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

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LiMn$_{0.50}$Fe$_{0.50}$PO$_4$ and LiMn$_{0.75}$Fe$_{0.25}$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, LiMn$_{0.50}$Fe$_{0.50}$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. LiMn$_{0.75}$Fe$_{0.25}$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 Fe$^{3+}$/Fe$^{2+}$ redox couple in phospho olivines was first reported in 1997, LiFePO$_4$ has been intensively studied as a promising cathode material 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 mechanism. On the other hand, attempts have been made to enhance the potential of olivine cathode materials by using manganese phosphate instead of iron phosphate. Despite the recent advances in cycling insulating materials, thanks to nano-coating techniques and new preparation routes and even though some authors have reported promising results, LiMn$_4$PO$_4$ 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. The main reason on that is the
large kinetic barrier at the mismatched interface of MnPO₄/LiMnPO₄. It is also worth noticing that during the charge, LiMnPO₄ exhibits higher volume change than LiFePO₄.²,¹⁵,¹⁷.

A good compromise between LiFePO₄ and LiMnPO₄ is the partially substituted phases LiMnₓFe₁₋ₓPO₄, that would introduce the advantage of combining good electrochemical performances of LiFePO₄ 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 LiMn₀.₆Fe₀.₄PO₄ composition exhibits the best electrochemical performances.¹⁵ LiMn₀.₄Fe₀.₆PO₄ has also been reported to give good specific capacity after 100 cycles.¹⁹ Chang et al. have reported that LiMn₀.₃Fe₀.₇PO₄ shows the excellent cycling performances, whereas Xu et al. found that LiMn₀.₁Fe₀.₉PO₄ shows the best cycling performances.²¹ Despite increasing interest in the Mn substituted phases, their electrochemical mechanisms are not yet well understood. It is for example not clear why the Fe³⁺/Fe²⁺ and Mn³⁺/Mn²⁺ redox potentials are shifted (vs. Mn content) and why the polarizations related to these two couples show an opposite behaviour.²²

Operando techniques are increasingly employed for the investigation of the batteries electrochemical behaviour. Few analyses of LiMnₓFe₁₋ₓPO₄ have been reported using XRD and X-ray absorption spectroscopy (XAS).²³-²⁵

We have recently reported an operando study of LiₓMnₓFe₁₋ₓPO₄/C composites (y = 0; 0.25).¹,²⁶ In order to establish a global mechanism, we have prepared LiMn₀.₅₀Fe₀.₅₀PO₄/C and LiMn₀.₂₅Fe₀.₇₅PO₄/C using solid-state reaction. Operando XRD and ⁵⁷Fe 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

LiMnₓFe₁₋ₓPO₄/C (y = 0.5; 0.75) composites were obtained by solid-state reaction from Li₂CO₃, FeC₂O₄•2H₂O, Mn(COOCH₃)₂•4H₂O, NH₄H₂PO₄ 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-2θ diffractometer equipped with the X’celerator detector) patterns were recorded using Cu Kα radiation (λ = 1.5418 Å) 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. $^{57}\text{Fe}$ 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 LiPF$_6$ (propylenecarbonate (PC): ethylene carbonate (EC):dimethyl carbonate (DMC)) 1:1:3, v/v)| LiMn$_{0.5}$Fe$_{1.5}$PO$_4$ 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 $^{57}\text{Fe}$ Mössbauer spectroscopy measurements for both LiMn$_{0.5}$Fe$_{1.5}$PO$_4$ ($y = 0.5; 0.75$) electrodes using an electrochemical cell designed especially for this aim.$^{27}$

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 $\Delta x = 0.025$ Li (where x is in Li$_x$Mn$_y$Fe$_{1-y}$PO$_4$/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
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. Lebail method has been used to estimate the lattice parameters respectively $a = 10.368(1)\,\text{Å}$, $b = 6.050(1)\,\text{Å}$, $c = 4.710(1)\,\text{Å}$ for LiMn$_{0.50}$Fe$_{0.50}$PO$_4$/C and $a = 10.397(1)\,\text{Å}$, $b = 6.073(1)\,\text{Å}$, $c = 4.726(1)\,\text{Å}$ for LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C. These values are in good agreement with the literature. Average crystallite sizes of 120 nm have been obtained using the Scherrer formula. The residual carbon content was evaluated at 4.89% and 4.82% for LiMn$_{y}$Fe$_{1-y}$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 LiMn$_{y}$Fe$_{1-y}$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 Å) and Fe$^{2+}$ high spin (0.92 Å).

LiMn$_{y}$Fe$_{1-y}$PO$_4$/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 $\Delta = 2.947(3)\,\text{mm/s}$ for $y = 0.5$ and an isomer shift of $\delta = 1.239(1)$ and a quadrupole splitting of $\Delta = 2.942(2)\,\text{mm/s}$ for $y = 0.75$ as discussed previously.

The voltage profiles of LiMn$_{y}$Fe$_{1-y}$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 Fe$^{3+}$/Fe$^{2+}$ and Mn$^{3+}$/Mn$^{2+}$. The length of the Mn plateau is proportional to manganese content.

Calculated capacities with the cycle rate for Li$_{1-x}$Mn$_{y}$Fe$_{1-y}$PO$_4$/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 LiMn$_{0.25}$Fe$_{0.75}$PO$_4$/C. The loss of capacity between C/10 and C is 12% and 62% respectively for the compositions LiMn$_{0.50}$Fe$_{0.50}$PO$_4$/C and LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C. The electrochemical performance decreases with the manganese content: for the phase LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C the reversible capacity calculated for a cycle rate of C/10 is 56 mAh.$\,\text{g}^{-1}$ against 125 mAh.$\,\text{g}^{-1}$ for the substituted phase with less manganese content LiMn$_{0.50}$Fe$_{0.50}$PO$_4$/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. \( \text{Li}^+/\text{Li}^0 \) 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, \textit{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 locate at 29.3°. In this domain, the Mössbauer spectra (Figure 7) indicate the transformation of initial \( \text{Fe}^{2+} \) into two components: the first is associated with \( \text{Fe}^{3+} \) with the parameters (\( \delta = 0.42 \text{ mm/s} \) and \( \Delta = 1.12 \text{ mm/s} \)) and a second component associated with a new \( \text{Fe}^{2+} \) component (\( \delta = 1.26 \text{ mm/s} \) and \( \Delta = 2.72 \text{ mm/s} \)). The quadrupole splitting of this new \( \text{Fe}^{2+} \) is lower than that of the initial \( \text{Fe}^{2+} \) indicating an increase of the distortion of the iron environment\(^{31}\) caused by the deintercalation of \( \text{Li}^+ \) and iron oxidation. This observation allows us to conclude to formation of a mixed valence phase with the following composition:

\[
\text{Li}_{x} \text{Mn}_{0.50}^{II} \text{Fe}_{0.50}^{II} \text{PO}_4
\]

It is worth noting that such phases (called ferrisicklerites \( \text{Li}_{x<1}(\text{Fe, Mn})\text{PO}_4 \)) have been reported by mineralogists and attributed to natural oxidation of triphylite \( \text{Li}(\text{Fe, Mn})\text{PO}_4 \). From the study of 45 ferrisicklerite minerals, Fanton \textit{et al.} have concluded on the absence of any structural order of the Mn and Fe cations in this family of materials\(^{32}\).

From these observations we conclude to a biphasic mechanism with the coexistence of \( \text{LiMn}_{0.50}^{II} \text{Fe}_{0.50}^{II} \text{PO}_4 \) and \( \text{Li}_{0.70} \text{Mn}_{0.50}^{II} \text{Fe}_{0.30}^{II} \text{PO}_4 \) for the charge and discharge in the range \( 0.70 \leq x < 0.95 \).

The electrochemical reaction in this region can be written:

\[
\begin{align*}
\text{Li}_{1.0} \text{Mn}_{0.50}^{II} \text{Fe}_{0.50}^{II} \text{PO}_4 & \leftrightarrow (\alpha)\text{Li}_{0.70} \text{Mn}_{0.50}^{II} \text{Fe}_{0.20}^{II} \text{Fe}_{0.30}^{III} \text{PO}_4 + \\
& (1 - \alpha)\text{Li}_{1.0} \text{Mn}_{0.50}^{II} \text{Fe}_{0.50}^{II} \text{PO}_4 + 0.30\alpha\text{Li}^{+} + 0.30\alpha\text{e}^{-} \quad (\text{where } 0 < \alpha \leq 1)
\end{align*}
\]
In the second region (0.50 ≤ x ≤ 0.70), shown in black in Figure 6a, the diffraction lines corresponding to the Li_{0.70}Mn_{0.50}Fe_{0.50}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 (~ 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:

\[
\text{Li}_{0.70}^\text{II} \text{Mn}_{0.50}^{\text{II}} \text{Fe}_{0.20}^{\text{II}} \text{Fe}_{0.30}^{\text{III}} \text{PO}_{4} \leftrightarrow \\
\text{Li}_{0.70-\alpha}^\text{II} \text{Mn}_{0.50}^{\text{II}} \text{Fe}_{0.20-\alpha}^{\text{II}} \text{Fe}_{0.30+\alpha}^{\text{III}} \text{PO}_{4} + \alpha \text{Li}^+ + \alpha \text{e}^- \\
\text{(where } 0 \leq \alpha \leq 0.2) 
\]

In the third region (~ 0.16 ≤ x < 0.5, shown in red in Figure 6a, the two-phase character is more evident. A new phase appears from x = 0.50 (Li_{0.50}Mn_{0.50}Fe_{0.50}PO_{4}) with diffraction peaks located at angles higher than the initial phase:

\[
\text{Li}_{0.50}^\text{II} \text{Mn}_{0.50}^{\text{II}} \text{Fe}_{0.50}^{\text{III}} \text{PO}_{4} \leftrightarrow \beta \text{Mn}_{0.50}^{\text{II}} \text{Fe}_{0.50}^{\text{III}} \text{PO}_{4} + \\
(1 - \beta) \text{Li}_{0.50}^\text{II} \text{Mn}_{0.50}^{\text{II}} \text{Fe}_{0.50}^{\text{III}} \text{PO}_{4} + 0.50 \beta \text{Li}^+ + 0.50 \beta \text{e}^- \text{ (where } 0 < \beta \leq 1) 
\]

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 LiMn_{0.25}Fe_{0.75}PO_{4}^{1}.

From x ≤ 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 Mn_{0.50}^{\text{III}}Fe_{0.50}^{\text{III}}PO_{4} exhibits a quadrupole splitting of 1.65 mm/s, which is higher than 1.55 mm/s observed for Mn_{0.25}^{\text{III}}Fe_{0.75}^{\text{III}}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 splitting^{31}. Similar spectra have been reported for natural purpurite (Fe,Mn)PO_{4}^{31}. The electromechanism of the charge and discharge of LiMn_{0.50}Fe_{0.50}PO_{4}/C is done in three steps as the LiMn_{0.25}Fe_{0.75}PO_{4}/C phase. At beginning, the mechanism is biphasic, with the coexistence of LiMn_{0.50}^{\text{II}}Fe_{0.50}^{\text{II}}PO_{4} and a mixed composition Li_{0.70}^\text{II}Mn_{0.50}^{\text{II}}Fe_{0.20}^{\text{II}}Fe_{0.30}^{\text{III}}PO_{4} up to x = 0.50. From x = 0.50, the second domain is a solid solution where the phase Li_{x}Mn_{0.50}^{\text{II}}Fe_{0.20}^{\text{II}}Fe_{0.30}^{\text{III}}PO_{4} oxidizes up to x = 0.16. The last domain is biphasic between Li_{0.50}^\text{II}Mn_{0.50}^{\text{II}}Fe_{0.50}^{\text{III}}PO_{4} and Mn_{0.50}^{\text{II}}Fe_{0.50}^{\text{III}}PO_{4}.
The electrochemical mechanism corresponding to the richest manganese phase LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/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 LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C (29.2° (2θ)) 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:

$$\text{Li}_{1.0}\text{Mn}_{0.75}^{\text{III}}\text{Fe}_{0.25}^{\text{II}}\text{PO}_4 \leftrightarrow \text{Li}_{1-\alpha}\text{Mn}_{0.75}^{\text{III}}\text{Fe}_{0.25}^{\text{I}+\alpha}\text{Fe}_{\alpha}^{\text{III}}\text{PO}_4$$

$$+\alpha\text{Li}^+ + \alpha\text{e}^-$$

(where $0 < \alpha \leq 0.25$)

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 (20 ~ 30.2°) 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 Mn$^{3+}$/Mn$^{2+}$ in the area shown in red. The electrochemical reaction in ($0.45 \leq x < 0.75$) can be written:

$$\text{Li}_{0.75}\text{Mn}_{0.75}^{\text{III}}\text{Fe}_{0.25}^{\text{III}}\text{PO}_4 \leftrightarrow \beta\text{Mn}_{0.75}^{\text{III}}\text{Fe}_{0.25}^{\text{III}}\text{PO}_4 +$$

$$(1-\beta)\text{Li}_{0.75}\text{Mn}_{0.75}^{\text{III}}\text{Fe}_{0.25}^{\text{III}}\text{PO}_4 + 0.25\beta\text{Li}^+ + 0.25\beta\text{e}^- \ (\text{where} \ 0 < \beta \leq 1)$$

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 Mn$^{3+}$/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 (Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$ and Mn$_{0.75}$Fe$_{0.25}$PO$_4$) are shown in Table 1. Component Mn$_{0.75}$Fe$_{0.25}$PO$_4$ is characterized by a quadrupole splitting of 1.705 mm/s.
In conclusion, the electrochemical mechanism of phase Li$_x$Mn$_{0.75}$Fe$_{0.25}$PO$_4$/C differs from the three previously studied compositions. The first part corresponding to the domain (0.75 ≤ $x$ < 0.95) is single-phase, the phase LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ evolves to the composition Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$. The second area (0.45 ≤ $x$ < 0.75) which is located at the "plateau" of the reaction Mn$^{3+}$/Mn$^{2+}$ is biphasic between the two compositions Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$ and Mn$_{0.75}$Fe$_{0.25}$PO$_4$ for the charge and discharge.

To summarize, all the mechanisms observed for these substituted phases LiMn$_y$Fe$_{1,y}$PO$_4$/C in charge are respectively represented in Figure 9. Other compositions LiMn$_y$Fe$_{1,y}$PO$_4$/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:

- The beginning of the charge corresponding to the reaction Fe$^{2+}$$\rightarrow$Fe$^{3+}$ is biphasic for all compositions, except LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C where the reaction is a single-phase.

- A domain of solid solution is also observed for all compositions, except LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C between the two "plateaus" corresponding to the two redox reactions, this domain decreases with the manganese content.

- The end of the charge where the potential is around 4.2 V corresponding to the Mn$^{3+}$/Mn$^{2+}$ reaction is biphasic for all the compositions.

An inductive effect has already been established in some intercalation compounds polyanionic lithium$^{35}$, it can result in changes in potential more than 1 V. In the case of compounds LiMn$_y$Fe$_{1-y}$PO$_4$/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 LiMn$_y$Fe$_{1-y}$PO$_4$/C with the values of potentials associated with the couple Fe$^{3+}$/Fe$^{2+}$ (Figure 10). Indeed, there is a correlation between the inductive effect and value of the isomer shift as demonstrated Menil$^{36}$. 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 compounds$^{37}$.

Finally we observed an excellent capacity retention over 100 cycles for all the studies 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 LiMn$_{y}$Fe$_{1-y}$PO$_4$/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 LiMn$_{0.50}$Fe$_{0.50}$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 LiMn$_{0.50}$Fe$_{0.50}$PO$_4$ and Li$_{0.70}$Mn$_{0.50}$Fe$_{0.20}$Fe$_{0.30}$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 Li$_{0.50}$Mn$_{0.50}$Fe$_{0.50}$PO$_4$ and Mn$_{0.50}$Fe$_{0.50}$PO$_4$ until $x \sim 0.1$. In conclusion, the electrochemical mechanism of phase Li$_x$Mn$_{0.75}$Fe$_{0.25}$PO$_4$/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 LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ evolves to the composition Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$ followed by a two phase mechanism with LiMn$_{0.25}$Fe$_{0.75}$PO$_4$ and LiMn$_{0.50}$Fe$_{0.50}$PO$_4$. The second area $(0.45 \leq x < 0.75)$ which is located at the "plateau" of the reaction Mn$^{3+}$/Mn$^{2+}$ is biphasic between the two compositions Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$ and Mn$_{0.75}$Fe$_{0.25}$PO$_4$ for the charge and discharge. An interesting correlation has been established between the isomer shift and the average potential of the Fe$^{3+}$/Fe$^{2+}$ redox reaction, which can be used to predict the potential indirectly from Mössbauer data.

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References

15. Yamada, A.; Kudo, Y.; Liu, K. Y., Reaction mechanism of the olivine-type Li-x(Mn0.6Fe0.4)PO4 (0 <= x <= 1). Journal of the Electrochemical Society 2001, 148 (7), A747-A754.
17. Kim, S. W.; Kim, J.; Gwon, H.; Kang, K., Phase Stability Study of Li1-xMnPO4 (0 <= x <= 1) Cathode for Li Rechargeable Battery. Journal of the Electrochemical Society 2009, 156 (8), A635-A638.


23. Nam, K. W.; Yoon, W. S.; Zaghib, K.; Chung, K. Y.; Yang, X. Q., The phase transition behaviors of Li1-xMn0.5Fe0.5PO4 during lithium extraction studied by in situ X-ray absorption and diffraction techniques. *Electrochemistry Communications* 2009, 11 (10), 2023-2026.


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 LiMn0.25Fe0.75PO4 as a cathode material for lithium ion batteries. *Solid State Ionics* 2009, 189 (20-22), 1215-1219.


Fig. 1 Powder X-ray diffraction patterns (a) and evolution of lattice parameters with manganese content of LiMn\text{y}Fe_{1-y}PO_4/C (b).
Fig. 2 $^{57}$Fe Mössbauer spectra for LiMn$_{0.50}$Fe$_{0.50}$PO$_4$/C, where $y = 0.50$ and $y = 0.75$. 
Fig. 3 Electrochemical curves (first cycle) (a) and rate capability (b) of LiMn$_y$Fe$_{1-y}$PO$_4$. 
Fig. 4 Average potential of redox reactions in LiMn$_y$Fe$_{1-y}$PO$_4$. 
Fig. 5 Evolution of the operando Mössbauer spectra (a) and hyperfine parameters of Fe$^{II}$ and Fe$^{III}$ species (b) of Li$_{x}$Mn$_{0.50}$Fe$_{0.50}$PO$_{4}$ recorded during the electrochemical process recorded at C/40 rate.
Fig. 6 Operando X-ray diffractograms of Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$/C (a) and Li$_{0.75}$Mn$_{0.75}$Fe$_{0.25}$PO$_4$/C (b) recorded during the electrochemical process at C/40 rate.
Fig. 7: Mössbauer spectra of Li$_x$Mn$_{0.50}$Fe$_{0.50}$PO$_4$/C obtained at the indicated x values.
Fig. 8 Mössbauer spectra of Li\(_{x}\)Mn\(_{0.75}\)Fe\(_{0.25}\)PO\(_4\)/C obtained at the indicated x values.
Table 1 Hyperfine parameters of the composition involved during the electrochemical charge process.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(\delta) (mm/s)</th>
<th>(\Delta) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Li}<em>{0.70}\text{Mn}</em>{0.50}\text{Fe}_{0.50}\text{PO}_4)</td>
<td>1.32</td>
<td>2.72</td>
</tr>
<tr>
<td>(\text{Li}<em>{0.50}\text{Mn}</em>{0.50}\text{Fe}_{0.50}\text{PO}_4)</td>
<td>0.43</td>
<td>1.02</td>
</tr>
<tr>
<td>(\text{Mn}<em>{0.50}\text{Fe}</em>{0.50}\text{PO}_4)</td>
<td>0.43</td>
<td>1.02</td>
</tr>
<tr>
<td>(\text{Li}<em>{0.75}\text{Mn}</em>{0.75}\text{Fe}_{0.25}\text{PO}_4)</td>
<td>1.28</td>
<td>2.71</td>
</tr>
<tr>
<td>(\text{Li}<em>{0.55}\text{Mn}</em>{0.25}\text{Fe}_{0.25}\text{PO}_4)</td>
<td>0.44</td>
<td>1.08</td>
</tr>
<tr>
<td>(\text{Mn}<em>{0.75}\text{Fe}</em>{0.25}\text{PO}_4)</td>
<td>0.41</td>
<td>1.30</td>
</tr>
<tr>
<td>(\text{Mn}<em>{0.75}\text{Fe}</em>{0.25}\text{PO}_4)</td>
<td>0.41</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Fig. 9 Schematic diagram of the different mechanisms observed during the first charge.
Fig. 10 Evolution of the Isomer Shift Vs. Average potential.