Operando ^{57}Fe Mössbauer and XRD investigation of $\text{Li}_x\text{MnyFe}_{1-y}\text{PO}_4/\text{C}$ composites ($y = 0.50; 0.75$)

Alexis Perea, Moulay Tahar Sougrati, Costana Ionica-Bousquet, Bernard Fraisse, Cécile Tessier, Laurent Aldon, Jean-Claude Jumas

► To cite this version:

Alexis Perea, Moulay Tahar Sougrati, Costana Ionica-Bousquet, Bernard Fraisse, Cécile Tessier, et al.. Operando ^{57}Fe Mössbauer and XRD investigation of $\text{Li}_x\text{MnyFe}_{1-y}\text{PO}_4/\text{C}$ composites ($y = 0.50; 0.75$). RSC Advances, 2012, 2, pp.9517-9524. 10.1039/C2RA20949G . hal-00736973

HAL Id: hal-00736973

<https://hal.science/hal-00736973>

Submitted on 1 Oct 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

RSC Advances

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard [Terms & Conditions](#) and the [ethical guidelines](#) that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Operando ^{57}Fe Mössbauer and XRD investigation of $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ composites ($y = 0.50; 0.75$)

Alexis Perea,^{*a} Moulay T. Sougrati,^a Costana M. Ionica-Bousquet,^a Bernard Fraisse,^a Cécile Tessier,^b Laurent Aldon^a and Jean-Claude Jumas^a

^s Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

$\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$ and $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ powders have been synthesized by ceramic route. A comparative investigation of their electrochemical behaviour using *operando* ^{57}Fe Mössbauer and X-ray diffraction is reported. The complementarity of *operando* techniques used in this study allows the monitoring of changes of the local electronic environment and the lattice modifications that are directly linked to the redox reaction mechanisms. During the charge, $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$ has been found to undergo three well defined and reversible reactions via an intermediate phase containing simultaneously Fe^{II} and Fe^{III} cations. $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ undergoes a two reactions mechanism. Fe^{III} Mössbauer signature has been found to be sensitive to the oxidation of Mn^{II} since this oxidation is accompanied with a significant increase of the iron quadrupole splitting. This study summarizes the different mechanisms observed for compositions with different manganese content.

1. Introduction

Since the work on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in phospho olivines was first reported in 1997, LiFePO_4 has been intensively studied as a promising cathode material¹⁻⁴ for the next generation of lithium-ion batteries because of its low cost, safety and environmental compatibility. Numerous studies have attempted to improve the electrochemical performances of the material and to get deeper insight in the lithium electrochemical mechanism⁵⁻⁹. On the other hand, attempts have been made to enhance the potential of olivine cathode materials by using manganese phosphate instead of iron phosphate^{3, 10}. Despite the recent advances in cycling insulating materials, thanks to nano-coating techniques and new preparation routes^{11, 12} and even though some authors have reported promising results¹¹⁻¹³, LiMnPO_4 is not used as active material in lithium battery. This is due to the fact that it shows much lower effective energy density than the lithium iron phosphate owing to the low practical capacity evidenced. In addition, LiMnPO_4 requires very slow charge and discharge rates^{2, 14-16}. The main reason on that is the

[View Online](#)

large kinetic barrier at the mismatched interface of $\text{MnPO}_4/\text{LiMnPO}_4$ ⁴. It is also worth noticing that during the charge, LiMnPO_4 exhibits higher volume change than LiFePO_4 ^{2, 15, 17}.

A good compromise between LiFePO_4 and LiMnPO_4 is the partially substituted phases $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ ^{3, 15, 18}, that would introduce the advantage of combining good electrochemical performances of LiFePO_4 with a higher potential for manganese (~ 4.1 V compared with ~ 3.4 V vs. Li^+/Li for iron) in order to enhance the energy density.

It is however not yet clear which composition has to be preferred for practical application. Yamada *et al.* suggested that $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ composition exhibits the best electrochemical performances¹⁵. $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ has also been reported to give good specific capacity after 100 cycles¹⁹. Chang *et al.* have reported that $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$ shows the excellent cycling performances²⁰, whereas Xu *et al.* found that $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$ shows the best cycling performances²¹. Despite increasing interest in the Mn substituted phases, their electrochemical mechanisms are not yet well understood. It is for example not clear why the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox potentials are shifted (vs. Mn content) and why the polarizations related to these two couples show an opposite behaviour²².

Operando techniques are increasingly employed for the investigation of the batteries electrochemical behaviour. Few analyses of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ have been reported using XRD and X-ray absorption spectroscopy (XAS)²³⁻²⁵.

We have recently reported an *operando* study of $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ composites ($y = 0; 0.25$)^{1, 26}. In order to establish a global mechanism, we have prepared $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$ and $\text{LiMn}_{0.25}\text{Fe}_{0.75}\text{PO}_4/\text{C}$ using solid-state reaction. *Operando* XRD and ^{57}Fe Mössbauer Spectroscopy analyses have been used to investigate the evolution of iron local environment, oxidation state and lattice structure during the electrochemical redox process.

2. Experimental section

2.1 Synthesis procedure

$\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y = 0.5; 0.75$) composites were obtained by solid-state reaction from Li_2CO_3 , $\text{FeC}_2\text{O}_4 \bullet 2\text{H}_2\text{O}$, $\text{Mn}(\text{COOCH}_3)_2 \bullet 4\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and a source of carbon (all chemicals of 99% purity from Aldrich) taken in stoichiometric quantities. The precursors were first ball milled during 90 minutes and then thermally treated in a furnace under argon flow at 600 °C.

2.2 Characterization of Materials

After preparation, the compounds were crushed in an agate mortar and powder XRD (PHILIPS X'Pert MPD θ -2 θ diffractometer equipped with the X'celerator detector) patterns were recorded using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a nickel filter.

The residual carbon content was evaluated by a Flash EA 1112 analyser based on the Dynamic Flash Combustion which produced complete combustion of the sample followed by an accurate and precise determination of the elemental gases produced. ^{57}Fe Mössbauer spectra were recorded in the constant acceleration mode and in transmission geometry on a standard Mössbauer spectrometer composed of electronic devices from Ortec and Wissel. A $^{57}\text{Co(Rh)}$ source with a nominal activity of 370 MBq was used. The source and the absorber were always kept at RT. All the isomer shifts are given relative to $\alpha\text{-Fe}$ at RT.

2.3 Electrochemical behaviour

Electrodes containing 80 wt. % sample and 20 wt. % carbon black were prepared for cycling tests. Standard Swagelok cells Li|1 M LiPF₆ (propylenecarbonate (PC): ethylene carbonate (EC):dimethyl carbonate (DMC)) 1:1:3, v/v| LiMn_yFe_{1-y}PO₄ were assembled in an argon-filled glove box and tested using a VMP system.

To identify the electrochemical reaction mechanisms, we carried out *operando* XRD and ^{57}Fe Mössbauer spectroscopy measurements for both LiMn_yFe_{1-y}PO₄ ($y = 0.5; 0.75$) electrodes using an electrochemical cell designed especially for this aim²⁷.

To preserve beryllium window from the oxidation due to high working voltage, it was covered by a 2 μm thick foil of pure aluminium (Goodfellow). Here, the cells were charged and discharged using a C/40 rate, at room temperature in the voltage ranges 2.75-4.6 V. Each *operando* XRD scan was recorded during 1h in which Li extraction/insertion was performed and the results correspond to a change of composition of $\Delta x = 0.025 \text{ Li}$ (where x is in Li _{x} Mn _{y} Fe_{1-y}PO₄/C ($y = 0.5; 0.75$)). A 2 hours acquisition time was used for the *operando* Mössbauer measurement. Each spectrum corresponds to $\Delta x = 0.05$ extracted/inserted Li. For $y = 0.75$. The spectra presented are obtained *in situ* but not *operando* due to the low amount of iron in the electrode.

3. Results and discussion

[View Online](#)

XRD patterns of the obtained powders are given in Figure 1a. As it can be seen, the powder are free of any crystalline impurity.

All the diffraction peaks can be indexed in the orthorhombic Pnma space group. Le Bail method²⁸ has been used to estimate the lattice parameters respectively $a = 10.368(1)\text{\AA}$, $b = 6.050(1)\text{\AA}$, $c = 4.710(1)\text{\AA}$ for $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$ and $a = 10.397(1)\text{\AA}$, $b = 6.073(1)\text{\AA}$, $c = 4.726(1)\text{\AA}$ for $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$. These values are in good agreement with the literature³. Average crystallite sizes of 120 nm have been obtained using the Scherrer formula²⁹. The residual carbon content was evaluated at 4.89 % and 4.82% for $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ ($y = 0.5$; 0.75) respectively.

Figure 1b give the variation of a , b and c for the olivine phases. All, the lattice parameters increase linearly with manganese content. The main effect of the substitution of iron-manganese in $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ is the expansion of the network that can be explained simply by the difference between the ionic radii of high spin Mn^{2+} ($0.97\text{\AA}$) and Fe^{2+} high spin ($0.92\text{\AA}$).

$\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y = 0.50$; 0.75) spectra (Figure 2) consist of sharp doublets with an isomer shift of $\delta = 1.235(2)$ and a quadrupole splitting of $\Delta = 2.947(3)$ mm/s for $y = 0.5$ and an isomer shift of $\delta = 1.239(1)$ and a quadrupole splitting of $\Delta = 2.942(2)$ mm/s for $y = 0.75$ as discussed previously¹.

The voltage profiles of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ are shown in Figure 3a. For LiFePO_4 , a flat plateau is observed at 3.4 V as previously reported. For the substituted phases, two pseudo plateaus are observed in agreement with the two redox reactions $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$. The length of the Mn plateau is proportional to manganese content.

Calculated capacities with the cycle rate for $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y = 0.25$, 0.50 , 0.60 , 0.75) are summarized in Figure 3b. This representation allows direct visualization of the reversible capacity of the material depending on the rate of cycling. The capacity is found to be a function of both cycling rate and Mn content. For our synthesis conditions, the material with the best performance is the composition $\text{LiMn}_{0.25}\text{Fe}_{0.75}\text{PO}_4/\text{C}$. The loss of capacity between C/10 and C is 12% and 62% respectively for the compositions $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$ and $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$. The electrochemical performance decreases with the manganese content: for the phase $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ the reversible capacity calculated for a cycle rate of C/10 is 56 mAh.g^{-1} against 125 mAh.g^{-1} for the substituted phase with less manganese content $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$.

The redox potentials have been obtained from the derivative curves (Figure 4). These potentials

associated with the redox couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ undergo an increase with the manganese content. Kobayashi *et al.*³⁰ explain this with an expansion of the volume of all compositions. These variations are sufficient to increase the average potential of the couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ from 3.45 V to 3.56 V vs. Li^+/Li^0 respectively for $y = 0$ and $y = 0.75$. This variation in potential of 0.11 V may appear negligible in the case of a battery with one cell, however it can be important in the case of batteries with many cells mounted in parallel that can be used for example for electrical vehicles.

To better understand the reaction mechanisms, *operando* analyses have been performed.

For $y = 0.50$ the Mössbauer spectra corresponding to the first cycle and the parameters associated with the first charge are represented respectively in Figure 5a and 5b. The diffractograms corresponding to the first cycle of phase $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$ are shown in Figure 6a. At the beginning of the charge (blue area) ($0.70 \leq x < 0.95$) a new phase appears in both XRD patterns and Mössbauer data. The (020) peak of the pristine material vanishes at the expense of a new peak located at 29.3° . In this domain, the Mössbauer spectra (Figure 7) indicate the transformation of initial Fe^{2+} into two components: the first is associated with Fe^{3+} with the parameters ($\delta = 0.42$ mm/s and $\Delta = 1.12$ mm/s) and a second component associated with a new Fe^{2+} component ($\delta = 1.26$ mm/s and $\Delta = 2.72$ mm/s). The quadrupole splitting of this new Fe^{2+} is lower than that of the initial Fe^{2+} indicating an increase of the distortion of the iron environment³¹ caused by the deintercalation of Li^+ and iron oxidation. This observation allows us to conclude to formation of a mixed valence phase with the following composition: $\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.20}^{\text{II}}\text{Fe}_{0.30}^{\text{III}}\text{PO}_4$. It is worth noting that such phases (called ferrisicklerites $\text{Li}_{x<1}(\text{Fe},\text{Mn})\text{PO}_4$) have been reported by mineralogists and attributed to natural oxidation of triphylite $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ ³²⁻³⁴. From the study of 45 ferrisicklerite minerals, Fanton *et al.* have concluded on the absence of any structural order of the Mn and Fe cations in this family of materials³².

From these observations we conclude to a biphasic mechanism with the coexistence of $\text{LiMn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{II}}\text{PO}_4$ and $\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{II,III}}\text{PO}_4$ for the charge and discharge in the range $0.70 \leq x < 0.95$.

The electrochemical reaction in this region can be written:

[View Online](#)

In the second region ($0.50 \leq x \leq 0.70$), shown in black in Figure 6a, the diffraction lines corresponding to the $\text{Li}_{0.70}\text{Mn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$ phase are shifted to upper angles, indicating the existence of a solid solution domain in charge and discharge. This also is supported by gradual increase ($\sim 21\%$) of the quadrupole splitting of Fe^{3+} with the oxidation of iron. Therefore, in this area the electrochemical reaction can be written as follow:

In the third region ($\sim 0.16 \leq x < 0.5$, shown in red in Figure 6a, the two-phase character is more evident. A new phase appears from $x = 0.50$ ($\text{Li}_{0.50}\text{Mn}_{0.50}^{\text{III}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$) with diffraction peaks located at angles higher than the initial phase:

All the Fe^{2+} was oxidized into Fe^{3+} at the end of the second region, however, the Mössbauer spectra continue to evolve (Figure 7), indicating that the environment of iron is affected by the oxidation of Mn^{2+} in Mn^{3+} as already observed for the phase $\text{LiMn}_{0.25}\text{Fe}_{0.75}\text{PO}_4$ ¹.

From $x \leq 0.50$ the spectra (Figure 7) are refined by adding a new Fe^{3+} doublet shown in magenta. The new doublet corresponding to Fe^{3+} phase $\text{Mn}_{0.50}^{\text{III}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$ exhibits a quadrupole splitting of 1.65 mm/s, which is higher than 1.55 mm/s observed for $\text{Mn}_{0.25}^{\text{III}}\text{Fe}_{0.75}^{\text{III}}\text{PO}_4$, and this further confirms that the Fe^{3+} is very sensitive to the oxidation state of Mn since an increase of the amount of Mn^{3+} around the Fe^{3+} site lead to a significant increase of the quadrupole splitting³¹. Similar spectra have been reported for natural purpurite $(\text{Fe},\text{Mn})\text{PO}_4$ ³¹. The electromechanism of the charge and discharge of $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$ is done in three steps as the $\text{LiMn}_{0.25}\text{Fe}_{0.75}\text{PO}_4/\text{C}$ phase. At beginning, the mechanism is biphasic, with the coexistence of $\text{LiMn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$ and a mixed composition $\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.20}^{\text{II}}\text{Fe}_{0.30}^{\text{III}}\text{PO}_4$ up to $x = 0.50$. From $x = 0.50$, the second domain is a solid solution where the phase $\text{Li}_x\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.20}^{\text{II}}\text{Fe}_{0.30}^{\text{III}}\text{PO}_4$ oxidizes up to $x = 0.16$. The last domain is biphasic between $\text{Li}_{0.50}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$ and $\text{Mn}_{0.50}^{\text{III}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$.

The electrochemical mechanism corresponding to the richest manganese phase $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ was also studied. The diffractograms corresponding to the first cycle with the galvanostatic curves are shown in Figure 6b. The three ^{57}Fe Mössbauer spectra (Figure 8) do not match the *operando* mode indeed the low iron content of this phase would not have sufficient quality for data processing. They were however recorded *in situ* with the battery paused at key points.

From $x = 0.95$ the diffraction line corresponding to the plane (020) phase $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ (29.2° (2 θ)) shifts to higher angles up to $x = 0.75$ (black area of Figure 6b). The reaction corresponding to the oxidation of iron is single phase in this area ($0.45 \leq x < 0.75$) for the charge and discharge:

After $x = 0.75$, the Mössbauer spectra show clearly that all the Fe^{2+} has been oxidized to Fe^{3+} (Figure 8).

From $x = 0.75$, the potential is 4.15 V, an olivine-type phase appeared, the main diffraction peak ($2\theta \sim 30.2^\circ$) corresponding to this new phase is shown Figure 6b. The coexistence of two phases in charge and discharge is established for the oxidation-reduction of $\text{Mn}^{3+}/\text{Mn}^{2+}$ in the area shown in red. The electrochemical reaction in ($0.45 \leq x < 0.75$) can be written:

Mössbauer spectra shown in Figure 8 (where $x = 0.60$ and 0.45) correspond to the spectra of Fe^{3+} on the "plateau" of redox reaction $\text{Mn}^{3+}/\text{Mn}^{2+}$. Indeed, it was interesting to see the indirect effect of Mn^{3+} on the environment of Fe^{3+} as in previous phases with less manganese. The spectra cannot be refined with a single component in this area, we must add a second doublet for a correct refinement. Mössbauer parameters for the two Fe^{3+} components ($\text{Li}_{0.75}\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ and $\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$) are shown in Table 1. Component $\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ is characterized by a quadrupole splitting of 1.705 mm/s.

[View Online](#)

In conclusion, the electrochemical mechanism of phase $\text{Li}_x\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ differs from the three previously studied compositions. The first part corresponding to the domain ($0.75 \leq x < 0.95$) is single-phase, the phase $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ evolves to the composition $\text{Li}_{0.75}\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$. The second area ($0.45 \leq x < 0.75$) which is located at the "plateau" of the reaction $\text{Mn}^{3+}/\text{Mn}^{2+}$ is biphasic between the two compositions $\text{Li}_{0.75}\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ and $\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ for the charge and discharge.

To summarize, all the mechanisms observed for these substituted phases $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ in charge are respectively represented in Figure 9. Other compositions $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ ($y = 0.4, 0.6, 0.67$) prepared under the same conditions have also been studied and can complete the graph of Figure 9. The regions corresponding to different types of mechanism are shown as a function of lithium content:

- 10 - The beginning of the charge corresponding to the reaction $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ is biphasic for all compositions, except $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ where the reaction is a single-phase.
- A domain of solid solution is also observed for all compositions, except $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ between the two "plateaus" corresponding to the two redox reactions, this domain decreases with the manganese content.
- 15 - The end of the charge where the potential is around 4.2 V corresponding to the $\text{Mn}^{3+}/\text{Mn}^{2+}$ reaction is biphasic for all the compositions.

An inductive effect has already been established in some intercalation compounds polyanionic lithium³⁵, it can result in changes in potential more than 1 V. In the case of compounds $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$, the ionicity or covalent bonds (Fe, Mn-O) is controlled by the size of the network (the length of these bonds). It was therefore interesting to compare the values of the isomer shifts of phases $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ with the values of potentials associated with the couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ (Figure 10). Indeed, there is a correlation between the inductive effect and value of the isomer shift as demonstrated Menil³⁶. The representation of values of δ and potentials in Figure 10 clearly shows a very similar tendency of the two parameters. This interesting result suggests that it is possible to predict the reaction potential from iron Mössbauer data as reported by Naille *et al.* for tin compounds³⁷.

Finally we observed an excellent capacity retention over 100 cycles for all the studied compositions (see Add. Data). Although the substitution of iron with manganese does not improve the capacity

(since it decreases with the manganese content), the possibility of tuning the working voltage may be useful for some applications as electric hybrid cars.

4. Conclusion

In this paper we report a comparative *operando* study for $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ for $y = 0.50$ and $y = 0.75$ combining XRD and ^{57}Fe Mössbauer spectroscopy. The electrochemical mechanisms have been studied by monitoring the evolution of the local electronic environment (Mössbauer probe) and the lattice changes (XRD). The solid solution phase $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$ exhibits a complex three steps mechanism during the charge. First a two biphasic reaction in the domain ($0.70 \leq x < 0.95$) between $\text{LiMn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{II}}\text{PO}_4$ and $\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.20}^{\text{II}}\text{Fe}_{0.30}^{\text{III}}\text{PO}_4$, the Mössbauer probe helps to determine the composition of this mixed valence phase. The reaction is followed by a solid solution in the domain ($0.50 \leq x \leq 0.70$). The third step is described by a biphasic reaction between $\text{Li}_{0.50}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$ and $\text{Mn}_{0.50}^{\text{III}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$ until $x \sim 0.1$. In conclusion, the electrochemical mechanism of phase $\text{Li}_x\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ differs from the three previously studied compositions. The first part corresponding to the domain ($0.75 \leq x < 0.95$) is single-phase, the phase $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ evolves to the composition $\text{Li}_{0.75}\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ followed by a two phase mechanism with $\text{LiMn}_{0.25}\text{Fe}_{0.75}\text{PO}_4$ and $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$. The second area ($0.45 \leq x < 0.75$) which is located at the "plateau" of the reaction $\text{Mn}^{3+}/\text{Mn}^{2+}$ is biphasic between the two compositions $\text{Li}_{0.75}\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ and $\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$ for the charge and discharge. An interesting correlation has been established between the isomer shift and the average potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox reaction, which can be used to predict the potential indirectly from Mössbauer data.

Acknowledgment

The authors would like to thank SAFT Company and CNRS (contract SAFT/CNRS N°029888) through the Ph.D. grant of Alexis Perea and ANR PHOSPHALION (National Research Agency) Stock-E program (ANR-09-STOCK-E-07) for financial support and Manfred Womes for fruitful discussions. Région Languedoc-Roussillon is gratefully acknowledged for the financial support to X-rays and gamma-rays platform (Contracts n° 2006 Q-086 and 2008 094192)

^a ICGM/AIME (CNRS UMR 5253), Université Montpellier II, CC 15-02

Place E. Bataillon, 34095 Montpellier Cedex 5, France. E-mail: alexis.perea@univ-montp2.fr

^b Saft Recherche Division, 111-113 Bld. Alfred Daney, 33074 Bordeaux, France

References

1. Perea, A.; Sougrati, M. T.; Ionica-Bousquet, C. M.; Fraisse, B.; Tessier, C.; Aldon, L.; Jumas, J.-C., Operando 57Fe Mossbauer and XRD investigation of $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ composites ($y = 0; 0.25$). *RSC Advances* **2012**, *2*, 2080-2086.
2. Delacourt, C.; Poizot, P.; Morcrette, M.; Tarascon, J. M.; Masquelier, C., One-step low-temperature route for the preparation of electrochemically active LiMnPO_4 powders. *Chemistry of Materials* **2004**, *16* (1), 93-99.
3. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B., Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *Journal of the Electrochemical Society* **1997**, *144* (4), 1188-1194.
4. Delacourt, C.; Laffont, L.; Bouchet, R.; Wurm, C.; Leriche, J. B.; Morcrette, M.; Tarascon, J. M.; Masquelier, C., Toward understanding of electrical limitations (electronic, ionic) in LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}$) electrode materials. *Journal of the Electrochemical Society* **2005**, *152*, A913-A921.
5. Delmas, C.; Maccario, M.; Croguennec, L.; Le Cras, F.; Weill, F., Lithium deintercalation in LiFePO_4 nanoparticles via a domino-cascade model. *Nature Materials* **2008**, *7* (8), 665-671.
6. Dedryvere, R.; Maccario, M.; Croguennec, L.; Le Cras, F.; Delmas, C.; Gonbeau, D., X-Ray Photoelectron Spectroscopy Investigations of Carbon-Coated LiFePO_4 Materials. *Chemistry of Materials* **2008**, *20* (22), 7164-7170.
7. Delacourt, C.; Rodriguez-Carvajal, J.; Schmitt, B.; Tarascon, J. M.; Masquelier, C., Crystal chemistry of the olivine-type Li_xFePO_4 system ($0 \leq x \leq 1$) between 25 and 370 degrees C. *Solid State Sciences* **2005**, *7* (12), 1506-1516.
8. Yamada, A.; Koizumi, H.; Sonoyama, N.; Kanno, R., Phase change in Li_xFePO_4 . *Electrochemical and Solid State Letters* **2005**, *8* (8), A409-A413.
9. Aldon, L.; Perea, A.; Womes, M.; Ionica-Bousquet, C. M.; Jumas, J. C., Determination of the Lamb-Mossbauer factors of LiFePO_4 and FePO_4 for electrochemical in situ and operando measurements in Li-ion batteries. *Journal of Solid State Chemistry* **2010**, *183* (1), 218-222.
10. Zhou, F.; Kang, K. S.; Maxisch, T.; Ceder, G.; Morgan, D., The electronic structure and band gap of LiFePO_4 and LiMnPO_4 . *Solid State Communications* **2004**, *132* (3-4), 181-186.
11. Li, G. H.; Azuma, H.; Tohda, M., LiMnPO_4 as the cathode for lithium batteries. *Electrochemical and Solid State Letters* **2002**, *5* (6), A135-A137.
12. Kwon, N. H.; Drezen, T.; Exnar, I.; Teerlinck, I.; Isono, M.; Graetzel, M., Enhanced electrochemical performance of mesoparticulate LiMnPO_4 for lithium ion batteries. *Electrochemical and Solid State Letters* **2006**, *9* (6), A277-A280.
13. Wang, C.; Lu, S.; Kan, S.; Pang, J.; Jin, W.; Zhang, X., Enhanced capacity retention of Co and Li doubly doped LiMn_2O_4 . *Journal of Power Sources* **2009**, *189* (1), 607-610.
14. Yonemura, M.; Yamada, A.; Takei, Y.; Sonoyama, N.; Kanno, R., Comparative kinetic study of olivine Li_xMPO_4 ($\text{M} = \text{Fe}, \text{Mn}$). *Journal of the Electrochemical Society* **2004**, *151* (9), A1352-A1356.
15. Yamada, A.; Kudo, Y.; Liu, K. Y., Reaction mechanism of the olivine-type $\text{Li}_x(\text{Mn}_{0.6}\text{Fe}_{0.4})\text{PO}_4$ ($0 \leq x \leq 1$). *Journal of the Electrochemical Society* **2001**, *148* (7), A747-A754.
16. Yang, J. S.; Xu, J. J., Synthesis and characterization of carbon-coated lithium transition metal phosphates LiMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) prepared via a nonaqueous sol-gel route. *Journal of the Electrochemical Society* **2006**, *153* (4), A716-A723.
17. Kim, S. W.; Kim, J.; Gwon, H.; Kang, K., Phase Stability Study of $\text{Li}_{1-x}\text{MnPO}_4$ ($0 \leq x \leq 1$) Cathode for Li Rechargeable Battery. *Journal of the Electrochemical Society* **2009**, *156* (8), A635-A638.
18. Yamada, A.; Hosoya, M.; Chung, S. C.; Kudo, Y.; Hinokuma, K.; Liu, K. Y.; Nishi, Y., Olivine-type cathodes achievements and problems. *Journal of Power Sources* **2003**, *119*, 232-238.
19. Shin, Y. J.; Kim, J. K.; Cheruvally, G.; Ahn, J. H.; Kim, K. W., $\text{Li}(\text{Mn}_{0.4}\text{Fe}_{0.6})\text{PO}_4$ cathode active material: Synthesis and electrochemical performance evaluation. *Journal of Physics and Chemistry of Solids* **2008**, *69* (5-6), 1253-1256.
20. Xu, J.; Chen, G.; Li, H. J.; Lv, Z. S., Direct-hydrothermal synthesis of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ cathode materials. *Journal of Applied Electrochemistry* **2010**, *40* (3), 575-580.

21. Chang, X. Y.; Wang, Z. X.; Li, X. H.; Zhang, L.; Guo, H. J.; Peng, W. J., Synthesis and performance of LiMn_{0.7}Fe_{0.3}PO₄ cathode material for lithium ion batteries. *Materials Research Bulletin* **2005**, *40* (9), 1513-1520.
22. Kobayashi, G.; Yamada, A.; Nishimura, S.; Kanno, R.; Kobayashi, Y.; Seki, S.; Ohno, Y.; Miyashiro, H., Shift of redox potential and kinetics in Li-x(MnyFe_{1-y})PO₄. *Journal of Power Sources* **2009**, *189* (1), 397-401.
23. Nam, K. W.; Yoon, W. S.; Zaghib, K.; Chung, K. Y.; Yang, X. Q., The phase transition behaviors of Li_{1-x}Mn_{0.5}Fe_{0.5}PO₄ during lithium extraction studied by in situ X-ray absorption and diffraction techniques. *Electrochemistry Communications* **2009**, *11* (10), 2023-2026.
24. Nedoseykina, T.; Kim, M. G.; Park, S. A.; Kim, H. S.; Kim, S. B.; Cho, J.; Lee, Y., In situ X-ray absorption spectroscopic study for the electrochemical delithiation of a cathode LiFe_{0.4}Mn_{0.6}PO₄ material. *Electrochimica Acta* **2010**, *55* (28), 8876-8882.
25. Chen, Y. C.; Chen, J. M.; Hsu, C. H.; Lee, J. F.; Yeh, J. W.; Shih, H. C., In-situ synchrotron X-ray absorption studies of LiMn_{0.25}Fe_{0.75}PO₄ as a cathode material for lithium ion batteries. *Solid State Ionics* **2009**, *180* (20-22), 1215-1219.
26. Aldon, L.; Perea, A., 2D-correlation analysis applied to in situ and operando Mossbauer spectroscopy. *Journal of Power Sources* **196** (3), 1342-1348.
27. Leriche, J. B.; Hamelet, S.; Shu, J.; Morcrette, M.; Masquelier, C.; Ouyard, G.; Zerrouki, M.; Soudan, P.; Belin, S.; Elkaim, E.; Baudelet, F., An Electrochemical Cell for Operando Study of Lithium Batteries Using Synchrotron Radiation. *Journal of the Electrochemical Society* **2010**, *157* (5), A606-A610.
28. Rodríguez-Carvajal, J., Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condensed Matter* **1993**, *192* (1-2), 55-69.
29. Eberhart, J. P., *Méthodes physiques d'étude des minéraux et des matériaux solides*. DOIN ed.; 1976.
30. Kobayashi, G.; Yamada, A.; Nishimura, S. i.; Kanno, R.; Kobayashi, Y.; Seki, S.; Ohno, Y.; Miyashiro, H., Shift of redox potential and kinetics in Li_x(MnyFe_{1-y})PO₄. *Journal of Power Sources* **2009**, *189* (1), 397-401.
31. Liu, Z. G.; Dong, D. W.; Liu, M. L.; Sui, Y.; Su, W. H.; Qian, Z. N.; Li, Z., Quadrupole splitting distributions in purpurite and related minerals. *Hyperfine Interactions* **2005**, *163* (1-4), 13-27.
32. Fontan, F.; Huvelin, P.; Orliac, M.; Permingeat, F., FERRISICKLERITE OF SIDI BOU OTHMANE PEGMATITES (JEBILET, MOROKKO) AND MINERAL GROUP WITH A TRIPHYLITE STRUCTURE. *Bulletin De La Societe Francaise Mineralogie Et De Cristallographie* **1976**, *99* (5), 274-286.
33. Liu, Z.; Dong, D.; Liu, M.; Sui, Y.; Su, W.; Qian, Z.; Li, Z., Quadrupole Splitting Distributions in Purpurite and Related Minerals. *Hyperfine Interactions* **2005**, *163* (1), 13-27.
34. Alberti, A., CRYSTAL-STRUCTURE OF FERRISICKLERITE, LI-LESS-THAN(1) (FE-3+, MN-2+) PO₄. *Acta Crystallogr. Sect. B-Struct. Commun.* **1976**, *32* (OCT15), 2761-2764.
35. Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Okada, S.; Goodenough, J. B., Effect of structure on the Fe³⁺/Fe²⁺ redox couple in iron phosphates. *Journal of the Electrochemical Society* **1997**, *144* (5), 1609-1613.
36. Menil, F., SYSTEMATIC TRENDS OF THE FE-57 MOSSBAUER ISOMER-SHIFTS IN (FEON) AND (FEFN) POLYHEDRA - EVIDENCE OF A NEW CORRELATION BETWEEN THE ISOMER-SHIFT AND THE INDUCTIVE EFFECT OF THE COMPETING BOND T-X (-)FE (WHERE X IS O OR F AND T ANY ELEMENT WITH A FORMAL POSITIVE CHARGE). *Journal of Physics and Chemistry of Solids* **1985**, *46* (7), 763-789.
37. Naille, S.; Jumas, J. C.; Lippens, P. E.; Olivier-Fourcade, J., ¹¹⁹Sn Mössbauer parameters as predictive tool for future Sn-based negative electrode materials. *Journal of Power Sources* **2009**, *189* (1), 814-817.

40

FIGURES

5

Fig. 1 Powder X-ray diffraction patterns (a) and evolution of lattice parameters with manganese content of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ (b).

20

Fig.2 ^{57}Fe Mössbauer spectra for $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$, where $y = 0.50$ and $y = 0.75$.

[View Online](#)

Fig.3 Electrochemical curves (first cycle) (a) and rate capability (b) of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$.

Fig.4 Average potential of redox reactions in $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$.

5

Fig.5 Evolution of the *operando* Mössbauer spectra (a) and hyperfine parameters of Fe^{II} and Fe^{III} species (b) of $\text{Li}_x\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ recorded during the electrochemical process recorded at C/40 rate .

25

Fig.6 Operando X-ray diffractograms of $\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$ (a) and $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ (b) recorded during the electrochemical process at C/40 rate .

5

10

15

Fig. 7: Mössbauer spectra of $\text{Li}_x\text{Mn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$ obtained at the indicated x values .

Fig. 8 Mössbauer spectra of $\text{Li}_x\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$ obtained at the indicated x values .

5

Table 1 Hyperfine parameters of the composition involved during the electrochemical charge process .

Composition	δ	Δ
	mm/s	mm/s
$\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{II,III}}\text{PO}_4$	1.32	2.72
	0.43	1.02
$\text{Li}_{0.50}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$	0.43	1.25
$\text{Mn}_{0.50}^{\text{III}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$	0.43	1.64
$\text{Li}_{0.55}\text{Mn}_{0.75}^{\text{II}}\text{Fe}_{0.25}^{\text{II,III}}\text{PO}_4$	1.28	2.71
	0.44	1.08
$\text{Li}_{0.25}\text{Mn}_{0.75}^{\text{II}}\text{Fe}_{0.25}^{\text{III}}\text{PO}_4$	0.41	1.30
$\text{Mn}_{0.75}^{\text{III}}\text{Fe}_{0.25}^{\text{III}}\text{PO}_4$	0.41	1.52

10

15

20

Fig. 9 Schematic diagram of the different mechanisms observed during the first charge .

Fig.10 Evolution of the Isomer Shift Vs. Average potential .