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

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

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$\text{LiMn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$  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*  $^{57}\text{Fe}$  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  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  cations.  $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4$  undergoes a two reactions mechanism.  $\text{Fe}^{\text{III}}$  Mössbauer signature has been found to be sensitive to the oxidation of  $\text{Mn}^{\text{II}}$  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,  $\text{LiFePO}_4$  has been intensively studied as a promising cathode material<sup>1-4</sup> 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<sup>5-9</sup>. On the other hand, attempts have been made to enhance the potential of olivine cathode materials by using manganese phosphate instead of iron phosphate<sup>3, 10</sup>. Despite the recent advances in cycling insulating materials, thanks to nano-coating techniques and new preparation routes<sup>11, 12</sup> and even though some authors have reported promising results<sup>11-13</sup>,  $\text{LiMnPO}_4$  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,  $\text{LiMnPO}_4$  requires very slow charge and discharge rates<sup>2, 14-16</sup>. The main reason on that is the

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

A good compromise between  $\text{LiFePO}_4$  and  $\text{LiMnPO}_4$  is the partially substituted phases  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ <sup>3, 15, 18</sup>, that would introduce the advantage of combining good electrochemical performances of  $\text{LiFePO}_4$  with a higher potential for manganese ( $\sim 4.1$  V compared with  $\sim 3.4$  V vs.  $\text{Li}^+/\text{Li}$  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 performances<sup>15</sup>.  $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$  has also been reported to give good specific capacity after 100 cycles<sup>19</sup>. Chang *et al.* have reported that  $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$  shows the excellent cycling performances<sup>20</sup>, whereas Xu *et al.* found that  $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$  shows the best cycling performances<sup>21</sup>. 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 behaviour<sup>22</sup>.

*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)<sup>23-25</sup>.

We have recently reported an *operando* study of  $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$  composites ( $y = 0; 0.25$ )<sup>1, 26</sup>. 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 <sup>57</sup>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  $\text{Li}_2\text{CO}_3$ ,  $\text{FeC}_2\text{O}_4 \bullet 2\text{H}_2\text{O}$ ,  $\text{Mn}(\text{COOCH}_3)_2 \bullet 4\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  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  $\theta$ -2 $\theta$  diffractometer equipped with the X'celerator detector) patterns were recorded using Cu K $\alpha$  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.  $^{57}\text{Fe}$  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  $^{57}\text{Co}(\text{Rh})$  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  $\alpha$ -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<sub>6</sub> (propylenecarbonate (PC): ethylene carbonate (EC):dimethyl carbonate (DMC)) 1:1:3, v/v| LiMn<sub>y</sub>Fe<sub>1-y</sub>PO<sub>4</sub> 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<sub>y</sub>Fe<sub>1-y</sub>PO<sub>4</sub> ( $y = 0.5; 0.75$ ) electrodes using an electrochemical cell designed especially for this aim<sup>27</sup>.

To preserve beryllium window from the oxidation due to high working voltage, it was covered by a 2  $\mu\text{m}$  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<sub>x</sub>Mn<sub>y</sub>Fe<sub>1-y</sub>PO<sub>4</sub>/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

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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 method<sup>28</sup> 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 literature<sup>3</sup>. Average crystallite sizes of 120 nm have been obtained using the Scherrer formula<sup>29</sup>. 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  $\text{Mn}^{2+}$  (0.97 Å) and  $\text{Fe}^{2+}$  high spin (0.92 Å).

$\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$  ( $y = 0.50; 0.75$ ) 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 previously<sup>1</sup>.

The voltage profiles of  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$  are shown in Figure 3a. For  $\text{LiFePO}_4$ , 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  $56 \text{ mAh.g}^{-1}$  against  $125 \text{ mAh.g}^{-1}$  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

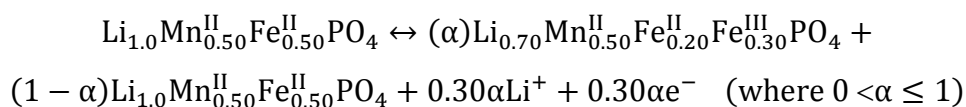
associated with the redox couples  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Mn}^{3+}/\text{Mn}^{2+}$  undergo an increase with the manganese content. Kobayashi *et al.*<sup>30</sup> explain this with an expansion of the volume of all compositions. These variations are sufficient to increase the average 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, *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  $29.3^\circ$ . 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 ( $\delta = 0.42$  mm/s and  $\Delta = 1.12$  mm/s) and a second component associated with a new  $\text{Fe}^{2+}$  component ( $\delta = 1.26$  mm/s and  $\Delta = 2.72$  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<sup>31</sup> 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:  $\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.20}^{\text{II}}\text{Fe}_{0.30}^{\text{III}}\text{PO}_4$ . 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  $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ <sup>32-34</sup>. 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 materials<sup>32</sup>.

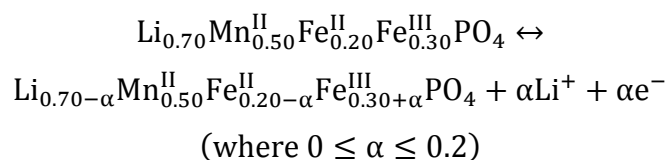
From these observations we conclude to a biphasic mechanism with the coexistence of  $\text{LiMn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{II}}\text{PO}_4$  and  $\text{Li}_{0.70}\text{Mn}_{0.50}^{\text{II}}\text{Fe}_{0.50}^{\text{II,III}}\text{PO}_4$  for the charge and discharge in the range  $0.70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

The electrochemical reaction in this region can be written:

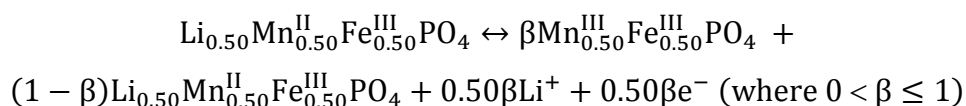


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In the second region ( $0.50 \leq x \leq 0.70$ ), shown in black in Figure 6a, the diffraction lines corresponding to the  $\text{Li}_{0.70}\text{Mn}_{0.50}\text{Fe}_{0.50}\text{PO}_4$  phase are shifted to upper angles, indicating the existence of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



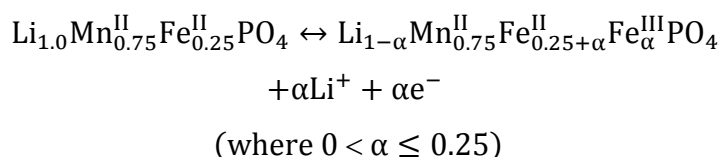
All the  $\text{Fe}^{2+}$  was oxidized into  $\text{Fe}^{3+}$  at the end of the second region, however, the Mössbauer spectra continue to evolve (Figure 7), indicating that the environment of iron is affected by the oxidation of  $\text{Mn}^{2+}$  in  $\text{Mn}^{3+}$  as already observed for the phase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

From  $x \leq 0.50$  the spectra (Figure 7) are refined by adding a new  $\text{Fe}^{3+}$  doublet shown in magenta. The new doublet corresponding to  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  is very sensitive to the oxidation state of Mn since an increase of the amount of  $\text{Mn}^{3+}$  around the  $\text{Fe}^{3+}$  site lead to a significant increase of the quadrupole splitting<sup>31</sup>. Similar spectra have been reported for natural purpurite  $(\text{Fe},\text{Mn})\text{PO}_4$ <sup>31</sup>. 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  $\text{Mn}_{0.50}^{\text{III}}\text{Fe}_{0.50}^{\text{III}}\text{PO}_4$ .



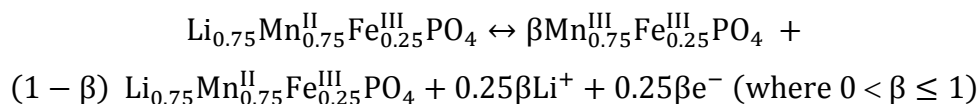
The electrochemical mechanism corresponding to the richest manganese phase  $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$  was also studied. The diffractograms corresponding to the first cycle with the galvanostatic curves are shown in Figure 6b. The three  $^{57}\text{Fe}$  Mössbauer spectra (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  $\text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$  ( $29.2^\circ$  ( $2\theta$ )) 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  $\text{Fe}^{2+}$  has been oxidized to  $\text{Fe}^{3+}$  (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  $\text{Fe}^{3+}$  on the "plateau" of redox reaction  $\text{Mn}^{3+}/\text{Mn}^{2+}$ . Indeed, it was interesting to see the indirect effect of  $\text{Mn}^{3+}$  on the environment of  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  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.

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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 lithium<sup>35</sup>, 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 Menil<sup>36</sup>. The representation of values of  $\delta$  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<sup>37</sup>.

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  $^{57}\text{Fe}$  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.

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## FIGURES

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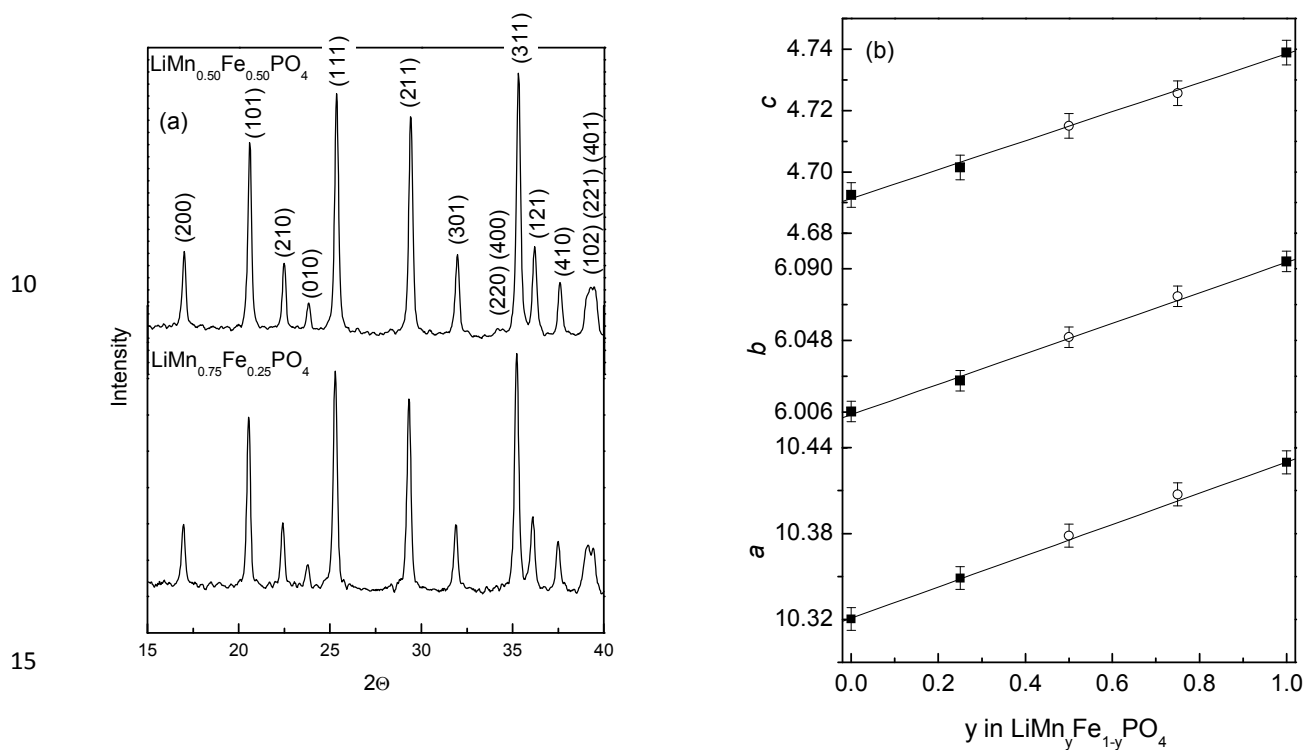
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Fig. 1 Powder X-ray diffraction patterns (a) and evolution of lattice parameters with manganese content of  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$  (b).

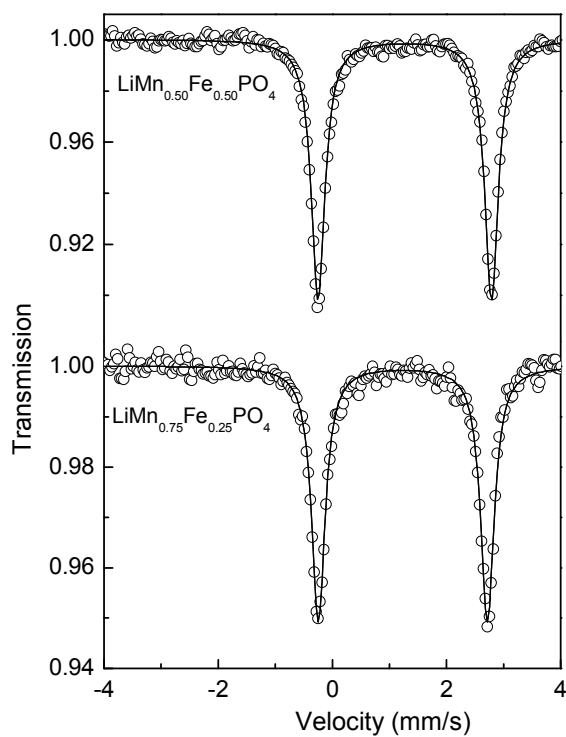
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**Fig.2**  $^{57}\text{Fe}$  Mössbauer spectra for  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4/\text{C}$ , where  $y = 0.50$  and  $y = 0.75$ .

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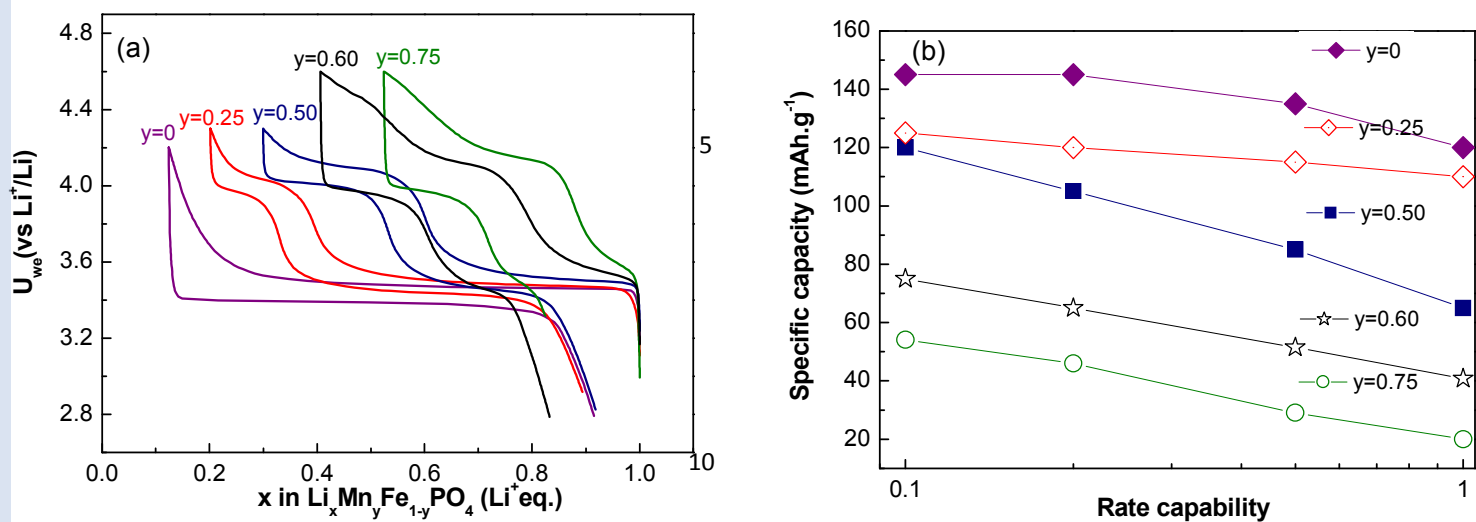
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Fig.3 Electrochemical curves (first cycle) (a) and rate capability (b) of  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ .

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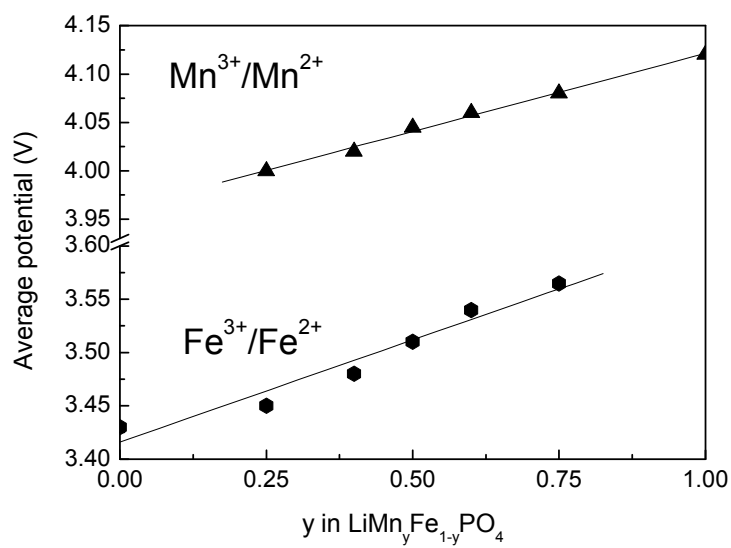
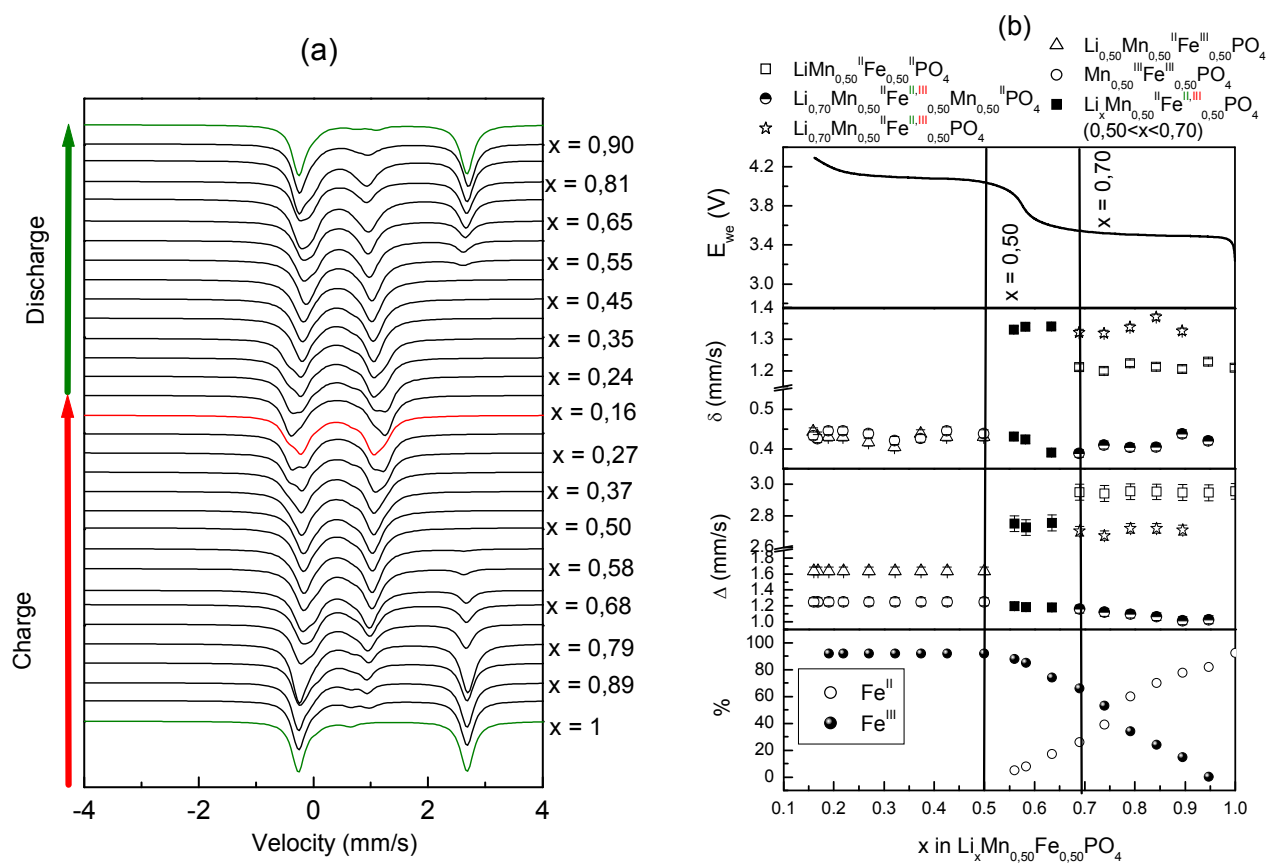


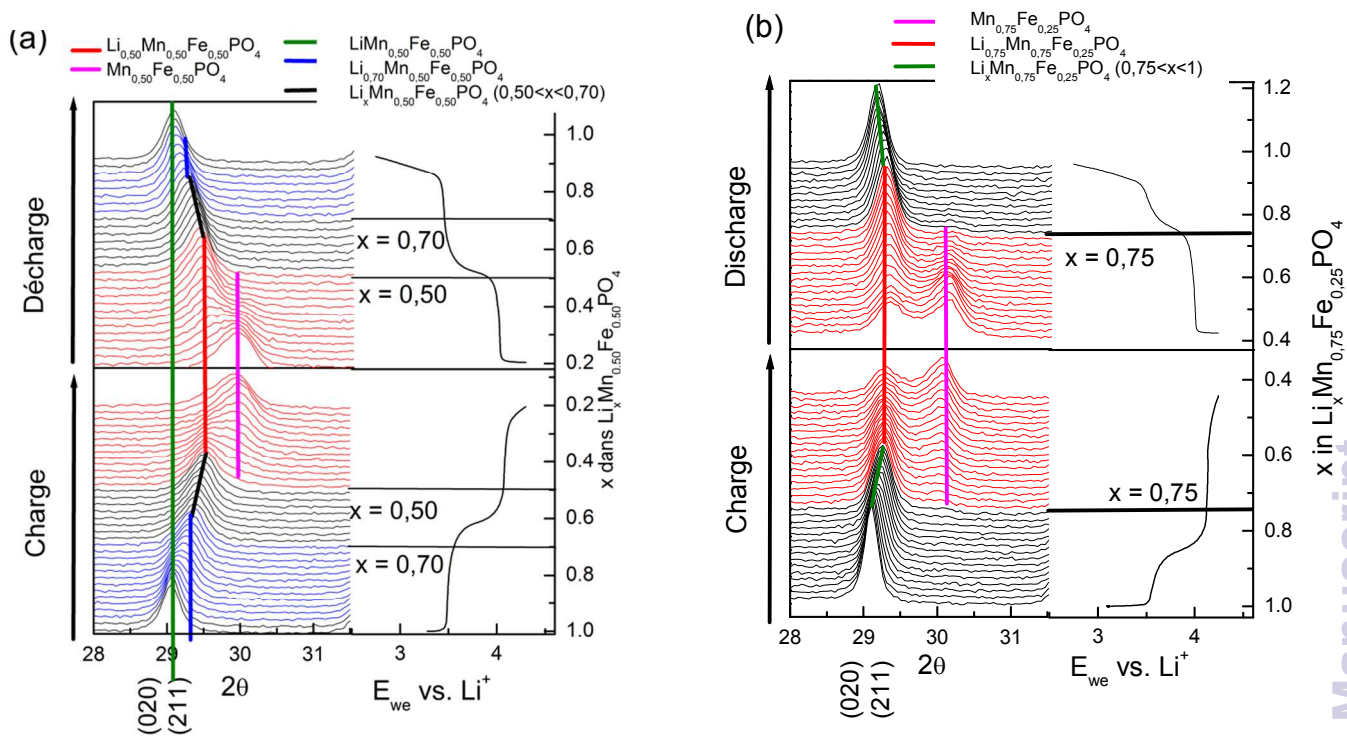
Fig.4 Average potential of redox reactions in  $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ .

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**Fig.5** Evolution of the *operando* Mössbauer spectra (a) and hyperfine parameters of Fe<sup>II</sup> and Fe<sup>III</sup> 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 .

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**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 .

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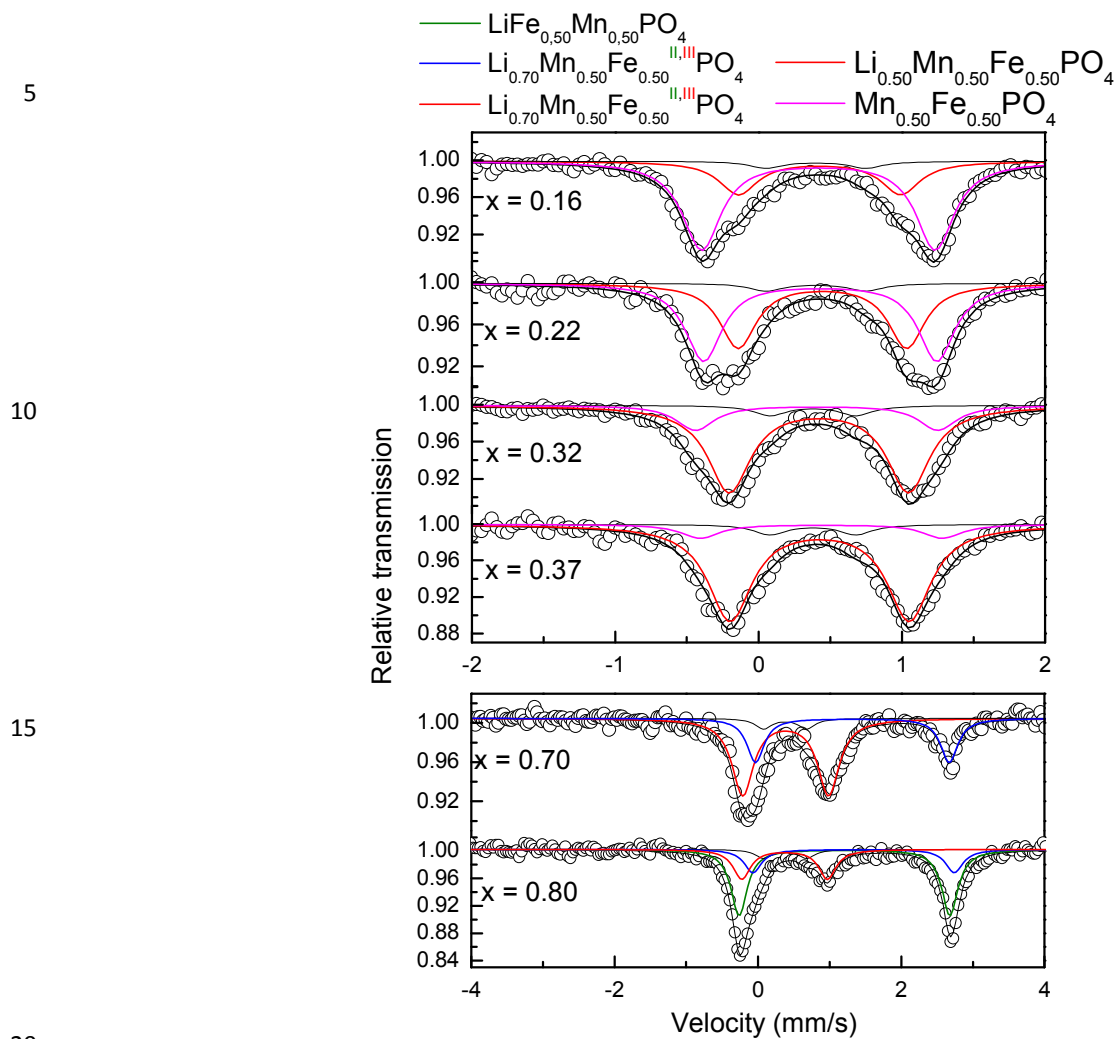


Fig. 7: Mössbauer spectra of  $\text{Li}_x\text{Mn}_{0.50}\text{Fe}_{0.50}\text{PO}_4/\text{C}$  obtained at the indicated  $x$  values .

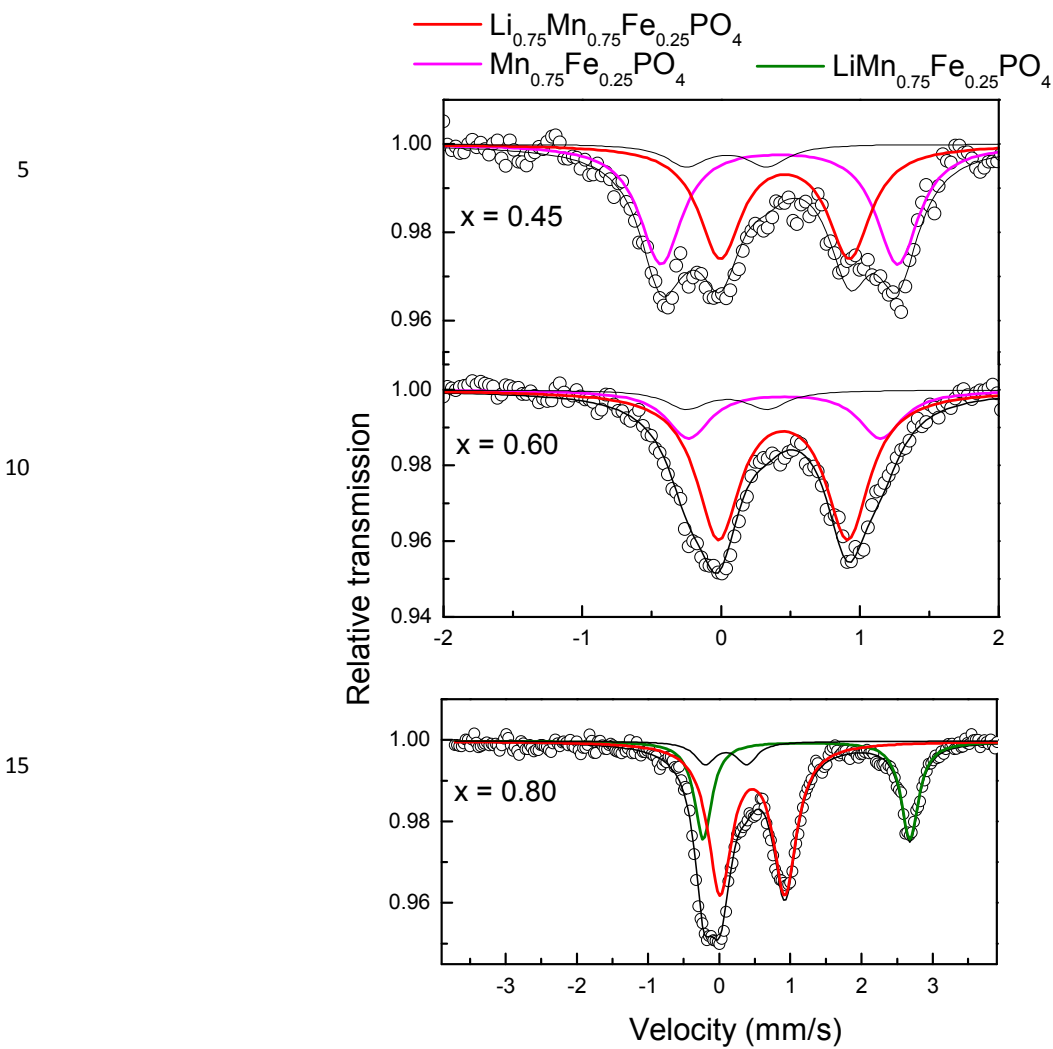


Fig. 8 Mössbauer spectra of  $\text{Li}_x\text{Mn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/\text{C}$  obtained at the indicated x values .

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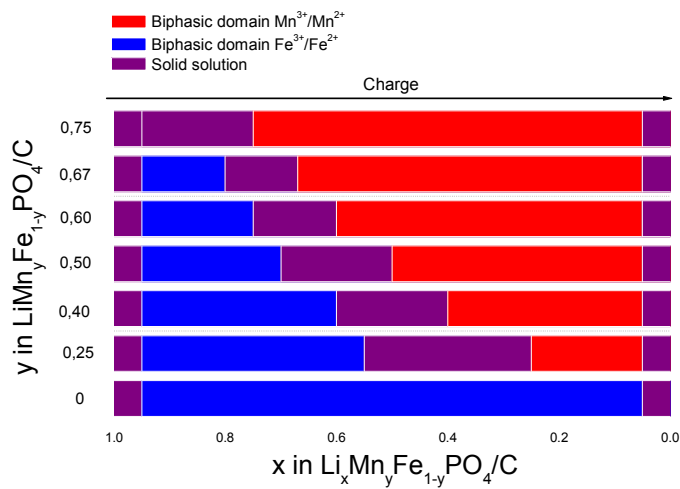
**Table 1** Hyperfine parameters of the composition involved during the electrochemical charge process .

Composition	$\delta$	$\Delta$
	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

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

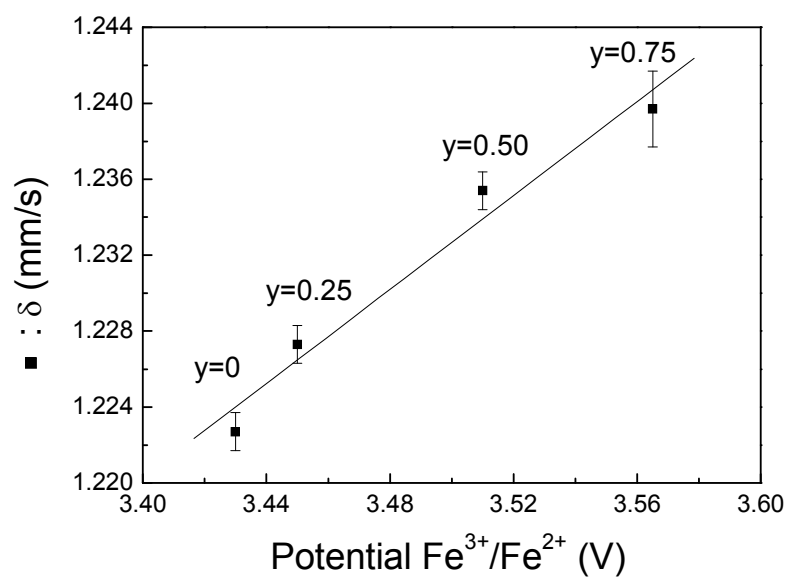


Fig.10 Evolution of the Isomer Shift Vs. Average potential .