary particles were observed, suggesting a low degree of sintering and high specific surface area.

The microstructures of the powders produced at 700°C and 1000°C are shown in Figure 5.7 (a) - (b) and (c) - (d) respectively. At 700°C a better crystallized powder than at 600°C was observed, where necking between particles and crystal growth could be appreciated. Crystals of 70 nm - 90 nm were observed. Moreover, powders at 1000°C grew up to form crystals in the range of 300 nm – 1 µm. Figure 5.7 (d) also shows how the sintering process through mass diffusion took place, binding together initial primary crystals to form larger crystals. At this temperature particles what used to be soft secondary particles or agglomerates composed of small crystals became a single, pre-sintered, porous particle.
Figure 5.6. SEM micrographs at of the LiTi$_2$(PO$_4$)$_3$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 500°C and (c) - (d) 600°C.

As expected, when crystals grow and sinter, the surface area must be reduced. This effect is clearly depicted by Figure 5.8, where the specific surface areas of the amorphous powder (500°C), and powders crystallized at 600°C, 700°C and 1000°C are presented. It can be observed that, as suggested by the SEM images (crystal sizes in the nano range), powders with high surface area could be obtained. For the amorphous powder the specific surface area was 121.0 m$^2$/g, and then, once crystallization started, the crystals rapidly grew and lost surface area. At 600°C, where it was believed that still not all of the powder was fully crystalline (due to a small hump in the XRD data), the surface area decreased by 62% to 46.1 m$^2$/g. At 700°C, powder considered to be crystalline and with crystals still in the nano range, the surface area was 16.2 m$^2$/g which was 13.4% and 35.1% of the surface area of the amorphous and the powder crystallized at 600°C, respectively. For the case of the
powder treated at 1000°C, the specific surface area was only 2.3 m²/g which was a reduction of 98.1%, 95.0% and 85.8% of the surface area of the amorphous (500°C), 600°C and 700°C powders, respectively. These results demonstrate the importance of the temperature on the crystal growth and sintering behavior, which in the end influences the specific surface area. This knowledge is useful from the process design point of view, where the synthesis variables can be tuned to obtain the single crystalline phase with a specific crystallite size and surface area which improve, for instance, the reactivity and sinterability of the powders. These desired improved features may influence the ionic transport and mechanical properties (density) of the end products.

Figure 5.7. SEM micrographs at of the LiTi₂(PO₄)₃ powder produced using a cation:organic ratio of 4:1, (a) - (b) 700°C and (c) - (d) 1000°C.
The particle size analyses of the agglomerates or secondary particles are shown in Figure 5.9. It is evident that these measurements do not reflect the nano-sized nature of the synthesized powders. While the effect of lower synthesis temperature on producing smaller the particles size has been proven by the SEM and surface area measurements, we can see that in these measurements the opposite occurred. This effect is attributed to the agglomeration of the small particles that took place due to the high surface area. The particle size distribution curves revealed humps in the upper and lower regions of the curves with suggested multimodal distributions due to the strong agglomeration of the particles. Multiple trials using different conditions such as different ultrasound and stirring levels as well as dispersant additions were tested. However, unless repeatable measurements were obtained, a monomodal distribution could not be achieved.

Figure 5.8. Specific surface area (SSA) of the LiTi$_2$(PO$_3$)$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1.
Finally, as previously stated in this work, it is important to know the carbon and nitrogen content of the powders produced by this method. The effect of the cation:organic ratio on the C and N amounts in the final powders was measured using LTP as the model compound. Figure 5.10 presents the C and N content for LTP powders produced using 2:1, 4:1 and 6:1 cation:organic ratios and crystallized at 500°C, 600°C, 700°C and 1000°C. In this case it is predictable that the higher the temperature and the longer the processing time, the lower the amount of C and N will be. This happens because by working in air, C and N remainders after the exothermic reaction will react with the oxygen in the air and they will form COx and NOx. However, the quality of the exothermic reaction, and thus the consumption of C and N during the combustion reaction will dictate the remnants of these two elements in the final powders. From Figure 5.10, it can be noticed that the highest amounts of C (2.04%) and N (2.36%) in the powders were encountered at 500°C when working with cation:organic ratio of 2:1. In contrast, working with cation:organic ratios of 4:1 and 6:1, the C and N amounts were virtually zero at 500°C. These results suggested that the combustion (exothermic) reaction is better balanced (in terms of C, N and O2) when working with cation:organic ratios of 4:1 and 6:1. In all cases, after 700°C the C and N amounts were virtually zero. This information could be relevant because unreacted carbon and nitrogen could form gases during the sintering process at higher temperature and be detrimental to the density properties.
Figure 5.9. Particle size distribution (PSD) of the LiTi$_2$(PO$_3$)$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1.

<table>
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<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500°C</td>
</tr>
<tr>
<td>Particle size</td>
<td></td>
</tr>
<tr>
<td>D$_{v10}$($\mu$m)</td>
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<tr>
<td>D$_{v50}$($\mu$m)</td>
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<td>D$_{v90}$($\mu$m)</td>
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Figure 5.10. Chemical analysis - carbon and nitrogen content (wt%) of the LiTi$_2$(PO$_3$)$_4$ powders produced at 500°C, 600°C, 700°C and 800°C using cation:organic ratio of 4:1.
5.3.3 Thermal Expansion Behavior of LiTi$_2$(PO$_3$)$_4$

As was described in the Experimental Section 3.2.6, the thermal expansion behavior of LiTi$_2$(PO$_3$)$_4$ phase was performed by packing the sample into a quartz capillary and then placing it in the center of the quadruple lamp furnace (QLF) which was centered at the center of the diffractometer. The specific wavelength was defined by the energy of the incident synchrotron X-ray radiation and it was accurately determined by the Rietveld refinement of the NIST LaB$_6$ standard (SRM 660a). X-ray diffraction patterns were collected at each temperature in the range of room temperature (~27°C) to 1037°C. The X-ray patterns were refined by the Rietveld method using the GSAS and EXPGUI software packages. From these refinements CIF files (crystallographic information files) containing the values of the lattice parameters, \(hkl\) and corresponding \(d\)-spacings were created. Additionally, by using the \(hkl\) listings and their corresponding \(d\)-spacings as a function of temperature, the thermal expansion coefficients (CTEs) were calculated by using the CTEAS program. The polynomial fitting used during the CTEs analysis was of the order two (a quadratic function) which gave an R-square fitting parameter of 0.99.

The lattice parameters (\(a\) and \(c\) of the hexagonal system), the volume of the cell and the coefficient of thermal expansion (\(\alpha_{11}\) and \(\alpha_{33}\)) as a function of temperature are plotted in Figure 5.11 and listed in Table 5.2.

It can be observed how both the \(a\)-axis and \(c\)-axis expanded (increased) upon increasing the temperature (Figure 5.11 (a) – (b)). Both the \(a\)- and \(c\)-axis expansion followed a second-order polynomial trend, but the \(a\)-axis reached a plateau above 1000°C before melting. Additionally, the volume of the cell expanded about 2.9% over the entire temperature range as depicted in Figure 5.11 (c). In order to compare the expansion of both \(a\)- and \(c\)-axis, they are plotted together in the same scale (Figure 5.11 (d)). It is shown that the expansion of both axes was very small and specifically for the \(a\)-axis, it showed a near zero thermal expansion over the 27°C – 1000°C range. Furthermore, it can be observed in Figure 5.11 (e) – (f) that the thermal expansion behavior of the \(\alpha_{11}\) and \(\alpha_{33}\) coefficients were not constant (single value) as has been erroneously reported in the literature. On the contrary, the values of the coefficients of thermal expansion varied with
temperature. For the case of $\alpha_{11}$, it was always positive (a-axis expanding) but decreased its value upon the increase of temperature which meant that the a-axis was expanding at a decreasing rate. Moreover, the $\alpha_{33}$ was always increasing and positive in the entire temperature range, which meant that the c-axis increased at an increasing rate upon an increase in temperature. Furthermore, these effects could also be seen in the thermal expansion quadric surfaces at 25°C, 500°C, and 1000°C (Figure 5.12). The blue color of the surface along the z direction represents the positive behavior of the $\alpha_{33}$, while the surfaces along the x and y directions (equal) cannot be seen (unless it is positive) because its value is very small (near zero). Moreover, a donut shape in the x–y plane would be expected due to the equivalent values for $\alpha_{11}$ and $\alpha_{22}$, which is also expected for hexagonal systems. These quadric surfaces are the 3-dimensional representation of the thermal expansion tensor which could be used to find the thermal expansion value for any crystallographic plane ($hkl$).

The mechanism for the low/near-zero/negative thermal expansion behavior of the $\text{M}_1\text{Ti}_2(\text{PO}_3)_4$ family has been explained previously [118, 140]. It is attributed not only to the cooperative rotations of linked polyhedra (TiO$_6$ and PO$_4$) but also, to the relative expansion/contraction of the occupied and vacant M1 sites. Additionally, it has been proposed that polyhedral distortions (Ti–O–P bridging bond angles) contribute to the low/near-zero/negative thermal expansion of $\alpha_{11}$ [104, 115, 116].

Using the refinements made from the synchrotron data (CIF files), a polyhedral model of the crystal structure of LTP was constructed (Figure 5.13), using VESTA software version 3.2.1. In this 3-D graphic representation, it can be observed how every cation (Li, Ti and P) is shielded by oxygen anions and that the titanium octahedra are linked in every corner with phosphorous tetrahedra. Additionally, there are channels along the a-axis where Li can easily move throughout the structure. This last fact is thought to be responsible for the fast ionic conductivity behavior of this type of materials. The inset table provides the lattice parameters, volume of the cells, angles and space groups of both the room temperature and maximum temperature evaluated in the in-situ high temperature synchrotron studies.
Figure 5.11. Lattice parameters for the a- and c-axes ((a), (b) and (d)), cell volume (c) and components of the thermal expansion tensor $\alpha_{11}$ and $\alpha_{33}$ ((e) – (f)) for the LiTi$_2$(PO$_3$)$_4$ in the hexagonal system.
<table>
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<tr>
<th>T (°C)</th>
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Table 5.2. Lattice Parameters, Volume and Coefficient of Thermal Expansion

Tensor Values of the LiTi₂(PO₃)₄
Figure 5.12. Quadric surfaces describing the thermal expansion in three-dimensions of the LiTi$_2$(PO$_3$)$_4$ at 25°C, 500°C and 1000°C.
5.4 Synthesis of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$ (PO$_4$)$_3$ Compound

The synthesis of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$ (PO$_4$)$_3$ (LATP) compound allowed us to explore how the LTP compound behaved when more cations were added to the mixture. Additionally, the LATP compound has received notable attention because partial substitution of Ti$^{4+}$ atoms with Al$^{3+}$ in the structure have shown enhanced ionic conductivity properties [135, 138, 141-143]. The polymeric steric entrapment method could provide some advantages over the traditional methods (solid state and glass-ceramic method) to produce this compound. The excellent control over the stoichiometry, purity and low synthesis temperature may avoid problems such as glassy phase formation, lithium evaporation and low density of the products due to lack of reactivity (surface area) of the LATP powders.

It is important to mention, that there is no information about the thermal expansion of this compound as well as there is no powder diffraction file (PDF) on the ICDD database. This work will provide good quality (synchrotron) information about the crystal structure of the pure LATP and its thermal expansion behavior in the range of 25°C to 1000°C.
5.4.1 Phase Evolution of the \( \text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3 \) Compound

The crystallization behavior at different cation:organic ratios is presented in Figures 5.14 through 5.16. Working with cation:organic ratio 2:1 (Figure 5.14), it can be observed that at 500°C the powder was already partially crystallized, unless high background and broad peaks were seen, suggesting a high content of amorphous phase. For LATP samples made using 4:1 and 6:1 ratios (Figure 5.15 and 5.16), the crystallization started somewhere between 500°C and 600°C. The differences in the cation:organic ratios also modified the nature (strength) of the exothermic reaction which could be the reason for inducing crystallization at lower temperatures for the 2:1 ratio condition. In all different cation:organic ratios conditions, unless LATP was the main phase formed, an unidentified peak was found at around 24° 2θ at temperatures below 700°C. During the search and match peak indexing procedure against the ICDD database, some C and N containing compounds matched and could be responsible for this diffraction peak. Moreover, in all cases above 700°C, the desired LATP single phase was produced. As mention before, all XRD patterns were indexed using the LTP 01-072-6140 ICDD PDF card and the unit cell characterization will be provided in detail using high resolution and Rietveld refinement techniques when the results for thermal expansion behavior will be presented.

Moreover, when the dissolution of the reagents and mixing procedures were no carefully carried out, some secondary phases such as \( \text{TiO}_2, \text{AlPO}_4 \) and \( \text{TiP}_2\text{O}_7 \) appeared at intermediate temperatures (800°C-900°C). However, at higher temperatures (1000°C), usually these secondary phases recombined by diffusion processes and formed LATP single phase.
Figure 5.14. X-ray diffractograms of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ synthesized in air using 2:1 cation:organic ratio in the range 500°C - 1100°C.

Figure 5.15. X-ray diffractograms of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ synthesized in air using 4:1 cation:organic ratio in the range 500°C - 1100°C.
Figure 5.16. X-ray diffractograms of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ synthesized in air using 6:1 cation:organic ratio in the range 500°C - 1100°C.

The thermal analysis performed on the LATP precursor pre-calcined at 200°C for 2 h is depicted in Figure 5.17. It can be pointed out that as in the case of LTP there were three regions of weight loss as well as three clear exothermic peaks. The three weight loss regions were located at 25°C – 200°C, 200°C – 290°C and 290°C – 700°C and gave a total weight loss of 24.56 wt%. These three regions corresponded to water and alcohol evaporation (3.2 wt%), nitrates and organic combustion reactions (17.06 wt%) and remnant C and N oxidations (3.96 wt%), respectively. Furthermore, the DSC profile agreed with some of the weight loses. For instance, the first strong exothermic peak (200°C – 310°C) corresponded to the combustion reaction (fast) between nitrates and organics and it appeared when the biggest weight loss occurred. On the other hand, the last exothermic peak (620°C – 710°C) represented the crystallization process. These exothermic reactions (combustion and crystallization) corresponded well with our observations during the synthesis procedure (powder coming out of the crucibles) and the XRD data.
Lastly, the idea that good dissolution and mixing of the reagents were more important that the cation:organic ratio for producing compounds in this family, was supported by the data presented in this section. Nevertheless, powders made using cation:organic ratio 4:1 was selected for further analysis in the next sections. This condition provided a safer entrapping condition and may have left less unreacted C and N at lower temperature as observed for LTP compound.

5.4.2 Physico-chemical Characterization of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$

The microstructure of the LATP powders produced using the cation:organic ratio 4:1 are presented in Figure 5.18 (500°C – 600°C) and Figure 5.19 (700°C – 1000°C). The images of amorphous powder (500°C) shown in Figure 5.18 (a) and (b) revealed agglomerated secondary particles composed of nanoparticles in the range of (10 nm -20
nm). No sintering between particles was evidenced at this temperature. Figure 5.18 (c) and (d) depict the microstructure of the LATP powders crystallized at 600°C. In these images, particles looked defined and crystalline compared to the particles obtained at 500°C. In Figure 5.18 (c), it can be appreciated how secondary agglomerates of about 1 µm in diameter were formed by nanoparticles of about 30 nm - 50 nm.

SEM micrographs of powders produced at 700°C are shown in Figure 5.19 (a) – (b), where evident crystal growth and necking was noticed, fact that suggest some degree of sintering, and thus, reduction in surface area. Crystals from 50 nm to 250 nm could be detected. These micrographs revealed how considerable crystal growth and sintering of the particles occurred in a short temperature range and time. Moreover, at 1000°C it can be observed that what used to be a soft agglomerate at low temperature became a sintered porous particle. A high degree of necking and sintering could be observed. Particles in the range of 0.5 µm to 10 µm were found. The maximum particle size in this case was dictated by the size of the initial secondary agglomerates which can be modified by a low intensity grinding process. In all cases there was not a specific crystal habit found in the powders, however, the lower the temperature, the more rounded the particles.
Figure 5.18. SEM micrographs at of the Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3 powder produced using a cation:organic ratio of 4:1, (a) - (b) 500°C and (c) - (d) 600°C.

As suggested by the crystal growth seen in the SEM images, upon increase in temperature, there should have been a decrease in specific surface area. This trend is supported by Figure 5.20 where the specific surface area of the amorphous phase was measured as 80.8 m²/g. After the crystallization took place at 600°C the specific surface area was reduced by close to a half (44.1 m²/g). Moreover, at 700°C the specific surface area was just about 23.7% (19.15 m²/g) of the amorphous powder surface area. Finally, at the maximum temperature tested (1000°C), the SSA was only 1.6 m²/g which represented 2% of the amorphous powder SSA. These results, coupled with the information obtained from the SEM images about the crystal sizes and growth and sintering behavior, clearly demonstrated the influence that the temperature and processing time had over the
microstructure. At the end, crystal structures, particle sizes, shapes and specific surface areas are characteristics that finally define reactivity, sinterability, electronic and ionic transport properties.

Figure 5.19. SEM micrographs of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 700°C and (c) - (d) 1000°C.
Figure 5.20. Specific surface area (SSA) of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ powders produced at different temperatures using a cation:organic ratio of 4:1.

The particle size analysis made by light scattering is presented in Figure 5.21. First, it can be noticed that for LATP powders made at different temperatures, the agglomerates follow a monomodal distribution. The inset table shows specific accumulated percentiles where the mean particle size for all samples was around 4 µm. It can be also observed that even though the amorphous sample revealed the lowest particle size by SEM analysis and highest surface area, the 90 cumulative number percent finer (Dv90) of the agglomerated particles was the highest one (21.10 µm) among all samples. This situation again proved that measuring the particle size distributions of high surface area powders was very difficult by this technique, even though multiple different sample preparation and instrument conditions were tested.
To conclude the physico-chemical characterization of the LATP powders produced by the polymeric steric entrapment method, chemical analysis (C, N and H) measurements were performed. Table 5.3 confirmed the low amount of these three elements (C, N and H) in the powders. As expected, the maximum amount of C (0.11%), N (0.06%) and H (0.28%) was found in the lowest temperature sample (500°C). As it can be seen in the table, the content of C, N and H were virtually zero in the crystalline samples. This fact supports the idea that the combustion reaction was well balanced so that the organics and nitrates were almost fully consumed during the exothermic reaction, leaving small amounts of unreacted compounds which oxidized and gasified at low temperature (<500°C).
Table 5.3. Chemical Composition of Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ Produced at Different Temperatures using a Cation:Organic Ratio of 4:1

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<th>Chemical Composition</th>
<th>Sample</th>
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<td>500°C</td>
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<tr>
<td>C (wt%)</td>
<td>0.11</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>0.28</td>
</tr>
<tr>
<td>N (wt%)</td>
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</tbody>
</table>

5.4.3 Thermal Expansion Behavior of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$

As described in the Experimental Section 3.2.6, the evolution of the lattice parameters and volume of the unit cell upon the increase in temperature, as well as the analysis of the thermal expansion behavior of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ phase, was performed using two different setups. The Advanced Photon Source (APS) at Argonne National Laboratory (ANL) and The National Synchrotron Light Source (NSLS-II) at Brookhaven National Laboratory (BNL) were used to confirm and compare the results. The LATP phase produced by the polymeric steric entrapment method using cation:organic ratio of 4:1 was evaluated in the 25°C ~ 1000°C temperature range using a quartz capillary in all cases. Moreover, the polynomial fitting used during the CTEs analysis by the CTEAS program was of the order two (a quadratic function) which gave a 0.96 R-Square fitting parameter in both sets of data.

It was noticed that in both cases (LATP and LTP phases), Li ions at high temperature (near to 1000°C) are both highly mobile and volatile, facts that make the measurement of the lattice parameters and therefore the thermal expansion behavior very variable and unreliable.

The lattice parameters (a and c of the hexagonal system), the volume of the cell and the coefficient of thermal expansion ($\alpha_{11}$ and $\alpha_{33}$) as a function of temperature are plotted in Figure 5.22 and are listed in Table 5.4 and Table 5.5.

It can be observed that in general the data for the lattice parameters, volume of the cell and the thermal expansion behavior are reproducible and follow the same trend in both setups, APS and NSLS-II. It can be noticed, that the a-axis (Figure 5.22 (a)) expanded...
upon the increased in temperature up to about 800°C where then become zero or slightly negative. Moreover, the c-axis expanded in the entire range of temperature (Figure 5.22 (b)). Furthermore, the volume of the cell is depicted in Figure 5.22 (c) and it was found that the total volume change in the 25°C – 950°C temperature range was about 2.6%.

In order to compare the expansion of both a- and c-axis, they are plotted together in the same scale (Figure 5.22 (d)). It is shown that the expansion of both axes was very small and specifically for the a-axis, it showed a near zero thermal expansion over the 25°C – 1000°C range. Additionally, they were reproducible in both experiment configurations (APS and NSLS-II).

Moreover, the thermal expansion behavior of the LATP phase is presented in Figure 5.22 (e) and (f). It can be seen that for the case of α_{11}, it was always positive (a-axis expanding) but decreasing its value upon the increased of temperature up to about 850°C. This means that the a-axis is expanding at a decreasing rate. After 850°C, the α_{11} became zero or slightly negative due to the contraction of the a-axis. Moreover, the α_{33} was always increasing and positive throughout the entire temperature range. This meant that the c-axis increased at an increasing rate upon the increase in temperature. These effects could also be seen in the thermal expansion quadric surfaces at 25°C, 500°C, and 1000°C (Figure 5.23) where the surfaces along the x and y directions were very small (near zero). On the other hand, the blue surfaces (positive) along the z direction increased in size.
Figure 5.22. Lattice parameters for the a- and c-axes ((a) – (b)), and components of the thermal expansion tensor $\alpha_{11}$ and $\alpha_{33}$ ((c) – (d)) for the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ in the hexagonal system.
Table 5.4. Lattice Parameters, Volume and Coefficient of Thermal Expansion
Tensor Values of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ Compound Obtained at Advanced Photon Source (APS) at Argonne National Laboratory (ANL)

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Table 5.5. Lattice Parameters, Volume and Coefficient of Thermal Expansion
Tensor Values of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ Compound Obtained at National Synchrotron Light Source (NSLS-II) at Brookhaven National Laboratory (BNL)

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Figure 5.23. Quadric surface describing the thermal expansion in three-dimensions of the Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ at 25°C, 500°C and 1000°C.
5.5 Synthesis of the NaTi$_2$(PO$_3$)$_4$ Compound

NaTi$_2$(PO$_3$)$_4$ is other member in the M$_1$Ti$_2$(PO$_3$)$_4$ that has recently attracted a lot of attention because upon the replacement of Li ion batteries in some applications by sodium ion batteries, as it will be necessary to find Na ion anodes and cathodes. Another reason for the interest in this material is that it exhibits negative thermal expansion behavior in the temperature range of 25°C -1000°C.

From the synthesis point of view, the incorporation of different cations into the structure of the compounds in the same family will provide an insight of how versatile the synthesis method is when different reagents are used and when different possible phases could be formed.

5.5.1 Phase Evolution of the NaTi$_2$(PO$_3$)$_4$ Compound

The phase evolution of the NaTi$_2$(PO$_3$)$_4$ phase was evaluated over the temperature range of 500°C – 1100°C using different organic cation:organic ratios (2:1, 4:1 and 6:1) and it is presented in Figures 5.24 through 5.26. As for the case of all materials in this family, there was no commercially available NTP powder, thus phase indexing was carried out using the NaTi$_2$(PO$_3$)$_4$ - 00-033-1296 ICDD PDF reference. At all cation:organic ratios, samples heat treated at 500°C were totally amorphous while samples at 700°C were crystalline. However at 600°C, samples were partially crystallized and characterized by an amorphous XRD profile with some low intensity peaks. This fact suggests that the onset of the crystallization was around 600°C.

Moreover, NaTi$_2$(PO$_3$)$_4$ single phase was obtained at all cation:organic ratios in the temperature range of 700°C – 1000°C. However, when proper dissolution and mixing were not carried out, secondary phases such as TiO$_2$, TiP$_2$O$_7$ were found at temperature above 800°C. It is important to mention that for the synthesis of this compound, the water-soluble cation solutions were always stable, thus pH modification was not required. However, if the formed gels (after water soluble solutions and TISO solutions were mixed) were not well mechanically re-dispersed, secondary phases appeared in the powders crystallized at temperature above 800°C and remained in the powder (did not recombine) at all
temperatures. Recombination through a diffusional process was not as effective as in the case of Li-based compound due to slow mass diffusion.

Figure 5.24. X-ray diffractograms of the NaTi$_2$(PO$_3$)$_4$ synthesized in air using 2:1 cation:organic ratio in the range 500°C - 1100°C.
Figure 5.25. X-ray diffractograms of the NaTi$_2$(PO$_3$)$_4$ synthesized in air using 4:1 cation:organic ratio in the range 500°C - 1100°C.

Figure 5.26. X-ray diffractograms of the NaTi$_2$(PO$_3$)$_4$ synthesized in air using 6:1 cation:organic ratio in the range 500°C - 1100°C.
The thermal analysis results for NTP over the 25°C – 1200°C temperature range are presented in Figure 5.27. The NTP behavior was similar to the one exhibited by LTP and LATP. Three weight loss regions at 25°C – 211°C (2.64 wt%), 211°C – 319°C (10.54 wt%) and 319°C – 600°C (4.12 wt%) could be observed. These three stages of weight loss could be attributed to removal of water and alcohol, combustion of nitrates and organics and gasification (oxidation) of the C and N remnant after the combustion reactions. The total mass loss of the NTP precursor powder between 20°C and 1200°C was 17.30 wt%. It can be also observed that there were three exothermic peaks. The first two peaks, located at 200°C – 300°C and 300°C – 620°C, corresponded to the combustion of nitrates and organics, while the third exothermic peak could be attributed to the crystallization process.

It is important to note that during the synthesis procedure many different endothermic and exothermic reactions occurred simultaneously, thus what the DSC/TGA curves represent the net contribution of both exothermic and endothermic reactions. If multiple different reactions occurred in the same temperature range it is not possible to separate and identify them unless more information about the specific reaction is known.

Figure 5.27. DSC/TGA curves of the NaTi$_2$(PO$_4$)$_3$ (NTP) precursor powders made by the polymeric steric entrapment method.
5.5.2 Physico-chemical Characterization of the NaTi$_2$(PO$_3$)$_4$

The microstructure of the NaTi$_2$(PO$_3$)$_4$ powders produced by the polymeric steric entrapment method using cation:organic ratio of 4:1 is presented in Figure 5.28 and 5.29. As discussed earlier with other compositions made by this method, the gas released and exothermic reactions which occurred during the synthesis, favored the formation of porous and soft agglomerates. Figure 5.28 (a) – (b) shows the microstructure of the NTP amorphous powder. Particles from 10 nm to 30 nm with no particular shape could be observed. Furthermore, it can be seen that the nanoparticles were agglomerated and formed secondary particles of 100 nm – 1 µm. At 600°C (Figure 5.28 (c) – (d)) no considerable crystal growth was noticed. This could be attributed to the fact that at 600°C the powders were still partially amorphous so, the energy applied to the system was spent to crystallize the powder and it was not enough to facilitate mass diffusion in order to induce pre-sintering or crystal growth.

Moreover, at 700°C (Figure 5.29 (a) – (b)) well-crystallized powders were identified. Crystals of about 50 nm - 90 nm were observed. Additionally, some degree of pre-sintering (necking between particles) and crystal growth were detected. Primary particles (nanocrystals) sintered together inside the bigger secondary particles, still showing high porosity could be appreciated. Finally at 1000°C (Figure 5.29 (c) - (d)), crystals were easily imaged at low magnification, showing clearly crystal growth and sintering. Crystals with rounded corners (not faceted) between 100 nm and 200 nm were found. These SEM images (Figure 5.28 and 5.29) demonstrate not only the real crystal size of the primary particles and secondary soft agglomerates, but also how fast the crystals grew and sintered upon the increase in temperature. As crystals grew and sintered, there was an expected reduction in specific surface area. Figure 5.30 depicts the change of specific surface area with the increase of temperature. For practical purposes the sample at 600°C was considered still amorphous as shown by the XRD analysis (Figure 5.25).
Figure 5.28. SEM micrographs of the NaTi$_2$(PO$_3$)$_4$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 500°C and (c) - (d) 600°C.

The SSA of the amorphous NTP (600°C) powders was found to be 83 m$^2$/g which was close to twice of the surface area (41 m$^2$/g) of the crystalline sample (700°C). For the sample heat treated at 1000°C, the specific surface area was 3.6 m$^2$/g which was the 4.3% of the amorphous SSA. These results support the observations of crystals sizes and pre-sintering behavior observed in the SEM images which suggested rapid decrease in surface area.
Figure 5.29. SEM micrographs of the NaTi$_2$(PO$_3$)$_4$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 700°C and (c) - (d) 1000°C.

Measurements of the particle sizes (agglomerates) by laser scattering (Figure 5.31) show how small particles with high surface area and surface energy tended to agglomerate strongly and made their measurement very difficult. Multiple variables such as sonication and stirring levels, diluted dispersions and dispersant additions were tested in order to have less agglomeration and stable measurement. In the inset table in Figure 5.31, different percentiles are shown. It can be noticed how a sample (600°C) which contains very small particles, exhibits the highest Dv50 and Dv90, 2.39 µm and 15.70 µm, respectively. These values show how small particles agglomerated to form larger secondary particles. If these laser scattering techniques wanted to be used for measuring individual nanoparticles, a dedicated procedure needs to be carried in order to find the correct sample preparation.
(grinding, dispersion stabilization, concentration and additives) as well as instrumentation (detectors, laser energy, stirring and sonication). In any case, the 90% of the particles and agglomerates of the crystalline samples were below 4.73 µm and 6.80 µm for the 700°C and 1000°C powders, respectively.

![Graph showing specific surface area vs temperature](image)

Figure 5.30. Specific surface area (SSA) of the NaTi$_2$(PO$_3$)$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1.

The final measurement for the physico-chemical analysis of the NTP powders was chemical analysis for C, N and H (Table 5.6). It can be noticed that for the amorphous powder heat-treated at 500°C the C and N amounts were 0.11% and 0.04%, respectively. These values were virtually zero and upon the increase in temperature it was expected that they would even decrease further. For the crystalline sample (700°C), the carbon and nitrogen amounts were 0.06% and 0.11%, which for practical purposes could be considered as zero. This information reflected how the combustion reaction between nitrates and organics was carried out up to completion and just traces of C and N were left behind. As the reaction was carried out in air, full removal of these two elements upon increasing temperature were expected.
Figure 5.31. Particle size distribution (PSD) of the NaTi$_2$(PO$_3$)$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1.

Table 5.6. Chemical Composition of the NaTi$_2$(PO$_3$)$_4$ Produced at Different Temperatures Using a Cation:Organic Ratio of 4:1

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These past sections demonstrated how synthesis variables such as dissolution and mixing of the reagents, cation:organic ratios, temperature and atmosphere played an important role on the formation of single phase of NaTi$_2$(PO$_3$)$_4$ and their physico-chemical characteristics (microstructure, particle size, surface area and purity).
5.5.3 Thermal Expansion Behavior of the NaTi$_2$(PO$_3$)$_4$

The evolution of the lattice parameters, volume of the unit cell and the thermal expansion coefficients of the NaTi$_2$(PO$_3$)$_4$ are presented in Figure 5.32 and Table 5.7. In the range between 25°C - 1200°C, the a-axis contracted but upon increasing temperature the rate of contraction slowed down, while the c-axis expanded, but the rate of expansion decreased. Additionally, the total volume change in the range 25°C - 1200°C was 1.6%. This work both confirmed the thermal expansion behavior of the R$^3$c family and reported it with greater accuracy than previously up to 1000°C [101, 104, 115, 117, 118] and continued the measurements to 1200°C.

It can be seen, from Figure 5.32, that the thermal expansion was non-equivalent between the a- and c-axes, and upon heating the $\alpha_{11}$ increased (while the a-axis was contracting), whereas $\alpha_{33}$ decreased (while the c-axis was expanding). Additionally, above 1000°C the a-axis and $\alpha_{11}$ were no longer contracting and negative, respectively, which is one of the attractive characteristics (negative thermal expansion) of this NASICON-type structure [102, 105, 106]. Furthermore, these effects could also be seen in the thermal expansion quadric surfaces at 25°C, 500°C, and 1000°C (Figure 5.33). The orange color of the surface along the x-y plane represents the negative behavior while the blue color of the surface along the z direction represents the positive behavior. Moreover, the donut shape in the x–y plane is a result of having equivalent values for $\alpha_{11}$ and $\alpha_{22}$, which is expected for hexagonal systems.

Additionally, Table 5.7 presents the results of the lattice parameters and cell volume change with temperature as well as the two components of the second rank-tensor of the thermal expansion and the average thermal expansion. This analysis was performed by means of CTEAS software using a second-order polynomial fit of each $hkl$ and corresponding $d$-spacing, which gave an R-square fitting parameter of 1.

The mechanism for the low/negative thermal expansion behavior of NTP has been explained previously [118, 140]. It is attributed not only to the cooperative rotations of linked polyhedra (TiO$_6$ and PO$_4$) but also, to the relative expansion/contraction of the occupied and vacant M$_1$ sites. Additionally, it has been proposed that polyhedral distortions
(Ti-O-P bridging bond angles) contribute to the negative thermal expansion of $\alpha_{11}$ [104, 115, 116].

Figure 5.32. Lattice parameters for the a- and c-axes ((a) – (b)), and components of the thermal expansion tensor $\alpha_{11}$ and $\alpha_{33}$ ((c) – (d)) for the NaTi$_2$(PO$_4$)$_3$ in the hexagonal system.
Table 5.7. Lattice Parameters, Volume and Coefficient of Thermal Expansion

Tensor Values of the NaTi$_2$(PO$_4$)$_3$

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Figure 5.33. Quadric surface describing the thermal expansion in three-dimensions of the NaTi$_2$(PO$_4$)$_3$ at 25°C, 500°C and 1000°C.
The 3-D graphic representation and information of the crystal structures of the room temperature and highest temperature NaTi$_2$(PO$_4$)$_3$ are presented in Figure 5.34. It can be noted that as in the case of LTP there are channels along the a-axis where Na ions can diffuse. Additionally, from the inset table, it can be seen that unless the a-axis contracts in the 27°C – 1214°C temperature range, the volume of the cell expands. This effect is caused by the greater expansion of the cell along the c-axis. In comparison, the unit cell of the NTP is larger than the LTP unit cell which can be attributed to the effect of the Na ion which is larger than the Li ion.

![Figure 5.34. Crystal structure model and information of the NaTi$_2$(PO$_4$)$_3$ at 27°C and 1214°C.](image)

5.6 Synthesis of the KTi$_2$(PO$_3$)$_4$ Compound

KTi$_2$(PO$_3$)$_4$ is the phase within the M$_1$Ti$_2$(PO$_3$)$_4$ which contains the largest alkali cation and provided us the opportunity to see if the entrapment behavior changed due to ionic size. Additionally, it helped us to expand our experience in managing different reagents in order to produce K-based compounds.
The thermal expansion of the KTi$_2$(PO$_3$)$_4$ phase (explained below) exhibits an intermediate behavior between LTP and NTP where it is negative (contracting) at low temperature (<500°C) and becomes positive (expanding) at high temperature (>500°C).

5.6.1 Phase Evolution of the KTi$_2$(PO$_3$)$_4$ Compound

The phase evolution of the KTi$_2$(PO$_3$)$_4$ compound at different cation:organic ratio is depicted in Figures 5.35 through 5.37. For this compound, the indexing of the phases was performed using the KTi$_2$(PO$_3$)$_4$ – 04-008-4780 ICDD PDF card. From the XRD data, it can be observed that in all cases the powders were amorphous at 600°C, partially crystallized at 700°C and fully crystalline at 800°C, for all cation:organic conditions. Qualitatively, the degree of crystallinity of the partially crystallized samples (700°C) could be inferred (for comparison purposes) from the background shape (hump) and sharpness and intenseness of the peaks. Unless there was not a large difference, by this qualitative comparison, it appeared that using the cation:organic ratio of 4:1, the powders started crystallizing at lower temperatures. This suggests that the exothermic reaction may perhaps have been stronger and the energy released helped to induce crystallization at lower temperatures.
Figure 5.35. X-ray diffractograms of the $\text{KTi}_2(\text{PO}_3)_4$ synthesized in air using 2:1 cation:organic ratio in the range 600°C - 1100°C.

Figure 5.36. X-ray diffractograms of the $\text{KTi}_2(\text{PO}_3)_4$ synthesized in air using 4:1 cation:organic ratio in the range 600°C - 1100°C.
In all cases (different cation:organic ratios), KTi$_2$(PO$_3$)$_4$ single phase was formed directly from the amorphous phase precursors without falling into any secondary or ternary stable phases. Furthermore, KTi$_2$(PO$_3$)$_4$ phases were stable over the entire temperature range, which was as expected if the dissolution, mixing and gel re-dispersion were carried out effectively. When the previous mentioned steps were not satisfactorily accomplished, secondary phases such as TiO$_2$, TiP$_2$O$_7$ were also obtained. From our experience and multiple repetitions of the synthesis of M$_1$Ti$_2$(PO$_3$)$_4$ compounds, KTi$_2$(PO$_3$)$_4$ was the easiest phase to stabilize compared to LiTi$_2$(PO$_3$)$_4$ which was the harder one. It is believed that the larger the cation (ionic size), after a good mixing of the reagents (at ionic level), the less probable the segregation of the cation at the same level of organic entrapment.

Additionally, at low temperature (800°C) the XRD data contained broad peaks and low intensity peaks which corresponded to a formation of nanoparticles as has been demonstrated before with other compounds. KTi$_2$(PO$_3$)$_4$ powder produced using cation:organic ratio 4:1 was selected for further characterization because, as mentioned
above. This was the ratio where the exothermic reaction appeared to be balanced and the entrapper amount seemed to be a safe condition to avoid segregation of the components.

The thermal analysis over the range of 25°C – 1200°C of the KTP precursor is shown in Figure 5.38. The KTP behavior was very similar to the LTP, LATP and NTP behavior. A total weight loss of 29.7 wt% distributed in three weight loss regions could be observed. The first one lay between 25°C – 170°C with a 5.9 wt% weight lost, the second one lay between 170°C and 290°C with a 18.1 wt% weight lost and the third one lay between 290°C and 550°C with a 5.7 wt% weight loss. Similar to the other compositions in this system, these three stages of weight loss could be attributed to the removal of water and alcohol, combustion of nitrates and organics as well as gasification (oxidation) of the C and N remnants after the combustion reactions. Additionally, three exothermic peaks could be observed in the temperature ranges of 210°C – 400°C, 400°C – 600°C and 800°C – 850°C. These exothermic peaks corresponded to the combustion of nitrates and organics, while the third exothermic peak could be attributed to the crystallization process.

Figure 5.38. DSC/TGA curves of the KT\textsubscript{i}\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (KTP) precursor powders made by the polymeric steric entrapment method.
5.6.2 Physico-chemical Characterization of the KTi$_2$(PO$_3$)$_4$

The microstructure and particle size of the KTi$_2$(PO$_3$)$_4$ synthesized at 600°C (amorphous), 700°C (crystalline) and 1000°C using cation:organic ratio 4:1 were performed by SEM and are seen in Figure 5.39. The porous agglomerates were characteristic of the powders produced by the polymeric steric entrapment method, where highly exothermic reactions accompanied by released of NO$_x$ and CO$_x$ gases occurred. For the amorphous powder (600°C), particles of 10 nm - 20 nm were found (Figure 5.39 (a) – (b)), while for the partially crystallized powder at 700°C, crystals of about 50 nm were encountered (Figure 5.39 (c) – (d)). Moreover, at 1000°C crystals grew (200 nm -400 nm) and necked together (sintered) displaying a decrease in porosity and surface area (Figure 5.39 (f) – (g)). Crystals did not show any particular shape, however they exhibited rounded edges (no faceted). The reduction of the specific surface area was also supported by the measurement of the specific surface area by nitrogen adsorption (Figure 5.40). It was found that the amorphous powder had a SSA of 47.7 m$^2$/g while the partially crystallized powder had 21.8 m$^2$/g which was 54% reduction of SSA. Additionally, the sample heat treated at 1000°C had 2.3 m$^2$/g corresponding to a 4.8% of the amorphous specific surface area. As the driving force for sintering is the reduction in surface area, this information is valuable for determining the desired powder characteristics for the subsequent processing steps. Both porosity and density of the final ceramic products are strongly dependent on the powders particle size, microstructure and specific surface area.
Figure 5.39. SEM micrographs of the KTi$_2$(PO$_3$)$_4$ powder produced using a cation:organic ratio of 4:1, (a) - (b) 600°C, (c) - (d) 700°C and (e) - (f) 1000°C.

The agglomerate size distributions of the KTi$_2$(PO$_3$)$_4$ powders synthesized at 600°C, 700°C and 1000°C are presented in Figure 5.41 and in the inset table. All distributions looked mono-modal and for the 600°C and 700°C samples they were very similar, where the Dv50’s were around 7 µm while the Dv90’s were between 23.7 µm – 28 µm. For the
case of the 1000°C sample, agglomeration of small particles was unlikely. However it was more likely that the particle size distribution corresponded to the pre-sintered larger agglomerates formed by the nanocrystals. These statements are supported by the microstructure observed in the SEM images (crystal growth and necking) and the low specific surface area (2.3 m²/g).

![Specific Surface Area](image)

Figure 5.40. Specific surface area (SSA) of the KTi₂(PO₃)₄ powders produced at different temperatures using a cation:organic ratio of 4:1.

Finally, the chemical analysis for carbon, nitrogen and hydrogen were performed on selected samples and are presented in Table 5.8. It was demonstrated that at low temperature, even when the sample was still amorphous (600°C) the amounts of C and N elements were practically zero. These trace amounts supported the idea that the combustion reaction was well balanced using cation:organic ratio 4:1 and small amounts of unreacted C and N were left behind after the reaction. Furthermore, it can be said (based on the XRD data) that the entrapment condition was accurate in order to avoid segregation of the components and formed KTi₂(PO₃)₄ single phase directly from the amorphous precursor.
Figure 5.41. Particle size distribution (PSD) of the KTi$_2$(PO$_3$)$_4$ powders produced at different temperatures using a cation:organic ratio of 4:1.

Table 5.8. Chemical Composition of the KTi$_2$(PO$_3$)$_4$ Produced at Different Temperatures Using a Cation:Organic Ratio of 4:1

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Sample</th>
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<tbody>
<tr>
<td></td>
<td>600°C</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>0.00</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>0.80</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.08</td>
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</table>
5.6.3 Thermal Expansion Behavior of the KTi$_2$(PO$_3$)$_4$

The thermal expansion behavior of the KTi$_2$(PO$_3$)$_4$ phase produced by the polymeric steric entrapment method using a cation:organic ratio of 4:1 was evaluated in the 25°C – 1300°C temperature range. The evolution of the lattices parameters (a and c), unit cell volume and coefficients of thermal expansion ($\alpha_{11}$, $\alpha_{33}$ and $\alpha_{\text{avg}}$) with increasing temperature are presented in Figure 5.42 and Table 5.9. This analysis was performed by means of CTEAS software using a second-order polynomial fit of each hkl and corresponding d-spacing which gave an R-square fitting parameter of 0.99. Figure 5.42 (a) shows how the a-axis contracted in the temperature range of 25°C – 500°C, while it changed its behavior to expanding over the temperature range of 500°C – 1300°C. This fact caused that the thermal expansion coefficient ($\alpha_{11}$) to be negative below 500°C and positive above it up to 1300°C (Figure 5.42 (e)). Moreover, the c-axis (Figure 5.42 (b)) was always increasing in the 25°C – 1300°C temperature range which resulted in the $\alpha_{33}$ (Figure 5.42 (f)) thermal expansion coefficient being always positive. It is important to mention that for both axes (a and c), the CTEs ($\alpha_{11}$ and $\alpha_{33}$) were always increasing (for either contraction or expansion) as is seen in Figures 5.42 (e) – (f). Additionally, the volume of the cell was always increasing (Figure 5.42 (c)) and gave a total volume change of 0.98% in the temperature range of 27°C – 1262°C. The KTi$_2$(PO$_3$)$_4$ compound experienced different behavior in comparison to LTP and NTP where the former was always expanding in the evaluated temperature range while the latter was always contracting.

The 3-dimensional representation of the thermal expansion tensor is depicted in Figure 5.43. It can be seen how the orange surface (negative) contracts up to 500°C, where it became zero. Then, it turned positive (blue surface) up to 1300°C. As the $\alpha_{11}$ values were positive but very small after 500°C, it is not possible to clearly see those effects on the quadric surface. However a distortion of the entire quadric surface can be appreciated, illustrating the behavior of the thermal expansion tensor at higher temperatures (500°C – 1200°C).
Figure 5.42. Lattice parameters for the a- and c-axes ((a), (b) and (d)), cell volume (c) and components of the thermal expansion tensor $\alpha_{11}$ and $\alpha_{33}$ ((e) – (f)) for the KTi$_2$(PO$_3$)$_4$ in the hexagonal system.
Table 5.9. Lattice Parameters, Volume and Coefficient of Thermal Expansion
Tensor Values of the KTi$_2$(PO$_3$)$_4$

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Lattice Parameters</th>
<th>T (°C)</th>
<th>Coefficients of Thermal Expansion</th>
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<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>V (Å$^3$)</td>
</tr>
<tr>
<td>27</td>
<td>8.35991(4)</td>
<td>23.0785(1)</td>
<td>1396.82(1)</td>
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Figure 5.43. Quadric surface describing the thermal expansion in three-dimensions of the KTi$_2$(PO$_3$)$_4$ at 25°C, 500°C and 1000°C
The 3-D graphic representation, as well as the information of the room temperature and highest temperature crystal structures are presented in Figure 5.44. Even though the KTP compound had the smallest $a$ lattice parameter, it possessed the largest cell volume. This occurred because K was the largest ion which stretched the unit cell along the c-axis. Still the structure possessed channels along the a-axis where K ion could still diffuse. However, the larger cation size (K) and smaller channels along the a- and b-axes may cause sluggish ionic mobility in comparison to the Na and Li counterparts.

![Crystal structure model and information of the KTi$_2$(PO$_3$)$_4$ at 27°C and 1214°C.](image)

**Figure 5.44.** Crystal structure model and information of the KTi$_2$(PO$_3$)$_4$ at 27°C and 1214°C.

5.7 **Summary**

This chapter has presented the synthesis conditions to produce materials in the M$_1$Ti$_2$(PO$_3$)$_4$ family and how the synthesis variables could be adjusted to obtain powders having different crystal sizes and specific surface areas.

In this family, the greater challenge was the segregation of the reagents during the mixing procedure because the Ti source rapidly decomposed with water. The decomposition of titanium isopropoxide (“TISO”) formed a gel, segregating the cations
and promoting formation of secondary phases upon heating. It has been found that if the reagents are dissolved in the proper solvent, mixed in the proper order and mechanically homogenized, thus, formation of single phase compounds can be achieved. Specifically, reagents that dissolve in water (nitrates) should be mixed together whereas TISO and EG should be mixed together in isopropyl alcohol. It was found that when Li + P solution as well as Li + P + Al solutions were mixed together, a cloudy or milky (precipitated) slurry was formed. This behavior (that occurs for LTP and LATP compounds) could segregate some components leading to the formation of multi-phase powders. It was found that modification of the pH below 4.4 by HNO$_3$ additions, hindered any precipitation and kept the clear solutions stable. Subsequently and after all solutions (nitrates and TISO + EG) were clear, well mixed and stable, the final mixing could be completed. At this stable state, a white gel was formed which could easily be re-dispersed by mechanical force (a practical approach). It was found that excess isopropyl alcohol slowed down the decomposition of the TISO as well as HNO$_3$ additions facilitated the re-dispersion of the precipitates. At the end and in all cases (LTP, LATP, NTP and KTP), it was found that working with cation:organic ratios of 4:1 and air atmosphere, single phase compound were produced at 700°C.

In this family ($\text{M}_1\text{Ti}_2(\text{PO}_3)_4$), the exothermic reaction produced by the reactions of nitrates and organics was not energetically strong enough to crystallize materials right after the exothermic reaction. However, the intimate mixing of the components reduced the synthesis temperature compared with synthesis methods such as solid state reaction and glass ceramic methods. Furthermore, it was found that the reducing power of nitrates and organic decomposition gases was not strong enough to affect the oxidation state of the Ti cation, as was the case in the synthesis of the $\text{M}_1\text{Mn}_x\text{O}_y$ compounds. For the reasons mentioned above, it was considered that the cation:organic ratio only played the role of controlling the entrapment of the cations once they are perfectly mixed.

It has been demonstrated how crystals sizes (in the nano to micron range) and specific surface areas (high reactivity) could be produced by modifying the calcining and annealing
temperatures. Nanocrystals with high surface areas and low contents of C, N and H could be obtained at temperatures as low as 700°C.

Finally, the thermal expansion behavior of LTP, LATP, NTP and KTP was evaluated by high resolution (synchrotron) in-situ high temperature X-ray diffraction. The nature of near zero/low/negative thermal expansion of these materials was confirmed. Additionally, the coefficients of the thermal expansion tensor ($\alpha_{11}$ and $\alpha_{33}$) have been reported for every phase, at a minimum temperature up to 1000°C. It has been shown that thermal expansion behavior of the $\alpha_{11}$ and $\alpha_{33}$ coefficients is not constant (a single value), as has been erroneously reported in the literature. On the contrary, the values of the coefficients thermal expansion vary with temperature. For instance $\alpha_{11}$ for LTP and LATP was positive but decreasing in its magnitude up to about ~800°C when it became zero or slightly negative. For the case of NTP, $\alpha_{11}$ was negative, but increasing in its magnitude up to about ~1000°C when it became zero or slightly positive. This effect was the consequence of the a-axis contracting over the evaluated temperature range. Finally, the KTP compound exhibited a mixed behavior where $\alpha_{11}$ was negative but increasing in its magnitude up to about ~600°C when it became positive and still increasing its magnitude. It is also important to mention that this is the first time (to our knowledge) that high resolution crystallographic information about the LATP compound has been reported.
CHAPTER 6
CONCLUSIONS

In this research work, we have shown how to synthesize multicomponent complex compounds based on intermetallic cations (Mn and Ti) which can adopt different oxidation states. Materials that belong to two main families (\(M_1Mn_xO_y\) and \(M_1Ti(PO_4)_3\)) such as \(Li\text{Mn}^{3+}O_2\), \(Li\text{Mn}_2^{3+/4+}O_4\), \(Li_2\text{Mn}^{4+}O_3\), \(Li\text{Ti}_2(PO_4)_3\), \(Li\text{Al}_{0.3}\text{Ti}_{1.7}(PO_4)_3\), \(Na\text{Ti}_2(PO_4)_3\) and \(K\text{Ti}_2(PO_4)_3\), were produced using the polymeric steric entrapment route and were selected due to their technological importance and technical information availability. We shed light over how variables such as the dissolution conditions, pH of the solution, mixing conditions, drying procedures, \(HNO_3\) addition, amount of polymer (cation:organic ratio), characteristic of the exothermic reaction (C/N ratio) calcination/crystallization atmosphere and temperature, affect the synthesis process and physico-chemical characteristics of the powders.

6.1 \(M_1Mn_xO_y\) Family

In chapter 4, it was demonstrated how the cation:organic ratio not only serves as a steric entrapper (avoiding segregation of the components), but also, has the power to modify the micro-atmosphere around the particles and hence influence the oxidation state of the intermetallic cations (e.g. Mn). It is important to mention, that in order to control the phase formation and oxidation state, a strict balance between the cation:organic ratio (micro - atmosphere) and the furnace atmosphere (macro atmosphere) needed to be accomplished. Additionally, the decomposition of the nitrates and organics produces a violent exothermic reaction which can induce crystallization at low temperatures (~200°C - 300°C). The strength and length of the exothermic reaction is also governed by the cation:organic ratio. Multiple unsatisfactory attempts were carried out in order to quantify the energy released during the exothermic reaction by DSC measurements. However, the fact that the reactions were that violent imposed a restriction over the use of open crucibles (powder always came out of the pans). When sealed pans were used, the built up pressure
inside the crucible affected the measurements and was not always efficient in containing the powder inside the Al pan. Furthermore, it did not fully reproduce the synthesis conditions since the atmosphere could not be modified.

It was shown that formation of the desired phases can be carried out in a single step and convert the reagents directly to the products without falling into secondary (undesirable) phases. This fact along with the low temperature synthesis may provide a technological and practical advantage for the polymeric steric entrapment method over the traditional ceramic method (solid-state), since multiple regrinding, re-processing, high temperature and long processing time can be minimized. Furthermore, it was demonstrated that with the process developed in this work, a fine control over the stoichiometry, purity, particle size (nano to micron range) and specific surface area could be achieved.

Finally, it has been demonstrated that the powder produced by the polymeric steric entrapment method (LMO4) performed similar or even better than LMO4 commercial powder. Half cells fabricated using LiMn$_2^{3+/4+}$O$_4$ produced at 300°C x 2h (10 nm to 60 nm crystals) exhibited discharge capacities at C/10 and C/5 of 93.3 mAh/g and 88.9 mAh/g, respectively. Furthermore, in the case of the batteries assembled with the powder produced at 500°C, the specific capacity at C/10 and C/5 were 110 mAh/g and 107 mAh/g, respectively, while, for the cells fabricated with the powder synthesized at 700°C cells, the specific capacities at C/10 and C/5 were 131.8 mAh/g and 128.3 mAh/g, respectively. It is important to mention that the theoretical specific capacity for LMO4 is 148 mAh/g, whereas the specific capacities for the half cells fabricated using commercial LMO4 and the same conditions of the powders produced in this work, were 99.8 mAh/g and 90.1 mAh/g at C/10 and C/5, respectively. These results prove that the powders were crystalline and pure (in terms of composition and crystalline phase) after the exothermic reaction (~300°C). They also yielded significantly superior electrical performance properties.

6.2 M$_1$Ti(PO$_4$)$_3$ Family

In Chapter 5, the proper way to synthesize materials was explained, where neither the cation sources dissolved in the same solvent nor did they form clear solutions (stable
solutions). In was effectively shown how modifying the pH of some solutions (as for LTP and LATP compounds), keeping them below 4.4, clear and stable solutions could be obtained. Furthermore, the decomposition of the alkoxide (titanium isopropoxide “TISO”) could be slowed down by diluting it in isopropyl alcohol and mixing it with ethylene glycol (EG). This procedure assured that the polymer entrapper and Ti cations were well mixed by the time that the water-soluble solutions (nitrates and P source) as well as the alcohol soluble solutions (TISO + EG) were mixed together and formed a white gel. It was found that the gel can be mechanically redispersed to obtain the single desired phase after the thermal process. This represented a significant saving in isopropyl alcohol.

Pure and single phases of LTP, LATP, NTP and KTP powders were obtained at calcination temperatures as low as ~700°C and cation:organic ratio 4:1, using an air atmosphere. The single phase was stable over the entire evaluated temperature range (700°C – 1100°C). It was demonstrated that due to the nature of the synthesis method (exothermic reactions and gas evolution), powders in the nano to micron range could be obtained. Furthermore, it was shown that by controlling the synthesis conditions, the crystallite sizes and specific surface areas could be controlled.

Finally, the thermal expansion behavior of the different compositions produced in this family was measured. It was confirmed that the interesting characteristic of these materials, was their low/negative/near zero thermal expansion behavior. Additionally, it was demonstrated that the values of the thermal expansion coefficients were not constant, but on the contrary, they varied with temperature. LTP and LATP exhibited a positive but decreasing thermal expansion along the a-axis. NTP displayed a negative but increasing thermal expansion. KTP revealed a negative increasing thermal expansion behavior up to ~500°C and then became positive increasing behavior up to ~1300°C. It is important to mention that the results presented in this chapter were obtained by high resolution X-ray diffraction techniques using synchrotron radiation analyzed by the Coefficient of Thermal Expansion Analysis Suite (CTEAS) program developed at UIUC. The coefficient of thermal expansion tensors were reported in broader temperature ranges than those reported in the literature to date. Crystallographic information for LATP composition has been also
provided, which is information (to our understanding) not yet available in the literature or in the ICDD crystallographic database.

These results demonstrate how to manage reagents that precipitate or decompose in different solvents and still produce highly reactive (small and high surface areas), pure and single-phase powder in a one step process.

The findings presented in this research project open the door to expand the use of the polymeric steric entrapment method to produce materials in the energy storage and low/near zero/negative thermal expansion fields. Additionally, this work places this synthesis method as a low temperature and energy efficient process that can be exploited for the production of ceramic powders for multiple low as well as high technology applications.
CHAPTER 7
SUGGESTIONS FOR FUTURE WORK

This research work had shed light on some topics related to the synthesis and characterization of low/near zero/negative thermal expansion and energy storage (ion batteries) materials. Furthermore, it opens the doors to keep working and expanding knowledge in this field toward the following specific directions:

- In order to really implement the synthesis method in an industrial scale, it would be desirable that the calcining and crystallization process be continuous. This improvement may increase the yield of the products, production rate and better interaction between the atmosphere (flowing gases) and reactants. Different continuous processes such as spray pyrolysis, flame combustion and rotary calcining coupled with the polymeric steric entrapment method, could be alternatives to take advantage of the findings of this research work and take it to the industrialization level. Research on the appropriate way to feed the reactants to the process and the effect of some process variables such as atmosphere, temperature and processing time need to be addressed. The new process may change the microstructure and some physico-chemical characteristics of the powders, so that they will need to be characterized. As mentioned in Chapter 4, a balance between the micro and macro atmosphere is necessary to control the oxidation state of the powders. It is believed that using a continuous process (where powders are always moving and in contact with the working gas), there will yield more homogenous redox conditions which facilitate control of the oxidation state.

- There are multiple ceramic materials that are usually produced at temperatures higher than 500°C by the solid state reaction, entropy stabilized and glass-ceramic methods. It could be valuable to try to make them instead at low temperatures taking advantage of the exothermic reaction generated by the polymeric steric entrapment method. Examples include, but are not limited to LiCo\textsubscript{1/3}Ni\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2},
Mg$_x$Ni$_x$Co$_x$Cu$_x$Zn$_x$O$_y$ and Na$_{1+x}$Zr$_2$Si$_3$P$_{3-x}$O$_{12}$, where 0 ≤ x ≤ 3). These example materials have cations that can adopt different oxidation states as well as reagents that decompose in water (e.g. Si alcoxide). Furthermore, these compositions have been proposed as promising compounds to be used as energy storage, colossal dielectrics and super ionic conductor materials.

- There is another possible way to expand even more the synthesis method and impact the energy storage field. A relatively new family of fluoride compounds has been proposed as electrode materials for Li and Na ion batteries. This family includes compounds such as Na$_2$(M$_{1-x}$M$_x$)PO$_4$F, LiM$_{1-x}$SO$_4$F, LiM$_1$PO$_4$F and LiM$_1$PO$_4$F.

- The thermal expansion has been usually reported as a linear thermal expansion. In this work, it was shown that to be accurate, the thermal expansion behavior should be represented by a rank two tensor, which is not always linear. There are other interesting materials that exhibit low/near zero and negative thermal expansion and it may be of great value to know the change in this property as a function of temperature and {hkl}s. By means of the polymer steric entrapment method, the quadruple lamp furnace, synchrotron radiation and CTEAS software, single phase materials in the following families can be produced and characterized: AM$_x$O$_y$-type structures (M = W or Mo), zirconium vanadates, AlPO$_4$, NASICON (NaZr$_2$(PO$_4$)$_3$) and some zeolites.

- It would be interesting to investigate the sintering conditions to produce dense ceramic samples of LTP, LATP, NTP and KTP, which then can be used to measure their ionic conductivity. These results could be compared with the performance of samples produced by other methods such as glass-ceramic and solid state reaction methods.
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