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Recent Progress in Structural and Electrochemical Properties of LiFePO_4 for Composite Based Batteries

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Abstract: Olivine LiFePO_4 have attracted considerable attention since last decade because of promising properties as a cathode material in Li ion based batteries (LIBs). It offers high theoretical capacity, environmental friendliness, and less toxicity. This review describe some recent developments in the composite doped cathode materials such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , LiMnO_2 with focus on LiFePO_4 . The electrochemical and structural characterization of these cathode materials will be discussed. The major goal of this review is to highlight the some new progress by using composite doped material as a cathode to develop Lithium ion batteries with high conductivity, high rate capacity and excellent cycling stability resulting from this composite doped material.

Keywords: Cathode material, Olivine structure, Electrochemical and structural properties.

1. INTRODUCTION

In 1991 the Sony Corporation commercialized the composite LiCoO_2/C cells. The Rechargeable Lithium Ion Batteries (LIBs) have become very important components in portable, telecommunication, computers, and entertainment devices required by information-rich systems. Lithium ion batteries (LIBs) are required in mobile society, such as camcorders, MP4-players, lap tops and cellular phones. LIBs LiCoO_2/C are used in the portable electronic devices, and presently manufactured at a rate of several millions of units per month. The rechargeable LIBs have a potential over 3.6 V, which is three times higher than that of alkaline systems. In addition the energy densities of LIBs are as high as 120–150 W h kg^{-1} which is two or three times larger than those of Ni–Cd batteries [1]. The major development in rechargeable lithium batteries is the replacement of lithium cobalt oxide with lithium cobalt/nickel oxide as the cathode material. In various applications in hybrid electric vehicles to consumer electronics the development of improved battery technology is the crucial issue. The improved performance of the LIBs battery depends on the material of the components used in the battery [2-5]. Most of the electrolyte used in

LIBs is organic solvents which is LiPF_6 , having low electrical resistance [6] and is mixed with carbonates. Now most of the transition metals used in LIBs are stable. So that structural stability is a particular challenge during charging when most of the lithium is removed from the cathode. During discharge lithium is inserted into the cathode material and electrons from the anode reduce the

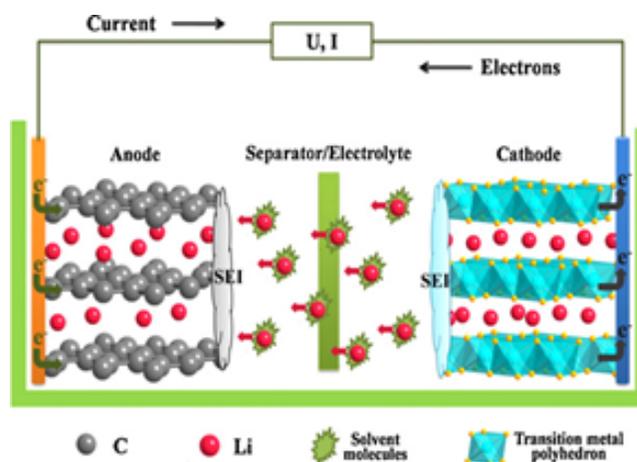


Figure 1. Working principles of LIB (charging) [4].

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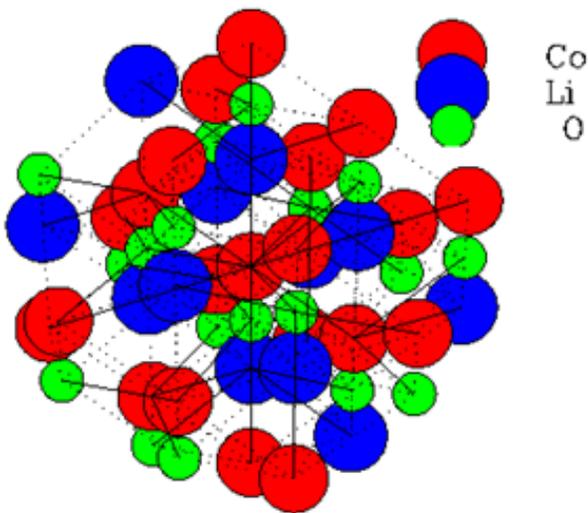


Figure 2. Crystal structure of layered LiCoO_2 [23] and refined lattice parameters [34].

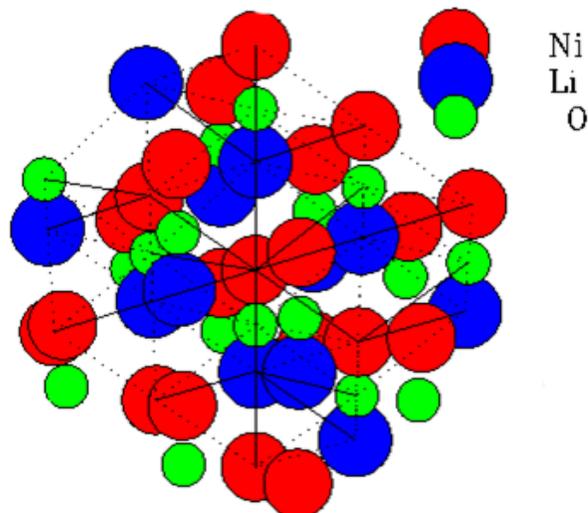


Figure 3. Crystal structure of layered LiNiO_2 [22] and refined lattice parameters [46].

transition metal ions in the cathode to a lower valence. The discharge current control during both processes because the large amount of Li ions moved through the electrolyte to the electrode surface. The cathode material most commonly used in lithium ion batteries is LiCoO_2 [4]. LiCoO_2 is thermally and chemically stable and environmental friendly [7-10]. But it also has some drawbacks such as its low conductivity and reversible capacity. Lot of research work going on to overcome these drawbacks. The basic working principles of LIB are shown in Fig. 1. A lithium ion battery is an electrochemical cell that transforms chemical energy into the electric energy. The key components of LIB are: Anode, cathode and electrolyte. For the commercialization of LIB system, both cathode and anode materials are intercalation materials. The anode made up of graphite and cathode made up of transition metal oxides i.e. $\text{Li}(\text{Co}, \text{Ni}, \text{Mn})\text{O}_2$. In charging process, Li ions are extracted from the cathode, move through the non-aqueous electrolyte and intercalate into the anode. While in discharge process all the Li ions are in the cathode sides and the process is vice versa. Meanwhile, the electrons also move from cathode to anode through the outside current collectors forming an electric circuit. The chemical potential of Li is much higher in anode than in the cathode, thus the electric energy is stored in the form of chemical energy. Such process is reversed when the battery is discharged where the electrochemical energy is released in the form of electric energy. The cathode and anode region are separated by the separator. A separator is a very thin sheet of (polymer) micro-porous membrane that allows the electrolyte to diffuse in it avoiding the short circuiting between the two electrodes and allow the ions to move through it. The electrolyte should be ionically conducting and electronically insulating in principle, however the actual properties of the electrolyte is more complicated [4], expensive and have low energy density. So Co was replaced with Ni. So LiNiO_2 , which also forms the $\alpha\text{-NaFeO}_2$ structure, is lower in cost and has a higher energy density (15% higher by volume, 20% higher by weight) but is less stable and less ordered [8] as compared to LiCoO_2 . Another promising cathode

material is LiMn_2O_4 , which is lower in cost and safer than LiCoO_2 . But it has lower capacity as compare to the cathode materials LiCoO_2 and LiNiO_2 . Among the long list of functional materials available as storage cathodes for rechargeable Li batteries (LIB), LiMPO_4 (M= Fe, Ni, Co, Mn etc.).

The olivine LiFePO_4 (triphylite) has attracted much attention as a suitable cathode material for high-power Li-based batteries [6-8]. LiFePO_4 has been extensively studied because of its attractive properties such as inexpensiveness, non toxicity, high theoretical capacity (170mAhg^{-1}), excellent cycling and thermal stability [1-5]. In particular, LiFePO_4 is one of the most promising candidates for use of hybrid electric (HEV) and electric vehicle (EV) batteries [5]. Key factors of using these materials in batteries are their electrical and ionic (Li^+) conductivities. And the key drawbacks of LiFePO_4 are its low electronic conductivity and reversible capacity. Various synthesis and processing approaches have been employed to improve the conductivity and cycleability of the LiFePO_4 [7-9]. Many studies have been devoted to optimize the material for better electrochemical performance and try to understand the lithium intercalation/ deintercalation mechanism [10-12]. The significant increase of the electrical conductivity can be induced by controlled non-stoichiometry and cation doping by improving the performance of current electrodes [5-6]. Structural changes in triphylite due to solid solutions of a metal M with iron ($\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$) may have significant effects on its solid electrolyte properties, including rates of Li diffusion and activation energies. Thus, detailed knowledge of structure in solid solutions is important in the development and design of Li-based olivine storage cathodes. Several structural studies have been performed on $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ solid solutions [12-18]. Few of them discussed the structural variations that occur as a function of M composition x [7, 19-27].

In this current review the main focus will be on the olivine LiFePO_4 with the comparison of different cathode materials. There is a discussion on the advantages of LiFePO_4 over different cathode materials. A detail on the recent work including the carbon coated

composite material of LiFePO₄, their electrochemical and structural applications is discussed. In this review we will discuss the recent progress in the research field and in the past decade of different cathode materials. The main focus is on the LiFePO₄ cathode material to see the modification in conductivity, capacity, rate performance and structural changes. For the better understanding of the main purpose, there is a discussion of different type of cathode materials.

2. LAYERED MATERIALS AS CATHODES IN LI-ION BATTERIES

In rechargeable Li-ion batteries, cathode materials are one of the key components affecting the final performance of the batteries. Among the various materials developed to act as cathodes in those cells, layered oxides are certainly very important. Layered oxide cathode materials, with a general formula LiMO₂ (where M=transition metal element such Co, Ni and Mn etc.) crystallize into a structure schematically depicted in Figs. 2 and 3. In these figures the oxide ions form a cubic-close-packed array with close-packed (111) octahedral site planes (rock-salt like structure). Li and M ions occupy the octahedral sites [28]. This structure can be described as a layered structure corresponding to the space group R⁻3m and unit cell parameters conveniently defined in terms of the hexagonal setting. Table 1 shows the comparisons of layered and non layered cathode materials, clearly suggesting that LiFePO₄ is better than all the other cathodes materials.

2.1. LiCoO₂

The cathode material most commonly used in lithium ion batteries is LiCoO₂ [28-29] because this material exhibits high specific capacity, low self discharge and excellent life cycle. LiCoO₂ has a theoretical capacity of 274 mAh g⁻¹. LiCoO₂ forms the α-NaFeO₂ structure which is rock-salt lattice where the cations order in alternating (1 1 1) planes. This ion ordering results in a trigonal structure (R 3m) and for LiCoO₂ planes of lithium ions through which lithiation and delithiation can occur [33-34].

Although LiCoO₂ is a successful cathode material, efforts are being done to improve the stability and cost of new cathode materials. In fact, cobalt is less available and more costly than other transition metals such as manganese, nickel and iron. In addition LiCoO₂ is not as stable as other potential electrode materials and when overcharged the performance undergoes degradation [35–37]. The cell capacity increases when charging voltage increases but can also lead to more rapid decrease in capacity as the cell is cycled during recharging. Several reasons have been given for the degradation during cycling. One is that cobalt is dissolved in the electrolyte when the electrode is delithiated during charging [38] such that

less lithium can be intercalated during discharge. Another reason is that a CoO₂ layer is formed after full delithiation and the deformation of the electrode surface [39] also results in less capacity for lithium intercalation.

Moreover, there is a sharp change in lattice parameters as a function of lithium content [40]. Heat treatment is needed to obtain stoichiometric LiCoO₂. A control of the surface phase content is needed to improve performance of cell during cycling [40]. Recently Zou et al [41-42] reported that small amount of foreign elements can give stable cycling performances due to a suppression of the phase transformation at 4.2 V during intercalation/deintercalation process (cut-off voltage higher than 4.5 V). Nowadays, Mg doped LiCoO₂ is used for commercial Li-ion batteries. It has been found that the cycle ability of the cathode material could be improved significantly by modifying its surface with metal oxides such as Al₂O₃ and ZrO₂ [43]. Some drawbacks, as previously mentioned, such as higher price and toxicity of cobalt element, accelerate extensive studies to investigate alternatives to LiCoO₂. So that is why Co is replaced with Ni. Table 2 shows the comparison of all three cathode materials and how doping effect their electrochemical and structural properties.

2.2. LiNiO₂

Another well know member of the LiMO₂ family of layered cathode materials is LiNiO₂, which also have the same α-NaFeO₂ structure. Its working voltage is more than 3.7 V and theoretical capacity is 275 mAh g⁻¹. LiNiO₂ provides important advantages such as less toxicity, lower price and higher reversible capacity as compare to LiCoO₂. On the other hand, it is less stable [44-45] and less ordered as compared to LiCoO₂. The lower degree of ordering results in nickel ions to occupy sites in the lithium plane. These hinder lithiation/delithiation also creates challenges in obtaining the appropriate composition. A small amount of doping of cobalt to LiNO₂ increases the degree of ordering. This leads to nickel ions to occupy sites in the nickel/cobalt plane rather than in the lithium plane. Thus LiNi_{1-x}Co_xO₂ has been used to take advantage of the low cost and higher capacity of nickel relative to cobalt [47]. Small amount of Mg doping causes strong increase in the electronic conductivity and slight decrease in the capacity. R. Sathiyamoorthi et al., has synthesized the Mg doped LiNiO₂ by low temperature solid state reaction. The Mg doped LiNiO₂ is single phase and stable. With the increase of Mg concentration the peak gets broaden, which shows small crystalline size. Enhanced reversibility of the Li intercalation/de-intercalation reaction is obtained. Charged/discharged studies showed the batter capacity retention and cycleability of Mg doped LiNiO₂. And it shows the high performance for Li-ion cells [48]. B.V.R. Chowdari et al., synthesized solid state reaction. Improve the cyclic behavior and performance

Table 1. Types of cathode materials for Lithium ion batteries (LIBS) [3, 29-32]

Cathode materials	Voltage (V) V	Charge V limit	Charge/discharge C-rates	Energy density Wh/kg	Applications
LiCoO ₂	3.60 V	4.20 V	1C limit	110-190	Cell phone, cameras, laptops
LiMnO ₂	3.7-3.80V	4.20 V	10C - 40C pulse	110-120	Power tools, medical equipment
LiNiO ₂	3.70V	4.10 V	~ 5C -30C pulse	95-130	Power tools, medical equipment
LiFePO ₄	3.2-3.30V	3.60 V	35 C cont.	95-140	Power tools, medical equipment

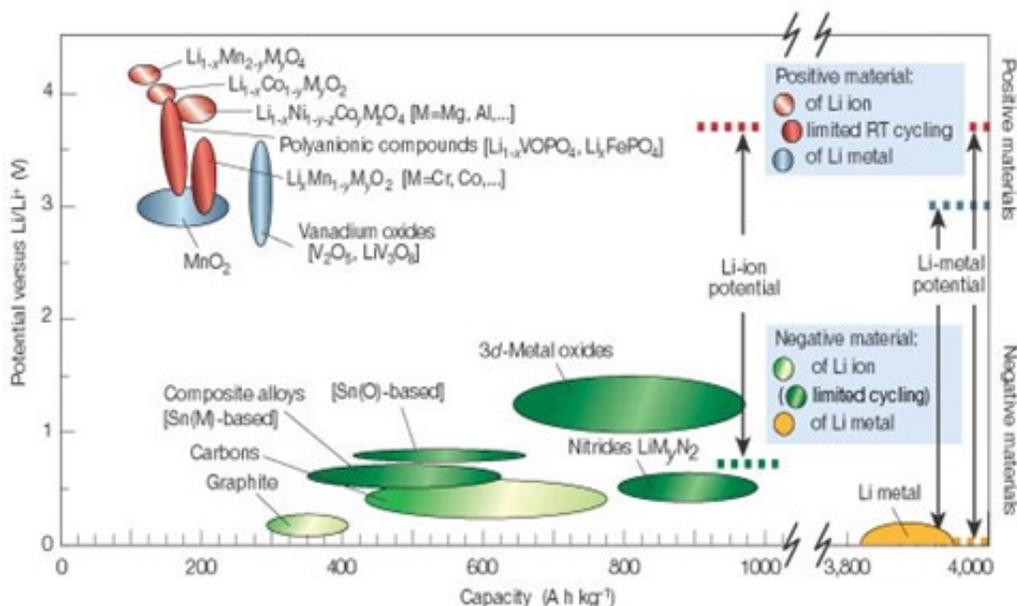


Figure 4. Voltage versus capacity for positive and negative electrode materials presently used or under serious considerations for the next generation of rechargeable Li-based cells. The output voltage values for Li ion cells or Li metal cells are represented. Note the huge difference in capacity between Li metal and the other negative electrodes, which is the reason why there is still great interest in solving the problem of dendrite growth [53].

of the cell [49]. Small amount of Co doping in $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ helps to reduce the amount of nickel in the lithium layer and have been shown to improve capacity. Increased cobalt content can also reduce the loss in capacity during cycling. The improved performance has been attributed to cobalt, which increases the conductivity and improves the structural stability of the cathode. Although nickel in the lithium layer can be detrimental to lithium transport, it is shown to stabilize the structure during delithiation and improve cycling performance [28, 47].

2.3. LiMnO_2

LiMnO_2 compounds have become of most interest as intercalation electrodes for rechargeable lithium batteries because of their high theoretical capacity 285 mAh^{-1} and low cost compared to

LiCoO_2 . LiMnO_2 forms a monoclinic structure which has the same cation ordering of the $\alpha\text{-NaFeO}_2$ structure [50]. The most commonly used Li (Ni, Mn, Co) O_2 composition contains equal amount of these three transition metals: $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$. This material has good rate capability, high capacity and can operate at high voltage. During cycling, the capacity of the cell leads to rapid loss while increase in voltage [47]. Yet-Ming Chiang et al., synthesized Al, Mn doped LiMnO_2 by using the Co-precipitation and freeze-drying route [51]. Al and Mn doping improves the capacity retention of the LiMnO_2 battery. It was also observed that the phase change and disorderness occurred in the structure [51]. T.J. Kim et al. synthesized the LiMnO_2 by using solid state route. The fluorine modified LiMnO_2 cathode exhibits improved capacity retention and rate capability [52].

Table 2. Comparison of layered structure and variation w. r. t. doped material in electrochemical and structural properties.

Cathode materials	Synthesis method	Electrochemical properties	Structural properties	Dopant
LiCoO_2	Solid-state method [42]. Thoroughly mixing of stoichiometric amounts of different materials under Ar atmosphere at 550°C [41]. Citrate precursor method	Stable high capacities over 30 charge / discharge. Fading at $165\text{-}170 \text{ mAh/g}$ when doped with Cu and Zn. Improved capacity retention. Cyclic stability.	Poor cycleability with increase of Li. Phase change [41]. Stable. Single phase	Mn, Cu, Fe, and Zn Mg [41, 43]. Mg
LiNiO_2	Conventional solid state reaction low temperature Solid state reaction	Lower capacity. Improved cyclic behavior. Improved capacity retention, cycleability and better cell performance. irreversible capacity	Phase transitions. Increase in thermal stability. Single phase and stable.	Co, Ti
LiMnO_2	Co-precipitation and freeze-drying route. Solid state reaction.	Al, Mn doping improves the capacity fading. Improved capacity retention and rate capability.	Phase change and disorderness in the structures.	Al, Mn, F and Li

3. NON-LAYERED CATHODES

Non-layered materials have also been the subject of intensive research. Guyomard and Tarascon worked at the Bell Communications Research Laboratory gave new motivation to the development of rocking-chair batteries by using graphite carbon as anode and LiMn₂O₄ as cathode. Lithium manganese spinel oxide and the Olivine LiFePO₄ are the most promising candidates up to now. These materials have interesting electrochemical reactions in 3-4 V region which can be useful when combined with a negative electrode of potential sufficiently close to lithium. The present performance of some electrode materials presently under consideration for Li-ion cells is summarized in Fig. 4. Recently, 5 V materials have emerged as a different option. They also include selected spinel oxides and Olivine related solids. These alternative materials increase the working potential sufficiently to provide acceptable cell voltages when combined with a negative electrode working significantly above 0 V versus lithium. The combination of 5 V electrodes with an appropriate anode can be considered to be a third generation of lithium-ion batteries, having high power density and avoiding electro deposition of lithium at the anode. Here we will briefly describe the main features of LiMn₂O₄ and Olivines.

3.1. Spinel LiMn₂O₄

The spinel compounds LiM_xMn_{1-x}O₄ (M = Metal element) are attractive cathode materials for replacing Co and Ni based layered cathode materials of Li-ion batteries [54]. In particular, they have been extensively studied as positive electrode materials of large size Li-ion batteries for power sources of hybrid electric vehicles (HEV), because they have several advantages such as lower cost, high capability and higher thermal stability, as compared to those of Co and Ni based layered materials [55-56]. As shown in Fig. 5, the LiMn₂O₄ crystallizes in the space group Fd3⁻m with Li and Mn present in tetrahedral and octahedral sites within the cubic close-packed oxygen array respectively [57]. However, those spinel compounds have a lower capacity as compared to the cathode materials that form the α-NaFeO₂ structure described above [55]. During cycling, control of phase change occurs in LiMn₂O₄ cathodes and is considered to be one of the challenges [58-59]. LiMn₂O₄ cathodes have been field tested in the DC power supply for an operating telecommunication transceiver. In these tests, rapid loss of capacity occurred in first few days but with the passage of time the capacity loss decreased [62]. During charging this initial loss is due to the loss of oxygen [60]. The dissolution of manganese in the electrolyte has also been observed during storage and capacity loss [61], associated with changes in crystallinity and morphology of the particles [62]. Other effects take place when other transition metals such as iron and cobalt are added to LiMn₂O₄ [64-67]. Discharge plateaus at high voltage were observed when adding iron in

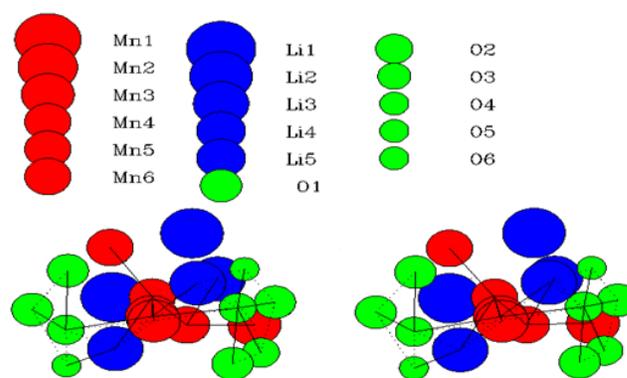


Figure 5. Crystal structure of LiMn₂O₄ [23] and refine parameters [63].

LiMn₂O₄, while the capacity retention improves during cycling for cobalt-doped electrodes. However, the most common doping is nickel, which has been found to decrease the electric conductivity and lattice parameters of LiMn₂O₄ [68]. The capacity was found to increase with increasing manganese content and a 3:1 Mn:Ni ratio (i.e. Mn_{1.5}Ni_{0.5}O₄) is the most commonly used composition [69]. Disordered spinel structure has been shown to have higher capacity while the manganese and nickel cations were found to be ordered on the octahedral sub-lattice [70-71]. Addition of nickel to the surface of LiMn₂O₄ through coatings rather than a dopant was also found to be effective in improving capacity retention during cycling [76]. Coating of LiMn₂O₄ spinel with LiCoO₂ was observed to improve the high temperature performances with the reduction in capacity and specific energy [72]. Table 3 shows the summary of doping effects (Co, Al, Cr, Ni, Li etc) on LiMn₂O₄.

3.2. Olivine LiFePO₄

LiFePO₄ has recently attracted considerable attention since it was first proposed by Padhi et al., [5] because of its potential application as the next generation cathode material in LIBs. Compared with conventional cathode materials LiCoO₂, LiNiO₂, LiMn₂O₄ and LiFePO₄ has many advantages such as high theoretical capacity (ca. 170 mA h g⁻¹) and moderate operating flat voltage (the Fe³⁺/Fe²⁺ redox couple is conveniently located at 3.4 V versus Li⁺/Li, which is compatible with common organic, as well as polymer electrolytes) [73]. In the past decade, a number of new cathode materials have been developed as alternative cathode materials for Li-ion batteries. However, none of them are in real industrial applications so far. A group of lithium transition metal polyanion compounds, incorporating polyanions XO³⁻₄ (X= S, P, As, Mo) has

Table 3. Variation in structural and electrochemical properties of the spinel structure by using different dopants.

Cathode Material	Synthesis method	Electrochemical properties	Structural properties	dopants
LiMn ₂ O ₄	Conventional method [60]. Solid-state reaction [64-65]. Sucrose-aided combustion method [66]. Sol-gel method [67]. spray-drying method & Tartaric acid gel method [72].	Li doping improved. Cycling performance. Improved capacity retention and Cycling performance Improve in capacity retention and cycling stability	Li doping improved the structure stability. Single Phase and stabilized spinel structure Single phase.	Li [65] Co, Li [64,65,67] Al ³⁺ , Ni ²⁺ , Cr ³⁺ , Co ³⁺ [66] LiNi _{0.05} Mn _{1.95} O ₄ [72]

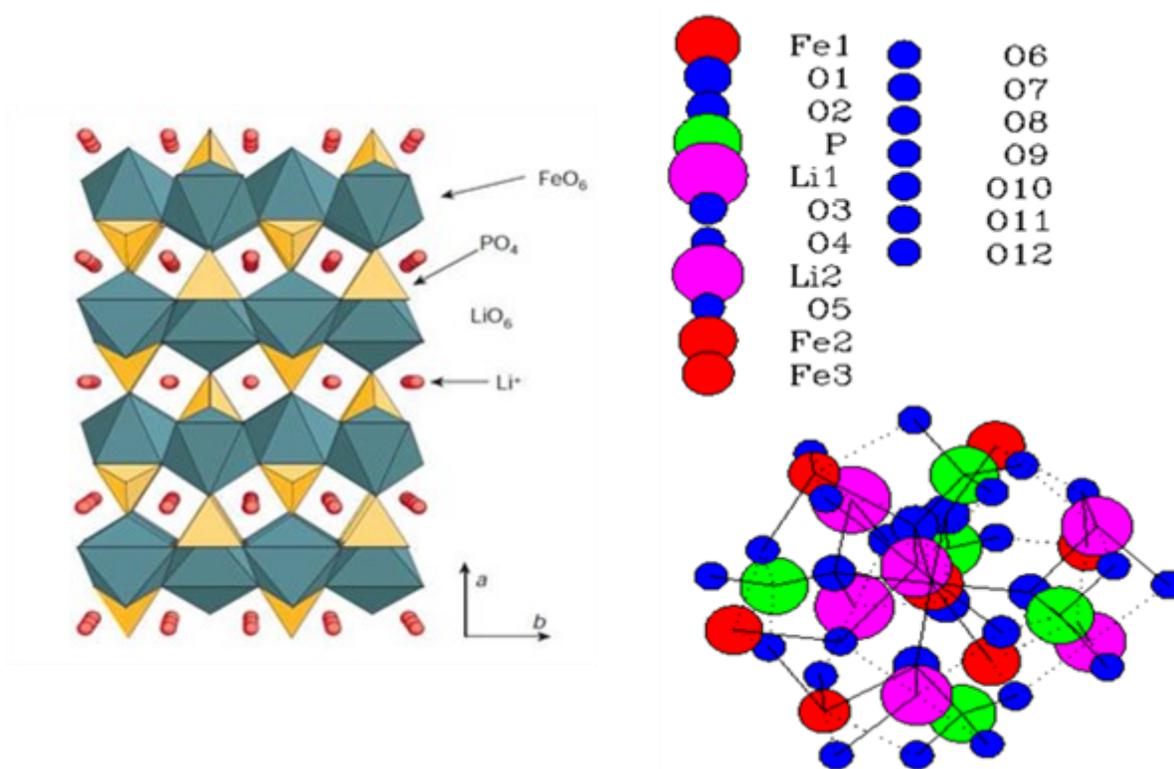


Figure 6. The crystal structure of olivine LiFePO_4 projected along $[001]$. FeO_6 structures are distorted octahedral and PO_4 are distorted tetrahedral, Li ions are surrounded by 6 oxygen atoms. Crystal structure of LiFePO_4 [23] and refine lattice parameters [78].

been extensively investigated as new cathode materials for Li-ion batteries [74]. Padhi first demonstrated that orthorhombic LiFePO_4 could be used as a cathode for rechargeable Li-ion batteries [5]. In particular, the olivine type LiFePO_4 (triphylite) has attracted much attention as a suitable cathode material [9, 75]. LiFePO_4 has been extensively studied because of its attractive properties such as inexpensiveness, non toxicity, high theoretical capacity (170mAhg^{-1}), excellent cycling and thermal stability [3, 8, 76-77].

LiFePO_4 has an ordered Olivine structure (space group Pnma) in which Li, Fe and P atoms occupy octahedral 4a, octahedral 4c and tetrahedral 4c sites, respectively. The oxygen atoms are arranged in a slightly distorted, hexagonal close-packed arrangement. The FeO_6 octahedral shares common corners in the b-c plane and the LiO_6 octahedral form edges sharing chains in the b direction. The separation of the FeO_6 octahedral by PO_4 polyanions significantly reduces the electrical conductivity of the material [74]. The key drawbacks of LiFePO_4 are its low electronic conductivity and reversible capacity. Various synthesis approaches have been employed to improve the conductivity and cycle ability of the LiFePO_4 [9, 11-12, 79].

4. DOPING EFFECT ON COMPOSITE LiFePO_4 CATHODE MATERIAL

Many studies have been devoted to optimize the material for better electrochemical performance and try to understand the lithium intercalation/deintercalation mechanism [13-15]. It has been shown [5, 10] that significant increase of the electrical conductivity can be induced by controlled non stoichiometry, carbon coating and

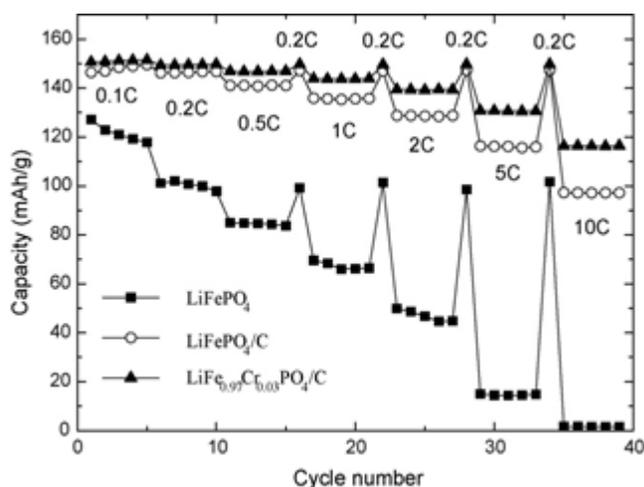


Figure 7. Rate performance of LiFePO_4 , LiFePO_4/C and $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$ during discharging at various rates (from 0.1 to 10 C) [18].

cation doping improves the performance of current electrodes. For example, olivine compounds $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ were studied in order to examine the doping effect of low concentration of Mn. It was observed that Mn influence on the electrochemical performance of the olivine cathode and enhanced the initial capacity and electrical

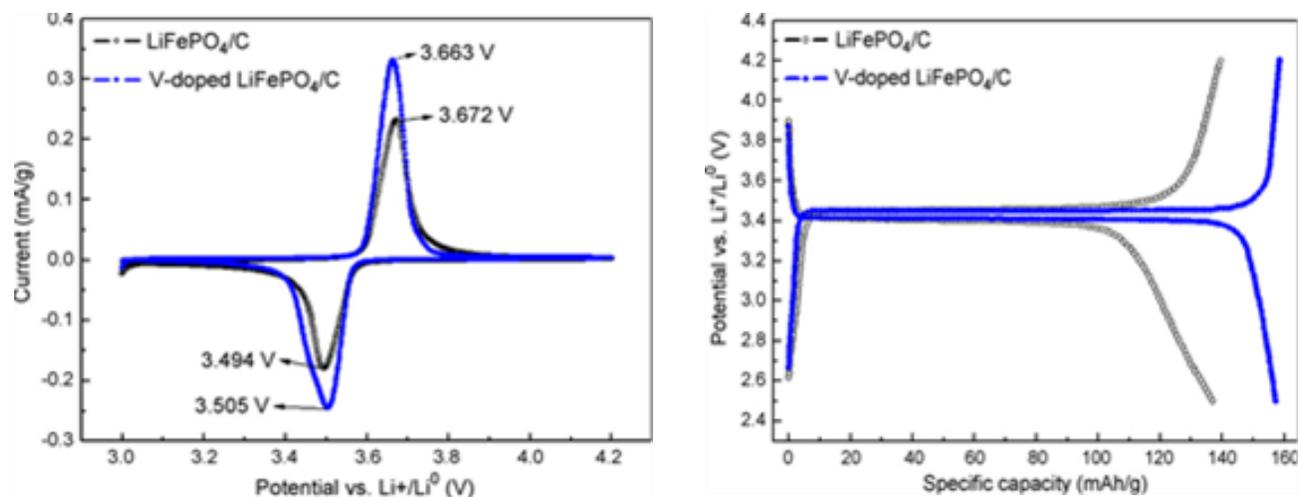


Figure 8. Cyclic voltammetry (CV) curves for pristine and V-doped LiFePO_4/C measured with a scanning rate of $50\mu\text{Vs}^{-1}$. Charge/discharge curves refer to the first cycle, measured at 0.1 C. Both Current-Potential (left) and Potential-Specific Capacity (right) curves are shown [92].

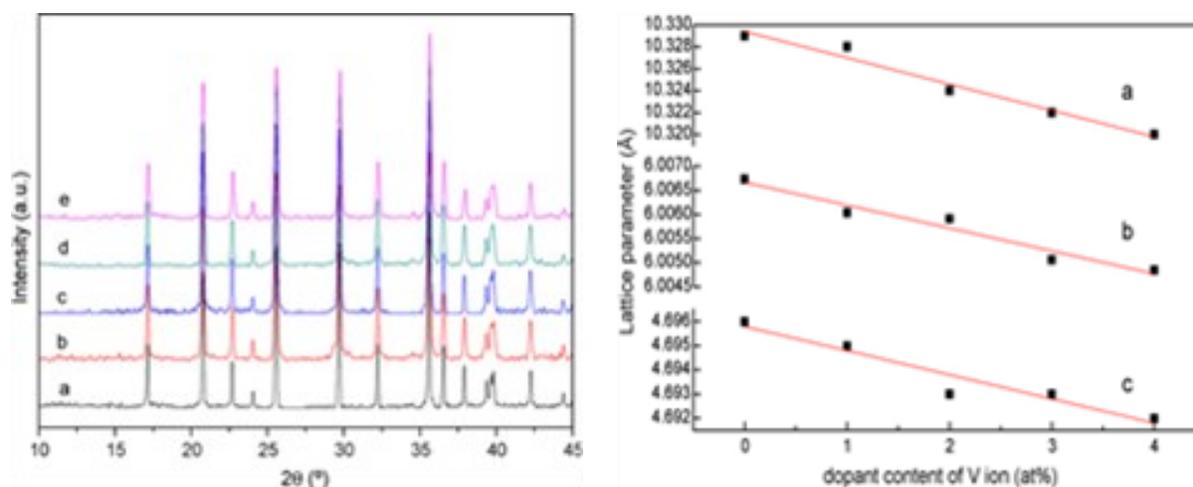


Figure 9. X-ray diffraction patterns of various V ion contention samples. Variation of lattice parameters with the substitution degree [76].

conductivity [80-81]. It has been shown also that chlorine doping also improve the electrochemical performances [82]. A significant example for the improvement in performance obtained by controlled doping is reported by Shin et al., [18]. In his work Cr doped LiFePO_4/C olivine compounds synthesized by mechano chemical methods are studied in detail. The simultaneous treatment of carbon coating and Cr doping improved the rate performance of the LiFePO_4 batteries. It is shown in Fig. 7, that Carbon coating and Cr doping allow excellent rate performances and discharging capacity (improved up to 120mAhg^{-1} at 10C rate). During cycling the structural change was also investigated. The Cr doping was found to assist the phase transformation between triphylite and heterosite during cycling and conductivity was improved by carbon coating. Liu et al., [83] synthesized the LiFePO_4/C composite by ball milling combined with spray- drying method.

This composite gives a high electronic conductivity with long term cyclability at a high C-rate. It also provides both the high specific energy and power required for a Li-ion battery. C.S. Sun et al., synthesized LiFePO_4/C and V-doped LiFePO_4/C cathode material by carbothermal reduction method. Figure 8 shows the CV and Charge/discharge curve of Pristine and V-doped LiFePO_4/C cathode materials. V-doped LiFePO_4/C showed a high discharge capacity at room temperature. The significantly improved high-rate charge/discharge capacity was attributed to the increased diffusion capability [76,92].

In V-doped LiFePO_4 olivine the lattice structure is not perturbed, but variations of the lattice parameter were observed as a function of doping. The XRD diffraction pattern of various V concentration and all peaks shows the olivine phase with orthorhombic ordered structure. And there was no evidence of any impurity peaks. Long-

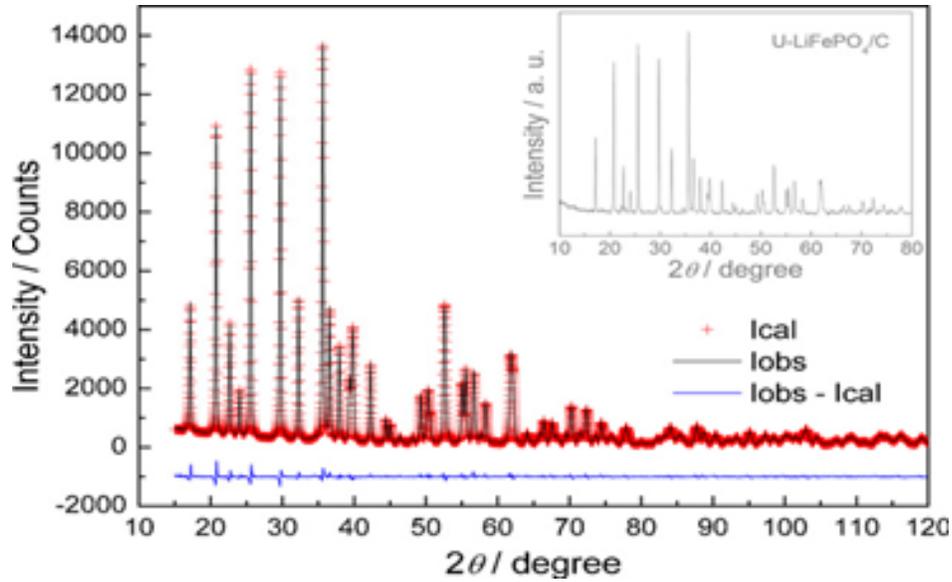


Figure 10. Rietveld profile refinement of XRD patterns for M-LiFePO₄/C powders (Rwp = 0.0876, Rp = 0.0688). In the inset we show the XRD pattern of U-LiFePO₄/C [90].

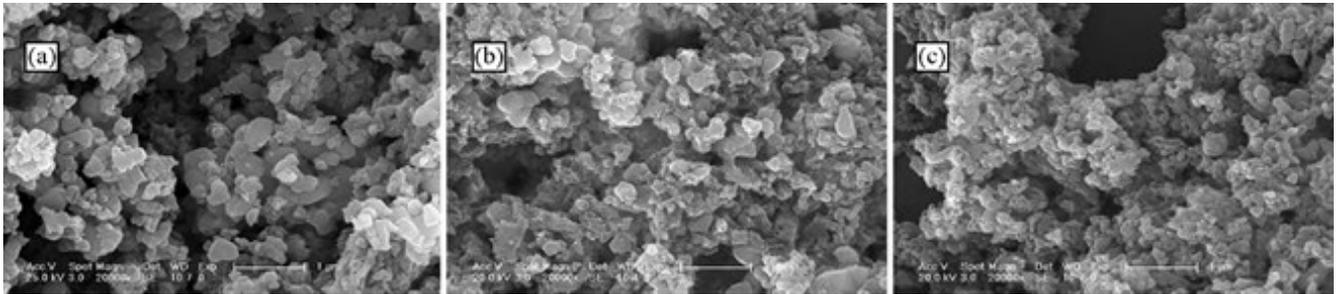


Figure 11. SEM images of pure LiFePO₄ (a), LiFePO₄/C (b) and Ni doped LiFePO₄/C (c) [19].

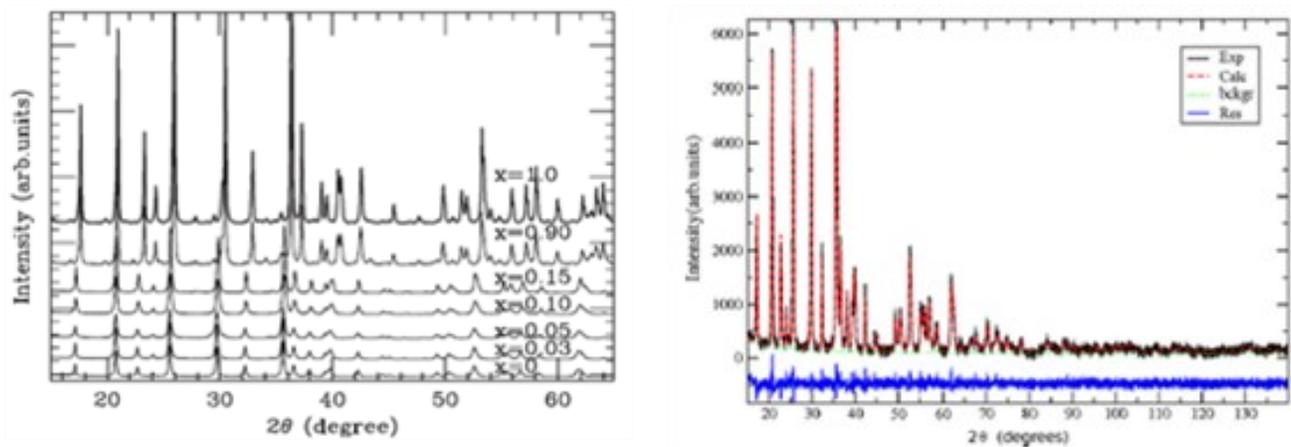


Figure 12: X-ray diffraction patterns of the LiFe_{1-x}Ni_xPO₄ solid solutions obtained in this work for different doping fractions x. Example of an XRD Rietveld refinement of the powder XRD pattern in the whole angular range (LiFe_{1-x}Ni_xPO₄, x = 0.1). Several curves are shown: experimental data (Exp, solid line), calculated pattern (Calc, dashed line), background (back, dotted), and residual curve (solid line, below) [8].

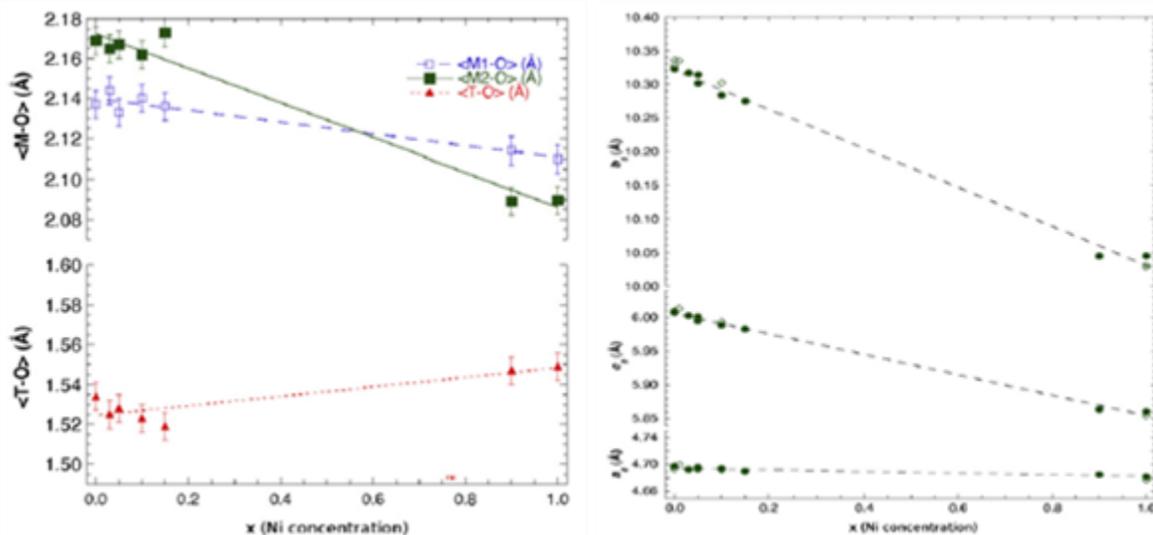


Figure 13. Average first-neighbor interatomic distances as determined by XRD Rietveld refinement, for different Ni concentrations x . $\langle \text{M-O} \rangle$ (metaleoxygen) average distances are reported as squares (filled or empty for M2 and M1 sites respectively). $\langle \text{T-O} \rangle$ distances are reported as filled triangles in the lower part of the figure. Linear interpolations of those distances are shown as dashed lines. Unit cell parameters a_0 , b_0 , and c_0 of $\text{LiFe}_{1-x}\text{Ni}_x\text{PO}_4$, as a function of Ni concentration x [9].

cycle performances were improved by optimizing the distribution of particles and improving the conductivity through carbon coating and V doping.

Doping of LiFePO_4 olivine with different ions ($\text{D}=\text{Zr}$, Nb , Cr) showed that the dopant resides primarily on the M1 (Li) site. The low doping level (3%) did not allow assessing a correlation between the dopants and improvement of the conductivity. On the other hand, the size of Li channels was found to be slightly increased (0.3 %) without influencing the Li-ion mobility [93]. Mg-doped LiFePO_4 showed a better rate performance [88]. Ti doped olivine LiFePO_4 have been synthesized by solid state reaction. To doping improved the rate capacity [84]. La-doped olivine LiFePO_4 cathode materials have been synthesized by solid-state method at high temperature. La doping did not affect the structure of the cathode material; improve capacity performance, cyclic stability and electronic conductivity [86]. Multi-doping with different ions was also carried out using novel synthesis routes. Multi-doped LiFePO_4/C composite is shown to improve the performance of the cells [90]. XRD (Rietveld-refinement) show that multidoped LiFePO_4/C is a single olivine phase, well crystalline with no evidence of presence of any impurity peaks (see Fig. 10 for a typical XRD pattern). XRD Rietveld refinement of the multi-doped alloy $\text{M-LiFePO}_4/\text{C}$ confirms that Mn, V, and Cr atoms occupy the Fe site and do not introduce any olivine LiFePO_4 . While the doped Li (M, Fe) PO_4 ($\text{M}=\text{La}$, Ce , Nd , Mn , Co , Ni) have also been synthesized by solvothermal method.

Electronic conductivity of LiFePO_4 is increased of the order of 1-3 by doping, but carbon coating is also needed to improve the conductivity of the cell. Among all these dopants, Nd was found to be the more effective [13, 94]. In recent times, LiMPO_4 ($\text{M}=\text{Mn}$, Fe , Co , and Ni) multiwalled carbon nanotubes have been studied, showing high capacity and excellent rate capability [74]. Also Zn-

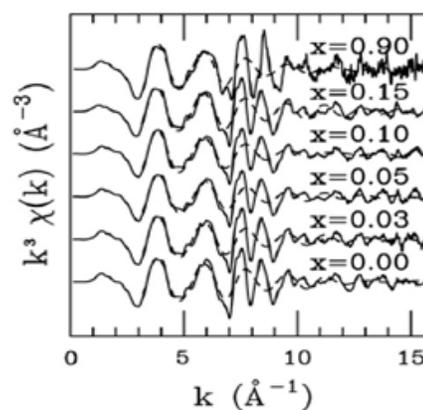


Figure 14: Fe K-edge experimental (solid) and calculated (dashed) spectra of $\text{LiFe}_{1-x}\text{Ni}_x\text{PO}_4$ samples. Calculated signals include only the first-neighbor component [9].

doped LiFePO_4 increases the conductivity, discharge capacity and rate capability [75]. Zinc doping was found to improve the reversibility, rate capability and conductivity of the cell. Zn doping was found to stabilize the crystal structure inducing a slight expansion of the lattice volume [76]. Cu-Sn-based negative electrode of the Li-ion battery was found to improve the charge/discharge performance [77]. Ni-doped LiFePO_4/C nanocomposites were synthesized by solid state reaction method, without affecting the olivine lattice structure. XRD results have shown that all the diffraction peaks are indexed to an olivine orthorhombic crystal structure, with no evidence of presence of any impurity phase. At 0.2 C rate Ni-

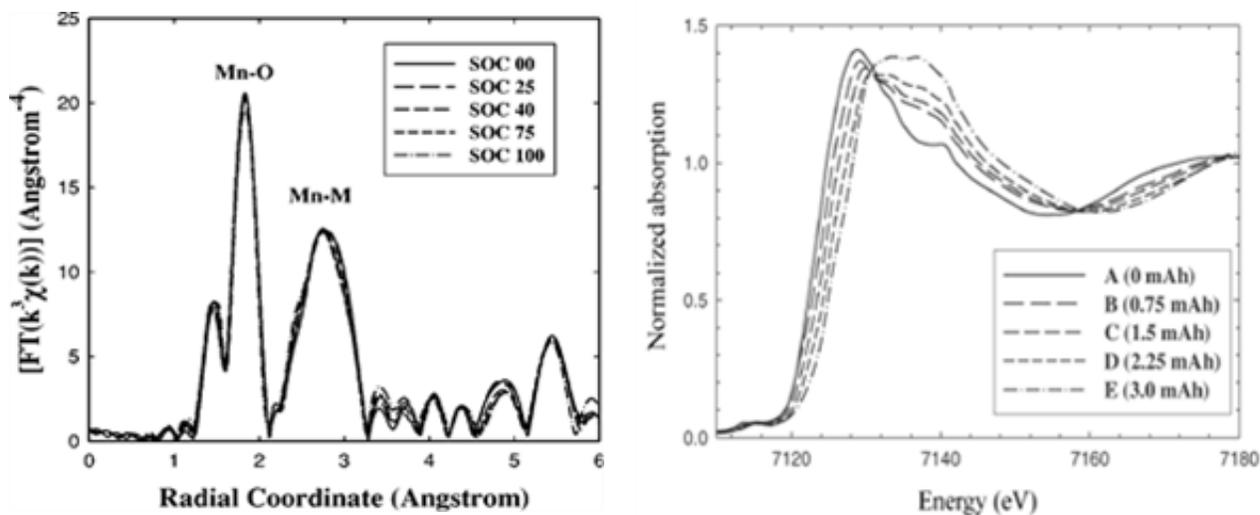


Figure 15. Left: Magnitude of the k^3 -weighted Fourier transform of $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ at the Mn K edge at selected SOC during the charge cycle (k range=1.5–15.1 Å). M represents the transition metal atom [95]. Right: calibrated and normalized XANES data at the Fe K edge during charge. A (0 mAh), B (0.75 mAh), C (1.50 mAh), D (2.25 mAh) and E (3.0 mAh) in the figure represent the different stages in the charge process at which the X-ray measurements were performed [26].

doped LiFePO_4/C nanocomposite shows a discharge capacity of 170mAhg^{-1} , which approximately coincides with the theoretical value. However this nanocomposite material shows excellent charge and discharge capability and long cyclability. At high C rate this material exhibits high capacities of 150mAhg^{-1} and 130mAhg^{-1} . Ni doping was found to enhance the electronic conductivity, reducing the particle size in the range of 20–60 nm [15, 19] (see also electron microscope images in Fig. 11).

L. Tabassam et al., synthesized the samples with solid solutions method. $\text{LiFe}_{1-x}\text{Ni}_x\text{PO}_4$ with x ranging from 0.0 to 0.15 and from 0.9 to 1.0 were successfully synthesized. Figure 12 shows the XRD diffraction patterns and Rietveld analysis of $x=0.1\%$ Ni doped LiFePO_4 . The Rietveld analysis shows that the unit cell volume decreases an-isotropically with increasing Ni content x .

The average equilibrium distances $\langle\text{M1-O}\rangle$, $\langle\text{M2-O}\rangle$ and $\langle\text{T-O}\rangle$ (where M1 and M2 are the octahedral and T is the tetrahedral site) and the average Ni-O and Fe-O inter-atomic distances [9] were obtained by XRD and XAS refinement respectively, showing that the overall linear decrease of the unit cell volume can be ascribed to the decrease of the M2 average size with increasing Ni occupancy.

XRD and XAS techniques indicate that Li occupies the M1 site, while both Fe and Ni reside mostly in the M2 site of the olivine structure. The shorter Ni-O bonding distances are found to induce a reduction of the average cell size, with an effect on the medium and long range structure. Moreover, the Ni-O octahedral sites have been found to be largely distorted, with two atoms at longer distances [9].

$\text{LiFePO}_4/\text{NiP}$ composite nanospheres with porous structures have been synthesized by spray technique. It was observed that by doping with NiP, the electric conductivity composite nanospheres improved by 3 to 4 order of magnitude as compared with pure LiFePO_4 . $\text{LiFePO}_4/\text{NiP}$ composite nanospheres with high capacity,

high power and long life cycle are promising candidate for rechargeable Li-Ion batteries [17]. Fe K-edge XANES and EXAFS have been used to study the stability and the changes in the local atomic and electronic structure upon repeated cycling. XANES peak positions of the powdered sample provide evidence that iron is in the Fe^{2+} (see Fig. 15).

EXAFS refinement reveals that there has been no change in the local atomic structure in the cycled LiFePO_4 electrodes [16, 30].

In a different study, LiFePO_4 was synthesized by the sol-gel technique. X-ray absorption spectroscopy (XAS) was used to investigate the local structure of lithium iron phosphate. Results of the Fe K-edge EXAFS showed that the sub microcrystalline iron phosphate material is characterized by a short range order structure slightly different from that of crystalline LiFePO_4 . Fe-O first-shell distance increases with the heat treatment. Changes in the structure disorderness were observed during the lithiation of the amorphous precursor. In fact, Li^+ ions cause deformations on the local structure of the host upon heating, the structure becomes more organized with the Li^+ ions reaching the crystallographic sites [31] (see also Fig. 16). Table 4 shows the doping effect of different dopants (M=Cr, Zn, V, Mn, Mo, Nb, Ti, Fe etc), and improvement in the structural and electrochemical characterization of composite LiFePO_4 . (this is just hole name of the composite material, both are correct, either composite lifepo4 or composite lifepo4/C), what ever you feel ok, no problem).

Arianna Moretti et al., Synthesized the V (vanadium) doped samples by using wet chemistry method. Different concentrations of V doped LiFePO_4 enhanced electrochemical performance which is the primary source in several morphological, structural and chemical effects with the reduction of crystallite size. The Vacancies of Li at M1 site cause the structural distortion around V and the single phase Li insertion/extraction enlarge the range of solid solution behavior. All the above factors that are responsible for

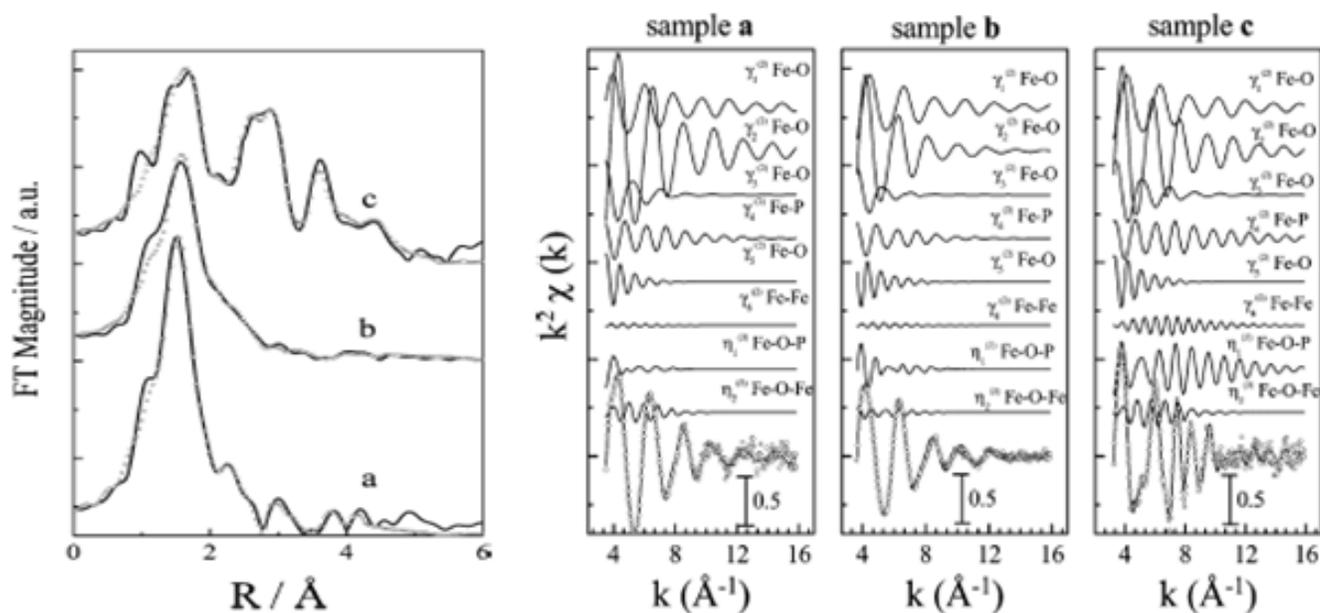


Figure 16. Left: Experimental (-) and theoretical FT EXAFS signals of the samples a-c obtained at the Fe K-edge. Right: Details of the EXAFS analysis of the Fe K-edge of the samples a-c. The figure shows the individual EXAFS contributions, in terms of two-body and three-body signals, to the total theoretical signal. At the bottom, the comparison of the total theoretical signal (-) with the experimental is also reported [31].

enhancing the performance of LiFePO₄ are related to the successful structural doping [80]. Different dopants are used to improve the structural and electrochemical performance of the batteries.

5. CONCLUSION

In this review article we have focused on the progress made in cathode materials in lithium ion batteries with layered and non layered cathodes. The progress is towards the high energy density, longer life cycle, good conductivity, high power density and safety characteristics of batteries. In different materials from the chemistry family; three layered and two non layered, we describe the crystal structures, ion mobilities and the stability of structures in rele-

vance to their electrochemical properties by using different doped transition metals in the LiFePO₄. The results showed that the phase transformation [17], dis-orderness in the structure by using different dopants [8, 99]. The very important aspect is reviewed as the modification of cathode material in lithium ion batteries. Over the past decade many experimentations, characterization and design have been made for the development of the batteries with long life time. Structural characterization shows the stability and improved performance of the lithium ion batteries. In the near future we will see the improved and less costly small size batteries with long life time. Structural study of different dopants is needed to understand the enhanced performance of batteries, their life time and conductivity that can be done by analyzing the symmetric, anti-symmetric

Table 4. Variation in structural and electrochemical properties by using different dopant in Olive LiFePO₄ structure.

Cathode Material	Synthesis Method	Electrochemical Properties	Structural Properties	Dopants
LiFePO ₄	Mechanochemical process [18].	Excellent rate performance and conductivity improvement [18].	phase transformation, Ordered structure [84].	Cr [17].
	Solid-state reaction method [84].	Improved rate capability [84].	single phase [79, 80, 83, 84, 97, 99].	Ti [84].
	Direct hydrothermal process. Mechanoactivation-assisted solid-state reaction [80-81].	Better life cycle and improved capacity [80-81].	Phase change [81].	Mn [80-81].
	Low-temperature solid-state method [82].	Improved conductivity [82].	Pure phase [85, 86].	Cl [82].
	Carbothermal reduction [84-85].	Higher rate capability and improved electrical conductivity [92, 76, 87].	Disorderness in the structure and single phase [8, 12].	V [76, 92, 87].
	Ball-milled [86].	Electrical conductivity improved [93].	Single phase [87].	Zr, Nb, Cr [93].
	Wet chemistry method [87].	Better rate performance [88].	Pure phase [90].	Mg [88].
	Co-precipitation route [88].	Improved capacity performance and cycling stability [89].		La [89].
	Solid-state method [89].	Improved electrochemical performance [9, 13, 90, 91].		Ni [9, 13].
	Solid solution method [9].			Multidoped
	Solid-state reaction [13].			LiFePO ₄ /C [90].
	Carbothermic method [90].			Mn, Fe, Co, and Ni [91].
	Solvothermal method [91].			

and change in type of the olivine structure. One of the major contributions is to study the nano size behavior due to the miniaturization of devices.

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