Doctoral Thesis in Chemical Engineering

Hybrid materials for lithium-ion batteries

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Doctoral Thesis in Chemical Engineering
KTH Royal Institute of Technology
Stockholm, Sweden 2022
Dedicated to:

My God
Way Maker
Miracle worker
Promise keeper
Light in the darkness

My wife
Naviana Leiva Quispe
without whom this thesis would not have been completed

My children:
Marcos Yoshiro Ajpi Leiva
Josue Kenji Ajpi Leiva
Micaela Zalles
without whom this thesis would not have been completed

My parents
Hermogenes Ajpi and Aurora Condori
Vicenta Pujro
Eugenia Quispe, Angel Leiva
Elena Quispe, Eulogio Aquino
Angel Quispe

My brothers and sister
Nelson, Johnny, Silvia, Roxana, Valeria, Valeriana, and Aurora
Berta Zalles
Abstract

The Lithium-ion batteries are the most important power source for electronic devices as electronics, storage and the different electric vehicles. The research and development of new materials for different applications has increased, especially in the development of materials with better electrochemical properties (Specific capacity, rate capability, high energy density and cyclability). Inorganic materials such as LiFePO₄, LiMn₂O₄ and organic materials such as Li₄C₆O₆, quinones and anthraquinones, polyaniline (PANI) and others have been extensively studied. Improvement of the electrochemical properties involve different aspects as: control in the particle size of the materials, doping with other elements and the combination of the different properties of the organic an inorganic materials. The development of hybrids materials with improved electrochemical properties need a combination between of inorganic and organic structures. This type of hybrids materials are a very attractive option for the development of advanced materials. For the design of this type of hybrid materials it is necessary to form interactions between the inorganic and organic part (supramolecular chemistry). This opens up for using an immense amount of organic materials such as conductive polymers and PANI (Polyaniline) are attractive alternatives in the development of hybrid materials due to their excellent electronic conductivity. Other attractive types of hybrid materials are compounds based on metal-organic frameworks (MOF), coordination polymers (CP) and coordination networks (CN).

This thesis work is focused in the synthesis, structural characterization and electrochemical characterization of two groups of hybrid materials:
1) LiFePO₄-PANI synthetized by different methods.  
2) Metal-organic compounds M-BDC-DMF with M=Ni²⁺, Fe²⁺, C₈H₄O₂=Terephthalate=BDC=Benzene dicarboxylate, DMF=N,N-dimethylformamide.

The materials were synthesized by chemical oxidation methods combined with thermal treatment (LiFePO₄-PANI-Li hybrid powder) and by solvothermal methods (M-BDC-DMF). The materials were characterized by SCXRD, PXRD, FTIR, SEM and electrochemical methods and the electrochemical characterization was carried out using CV, EIS and galvanostatics methods. The specific capacities of PANI was 95 mAh/g, of LiFePO₄ was 120 mAh/g and of LiFePO₄-PANI was 145 mAh/g at 0.1C. At 2C the capacity of LiFePO₄ was 70 mAh/g and LiFePO₄-PANI was 100 mAh/g. The specific capacities of Ni₃(C₈H₄O₄)₃(C₃H₇NO)₄ is ~50 mAh/g and Fe-BDC-DMF was ~175 mAh/g.

The work has shown that PANI can improve the performance of LFP also at higher discharges rates. For M-BDC-DMF stability seems to be an issue which should be studied more in the future.

Keywords

Hybrid battery materials, conducting polymer composite, metal organic compounds, lithium-ion batteries.
List of appended papers

Paper I

Synthesis and spectroscopic characterization of LiFePO4-PANI hybrid material as cathode for lithium-ion batteries

Cesario Ajpi, Naviana Leiva, Max Vargas, Anders Lundblad, Göran Lindbergh, Saul Cabrera.
Materials 2020, 13(12), 2834.
https://doi.org/10.3390/ma13122834

Paper II

Crystal structure and Hirshfeld surface analysis of poly-[tris(μ₄-Benzene-1,4-dicarboxylato)-tetrakis(μ₁-dimethylformamide-κ¹O)-trinickel(II)] 2D coordination network

Cesario Ajpi, Leopoldo Suescun, Naviana Leiva, Anders Lundblad, Göran Lindbergh and Saul Cabrera
https://doi.org/10.1107/S2056989019014658

Paper III

Synthesis and spectroscopic characterization of Ni²⁺ coordination network: poly-[tris(μ₄-Benzene-1,4-dicarboxylato)-tetrakis(μ₁-dimethylformamide-κ¹O)-trinickel(II)] as material for lithium ion batteries

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Paper IV

Synthesis and spectroscopic characterization of Fe³⁺-MOF metal organic network as material for lithium ion batteries

Cesario Ajpi, Naviana Leiva, Anders Lundblad, Göran Lindbergh, Saul Cabrera.
Journal of Molecular Structure
Submitted
The contributions of the author to these papers are:

**Paper I**

Principal author. I performed synthesis-design and experimental work, analyzed all the experimental data and wrote most of the paper. Synthesized the crystals for single crystal X-ray diffraction in collaboration with Naviana Leiva.

**Paper II**

Principal author. I performed synthesis-design and performed all the experimental work and I performed the data analysis and wrote of the paper. Under my supervision Naviana Leiva and Max Vargas performed some parts of the experimental in the electrochemical characterization.

**Paper III**

Principal author. I performed all the synthesis and experimental work, I performed synthesis-design and analyzed all of the data and wrote the paper. Naviana Leiva and Max Vargas performed some parts of the electrochemical characterization under my supervision.

**Paper IV**

Principal author. Naviana and I performed all the synthesis and experimental work, I designed the synthesis and analyzed all of the data and wrote the paper. Under my supervision Naviana Leiva and Max Vargas performed some parts of the electrochemical characterization under my supervision.
### List of abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>CN</td>
<td>Coordination network</td>
</tr>
<tr>
<td>CP</td>
<td>Coordination polymer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EDS</td>
<td>Electron dispersion spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
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<tr>
<td>LED</td>
<td>Light emitting diode</td>
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<tr>
<td>LFP</td>
<td>LiFePO$_4$</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium-ion batteries</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal organic framework</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly (vinylidene fluoride)</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder x-ray diffraction</td>
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<tr>
<td>SCXRD</td>
<td>Single crystal x-ray diffraction</td>
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<tr>
<td>SEI</td>
<td>Solid-electrolyte interface</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SPC</td>
<td>Super P carbon</td>
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1 Background

1.1 Introduction

Since Sony developed the first lithium battery based on LiCoO₂ in 1990 [1] and its commercialization, the research and development of new materials for different applications has increased, especially in the development of materials with better electrochemical properties (Capacity, rate capability, high energy density and cyclability) mainly for hybrid vehicles and energy storage systems. Inorganic cathode materials such as LiFePO₄ [1-2], LiMn₂O₄ [2-4] and organic materials such as Li₄C₆O₆, quinones and anthraquinones [5], polyaniline (PANI) and others have been extensively studied.

One option in order to improve the electrochemical properties are to combine structure and electrochemical characterization of inorganic and organic materials thereby obtaining better understanding of the electrode materials. For the design of these types of hybrid materials it is necessary to have an interaction between the inorganic and organic parts (supramolecular chemistry), which opens an immense amount of organic materials such as conductive polymers: Polyacetylene, Polyphenylene, PANI (Polyaniline), PPY (Polypyrrole) and PT (Polythiophene) [6] are an attractive compounds for the development of hybrid materials due to their high electronic conductivity.

Inorganic materials such as LiFePO₄ has a good structural stability and cyclability but has low conductivity. This can be solved by combining with organic materials as PANI. For that purpose, LiFePO₄-polyaniline, have been developed showing improved electrochemical properties [6], such as high loading speeds, increased cyclability and material capacity. Lithium-ion batteries are commonly used for portable devices, electric vehicles and energy storage.

1.2 Active materials electrodes for Lithium-Ion Batteries

The lithium ion battery is a rechargeable battery which includes current collectors, positive electrode, electrolyte, separator and negative electrode as shown in the Figure 1.1.
The lithium ions move from the negative electrode through the electrolyte and to the positive electrode during the discharge process. In the charge process the lithium ion moves back to the negative electrode. The process is known as lithiation and delithiation.

Most of the electrolytes used in commercial lithium-ion batteries are non-aqueous solutions, in which lithium hexafluorophosphate (LiPF$_6$) salt dissolved in organic carbonates, in particular mixtures of ethylene carbonate (EC) with dimethyl carbonate (DMC), propylene carbonate (PC), diethyl carbonate (DEC), and/or ethyl methyl carbonate (EMC) [7]. Research has been under way in the area of non-flammable electrolytes as a pathway to increased safety based on the flammability and volatility of the organic solvents used in the typical electrolytes. Strategies include aqueous lithium-ion batteries, ceramic solid electrolytes, polymer electrolytes, ionic liquids, and heavily fluorinated systems.

Recently developed solid state electrolytes such as gel polymer electrolytes and ceramic electrolytes can be considered as excellent substitutes for the liquid electrolytes. Most important are perovskite type Li$_{3x}$La$\left(\frac{2}{3}\right)$−$x$TiO$_3$ (LLTO) and NASICON-type (Na$_{1+x}$Zr$_2$P$_{3−x}$Si$_x$O$_{12}$) Li-ion conductors [7].

1.2.1 Cathode materials

The most common cathode materials for lithium batteries contain lithium in their structures as LiCoO$_2$, LiFePO$_4$, LiMn$_2$O$_4$, LiNiMnCoO$_2$ (NMC) [7-8], with capacities 140 mAh/g, 160 mAh/g, 110 mAh/g and 170 mAh/g respectively. This type of materials are inorganic and the structures and redox reactions for the most common cathode materials are shown in Figure 1.2.

These materials have some disadvantages which need to be overcome. For example, LiFePO$_4$ has low electrical conductivity, which can be improved by coating with thin
carbon layer. LiMn$_2$O$_4$ is known to dissolve Mn ions into the electrolyte. For LiCoO$_2$ only 0.5 lithium can be extracted from the structure.

There are also organic cathode materials, which requires less of scarce metals, which have been studied. There are known as eco-friendly materials and some examples are: dilithium rhodizonate (Li$_2$C$_6$O$_6$), carboxylates and amide salts [9]. Some structures and redox reactions are shown in Figure 1.3.

Research areas for lithium-ion batteries include life extension, improved energy density, safety, cost reduction, and charging rate, [10] among others.

![Figure 1.3. Structure and electrochemical reactions of some organic cathode materials.](image)

### 1.2.2 Anode materials

Anode materials for lithium batteries have been development with several different elements, mainly of group IV (C, Si, Ge, Sn) and group V (P, Sb). The most common anode is conventional graphite, which has been used in batteries without any safety issues [11-14]. Other alternative materials [15-19] including Si, Sn, other type C, alloyed materials, and Li$_4$Ti$_5$O$_12$ have been used for improving anode performance. The structures of the most common anode materials are show in Figure 1.4.

The group IV elements (Si, Ge, Sn) have a higher specific capacities (3579 mAh/g, 1600 mAh/g, 994 mAh/g, respectively) than commercial carbon-based anodes (372 mAh/g) [20-24]. They have been considered the most promising anode candidates for the next generation of the LIBs. However, the use of bulk Si, Ge and Sn have a disadvantage due to the high volumetric change of ~300% (297%, 270%, 257%, respectively) during the lithiation and delithiation process.

It leads to particle pulverization and destabilization of a solid electrolyte interphase (SEI) film, and result in fast capacity fading and low coulombic efficiency. New anode materials with higher redox potential along with high charge rate and low strain as Li-based (LixMy) alloys have been developed with composition of Li$_4$S, LiSi with an energy capacity of more than 1000 mAh/g has been reported [25].

![Figure 1.4. Structures of the most common anode materials.](image)
There are also organic anode materials that have been studied. There are known as eco-friendly materials and some examples are quinones and nitroxide radicals [9]. Some structures and redox reactions are shown in Figure 1.4.

![Figure 1.4. Structure and electrochemical reactions of some common anode materials.](image)

\[
\begin{align*}
C_6 + Li^+ + e^- & \xrightarrow{\text{Charge}} LiC_6, \\
Li_4Ti_5O_{12} + 3Li^+ + 3e^- & \xrightarrow{\text{Charge}} Li_7Ti_5O_{12}, \\
\end{align*}
\]

1.3 Conducting polymers

Among the conductive organic polymers that have been extensively studied, one type is more precisely called intrinsically conducting polymers (ICPs). These are organic conjugated polymers, a type of materials having the property of conducting electrons. The conducting polymers may have metallic conductivity or semiconductors properties depending on the grade of doping. Some common conducting polymers are shown in Figure 1.5 [26-27].
The electrical conductivity of the π-conjugated polymers is mainly determined by their electronic structure. The conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied [28-29] as illustrated in Figure 1.6.

Figure 1.6. Chemical structures of polyacetylene showing the effect of doping in presence of I$_3^-$. 

Figure 1.7 shows the conductivity values of the different π-conjugated polymers. The electrical conductivity of an ICPs is mainly determined by its electronic structure. The π-conjugated polymers have an alternating single (σ) and double (π) bonds, and these π-conjugated systems give the ICPs their inherent optical, electrochemical, and electrical-electronic properties. These parameters are mostly affected by the physical properties of the ICPs: their conjugation length, degree of crystallinity, and intra- and inter- interactions in the polymer chain. The energy band theory is a useful way to visualize the differences between conductors, insulators and semiconductors.
The electrical conduction can be explained by formation of polaron and bipolaron as shown in Figure 1.8. The effects of polarons and bipolarons can be explained in terms of energy band gap theory. Undoped electrically conducting polymers can be thought of as semiconductors, and for example doping with Li$^+$ decreases the band gap.

The mechanism of the formation of polaron and bipolaron is shown in Figure 1.9. The CPs can be doped as p-type and n-type. The doping process generates positive or negative polarons-bipolarons. These charge carriers are delocalized in the polymer chains, which facilitates the electronic conductivity along the polymer chain. The negative charged carriers in n-type are not as stable as positively charged forms. As an example Figure 1.8 shows the formation mechanism in Ppy as p-type doped. The PPy chain exhibits four distinct electronic band structures with different doping levels.
the undoped state, PPy is an insulator with a large band gap of approximately 3.16 eV [28].

![Figure 1.9. Mechanism of formation of polaron and bipolaron in polypyrrole (PPy)](image)

The electrical properties of conducting polymers change with the oxidation or reduction, and depend on state and structure. For example, when PPy has high doping level the structure has low resistance and the behavior is like a conductor but if the structure has low doping, the behavior is like an insulator (Figure 1.10).

![Figure 1.10. Chemical structures of π-conjugated polypyrrole (Ppy)](image)

The most studied π-conjugated polymer is polyaniline (PANI). Polyaniline can be synthesized by different methods: chemical synthesis and electro-polymerization. Chemical oxidation is the most common method to synthesize polyaniline (PANI) using different oxidants as ammonium persulfate (APS), iron chloride (FeCl₃), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂) and others [30]. APS is the oxidant most commonly used in the synthesis by chemical oxidation according to the following reactions, Figure 1.11:

![Figure 1.11. Chemical reaction for the synthesis of PANI](image)

Two types of units are present in the structure of PANI, the quinoid diimine (oxidized unit) and benzoid diamine (reduced unit), Figure 1.12.
The structure of PANI depends on the doping, and usually inorganic acids like HCl, H₂SO₄ and H₃PO₄ are used as dopants but it is also possible to use organic acids. Five chemical species are possible in the synthesis of PANI, shown in Figure 1.13.

![Figure 1.12. Oxidized and reduced units in the structure of PANI](image)

The monomer units are built from reduced (x) and oxidized (1-x) blocks: where 0 ≤ x ≤ 1. The redox state of the PANI is determined by the value of x, which may vary continuously from zero to unity. At x=0.5, PANI occurs in the form of emeraldine; x=0 corresponds to the fully oxidized form pernigraniline, x=1 corresponds to the fully reduced form leucoemeraldine [31]. Pernigraniline and emeraldine may occur as either salts or bases [32-33].

![Figure 1.13. Structures of different forms of PANI and their electrochemical reactions in e.g sulphuric acid.](image)
The forms of PANI have different colors, stabilities and conductivities. Leucoemeraldine is colorless, emeraldine base is blue, emeraldine salt is green, pernigraniline base protonated is blue and pernigraniline base is violet, see Figure 1.13.

PANI has been studied and described as the most stable conductive polymer and can be used as cathode material for lithium rechargeable batteries [34]. The PANI electrode has the possibility to work by two mechanisms for the charge process: a) Charge separation mechanism and b) Intercalation mechanism [35], as illustrated in Figure 1.14.

Figure 1.14. The proposed charge mechanisms of PANI cathode materials: (a) charge separation mechanism and (b) intercalation mechanism.

The charge separation mechanism was indicated by X-ray photoelectron spectroscopy (XPS) and electron-spin-resonance (ESR) signals for the polyaniline before and after charging [35].
1.4 Hybrid materials

A hybrid material is a combination of inorganic and organic components, homogeneously distributed to molecular level and/or nanometer level. There are also so-called nanocomposites, having at least one component with nanometer dimensions (1-100 nm). The boundary between the hybrid materials and nanocomposites is not clear in the literature but for both materials the properties are determined by the synergistic combination of the inorganic-organic components. Hybrid materials can be classified according to the possible interactions between the inorganic and organic components: Class I hybrid materials are those with weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions. Class II hybrid materials are those with strong chemical interactions between the components [36], see Figure 1.15.

Figure 1.15. Illustration of hybrid materials: Class I, blends and interpenetrating networks (upper) with weak interactions and Class II, with covalently bonded blocks or polymers with strong chemical interactions.
As illustrated in Figure 1.16 there is a steady transition between weak and strong chemical interactions for different hybrid materials.

![Figure 1.16. Different hybrid materials and their chemical interactions (Contributed with pi-pi interactions) [36].](image)

In addition to the bonding characteristics, structural properties can also be used to distinguish between various hybrid materials. An organic moiety contains a functional group that allows the attachment to an inorganic network.

The general strategies for the design of hybrids materials and their synthesis routes are independent of their types or applications. The synthesis routes are determined by the nature of the interaction and interface between organic and inorganic components as a first feature. As a second important feature in the tailoring of hybrid networks concerns the chemical pathways that are used to design a given hybrid material.

The design and synthesis of hybrid materials depends on the type of hybrid sought. Class I and class II hybrids differ in the type of synthesis approaches and this is relevant for their successful use in different applications. In Figure 1.17 various types of hybrids are shown and will require different strategies for their synthesis. The solvent may or may not contain a specific organic molecule, a biocomponent or polyfunctional polymers that can be crosslinked. The molecule can also interact or be trapped to the inorganic components through long or short-range interactions as hydrogen-bonds, π–π interactions, and van der Waals-interactions.

The synthesis strategies can be divided into four categories: Conventional sol-gel route (Route A), self-assembly (Route B and D) and assembly building blocks (Route C). These strategies are simple, low cost and yield hybrid materials [37].
Route A corresponds to conventional sol-gel chemistry. The hybrid networks are obtained through hydrolysis of organically modified metal alkoxides or metal halides condensed with or without simple metallic alkoxides.

Route B and D corresponds to the self-organization (self-assembly) or the texturation of growing inorganic or hybrid networks, templated by the directing agents of the organic structure. The advantage of this strategy is the ability to control and tune hybrid interfaces. The hybrid organic-inorganic phases formed by this strategy are very interesting, due to the versatility they demonstrate in the building of a whole continuous range of nanocomposites with different pore sizes.

Route C is another suitable synthesis route. The inorganic component consists in the use of preformed objects that keep their integrity in the final hybrid material. These assemblies of building blocks can be clusters, organically pre-functionalized or post-functionalized nanoparticles (metallic oxides, metals, chalcogenides, etc.), nanocore-shells [38] or layered compounds able to intercalate organic components [39]. The building blocks (BB) can be capped with polymerizable ligands or connected through organic linkers like telechelic molecules or polymers, functional dendrimers, etc.

The strategy of combining the building blocks with organic templates by self-assemble allows to control the formed structures. This combination between the “building block approach” (D) and “templated assembling” have an importance in the exploring of “synthesis with building blocks”. The synthesized materials show a large variety of interfaces between the organic and the inorganic components by covalent bonding, complexation, electrostatic interactions, etc.
Metal-organic compounds belong to one type of hybrid materials that have been of great interest during the last decade. They have potential applications in coordination chemistry, catalysis, sensors, biological and magnetic fields [40-42], and could be used in energy applications as materials for lithium batteries [43-45], luminescent compounds [46] and potential substitutes for dye-sensitized solar cells (DSSCs) [47-49]. One characteristics of those materials are the high surface and their high porosity which can be compared with other porous materials such as covalent organic frameworks (COFs) and zeolites, Figure 1.18.

![Figure 1.18. Structures of different porous materials.](image)

The coordination polymers (CP) [50], coordination networks (CN) and metal–organic frameworks (MOFs) [51], constitute a field with its origin in so-called coordination chemistry that has expanded rapidly the last two decades because they are attracting the interest of the chemical industry [52].

![Figure 1.19. Examples of coordination compounds and their structures.](image)
The terminology of this type of compounds are according to IUPAC [53]:

- Metal–organic framework (MOF) abbreviated to MOF, is a coordination network with organic ligands containing potential voids. One example of a MOF is shown in Figure 1.19a, presented without acetonitrile, acetone solvent, and anions [54].

- Coordination networks (CNs) are coordination compounds extending through repeated coordination entities in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links. Alternatively, they are coordination compound extending through repeated coordination entities in 2 or 3 dimensions. Nets can also be formed by cross-links between single chains as shown in Figure 1.19b.

- Coordination polymers (CPs) are coordination compounds with repeated coordination entities extending in 1, 2, or 3 dimensions. A classical type of single-chain coordination polymer is the (4,4'-bipyridine-N,N)-bridged cobalt(II) compound depicted in Figure 1.19c [55].

The synthesis and design of these type of compounds are influenced by many factors, such as the metal ions, organic linkers, solvents, temperature and pH [56-58]. The metal ions and organic ligands are especially important for the design, because they play a key role as linker between the metal nodes and the organic structures [59-60]. A very effective method for regulating the properties of MOFs, CNs and CPs is the selection of organic linkers [61]. The organic linker and the metal ion will define the type of the metal-organic compound that is formed as a final product.

The MOFs has been studied for lithium ion batteries applications. The first MOF used as an anode material for LIBs was MOF-177 reported in 2006 [62]. The Li-ion storage occurs through conversion reactions, which destroys the MOF structure (Figure 1.20) and the formation of metallic Zn, see reactions:

\[
\begin{align*}
Zn_4O(BTB)_{2}(DEF)_{m}(H_2O)_n + e + Li^+ & \rightarrow Zn + Li_2O \\
DEF + H_2O + e + Li^+ & \rightarrow Li_2(DEF) + LiOH \\
Zn + Li^+ + e & \rightarrow LiZn
\end{align*}
\]
The irreversible degradation of MOF-177 leads to a poor cycling performance. MOF-177 shows a high initial discharge capacity of 400 mAh/g under 50 mA/g, but this drops to 105 mAh/g in the second cycle. The inorganic and organic units can serve as redox active sites during the electrochemical process. Thus, compounds using Fe, Co, Zn, or Mn with different linkers can potentially be used as electrode materials for LIBs and fuel cells. Recently, several different MOFs, CNs and CPs have been investigated as anode, cathode, and electrolyte materials for LIBs [63-64].
2 Scope of the thesis

The main aim of this thesis work is to understand the relationship between the structure and electrochemical properties of the hybrid materials as potential materials for lithium-ion batteries. This involves synthesis, structural characterization and electrochemical characterization of the materials.

The first goal is to design the synthesis strategy for two groups of hybrid materials with expected interesting electrochemical properties. These materials are going to be electrochemically investigated. Together with the analysis of their structures, the suitability of the materials as cathodes or anodes in lithium-ion batteries will be analyzed and evaluated.

The second goal is the structural characterization by single crystal x-ray diffraction (SCXRD), powder x-ray diffraction (PXRD), infrared spectroscopy (IR) and TGA-analysis to understand the structure or propose a possible structure of the synthesized materials in order to explain their chemical and electrochemical properties.

The third goal is to perform the electrochemical characterization of the synthesized hybrid materials by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge-discharge processes to explain the relationship between the structure and electrochemical properties of each hybrid materials.
3 Experimental

3.1 Materials and reagents

3.1.1 Synthesis of materials

The reagents used in the synthesis of PANI and LiFePO$_4$-PANI were aniline (C$_6$H$_5$NH$_2$), ammonium persulphate (APS), phosphoric acid (H$_3$PO$_4$), LiFePO$_4$ (LFP) provided by Phostech Lithium Inc., lithium acetate (LiOAc) and ethanol. Some of the synthesis was carried out in a furnace at 300 °C with Ar atmosphere. FeCl$_3$.4H$_2$O, NiCl$_2$.6H$_2$O, terephthalic acid (H$_2$BDC) and N,N-dimethylformamide (DMF, as solvent) were used for the synthesis of Ni$_3$($C_8$H$_4$O$_4$)$_3$($C_3$H$_7$NO)$_3$ and Fe-BDC. The synthesis was carried out by a solvothermal process in an autoclave at 150 °C for 24 h.

3.1.2 Synthesis of PANI

The synthesis of PANI (Paper 2) was carried out by dissolving 25 mmol of APS in 50 ml of distilled water. 20 mmol of aniline were dissolved in 50 ml of 1M H$_3$PO$_4$ in aqueous medium. Both solutions were added at room temperature. The APS solution, containing the aniline, was added to the previous solution. The mixture was stirred for 1 h at 5 °C. A dark blue precipitate of emeraldine base (EB) was collected by filtration and washed with distilled water and ethanol and dried under vacuum at 60 °C for 8 h (yield 99.99%). The reaction 1 is shown below:

\[
\begin{align*}
4n & \quad + 5n(NH_4)_2S_2O_8 \quad \xrightarrow{H^+} \quad H_2O + 5n(NH_4)_2SO_4 \\
\text{Reaction 1.}
\end{align*}
\]

3.1.3 Synthesis of LiFePO$_4$-PANI by thermal treatment

The synthesis of LiFePO$_4$-PANI with ~25 wt% polyaniline was carried out using 0.75 g of commercial LiFePO$_4$ (Phostech Lithium Inc.), 0.25 g synthetized PANI (i.e. EB) and 0.1675 g LiOAc (lithium acetate), which were mixed in a mortar for 0.5 h, subsequently transferred to crucible and exposed thermal treatment at 300 °C for 1 h in Ar atmosphere. A black powder with a mass yield of 99.95% was obtained. A schematic reaction scheme is shown in Figure 3.1.
3.1.4 Synthesis of Ni-BDC-DMF

The Ni-BDC-DMF hybrid compound was synthesized by the solvothermal method via reaction between NiCl$_2$.6H$_2$O (0.6143 g, 2.58 mmol), terephthalic acid (H$_2$BDC) (0.8587 g, 5.20 mmol) and N,N-dimethylformamide (DMF) (50 ml) as a solvent. The reactants were dissolved in DMF and the solution was transferred to a steel autoclave at 150 °C for 24 h. Figure 3.2 shows a scheme of the reaction.

The green crystals obtained were collected by filtration, washed several times with DMF and dried at 100 °C. The yield of the collected green crystals was 0.7004 g, corresponding to a yield of 70%. The reaction of the synthesis is shown in reaction 2:

\[
3\text{NiCl}_2.6\text{H}_2\text{O} + 3\text{C}_8\text{H}_6\text{O}_4 + 4\text{C}_3\text{H}_7\text{NO} \xrightarrow{\text{DMF}} \text{Ni}_3(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_3\text{H}_7\text{NO})_4 + 6\text{HCl} + 6\text{H}_2\text{O}
\]
3.1.5 Synthesis of Fe-BDC-DMF

The hybrid compound Fe-BDC-DMF was synthezized by solvothermal method via reaction between FeCl$_3$.4H$_2$O (0.6143g, 2.58 mmol), terephthalic acid (H$_2$BDC)(0.8587 g, 5.20 mmol) and N,N-dimethylformamide (DMF)(50 ml) as a solvent. The reactants were dissolved in DMF, afterwards the solutions were transfer to a steel autoclave kept at 150 °C for 24 h. The green crystals obtained were collected by filtration, washed several times with DMF and dried at 100 °C. The mass of the yielded green crystals collected was 0.4954 g, corresponding to a yield of 50%. Figure 3.3 show a scheme of the reaction.

Figure 3.3. The schematic reaction of the synthesis of Fe-BDC-DMF.

3.2 Structural characterization

3.2.1 Methods and equipment

The LiFePO$_4$ and LiFePO$_4$-PANI was characterized by X-ray powder diffraction (PXRD) was carried out by using X’Pert Panalytical, with a scan rate of 0.02°/s, by Cu–Kα radiation (λ = 1.5406 Å). X’pert Highscore software (Panalytical. B. V, Lelyweg, the Netherlands) was used for identification of the phases.

The morphologies of the samples were determined by S-4800 series field-emission high-resolution scanning electron microscope (SEM) (Hitachi, Tokyo, Japan), equipped with EDS detector. The powder samples were mounted in the sample holder and sputtered with a thin layer of Pt/Pd.

The Fourier transform infrared spectroscopy (FTIR) was detected on Spectrum 100 (Perkin Elmer) in the wavelength range of 4000–400 cm$^{-1}$ with a resolution of 1 cm$^{-1}$. The TG was carried out by placing 20 mg of the specimen of the TG instrument (LABSYS evo STA 1150, SETARAM Instrumentation), with Temperature Range; Room temperature to 1150 °C and 0.01 to 100 °C/min.

The samples of Ni-BDC and Fe-BDC was characterized by powder X-ray diffraction (PXRD). The data were collected on a Panalytical Xpert, X-ray diffractometer with Cu
Kα1. The FT-IR spectra were measured with a Perkin-Elmer Spectrum 65 instrument in the range 4000–500 cm⁻¹.

The electrochemical characterization was performed at 20 °C using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge-discharge curves measured with a Gamry 600 potentiostat.

3.3 Electrochemical characterization

3.3.1 Preparation of electrodes and cells

The active cathode material LiFePO₄-PANI was made by preparing a mixture with relation to 80:10:10 of active materials: (LFP-PANI), conducting agent (Super P) and binder (PVDF), respectively. The components of the mixture were weighed and subsequently grounded in a mortar for 15 min. Then NMP (N-methylpyrrolidone) was added as solvent and the mixture was stirred for 1 h using a magnetic stirrer. The electrode was tape-casted by a doctor blade process on an Al foil with a slitt height of 100 μm.

The Ni-BDC-DMF and Fe-BDC-DMF powders were used to prepare electrodes by dispersing the active material, carbon super P, and poly(vinylidene fluoride) (PVDF) binder in a composition of 80:10:10 %wt in 1-methyl-2-pyrrolidinone (NMP) solvent, with the mixture ground until it became homogeneous, using an agate mortar. The resulting slurry was pasted onto copper foil and dried in vacuum at 90 °C for 24 h to remove the NMP solvent.

To investigate the electrochemical performance test-cells were assembled in an argon-filled glove box (H₂O, O₂ < 0.1 ppm). The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) and a microporous polypropylene film (Celgard 2325) was used as the separator. Electrode discs with a diameter of up to 14 mm were cut out and coin-type test-cells were fabricated according to the schematic diagram presented in Figure 3.4.

Figure 3.4. Schematic diagram of the coin-type test-cell with the active materials used for electrochemical testing, e.g. for Fe-BDC-DMF cathode.
The electrochemical testing of LiFePO$_4$, PANI and LiFePO$_4$-PANI was done in a coin-cell of 0.9 cm$^2$ active area, using metallic Li as counter and reference electrode, Celgard (2325) as separator and a solution of 1M LiPF$_6$ dissolved in EC-DMC (1: 1 vol) as electrolyte.

### 3.3.2 Electrochemical measurements

For the electrochemical testing of LiFePO$_4$, PANI and LiFePO$_4$-PANI electrodes were subjected to charge-discharge cycling at 0.1C between 2.5 and 4.2 V vs. Li$^+/Li^0$ and electrochemical impedance spectroscopy (EIS) at 0.1 Hz-100 kHz and an AC voltage amplitude of 10 mV.

The electrochemical impedance for Ni-BDC-DMF and Fe-BDC-DMF was measured at 1 mHz – 1 MHz and an AC voltage of 10 mV. The cyclic voltammograms were recorded with a scan rate of 0.1 mV/s for Ni-BDC-DMF and 10 mV/s for Fe-BDC-DMF at 20 °C. The charge and discharge curves recorded at 0.1 C rate in the potential window 0.5-3.5 V vs. Li$^+/Li^0$. 
4 Results and discussion

4.1 PANI

4.1.1 Synthesis and structural characterization

4.1.1.1 Synthesis of PANI

The synthesis of PANI was performed by chemical oxidation of the aniline with APS. The addition of aniline on the solution of H$_3$PO$_4$, leads to the formation of protonated species of C$_6$H$_5$NH$_3^+$ -H$_2$PO$_4^-$, which is much more soluble compared to aniline and it reacts with the APS initiating the polymerization. The mechanism of the polymerization is shown in the Figure 4.1.

![Mechanism of polymerization of aniline in the synthesis of PANI](image)

After the addition of the APS solution, the polymerization reaction begins with the appearance of a green coloration due to the formation of a polyaniline species called emeraldine salt (ES). Later the coloration change to blue due to the formation of the chemical species emeraldine base (EB). The structures of species are shown in Figure 4.2.
4.1.1.2 PXRD characterizations of PANI

The crystallographic characterization of the dark blue powder obtained was carried out by X-ray Powder Diffraction (XRD). The diffraction pattern of the product is shown in Figure 4.3.

The diffraction pattern shows a good crystallinity of the PANI. The diffraction planes (011) correspond to the orientation parallel to the polymer chain. The plane (100) correspond to the parallel and perpendicular periodicity of the polymer chain. The planes (200) correspond to the periodicity perpendicular to the chain. [65].

Figure 4.3. X-ray diffraction pattern of the PANI sample.
4.1.1.3 SEM and EDS

Figure 4.4 shows SEM images of PANI. The synthetized PANI by a self-assembly process has globular morphology with aggregates of an average diameters of 2.75 µm. The primary particles of an average diameter of 310 nm, the globular morphology, characteristic of PANI synthesized by chemical oxidation as shown in Figure 4.4.

The spectrum of energy dispersive spectroscopy (EDS) in Figure 4.5, shows the presence of C and N, from PANI, P from $\text{H}_2\text{PO}_4^-$, S from HSO$_4^-$ and O from $\text{H}_2\text{PO}_4^-$ and HSO$_4^-$ in the PANI powder.

![SEM images of PANI](image1)

![EDS spectrum](image2)

Figure 4.4. SEM images of the PANI synthesized showing the agglomerates.

Figure 4.5. EDS spectrum of the synthetized PANI.
4.1.1.4 FT-Infrared spectroscopy

The IR spectrum of PANI shown in Figure 4.6, shown the presence of a band around 1136 cm\(^{-1}\), which is known as an "electronic band" being associated, the doped form of polyaniline, specifically the vibration mode of the structures -NH\(^+\) = [66]. The spectra show characteristic peaks at about 1575 cm\(^{-1}\) for C=N stretching mode of the quinonoid rings, 1486 cm\(^{-1}\) for C=C stretching mode of benzenoid rings, 1299 cm\(^{-1}\) for C-N stretching mode. The vibrational bands at about 1144 and 708 cm\(^{-1}\) are assigned to the aromatic ring in-plane and out-of-plane C-H bending [67-68]. The peaks in 796 cm\(^{-1}\) is assigned to N-H wag vibration, characteristics of primary and secondary amines only, the 3229 cm\(^{-1}\) is assigned to N-H stretching vibration, which is seen in case of PANI-EB. The peaks around 3230 cm\(^{-1}\) and 2464 cm\(^{-1}\), correspond to stretching of O-H of the group HSO\(_4^-\)[69].

![Figure 4.6. FTIR spectra for PANI.](image)

The ratio of the quinoid and benzenoid units (C=N/C-N) can be estimated by taking the ratio of the areas of the IR bands at \(~1300\) and \(~1590\) cm\(^{-1}\) (Figure 4.7). This ratio
is directly related to the oxidized state of the PANI polymer. The ratio of the two bands is less than one indicating that there are more benzene units within the PANI polymer. The ratio R is calculated on the basis of the following equation (1) [70]:

\[ \frac{V_{HN\equiv NH}}{V_{N\equiv \pi N}} = R = \frac{1-X}{X} \]  

(1)

The values of the area calculated from the FTIR data are R=0.462 for PANI. Therefore, the structure of PANI can be represented as Figure 4.7.

A possible structure and interactions in the PANI is shown in Figure 4.8.

The possible interactions present in the structure are hydrogen bonds, ion-ion and interaction as oxygen one pair-\(\pi\) and ion-\(\pi\). These interactions are weak except the hydrogen bond. The role of those interaction define the crystallinity of the PANI and the packing on the chains in the structure.
4.1.1.5 **Thermogravimetric analysis**

The TGA measurements of the PANI powder was carried out in air atmosphere. It is shown in Figure 4.9. The mass loss from room temperature 25 to 150 °C is due to the elimination of a small amount of water and the rupture of the hydrogen bonds. The pristine PANI is completely decomposed between 150-600 °C. In the range of 180-300 °C is the formation of a cross linked PANI (see Figure 4.10).

![Figure 4.9. Thermogravimetric curves for PANI](image)

The PANI sample displayed an accelerated weight loss at 350–600 °C due to the pyrolysis of the polymer. For pure PANI, the gradual weight loss between 100 and 349°C produce the elimination of dopant H2SO4 of acid PANI and the major weight loss above 349°C was assigned to the decomposition of PANI.

![Figure 4.10. Conversion reaction and structure of cross linked PANI.](image)
4.1.2 Electrochemical characterization of PANI

4.1.2.1 Charge-discharge

The PANI composites was electrochemically tested in a cell by charging and discharging at room temperature over 10 cycles at a rate 0.1C. Figure 4.11 and Figure 4.12 show the charge-discharge capacity vs. cycle number and capacity vs. voltage. The PANI was tested in the range of 2.5-3.9 V. The PANI shows a low capacity of 95 mAh/g.

The theoretical capacity of the PANI is 142 mAh/g compared with the experimental results of 95 mAh/g. Figure 4.12 shown the discharge capacity is increases with increasing number of cycles.

Figure 4.13 shows the charge-discharge at different C-rates. The PANI shows the best rate capability with discharge capacity of 95 mAh/g at 0.1C compared with other C-rates. This means that PANI has low capacity when charged-discharged at high current.

Figure 4.13. Specific discharge capacity at different C-rates for the PANI.
4.1.2.2 Electrochemical Impedance Spectroscopy

The Nyquist diagram of the PANI shown in Figure 4.14. The values of R1 (high frequency intercept) represents the ionic resistance and has a value of about 4 Ohm. The value of Rct (charge transfer resistance) is indicated by a minimum of the imaginary part of the Nyquist diagram. This represents the internal resistance of the film formed and the charge transfer and has a value of 260 Ohm.

![Nyquist diagram](image)

Figure 4.14. Impedance spectroscopic study at OCP 2.4V) at 10 mV, frequency range 10 mHz-1MHz, T=20 °C, 1M LiPF₆ dissolved in EC-DMC (1: 1 vol) as electrolyte, Celgard as separator.
4.2 LiFePO$_4$-PANI

4.2.1 LiFePO$_4$-PANI by thermal processes

4.2.1.1 Synthesis of LiFePO$_4$-PANI

The reaction between LiFePO$_4$, PANI and LiOAc starts during the mixing and a characteristic smell of acetic acid was detected, also a change in the color of the PANI from blue to green occurred. The observed change of color was attributed to the formation of EB and ES in Figure 4.2.

The EB reacts with LiOAc through lithiation and protonated ES in the PANI structure. During the thermal treatment at 300°C for 1 h in inert atmosphere of Ar/H$_2$ the HOAc is removed by evaporation.

During the thermal treatment the PANI is converted by a chemical reaction between two chains of PANI to form cross linked PANI.

The quinoid unit of the PANI chain (blue color) react with a quinoid unit of another PANI chain to form the cross linked PANI [71]. Probably only a small amount of PANI reacts to form cross-linked PANI. The HOAc react with H$_2$PO$_4^-$ and HSO$_4^-$ in the structure of PANI according to reactions in Figure 4.15.

![Figure 4.15. Reactions of the HSO$_4^-$ and H$_2$PO$_4^-$ in the PANI with LiOAc](image-url)
4.2.1.2 PXRD characterizations of LiFePO$_4$-PANI

The XRD diffraction pattern of the LiFePO$_4$-PANI composite show diffraction peaks corresponding to the group Pnmb for LiFePO$_4$. The structure of LiFePO$_4$ is shown in Figure 4.16. A qualitative structure of the LiFePO$_4$-PANI is shown in Figure 4.17. The surface of the LiFePO$_4$ particles are coated with PANI, as can be seen.

A low amount of phase impurity is detected as Li$_2$SO$_4$ (01-075-0929) and Li$_3$PO$_4$ (01-071-1528) as shown in Figure 4.18. It is the reaction product between Li$^+$ of the LiOAc and SO$_4^{2-}$ or PO$_4^{3-}$ in the structure of PANI. The diffraction pattern of PANI is not observed in the patterns of the composite due to its small amount, amorphous state, and the low intensity of its diffraction peaks.
4.2.1.3 SEM and EDS of LiFePO$_4$-PANI

Figure 4.19 shows SEM images of LiFePO$_4$ and LiFePO$_4$-PANI respectively. From the SEM images it can be seen that the particles size of LiFePO$_4$ is distributed with an estimated average diameter of 300 nm and the LiFePO$_4$-PANI particles have an estimated average diameter of 180 nm. The particles were split to smaller particles via milling and stirring in a mortar before the thermal treatment and they seem to be coated by PANI homogeneously. This is advantageous for the electrolyte and diffusion of Li$^+$ into the active particles, which improves the rate capability of the material [72].

![SEM images](image1)

Figure 4.19. SEM images of the a) LiFePO$_4$ and b) LiFePO$_4$-PANI composite.

The particle size and shape of the LiFePO$_4$-PANI composite are similar to the LiFePO$_4$ particles but the surfaces morphologies are different. A comparison of the surfaces between LiFePO$_4$ particles and LiFePO$_4$-PANI particles show differences in roughness. This can be attributed to a possible homogenous coating of PANI on the surface of the LiFePO$_4$ particles. The SEM imaging coupled with EDS element mapping provide a qualitative elemental and semiquantitative analysis of the LiFePO$_4$-PANI powder which is presented in Figure 4.20.

![SEM with EDS](image2)

Figure 4.20. Scanning electron microscopy (SEM) of LiFePO$_4$-PANI coupled with energy dispersive spectroscopy (EDS).
The experimental results shown a good correlation between the PXRD, SEM images and the EDS. Figure 4.20 and the spectrum in Figure 4.21 show the presence of C, N, P, S and Fe. The mapping of N, S and C indicates a homogenous distribution of PANI on the LiFePO$_4$ particles. However, some flakes of PANI extending from the particle surfaces can also be observed. The mapping of the S shows a small high concentration of S attributed to a small amount of Li$_2$SO$_4$.

**4.2.1.4 FT-Infrared spectroscopy**

The IR spectrums in Figure 4.22 show a comparison of PANI, LiFePO$_4$ and LiFePO$_4$-PANI. The LiFePO$_4$ shows four fundamental modes. The bands around 1136, 1092, 1058, and 977 cm$^{-1}$ correspond to the P–O antisymmetric stretching vibration of the olivine phosphate groups [73, 74]. The bands around 647 and 632 cm$^{-1}$ correspond to the O–P–O symmetric and anti-symmetric stretching vibrations. [75].

![FTIR spectra for LiFePO$_4$, PANI and LiFePO$_4$-PANI](image)

Figure 4.22. FTIR spectra for LiFePO$_4$, PANI and LiFePO$_4$-PANI.
The IR spectrum of LiFePO$_4$-PANI shows shifts in the broad bands (LiFePO$_4$ band to LiFePO$_4$-PANI band); 1092 to 1194, 1058 to 1031, and 977 to 983 cm$^{-1}$ compared to LiFePO$_4$ and corresponding to the P–O antisymmetric stretching vibrations. We believe that these shifts probably are due to the chemical interaction of hydrogen bonds between LiFePO$_4$ and PANI by P-O---H-N. The O–P–O symmetric and antisymmetric stretching vibrations shown at 632 cm$^{-1}$ has changed with the P vibration and a new peak appears at 610 cm$^{-1}$, attributed to O–P–O--H-N interaction.

The vibration mode of the NH$^+$= structures at 1136 cm$^{-1}$ associated with the doped form of polyaniline, in this case doped with Li$^+$, is overlapped with the P-O vibration. The peaks change from 1299 to 1307 cm$^{-1}$ for C-N stretching and peaks at about 1575 to 1592 cm$^{-1}$ for C=N stretching mode of the quinonoid rings, 1486 to 1505 cm$^{-1}$ for C=C stretching mode of benzenoid rings, compared with polyaniline, reveal that the polyaniline in the LiFePO$_4$-PANI has more quinoid units than the PANI. This is probably because the chain of PANI deposited on the surface of the particles of LiFePO$_4$ has a greater conjugation [76]. The peak at 796 cm$^{-1}$ is assigned to N-H wag vibration and the one at 3229 cm$^{-1}$ is assigned to N-H stretching vibrations. This last peak is not present in the LFP-PANI spectrum and this can be attributed to chemical interaction by the hydrogen bond N-H--O-P. The change in the vibration values in the LiFePO$_4$-PANI compared with LiFePO$_4$ and PANI is attributed to chemical interaction by hydrogen bonds between the electronic cloud of PANI and LiFePO$_4$ caused by polarization and the change in the dipolar moment. The structure of LiFePO$_4$-PANI could be represented by the structure in Figure 4.23, where X=0.5 for the polyelemeraldine salt.

![Figure 4.23. Oxidized and reduced units of LiFePO$_4$-PANI.](image)

The ratio R is calculated using equation (1). The values based on the area calculated from the FTIR data are R=0.462 for PANI and R=0.500 for LiFePO$_4$-PANI respectively. Therefore, the structure of PANI and LiFePO$_4$-PANI can be represented as in Figure 4.24.

![Figure 4.24. Oxidized and reduced units of PANI and LiFePO$_4$-PANI.](image)
The ratio between quinoid and benzoid units in the PANI and LiFePO$_4$-PANI are similar. This indicates that the thermal treatment does not produce any significant changes in the structure of the PANI.

According to results of PXRD, SEM, IR and EDS a possible structure and the interaction between the LiFePO$_4$ particles and PANI is shown in Figure 4.25.

Possible interactions present in the structure are hydrogen bonds, ion-ion, oxygen lone pair-π and ion-π. These interactions are weak and indicate the possibility of interaction and formation of a small amount of cross linked PANI during the thermal treatment.

### 4.2.1.5 Thermogravimetric analysis

The TGA curves are shown in Figure 4.26. The mass loss from 25 to 150 °C is due to the elimination of a small amount of water, absorbed in the LiFePO$_4$-PANI. The pristine PANI is completely decomposed between 150-600 °C. The PANI in LiFePO$_4$-PANI decomposes at 100–500 °C because LiFePO$_4$ is still stable at 850 °C and the residual mass of carbon formed by decomposition of the polymer can be neglected. The calculated mass contents of PANI in the LiFePO$_4$-PANI composites is 25 %, which corresponds well to the precursor mass in the synthesis step.
Figure 4.26. Thermogravimetric curves for pristine PANI and LiFePO₄-PANI.

4.2.2 Electrochemical characterization of LiFePO₄-PANI

4.2.2.1 Charge-discharge

The LiFePO₄-PANI composites was electrochemically tested in a button-type test cell by charging and discharging at room temperature over 50 cycles at a rate 0.1C. Figure 4.27 shows the charge-discharge capacity vs. cycle number for the LiFePO₄-PANI composite. The LiFePO₄ and LiFePO₄-PANI with Li⁺ are electrochemically active in the range of 2.4-4.2 V. The LiFePO₄-PANI shows a small capacity fade of about 0.2% over 50 cycles.

The cell voltage as a function of specific capacity for LiFePO₄-PANI composites tested at 2.4-4.2 V is shown in Figure 4.28. At 0.1C, the specific discharge capacity of LiFePO₄-PANI composite doped with 25 wt% PANI is 145 mAh/g and the corresponding results for pure LiFePO₄ is 120 mAh/g and for PANI is 95 mAh/g (theoretical capacity of PANI is 142 mAh/g and of LiFePO₄ 170 mAh/g), as shown in Figure 4.29. The coulombic efficiency of the LiFePO₄-PANI is 98%. The superior performance of LiFePO₄-PANI can be ascribed to the improved electrical conductivity of LiFePO₄ by the interaction with PANI in the composite.
Figure 4.29. Comparison of discharge cycling performances for the LiFePO$_4$-PANI composite, PANI and LiFePO$_4$ charging and discharging at 0.1C.

Figure 4.30. Specific discharge capacity at different C-rates for the LiFePO$_4$-PANI, PANI and pure LiFePO$_4$.

Figure 4.30 is comparing LiFePO$_4$, PANI and LiFePO$_4$-PANI at different C-rates. LiFePO$_4$-PANI shows the best rate capability with a discharge capacity of 145 mAh/g at 0.1C and 100 mAh g$^{-1}$ at 2C. This means that incorporation of PANI on the surface of the particles of LiFePO$_4$ results in 21% capacity enhancement at 0.1C and 45% enhancement at 2C. The enhanced rate capability is attributed to the improved electrical and ionic conductivity, and Li$^+$ diffusion promoted by PANI on the surface of the LiFePO$_4$ particles.

The electrochemical impedance spectroscopy (EIS) curves for the LiFePO$_4$, PANI and LiFePO$_4$-PANI composite cathodes at OCV, 2.17 V for LiFePO$_4$ and 3.42V for LiFePO$_4$-PANI and 2.4V for PANI as shown in Figure 4.31. It should be noted that these EIS-curves were measured directly after assembly of the cells.

The semicircle formed by the middle frequency range of the impedance spectra is compared between PANI, LiFePO$_4$ and LiFePO$_4$-PANI. The smaller diameter of the LiFePO$_4$-PANI semicircle suggest a lower charge transfer impedance (Rct) [77-78] for the composite electrode. This indicates that the LiFePO$_4$ coated or combined with conductive PANI can effectively improve the charge transfer and the electrochemical properties of LiFePO$_4$ particles. The results are shown in the Table 4.1.
The results can be correlated with the structure proposed in Figure 4.32. It shows the different processes in the proposed structure. PANI also improves the contact resistance by increasing the contact area between LiFePO$_4$ particles and the current collector. In the charge transfer process the electron first moves through the molecular orbitals of the network in the LiFePO$_4$. After that the electron is transferred to the PANI chain, and moves through the polymer chain to the current collector. The Li$^+$ moves through the network of the LiFePO$_4$ and the PANI structure to the electrolyte.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_1$ (Ohm)</th>
<th>$R_{ct}$ (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO$_4$ as assembled (OCV)</td>
<td>14</td>
<td>180</td>
</tr>
<tr>
<td>LiFePO$_4$-PANI as assembled (OCV)</td>
<td>3.6</td>
<td>61</td>
</tr>
<tr>
<td>PANI as assembled (OCV)</td>
<td>4.1</td>
<td>240</td>
</tr>
</tbody>
</table>

4.3 Ni-BDC-DMF

4.3.1 Synthesis and characterization of Ni-BDC-DMF

4.3.1.1 Synthesis of Ni-BDC-DMF

Ni-NDC-BDC with the formula Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ is synthesized by complexations and condensation of the precursors to form the trinuclear Ni$^{2+}$. In general, carboxylic acids undergo a nucleophilic substitution reaction where the nucleophile (-OH) is substituted by another nucleophile (Nu). Also –OH can form complexes with metallic cations. The carbonyl group (C=O) becomes polarized, since oxygen is more electronegative than carbon and pulls the electron density towards
itself. As a result, the carbon atom develops a partially positive charge ($\delta^+$) and the oxygen atom develops a partially negative charge ($\delta^-$). In some cases, in the vicinity of a strong electrophile, the partially negatively charged carbonyl oxygen ($\delta^-$) can act as a nucleophile and attack the electrophile, in this case an attack to the Ni$^{2+}$ ions.

The nucleophiles that can attack through two different sites are known as amphoteric nucleophiles. In this case the terephthalic acid reacts with the H$_2$O from NiCl$_2$.6H$_2$O by an acid-base reaction to form a terephthalate anion which is more nucleophilic than terephthalic acid. The reaction is shown in the Figure 4.33.

![Figure 4.33. Scheme of the reaction acid-base of the terephthalic acid and the resonance structures.](image)

The DMF is a polar (hydrophilic) aprotic solvent. It facilitates reactions that follow polar mechanisms, such as SN2 reactions. The DMF also can be a nucleophile by the O atom and the negative density. The resonant structure is shown in Figure 4.34.

![Figure 4.34. Resonance structures of the DMF.](image)

The amides as DMF can be hydrolyzed to carboxylic acids by either acid-promoted or base-promoted processes. In the DMF there are two basic sites in function which could potentially be protonated, namely the carbonyl oxygen and the amide nitrogen.
The protonation of DMF by the H\(^+\) of the terephthalic acid occurs preferentially on the carbonyl oxygen because the electron pair on trivalent nitrogen is typically much less strongly held to the nucleus than are electron pairs on neutral, divalent oxygen. The carbonyl oxygen-protonated conjugate acid is highly resonance stabilized as seen in Figure 4.33. Three resonance structures can be seen, including one in which the unshared pair on nitrogen is used to stabilize the cation. Figure 4.35 shows a possible mechanism for DMF hydrolysis.

![Chemical Structures]

The DMF acts as a catalyst of the reaction with the H\(_2\)O provided in the NiCl\(_2\).6H\(_2\)O. As shown in Figure 4.33 and Figure 4.35, the formation of the anion is promoted by the terephthalate which is more nucleophilic due to the charge on the O atom. The reaction of complexation and condensation starts with the attack of the Tp anion to the Ni\(^{2+}\) complex coordinated with Cl\(^-\) and H\(_2\)O. The Cl\(^-\) is a good leaving group compared with H\(_2\)O and the reaction results in the formation of the Intermediate A as shown in Figure 4.36. The intermediate proceeds to the formation of the complex A.
Finally two complex A can coordinate a Ni$^{2+}$ forming the trimer by a condensation via olation mechanism (see Figure 4.37).

Figure 4.36. A possible mechanism for the formation of Complex A.

Figure 4.37. Condensation of the complex A to form the structure.
4.3.1.2 SCPXR Crystal structure solution of the Ni-BDC-DMF

The single crystal X-ray crystallographic analysis revealed the compound crystallizes in the monoclinic space group P21/c with Z = 2. The Ni\(^{2+}\) atom has a sixfold coordination sphere NiO\(_6\) and trinuclear Ni\(^{2+}\) atoms are coordinated to six molecules of the terephthalic acid with the two O atoms of the carboxylic group. They are also coordinated with O atoms of the four molecules of N,N-dimethyl formamide (DMF). As a result, two of the four molecules show disorder in the structure (see Figure 4.38).

In the structure of the Ni\(_3\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\)\(_n\), the terephthalate (tp) ligand coordinates in a tetradentate and a bis-dentate manner, thereby bridging three equivalent Ni atoms as a trinuclear part in the structure and the N,N-dimethylformamide (DMF) coordinates with the O atom. One of them is ordered and one disordered, see Figure 4.39a. This gives rise to the formation of a 2D and 3D coordination network in the structure, as shown in Figure 4.38b.

In the crystal structure, the aliphatic–COO group of the tetradentate ligand actively participate in the formation of bonds with Ni atoms, connecting to one other unit of Ni and resulting in a 2D chain along the b axis, and a 3D structure along the a and c axis. The 2D structure formed by terephthalate (tp) molecules linked by Ni atoms is shown in Figure 4.39.

---

**Figure 4.38.** a) Scheme of the transfer and electron and diffusion of Li\(^+\), b) Structure of [Ni\(_3\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\)]\(_n\), View along the a axis of the coordination network structure.

**Figure 4.39.** Structure of Ni\(_3\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\) along b axis, illustrating the 2D terephthalate chains. The DMF molecules were deleted for clarity.
4.3.1.3 Hirshfeld surface analysis

In order to visualize the intermolecular interactions in the asymmetric unit and the crystal of the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$, a Hirshfeld surface (HS) analysis [79,80] was carried out by using Crystal Explorer 17.5 [81]. In the HS plotted over $d_{norm}$ (Figure 4.40), the white surfaces indicate contacts with distances equal to the sum of van der Waals radii, and the red and blue colors indicate distances shorter (in close contact) or longer (distinct contact) than the van der Waals radii, respectively.

![Hirshfeld surface](image)

Figure 4.40. View of the three-dimensional Hirshfeld surface of the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ complex plotted over $d_{norm}$ in the range -0.7548 to 1.5398 a.u.

The bright red spots appearing near C and Ni indicate their role as the donors and acceptors, respectively. They also appear as blue and red regions, corresponding to positive and negative potentials on the HS mapped over electrostatic potential. The blue regions indicate the positive electrostatic potential (bond donors), while the red regions indicate the negative electrostatic potential (bond acceptors).

The disorder of DMF showed in the structure can be classified as a dynamic disorder [82]. In this case due to different interactions as type O--H and H--H, it is attributed to rotating disorder around the bond Ni--O (O=C in the DMF) in three positions, due to different contacts or interactions. The overall two-dimensional fingerprint plot and the dashed lines between H--H, O--H/H--O, C--H contacts and the percentage contributions are illustrated in Figure 4.41, respectively, together with their relative contributions to the Hirshfeld surface.

![Fingerprint plots](image)

Figure 4.41. The two-dimensional fingerprint plots for the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$, showing (a) all interactions, and (b) H--O/O--H, (c) H--H, (d) H--C/C--H, interactions.
The Hirshfeld surface (HS) analysis suggests the importance of H-atom contacts in establishing the structure. The large number of H---H and H---C/C---H interactions suggest that van der Waals interactions and carbon-hydrogen bonding play the major roles in the crystal packing, see Figure 4.42.

![Figure 4.42. Illustration of the one-dimensional H--H interaction in the chain structure. Dotted lines indicate H--H interactions.](image)

4.3.1.4 Calculation of the channels and cavities

In order to understand the insertion and diffusion possibility for Li\(^+\) ion through pores and channels of the structure, the calculation of voids was carried out using “Voids calculation” implemented in Mercury software [83] searching for voids with Li\(^+\) radius (0.75 Å) as spherical “probe” and a 0.7 Å grid. The results give a void volume of 262 Å\(^3\), equivalent to 12.4 % of the unit cell volume. The void volume is illustrated in Figure 4.43.

![Figure 4.43. The voids illustrated as volume of channels in the unit cell.](image)

To understand the occupation of Li\(^+\) in the structure, the calculation of cavities was carried out using “Cavities calculation” implemented in CrystalMaker Software 10.4.5 [84], searching for cavities with radius greater than 0.75 Å since the ionic radius of Li\(^+\) is 0.75 Å. The result is shown in Figure 4.44, where the cavities are represented by grey-yellow spheres (Zz).
The calculation result in cavities with different radius between 1.09 and 2.38 Å with 36 cavities per unit cell. Assuming that cavities are occupied by Li$^+$ it is possible to study the insertion in the structure and the type of interaction, according to the hypothesis that the Li$^+$ can occupy the voids. The structure was studied considering the interaction of the Li$^+$ as Li$^+$--O or Li$^+$--π. The length of the distances was calculated in the range 1.000-3.427 Å. The results are shown in Table 4.2. This figure illustrates the difference between these materials and conventional inorganic materials (e.g. LFP) which contains less voids.

**Table 4.2**
Type of interaction of Li$^+$ in the structure.

<table>
<thead>
<tr>
<th>Nº</th>
<th>Cavities</th>
<th>Radius of cavities (Å)</th>
<th>Number of Cavities and number of Li$^+$</th>
<th>Type of interaction</th>
<th>Length of interaction Li$^+$--O and Li$^+$--π (Å)</th>
<th>Coordination of Li$^+$ and geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cav2.4</td>
<td>2.38</td>
<td>4</td>
<td>Li$^+$--π</td>
<td>2.615 to ring</td>
<td>1 (one-side)</td>
</tr>
<tr>
<td>2</td>
<td>Cav2.0</td>
<td>2.00</td>
<td>4</td>
<td>Li$^+$--π</td>
<td>2.292 to ring</td>
<td>1 (one-side)</td>
</tr>
<tr>
<td>3</td>
<td>Cav2.1</td>
<td>2.07</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>3.280</td>
<td>1 (one-side)</td>
</tr>
<tr>
<td>4</td>
<td>Cav1.8</td>
<td>1.84</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>2.375-3.047</td>
<td>3 (Triplanar)</td>
</tr>
<tr>
<td>5</td>
<td>Cav1.4</td>
<td>1.36</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>2.637-3.357-3.017-3.163</td>
<td>4 (Cuboid)</td>
</tr>
<tr>
<td>6</td>
<td>Cav1.4</td>
<td>1.43</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>3.027-2.640-3.106</td>
<td>5 (Cuboid)</td>
</tr>
<tr>
<td>7</td>
<td>Cav1.2</td>
<td>1.22</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>3.121</td>
<td>1 (one-side)</td>
</tr>
<tr>
<td>8</td>
<td>Cav1.2</td>
<td>1.21</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>2.359-3.181-2.660</td>
<td>3 (Trigonal)</td>
</tr>
<tr>
<td>9</td>
<td>Cav1.1</td>
<td>1.09</td>
<td>4</td>
<td>Li$^+$--O</td>
<td>2.302</td>
<td>1 (one-side)</td>
</tr>
</tbody>
</table>

The cavities to each radius and the type of interaction are shown in Figure 4.45.
1.- Cav2.4 and Cav2.0 show the Li$^+$--π interaction.

3.- Cav2.1 show the Li$^+$--O interaction.

4.- Cav1.8 show the Li$^+$--O interaction.

5.- Cav1.4 show the Li$^+$--O interaction.

6.- Cav1.4 show the Li$^+$--O interaction.

7.- Cav1.2 show the Li$^+$--O interaction.

8.- Cav1.2 show the Li$^+$--O interaction.

9.- Cav1.1 show the Li$^+$--O interaction.

Figure 4.45. Cavities of Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ show the substitution of cavities by Li$^+$ and the interaction with the oxygen atom.
4.3.1.5 Powder X-ray diffraction pattern

Powder X-ray diffraction (PXRD) experiments were carried out to investigate the purity of Ni-BDC. The PXRD results showed that the peak positions match well with those from the simulated PXRD patterns based on single-crystal structure data, indicating reasonable crystalline phase purity (see Figure 4.46). The pattern (a) was simulated from the CIF, the pattern (b) was simulated from the CIF considering the preferred orientation by the plane (1,0,-1) with March-Dollase parameter as 0.43476. The two simulated patterns are compared with the experimental pattern. The experimental matching with “preferred orientation” can be explained by the flaky nature of the crushed particles as can be observed in the SEM image of Figure 4.47b below.

![Figure 4.46. Powder X-ray diffraction pattern of the powder. The blue line (a) represents the pattern simulated from the CIF, the black line (b) represents the pattern simulated from the CIF with (1,0,-1) orientation and Marchdollase 0.43476. The red line represents the experimental pattern and pink after 50 cycles.](image)

Ex-situ XRD of the pristine Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ and the electrode after 50 cycles were performed in order to investigate the electrochemical reversibility and the structural changes during the charge-discharge processes. The XRD profile after 50 cycles have features of the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ pristine material but in a small amount, which shows probably that the material is decomposed during the cycles in the charge-discharge process. The XRD profile also shows the amorphous phase which is attributed to the Super P carbon, PVDF and a possible amorphization of the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ during the charge-discharge processes. The comparison of the XRD profile after 50 cycles with the pristine experimental, and simulated from CIF show the possible changes in the crystal structure, probable due to collapse of the of the twinning crystal. The peaks corresponding to plane (1,0,-1) disappear after 50 cycles due to collapse of the twinning crystals which correspond to the crystal with preferred orientation. In the sample after 50 cycles the spectrogram indicates a loss of crystallinity (more amorphous) and the preferred orientation has disappeared. The peak at 21 degree corresponds to PVDF and the amorphous carbon Super-P.
4.3.1.6 SEM analysis

The Scanning electron microscopy (SEM) images in Figure 4.47 was obtained by first coating with Pt. Figure 4.47a shows the image of the powder crystals before crushing in a mortar. From Figure 4.47b the diameter of the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ particles can be estimated. They are mostly distributed as flaky crystals between 2 and 140 µm with an average diameter of 11 µm. The SEM image shows crystals with irregular shapes due to that the sample was crushed in a mortar to obtain the PXRD. It is the same powder as used to obtain the PXRD and thus, it explains the preferred orientation of the crystals seen in the PXRD. The SEM image of the synthetized crystals shows hexagonal shapes and also the crystals show a twinning [85-87].

![SEM images](image1)

**Figure 4.47.** Scanning electron microscopy (SEM) image of the a) powder before crushing in a mortar and b) flaky crystals after crushing in a mortar.

4.3.1.7 IR Spectroscopy

Figure 4.48 shows the FT–IR spectrum of the material. It is consistent with the structure determined by single-crystal X-ray diffraction and powder X-ray diffraction. By comparing the IR spectra of Terephthalic Acid (H$_2$BDC) and Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$, the coordination of the ligand bound to the metal ion were explored. In the coordination network, the stretching vibrations for the γ(C=O) and γ(C-O) bonds show a significant shift from 1648 to 1633 cm$^{-1}$ and from 1204 to 1167 cm$^{-1}$ for terephthalic acid. The absorptions between 2964 and 2855 cm$^{-1}$ are characteristic of the C-H aromatic and aliphatic stretching vibrations for both structures. The absorptions between 729 and 696 cm$^{-1}$ are characteristic of ring aromatic torsion vibrations for both structures.

![IR spectrum](image2)

**Figure 4.48.** The IR spectra of (a) Terephthalic acid (H$_2$BDC) black line and (b) Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ (1) red line.
The absorptions between 3500 and 2700 cm\(^{-1}\) are characteristic of the O-H hydrogen bond stretching vibrations for the H\(_2\)BDC but in the Ni\(_3\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\) its signal disappear due to the formation of the Ni-O bond.

### 4.3.2 Electrochemical properties

#### 4.3.2.1 CV Cyclic Voltammetry

The electrochemical performance of the synthetized Ni\(_3\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\) versus Li/Li\(^+\) was evaluated by cyclic voltammetry (CV) in the potential window 0.5–3.5 V to identify the redox processes, and three successive CV scans are shown in Figure 4.49.

![Cyclic voltammograms](image)

Figure 4.49. Cyclic voltammograms of Ni\(_3\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\) at potential window of 0.5-3.5 V, T=20\(^\circ\)C, 1M LiPF\(_6\) dissolved in EC-DMC (1: 1 vol) as electrolyte, Celgard as a separator.

The 1\(^{st}\) cathodic scan has five peaks observed at 1.65, 1.50, 1.33, 0.85 and 0.72 V. These peaks being visible during the first lithiation correspond to the initial formation of Li\(_6\)(C\(_8\)H\(_4\)O\(_4\))\(_3\)(C\(_3\)H\(_7\)NO)\(_4\) due to Li\(^+\) insertion, and the Ni metal formation, reaction (1) [88]. The peak at 0.85 V correspond to the formation of solid-electrolyte interphase (SEI) layer, i.e. amorphous Li\(_2\)O, according to reaction (2) [89]. The Ni metal atoms can also act to decompose the electrolyte by a catalytic process during the discharge process and contribute to form the solid electrolyte film (SEI) [90].
Three of the cathodic peaks disappear after the first cycle, leading to an initial loss of reversible capacity. Furthermore, the capacity is severely attenuated during the initial charge-discharge process, accompanied by the higher than theoretical capacity and a large irreversibility of the initial discharge.

The conjugated carboxylates containing lithium [91-92] as Li$_2$BDC, are considered as weakly electron withdrawing ligands. They can act as redox centers for coordination of Li$^+$ with -COO$^-$. Therefore, it is likely that redox participation of the organic molecule through the COO$^-$ groups plays an important role for Li$^+$ insertion and extraction in Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$. The resonance structures for the BDC is shown in Figure 4.50.

![Resonance structures of the BDC anion](image)

Figure 4.50. Reversible oxidation-reduction reactions of the BDC anion.

Two electrons are involved in the reduction processes of Tp. In the first stage one electron is added in the –COO- group. It is delocalized in the aromatic ring to the O marked in red. In the second stage one more electron is added to complete the electron structure in the O atom.

In the delithiation process, the Ni metal react with Li$_2$O and generate NiO and Li$^+$, reaction (3). After the initial scan the peak at 2.12 V is slightly shifted towards the left to 2.08 V. During the consecutive discharge the NiO is reduced again. These peak potential values are comparable to the expected potential range for Ni-NiO oxidation and the corresponding reduction.

The two redox reactions (4) and (5) in the range 0.5 to 3.5 V are only partially reversible and leads to destruction of the structure.

$$\text{NiO} + 2\text{Li}^+ + 2\text{e}^- \rightleftharpoons \text{Ni} + \text{Li}_2\text{O} \quad (3)$$

$$\begin{array}{c}
\begin{array}{c}
\text{O}^- \\
\text{O}^-
\end{array}
\rightleftharpoons \\
\begin{array}{c}
\text{O}^- \\
\text{Li}^+
\end{array}
\end{array} \quad \begin{array}{c}
\begin{array}{c}
\text{O}^- \\
\text{O}^-
\end{array}
\rightleftharpoons \\
\begin{array}{c}
\text{O}^- \\
\text{Li}^+
\end{array}
\end{array} \quad (4)$$

Each of three units of terephthalate undergo reversible electron redox processes. The theoretical capacity was calculated by the following reaction to be 160 mAh/g.
Assuming that one oxygen atom in the carboxylate can attach one Li$^+$ and each aromatic ring can accommodate one Li$^+$ ion which possibly remains coordinated with the aromatic ring. [93]. The observed irreversible capacity loss can be attributed to increased side reactions with the electrolyte and formation of SEI layer and remaining coordination of Li$^+$ with the aromatic ring, as shown in Figure 4.51.

Figure 4.51. Sites of insertion and coordination of Li$^+$ with aromatic rings in the structure.

The Li$^+$ ion insertion and deinsertion in the structure are in the empty spaces (voids) around the aromatic ring and the trinickel core in the structure. It is possible to identify the sites for the insertion of Li$^+$ and for the coordination of Li$^+$ with the aromatic rings by calculations using the software Mercury, as shown in Figure 4.51.
4.3.2.2 Charge-discharge

The charge-discharge capacity, Figure 4.52, and voltage profiles, Figure 4.53, of Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ observed in the potential range of 0.5−3.5 V. The open circuit potential (OCP) of the as-assembled cells was 2.4 V. The cell presents a specific capacity of ~420 mAh/g during the initial discharge and with a capacity of ~50 mAh/g and coulombic efficiency of 99.9 %, respectively, even after 50 cycles. The observed irreversible capacity loss can be attributed to increased side reactions with the electrolyte, formation of SEI layer and the retention of Li$^+$ inside the structure due to the coordination of Li$^+$ with the aromatic core, Figure 4.51.

4.3.2.3 EIS Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) has been carried out in the frequency range 10 mHz to 1 MHz with an AC amplitude of 10 mV, in order to understand the electronic and ionic transport processes. The electrochemical impedance spectra of the Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$ electrodes at open circuit voltage (OCV= 2.4V) and at discharged state (3.5V) during the first and 10$^{th}$ cycle are shown in Figure 4.54.

Figure 4.52. Electrochemical performance of Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$: cycling performance profiles.

Figure 4.53. Electrochemical performance of Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$: galvanostatic discharge−charge profiles.

Figure 4.54. Impedance spectroscopic study at OCV 2.4V and discharged after 10 cycles (3.5 V) at 10 mV, frequency range 10 mHz-1MHz, T=20 °C, 1M LiPF$_6$ dissolved in EC-DMC (1: 1 vol) as electrolyte, Celgard as separator.
From the EIS curves of $\text{Ni}_3(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_3\text{H}_7\text{NO})_4$ electrodes at OCV, a smaller semicircle of the cell demonstrates that the cell has a lower resistance at OCV, moreover the semicircle increased with further discharge–charge cycling, Figure 4.54. It demonstrates that the charge transfer resistance of the cell increases during the electrochemical cycling process. The parameters are summarized in Table 4.3.

Table 4.3. Data for Impedance Spectra at Different Cycling Stages

<table>
<thead>
<tr>
<th>State</th>
<th>$R_1$ (Ohm)</th>
<th>$R_2$ (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As assembled (OCV = 2.4 V)</td>
<td>5.121</td>
<td>24.18</td>
</tr>
<tr>
<td>After formation cycle (Charged)</td>
<td>8.392</td>
<td>1190.00</td>
</tr>
</tbody>
</table>

Figure 4.55 shows the EIS of the $\text{Ni}_3(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_3\text{H}_7\text{NO})_4$ in the assembled cell in charged state (0.5 V) after the first charging. The semicircle is typical for a charge transfer process. After 10 cycles the material shows a hooked shape [94]. This could indicate a process of electron transport through a mixed conducting thin film. When a charging current is applied, it induces the migration of ion $\text{Li}^+$. The $\text{Li}^+$ ions gather at the interface and change the stoichiometry in the entire film, which in turn influences the electronic charge transport and its characteristic resistance. An additional explanation for the low frequency hook is a two-step reaction attributed to BDC ($\text{C}_8\text{H}_4\text{O}_4$).

Figure 4.56. Probable Lithiation process in the sites for coordination with $\text{Li}^+$ in the $\text{Ni}_3(\text{C}_8\text{H}_4\text{O}_4)_3(\text{C}_3\text{H}_7\text{NO})_4$
It can be argued that a two-step reaction competing for reaction and absorption sites will cause such behavior and the high-frequency shape of the curve is typical for a diffusion process in a porous electrode [95]. The presence of an inductive hook can be attributed to the surface relaxation of species in the SEI layer. A possible mechanism is illustrated in Figure 4.56 and with reference to Figure 4.50.

4.4 Fe-BDC-DMF

4.4.1 Synthesis and characterization of Fe\textsuperscript{3+}-BDC-DMF

4.4.1.1 Synthesis Fe-BDC-DMF

The synthesis of Fe-BDC produce a mixture of the monoclinic structure of Fe(OH)(BDC) and Fe(OH)(BDC)(H\textsubscript{2}O), in analogue of MIL-53 and Fe\textsubscript{3}O(BDC)\textsubscript{3}(DMF)\textsubscript{3} called MOF-235. (See paper 4)

According Scherb et al. [96] in this system Fe\textsuperscript{3+}:H\textsubscript{2}BDC the products are depending on the nucleation it can be homogenous and heterogeneous. In our synthesis, the molar ratio was 1:1 of the Fe\textsuperscript{3+}:H\textsubscript{2}BDC. The Fe-MIL-53 is the product of homogeneous nucleation and Fe-MOF-235 is the product of heterogeneous nucleation.

The chains of FeO\textsubscript{6} octahedral are connected by 1,4-benzenedicarboxylate anions in one-dimensional (1D) channels in the structure. The hexagonal three-dimensional (3D) structure of MOF-235, which is an analogue to MIL-88B, are built up from trinuclear Fe of FeO\textsubscript{6} octahedral linked by one oxygen and the trinuclear Fe linked by 1,4-benzenedicarboxylate anions with others trinuclear Fe. The tunnels connected by bipyramidal cages as shown in Figure 4.57 and form the 3D pore system of MOF-235 and MIL-88B (See paper 4).

![Figure 4.57. The schematic reaction of the synthesis Fe-BDC-DMF](image-url)
The reaction of the condensations of the Fe\(^{3+}\) occur by an oxolation processes since the ratio between charge and radius is high compared with the Ni\(^{2+}\) which occur by an olation mechanism.

### 4.4.1.2 XRD characterizations

The orange powder obtained was characterized by powder X-ray diffractometry (PXRD). The diffraction pattern of the product is shown in Figure 4.58. To further identify the phases a Rietveld refinement of the diffraction pattern was performed using the Xpert-high Score v.3.0 program, and the result is shown in Figure 4.59 and Table 4.4. The CIFs used in the refinement were MOF-235 ([Fe\(_3\)O(1,4-BDC)\(_3\)(DMF)\(_3\)][FeCl\(_4\)]*(DMF)\(_3\)) reported by Andrea C et al. [97] in the supporting information and Millange et al. [98] reported as supplementary files for MIL-53(Fe) (Fe\(^{III}\)(OH){O\(_2\)C-C\(_6\)H\(_4\)-CO\(_2\)}*H\(_2\)O) and (Fe\(^{III}\)(OH){O\(_2\)C-C\(_6\)H\(_4\)-CO\(_2\})). A pseudo-Voigt function convoluted with an axial divergence symmetry function was used to model the peak profile of Fe-BDC-DMF.

![Diffraction pattern and Rietveld refined intensity pattern of the Fe-BDC sample.](image)

The agreement indices between the calculated and the observed intensities were satisfactory and the structure of the phases identified are:

- **Phase 1** ([Fe\(_3\)O(1,4-BDC)\(_3\)(DMF)\(_3\)][FeCl\(_4\)]*(DMF)\(_3\))(34.7%)
- **Phase 2** (Fe\(^{III}\)(OH){O\(_2\)C-C\(_6\)H\(_4\)-CO\(_2\})\(\cdot\)H\(_2\)O) (5.8%)
- **Phase 3** (Fe\(^{III}\)(OH){O\(_2\)C-C\(_6\)H\(_4\)-CO\(_2\})\(\cdot\)H\(_2\)O) (59.5%)

### Table 4.4. Details of Rietveld refined PXRD parameters for Fe-BDC-DMF

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(\theta) range (deg.)</td>
<td>05–70°</td>
<td>05–70°</td>
<td>05–70°</td>
</tr>
<tr>
<td>Step size (deg.)</td>
<td>0.0710°</td>
<td>0.0710°</td>
<td>0.0710°</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.5406 Å</td>
<td>1.5406 Å</td>
<td>1.5406 Å</td>
</tr>
<tr>
<td>Zero point (2(\theta),°)</td>
<td>0.000102</td>
<td>0.000102</td>
<td>0.000102</td>
</tr>
<tr>
<td>Pseudo-Voigt function</td>
<td>(\eta = 0.60)</td>
<td>(\eta = 0.60)</td>
<td>(\eta = 0.60)</td>
</tr>
</tbody>
</table>

\(pV(x) = \eta C(x) + (1 - \eta)G(x)\)
The structures of the phases identified are shown in Figure 4.59.

![Figure 4.59a. Structure Phase 1 ([Fe₃O(1,4-BDC)₃(DMF)₃][FeCl₄]⁺(DMF)₃)](image1)

![Figure 4.59b. Structure Phase 2 (Fe³⁺(OH){O₂C-C₆H₄-CO₂})](image2)

![Figure 4.59c. Structure Phase 3 (Fe³⁺(OH){O₂C-C₆H₄-CO₂})·H₂O)](image3)

The simulated XRD pattern using the CIFs coincide well with the measured XRD pattern is shown in Figure 4.60. Ex-situ XRD of pristine Fe-BDC and an electrode after 100 cycles were performed in order to investigate the electrochemical reversibility and the structural changes during the charge-discharge processes.
The XRD profile after 100 cycles have features of the pristine material but shows changes in the structure of phase 3 during the charge-discharge process. The XRD profile also shows amorphous phases which are attributed to the Super P carbon and PVDF. The peak at 20.0° corresponds to PVDF and the peak at 24° corresponds to amorphous carbon Super-P. The comparison of the XRD profile after 100 cycles with the pristine material and the simulated from CIFs shows good stability of the structures of phase 1 and 2. The peak at 12.7° disappear after 100 cycles and this peak corresponds to the crystallographic plane (1,2,0) of phase 3, which contains the O atoms of the water molecules labeled Ow1 and Ow2 in Figure 4.61.

The disappearance of this peak can, for example, be attributed to loss of the water molecules in the structure by the reaction with the electrolyte:

\[
\text{LiPF}_6 + 4\text{H}_2\text{O} \rightarrow \text{LiF} + \text{H}_3\text{PO}_4 + 5\text{HF}
\]

Figure 4.61 is showing the crystallographic plane (1,2,0) in the structure of the phase 3. Phases 1 and 2 do not show any significant changes in the structure, indicating the good stability of their structures in the charge-discharge processes.
4.4.1.3 SEM analysis

The Scanning electron microscopy (SEM) image, shown in Figure 4.62, was carried out by coating with Pt to reduce charging induced distortion. From the SEM image, the diameter of the Fe-BDC particles can be estimated. The powder is mostly distributed as small crystals with a size between 0.140 to 0.559 µm with an average diameter of 0.213 µm. The SEM shown the crystals with different morphologies and agglomeration of smaller primary particles.

Figure 4.62. Scanning electron microscopy (SEM) of powder.

The SEM coupled with energy dispersive spectroscopy (EDS) is providing a qualitative elemental and semi quantitative analysis of the Fe-BDC-DMF composition. The EDS spectrum and an elemental composition is presented in Figure 4.63. The results of the EDS are in concordance with the identified structures of each phases.

Figure 4.63. Spectrum EDS of the Fe-BDC-DMF.

4.4.1.4 IR Spectroscopy

The FT–IR spectrum of Fe-BDC-DMF in Figure 4.64 is consistent with the structural characteristics determined by powder X-ray diffraction, Figure 4.60. By comparing the IR spectra of terephthalic acid (H₂BDC) and Fe-BDC-DMF, the coordination parts of the ligand bound to the Fe³⁺ ion were explored. In the mixture, the stretching vibrations for the ν(C=O) and ν(C-O) bonds show a significant shift from 1648 to 1633 cm⁻¹ and from 1204 to 1167 cm⁻¹ for terephthalic acid. The absorptions between
2964 and 2855 cm\(^{-1}\) are characteristic of the C-H aromatic and aliphatic stretching vibrations for both structures. The absorptions between 729 and 696 cm\(^{-1}\) are characteristic of ring aromatic torsion vibrations for both structures. The range of 579–635 cm\(^{-1}\) corresponds to the vibration of the ν(Fe-O) bonds and two bands of ν(Fe-OH) were identified at 1609 and 3369 cm\(^{-1}\), representing the stretching vibration of the hydroxyl groups in the Fe-BDC-DMF [99]. The absorptions between 3500 and 3000 cm\(^{-1}\) are characteristic of the O-H hydrogen bond stretching vibrations for the H\(_2\)BDC but in the Fe-BDC-DMF its signal disappear due to the formation of the Fe-O bond.

![IR spectra](image)

Figure 4.64. The IR spectra of (a) Terephthalic acid (H\(_2\)BDC) black line and (b) Fe-BDC (1) red line.

### 4.4.2 Electrochemical properties

#### 4.4.2.1 CV Cyclic Voltammetry

The electrochemical performance of the synthetized Fe-BDC-DMF mixture versus Li/Li\(^+\) was evaluated by cyclic voltammetry (CV) in the potential window 0.5–3.5 V to identify the redox processes by six successive CV scans is shown in Figure 4.65. The peaks at 1.38 and 2.54 V can be attributed to the formation of LiFeO\(^-\), Reaction 6 and the Li\(^+\) insertion in the structure during discharge.

\[
\begin{align*}
\text{Fe-O} & \quad \text{O} \quad \text{Fe-O} \\
\text{ Stretch} & \quad \text{O-H} \quad \text{Bend} \\
\text{C-O} & \quad \text{C-O} \\
\text{Stretch} & \quad \text{Stretch} \\
\text{O-H} & \quad \text{O-H} \\
\text{Bend} & \quad \text{Bend} \\
\text{Ring} & \quad \text{tortion} \\
\end{align*}
\]

At low voltages (i.e. down to 0.52 V) the reduction current is partly responsible for the formation of amorphous Li\(_2\)O (Reaction 7) and the formation a solid-electrolyte
interphase (SEI) layer [100]. This reaction decreases the capacity of the material during cycling.

![Cyclic voltammograms of Fe-BDC-DMF](image)

**Figure 4.65.** Cyclic voltammograms of Fe-BDC-DMF at potential window of 0.5-3.5 V, T=20 °C, 1M LiPF₆ dissolved in EC-DMC (1: 1 vol) as electrolyte, Celgard as a separator.

The peaks at 0.52 V and 1.54 V also correspond to reaction 8 and can be attributed to the oxidation and reduction of \((C_8H_4O_4)_2^-\) in the structure being positioned at the expected potentials [92-93].

The conjugated carboxylates containing lithium [92-93] are considered as weakly electron withdrawing ligands. They can act as redox centers for coordination of Li⁺ with -COO⁻. Therefore, it is likely that redox participation of the organic through the COO⁻ groups plays an important role for Li⁺ insertion and extraction in the structure.

The possible redox reactions of MOFs phases of Fe-BDC-DMF and ((6) and (8)) are shown in Figure 4.66. In the range from 0.5 to 3.5 V the material can be working as anode by Fe atoms and terephthalate units undergoing reversible redox processes.
The channels of the different phases are shown in Figure 4.67. It was calculated using the software Mercury [83] in order to understand the insertion and deinsertion of the Li$^+$ ions in the structure using a "probe radius of 0.75 Å and 0.2 grid spacing" and calculate voids using the contact surface. The transport of the Li$^+$ ions in the insertion and deinsertion process in the structure are through empty spaces (voids) in the structure. The pore channels provide a conduction pathway for the Li$^+$ ions through the structure of the Fe-BDC and produce a low resistance for ion transfer.

It is possible to identify the sites for the insertion by Li$^+$ and the sites for the coordination of Li$^+$ with the aromatic ring. In order to understand the occupation of the Li$^+$ ion in the structure, the cavities of the different phases were calculated using the software CrystalMaker [84]. The cavities provide possible sites, which can be occupied by the Li$^+$ ions in the structure. It was calculated using a "cavitie search" with 0.75 Å as minimum radius, which correspond to the ionic radius of Li$^+$ ion. Figure 4.68 shows the different sizes of cavities represented by yellow spheres.

However, further work is necessary to understand the exact electrochemical mechanism. According to the structures illustrated in Figure 4.67 there are possible two type of interaction sites for Li$^+$ insertion in the cavities of phase 2 and 3. The first interaction is Li$^+$--O around the oxygen bonded with the Fe$^{3+}$. The second interaction is Li$^+$--π interaction.

However, further work is necessary to understand the exact electrochemical mechanism. According to the structures illustrated in Figure 4.68 there are possible two type of interaction sites for Li$^+$ insertion in the cavities of phase 2 and 3. The first interaction is Li$^+$--O around the oxygen bonded with the Fe$^{3+}$. The second interaction is Li$^+$--π interaction.
Figure 4.67. Illustration of the channels for Li\textsuperscript{+} ion diffusion and cavities for Li\textsuperscript{+} insertion. a) Phase 1 ([Fe\textsubscript{3}O(1,4-BDC)\textsubscript{3}(DMF)]\textsubscript{3}[FeCl\textsubscript{4}]\textsuperscript{+}(DMF)\textsubscript{3}), b) Phase 2 (Fe\textsuperscript{III}(OH){O\textsubscript{2}C-C\textsubscript{6}H\textsubscript{4}-CO\textsubscript{2}}) and c) Phase 3 (Fe\textsuperscript{III}(OH){O\textsubscript{2}C-C\textsubscript{6}H\textsubscript{4}-CO\textsubscript{2}}\textsuperscript{+}H\textsubscript{2}O).

The results for the phase 2 and 3 can be compared with the results obtained by Combelles et al. [101]. They suggest 4 positions calculated by DFT computation to determine the different sites accessible for Li\textsuperscript{+} ions. They use an algorithm with spheres of a particular radius for the solvent and Li\textsuperscript{+} ions with a radius r = 1.0 Å to probe the accessible surface area of the porous material. Our study gives the same results as obtained by them.

The oxygen atom in the carboxylate can attach one Li\textsuperscript{+} and each aromatic ring can accommodate Li\textsuperscript{+} ions, which possibly remain coordinated with the aromatic ring. This
possibly explains the decrease in capacity of the material that occurs in the carbon anodes [93].

![Two crystallographic sites Li1 and Li2 for possible lithium insertion.](image1)

Figure 4.68. Two crystallographic sites Li1 and Li2 for possible lithium insertion.

Possible sites for occupation of the Li$^+$ and its interactions in the structure of 1, 2 and 3.

### 4.4.2.2 Charge-discharge

The charge–discharge capacity and voltage profiles observed in the potential range of 0.5–3.5 V of the Fe-BDC electrode are shown in Figure 4.69 and 4.70, respectively. It was performed at charge and discharge rate of 13 mA/g. The first cycle discharge capacity of the Fe-BDC electrode is 310 mA h/g, but the second cycle discharge capacity is only 275 mA h/g. Comparing the capacity of the first and second cycles, capacity loss is 11%. However, from the fortieth cycle, the Fe-BDC electrode demonstrates a stable capacity for reversible lithium storage. After 50 cycles, the electrode maintains a capacity of about 175 mA h/g, indicating good cycling stability of the Fe-BDC electrode. The voltage profile corresponds to reaction 6 and 8 in the charge-discharge processes.

![Charge-discharge cycling performances for the Fe-BDC at 13 mA/g.](image2)

Figure 4.69. Charge-discharge cycling performances for the Fe-BDC at 13 mA/g.

![Cell voltage as a function of specific capacity obtained by charging and discharging at 13 mA/g.](image3)

Figure 4.70. Cell voltage as a function of specific capacity obtained by charging and discharging at 13 mA/g.
4.4.2.3 EIS Electrochemical impedance spectroscopy

The Nyquist plot from impedance spectroscopy is shown in Figure 4.71. That show the Fe-BDC has a very low resistance of 15.1 ohm and the charge transfer resistance is nearly 275 Ohm in the first semicircle and 1.15 kOhm in the second semicircle as assembled. After 100 cycles it has decreased to 6.75 ohm and one semicircle at 270 ohm. The results are shown in the Table 4.5.

The good conductivity of Fe-BDC-DMF can be attributed to that pore channels provide a conduction pathway, and the conducting nature of the Fe-BDC anode leads to a low resistance for ion transfer. Figure 4.72.

The semicircle at high frequency can be ascribed to the electrolyte resistance and the surface film impedance, while the semicircle at lower frequency can be ascribed to the lithium-intercalation process. This second semicircle could be explained by reversible charge adsorption [102]. The adsorption and desorption of charges might account for the observed behavior. The charge carriers in the electrolyte arrive at electrode surface. They can: (1) accumulate on the surface of Fe-BDC or (2) be adsorbed into (desorbed from) the electrode structure of Fe-BDC-DMF.

Table 4.5. Data for Impedance Spectra at Different Cycling Stages.

<table>
<thead>
<tr>
<th>State</th>
<th>R1 (Ohm)</th>
<th>R2 (Ohm)</th>
<th>R3 (Ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As assembled (OCP) (Charged)</td>
<td>15.1</td>
<td>275.0</td>
<td>1150</td>
</tr>
<tr>
<td>After 100 cycles (Charged)</td>
<td>6.75</td>
<td>270.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Low resistance and charge transfer resistance are a very good for lithium ion batteries application as they facilitate easy ion transfer from electrolyte to the surface and then to the bulk of the electrode.

Figure 4.71. Nyquist plot of the Fe-MOF half-cell in the frequency range of 300 kHz to 1 mHz with peak to peak amplitude of 10 mV

Figure 4.72. The adsorption and desorption of charge in the Fe-BDC-DMF
5 Conclusions and outlook

The thesis has investigated Hybrid materials for Lithium-ion batteries in order to understand the relationship between structure and electrochemical properties.

The PANI was synthesized by chemical oxidation with a good crystallinity and globular morphology such as emeraldine base (EB) form. The PANI has five forms with different electrochemical properties. The PANY has 95 mAh/g and its electrochemical properties show PANI has properties for materials for capacitors.

The LiFePO$_4$-PANI hybrid material has been prepared via two methods: 1) Via self-assembly processes and 2) via thermal processes. The self-assembly processes produce the dissolution of the LiFePO$_4$ commercial particles during the synthesis. The structural characterization shown as mainly product to FePO$_4$-PANI with 25 wt% of PANI, which is a hybrid material with anode application for lithium-ion batteries but this materials was not the aim of the thesis and further work is in progress with this material.

The LiFePO$_4$-PANI hybrid material prepared via a thermal process using synthetized PANI, LiFePO$_4$ commercial and LiOAc. The structural characterization shown as mainly product to LiFePO$_4$-PANI with 25 wt% of PANI. The morphologies of the LiFePO$_4$-PANI and LiFePO$_4$ particles are similar. The comparison of the surfaces shown different surface structure and supported with EDS mapping shows a homogeneous distribution of PANI elements (C,S) on the surface of LiFePO$_4$ particles showing the good method for the coating of the LiFePO$_4$ particles.

The LiFePO$_4$-PANI good electrochemical properties showing good capacity, rate capability and cyclability. The composite containing 25 wt% PANI show the better electrochemical performance, compared with the PANI and LiFePO$_4$ commercial. The discharge capacity of LiFePO$_4$ was 120 mAh$^{-1}$ and the LiFePO$_4$-PANI is 145 mAh$^{-1}$ at 0.1C. The PANI can be considered as electronic conductor for the electronic transfer between the LiFePO$_4$ particles but also improve the contact between the electrolyte and LiFePO$_4$ particles during the charge-discharge process. The PANI also can act as host for Li$^+$ ion insertion-extraction, it gives to additional contribution to the capacity of the composite and PANI can also serve as a binder network between LiFePO$_4$ particles and to the current collector surface.

The CN compound Ni-BDC (Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$) synthetized and characterized in this work is a new example of a hybrid material with a coordination network complex of nickel (II). The structure and electrochemical properties was investigated at the first time. The structure solution was carried out by SCXRD.

The crystal structure of the compound, [Ni$_3$(C$_8$H$_4$O$_4$)$_3$(C$_3$H$_7$NO)$_4$], is a two-dimensional coordination network formed by trinuclear linear Ni$_3$(BDC)$_3$(DMF)$_4$ units of (BDC=benzene-1,4-di-carboxyl-ate and DMF = di-methyl-formamide). Individual trinuclear units are connected through tp anions in a triangular network that forms layers. One of the DMF ligands points outwards and provides interactions with equivalent planes above and below, leaving the second ligand in a structural void much larger than the DMF molecule, which shows positional disorder. The structure are connected by weak C—H⋯O, H⋯H and H⋯C interactions between DMF molecules, as shown by Hirshfeld surface analysis.
The compound has channels and cavities for the insertion of ion lithium in the structure. The electrochemical properties stability and reversibility of the Ni$_3$(CsH$_4$O$_4$)$_6$(C$_3$H$_2$NO)$_4$ electrode is strongly influenced by the Ni and the linker (BDC) moreover, also influenced by the porosity of the compound. However, the specific capacity is not very high (~50 mAh/g) because of the high molecular weight and the high amount of inserted Li$^+$ ions compared to the limited number deinserted of Li$^+$ ions per formula unit. The compound demonstrates electrochemical properties at 0.5-3.5 V and can work as anode in lithium-ion batteries but at this range it is possible the collapse of the structure of some amount of the material.

The synthetized MOF, Fe-BDC is a mixture of the Fe$^{III}$(OH)[O$_2$C–C$_6$H$_4$–CO$_2$], Fe$^{III}$(OH)[O$_2$C–C$_6$H$_4$–CO$_2$].H$_2$O and [Fe$_3$O(1,4-BDC)$_3$(DMF)$_3$][FeCl$_4$]$_n$(DMF)$_3$. The Fe-BDC exhibited a good electrochemical behavior when was applied as an anode material in lithium-ion cells, it is shown capacity up to about 175 mA h/g at the forty cycle at 13 mA/g.

The Fe-BDC is stable during lithium-ion insertion and extraction. The three phases can be used as anode. The electrochemical properties of those materials are due to structures and excellent structural stability. It necessary identifies the most important active phase. It is possible to obtain one phase by the control of the ratio of the reactants and conditions of the reaction. A comparison with other similar structures such as Fe$^{III}$(OH)$_{0.8}$Fe$_{0.2}$[O$_2$C–C$_6$H$_4$–CO$_2$], with 70 mAh/g, which has similar structure of the phases Fe$^{III}$(OH)[O$_2$C–C$_6$H$_4$–CO$_2$], Fe$^{III}$(OH)[O$_2$C–C$_6$H$_4$–CO$_2$].H$_2$O and the compound [Fe$_3$O(BDC)$_3$(H$_2$O)$_2$(NO$_3$)]$_n$ (Fe-MIL-88B) with 144.5 mAh/g, tested at 60 mA/g with similar structure to [Fe$_3$O(1,4-BDC)$_3$(DMF)$_3$][FeCl$_4$]$_n$(DMF)$_3$ (MOF-253) show a good capacity. It is necessary study the individual phases to determinate if the good capacity is due to mixture by synergic interaction between phases or is only attributed at each phases.

The high capacity and good cycling stability confirm the advantages of Fe-MOF-253, Fe-MIL-53 and Fe-MIL-88 B as the electrode materials of a lithium battery.

The mechanism of the condensation in the Fe$^{3+}$ is via oxolation mechanism and the Ni$^{2+}$ is via olation mechanism in the synthesis of each materials.

In this work, we develop a new route to synthesize the LiFePO$_4$-PANI hybrid via thermal treatment using lithium iron phosphate (LiFePO$_4$), polyaniline (PANI) and Lithium acetate (LiOAc) as raw materials. The synthesis process has a high yield (99.99%).

The calculation of cavities and channels was used at the first time in this study of the possible insertion sites of Li$^+$ ions and diffusion through the channels in the structures of Ni-BDC, Fe-BDC materials and it can be applied in other materials.

Also a possible potential material FePO$_4$-PANI was synthetized which is not reported in the thesis with possible application as anode in lithium ion-batteries.

Further investigation is still in progress.
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