



Determination of the Lamb-Mössbauer factors of LiFePO_4 and FePO_4 for electrochemical *in situ* and *operando* measurements in Li-ion batteries

L. Aldon*, A. Perea, M. Womes, C.M. Ionica-Bousquet, J.-C. Jumas

ICGM/AIME (CNRS UMR 5253), Université Montpellier II, CC 15-02 Place E. Bataillon, 34095 Montpellier Cedex 5, France

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ABSTRACT

^{57}Fe Mössbauer spectroscopy is a powerful tool to investigate redox reactions during in electrochemical lithium insertion/extraction processes. Electrochemical oxidation of $\text{LiFe}^{\text{II}}\text{PO}_4$ (triphylite) in Li-ion batteries results in $\text{Fe}^{\text{III}}\text{PO}_4$ (heterosite). LiFePO_4 was synthesized by solid state reaction at 800°C under Ar flow from Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ precursors in stoichiometric composition. FePO_4 was prepared from chemical oxidation of LiFePO_4 using bromine as oxidative agent. For both materials a complete ^{57}Fe Mössbauer study as a function of the temperature has been carried out. The Debye temperatures are found to be $\theta_M=336\text{K}$ for LiFePO_4 and $\theta_M=359\text{K}$ for FePO_4 , leading to Lamb-Mössbauer factors $f_{300\text{K}}=0.73$ and 0.77 , respectively. These data will be useful for a precise estimation of the relative amounts of each species in a mixture.

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1. Introduction

Lithium iron phosphate LiFePO_4 with olivine structure has become of great interest [1,2] as potential storage cathode for the next generation lithium ion batteries, particularly for hybrid electric vehicles. Low toxicity of the element makes this material family environmental friendly [3].

The electrochemical intercalation/deintercalation of lithium proceeds via a two-phase process between $\text{LiFe}^{\text{II}}\text{PO}_4$ and $\text{Fe}^{\text{III}}\text{PO}_4$ who are very close from a structural point of view. This material has good electrochemical performances with a high potential ($\sim 3.4\text{V}$ vs. Li^+/Li).

^{57}Fe Mössbauer spectroscopy is an efficient tool for the phase analysis of the multi-phased samples and helpful for the comprehension of the redox mechanism in Fe-containing electrode materials [4–7]. Quantitative phase analysis is possible provided that f -factors are known. Robert et al. have shown the interest of such a knowledge applicated to Li-ion electrode materials in the case of ^{119}Sn isotope [8,9]. In a spectrum, the relative contributions C_i of species i are given by :

$$C_i = \frac{A_i}{\sum_i \frac{A_i}{f_i}}$$

where A_i and f_i represent respectively, the experimental absorption area and the Lamb-Mössbauer factor of the i th specie, respectively.

From our knowledge the f -factors are currently not known for either Triphylite or Heterosite. In this study we will present the evaluation of the Lamb-Mössbauer factors of LiFePO_4 and FePO_4 compounds over the temperature range $120 \leq T \leq 300\text{K}$. These results will be then employed in future work for the interpretation of the electrochemical mechanism of the $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ ($M=\text{Co}, \text{Ni}, \text{Cr}, \text{Mn}$) systems investigated by *in situ* Mössbauer and XRD measurements during Li extraction/insertion processes. Yamada et al. showed the interest of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ composition which is the one who exhibits the most interesting electrochemical performances [10,11] in this family of compounds [12].

2. Experimental

2.1. Synthesis procedure

To investigate the factor Lamb-Mössbauer, two different synthesis methods have been used to obtain the raw materials. LiFePO_4 triphylite was obtained by solid-state reaction. The precursors: Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Labosi, 99.99%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Acros Organics, 99.99%) have been first ball milled during 1 h 30 min and then thermally treated in a tube furnace under argon flow for 8 h at 800°C . The heterosite FePO_4 was prepared by chemical delithiation of the triphylite phase. To this end the

* Corresponding author.

E-mail address: laurent.aldon@univ-montp2.fr (L. Aldon).

LiFePO₄ was immersed in a solution of bromine in acetonitrile for two days at the temperature of 60 °C under vigorous magnetic stirring. Then powders have been dried at 110 °C under vacuum in order to remove both acetonitrile and excess of bromine reactant.

2.2. XRD measurements

Pristine and delithiated samples have been characterized by X-ray Powder Diffraction (XPD) with a Philips θ - 2θ diffractometer using CuK α radiation ($\lambda=1.5418$ Å) and a nickel filter.

Crystallographic reference data for the LiFePO₄ triphylite and the FePO₄ heterosite have been taken from Powder Diffraction File (JCPDS no. 81-1173, $a=10.332$ Å, $b=6.010$ Å and $c=4.692$ Å) and (JCPDS no. 42-0579, $a=9.790$ Å, $b=5.830$ Å and $c=4.769$ Å). These values have been used in the initial stages of refinement of the cell parameters. The structures of both phases are usually described in the orthorhombic $Pnma$ space group.

2.3. ⁵⁷Fe Mössbauer measurements

Mössbauer spectra have been recorded in the constant acceleration mode and in transmission geometry on a standard Mössbauer spectrometer composed of devices from Ortec and WissEl. A ⁵⁷Co(Rh) source with a nominal activity of 10 mCi has been used. Low temperature spectra have been recorded by cooling the sample in a flow cryostat from Air Liquide, using liquid nitrogen as cooling agent. The source has been always kept at RT. Isomer shifts are given relative to α -Fe. Calibration of the velocity scale has been done using absorption lines of a 25 μ m iron foil.

3. Results and discussion

For LiFePO₄ sample, XRD measurements suggest pure phase within the detection limit of the apparatus as shown in Fig. 1. FePO₄ sample presents small diffraction lines owing to unreacted LiFePO₄. Both LiFePO₄ (Triphylite) and FePO₄ (Heterosite) present characteristic diffraction lines indexed in the $Pnma$ space group with a set of cell parameters $a=10.328(9)$ Å, $b=6.007(5)$ Å, $c=4.692(4)$ Å and $a=9.814(9)$ Å, $b=5.791(5)$ Å, $c=4.782(3)$ Å, respectively. Refined cell parameters have been obtained by pattern matching using FullProf [13] program. These values are in agreement with those found in the literature [14].

It is important for the comprehension of the reaction mechanism with lithium to get a precise determination of the amounts of each species during the electrochemical process. Mössbauer spectroscopy can furnish these informations provided the f -factors of all occurring phases are known. For LiFePO₄ and FePO₄, however, these data have not yet been reported in the literature to our knowledge. The present study of the Mössbauer parameters of both compounds as a function of temperature allows us to determine the Debye temperature for both LiFePO₄ and FePO₄ and to derive thereof the fractions f of recoilless γ absorption (Lamb-Mössbauer factors) at room temperature.

Using the Debye model for the phonon spectrum and assuming that the variation of IS with T is entirely due to the second order Doppler shift, we can write [15,16] the following:

$$d(\text{IS})/dT = -3E_0k_B/2M_{\text{eff}}c^2$$

M_{eff} represents the effective vibrating mass involved in the recoil process due to the absorption of the gamma radiation owing the energy E_0 (14.4 keV for ⁵⁷Fe, 23.9 keV for ¹¹⁹Sn). Physical constants are k_B , the Boltzman constant and c , the velocity of light. From this first expression we have access to M_{eff} , which is needed to evaluate the Debye temperature. The second expression

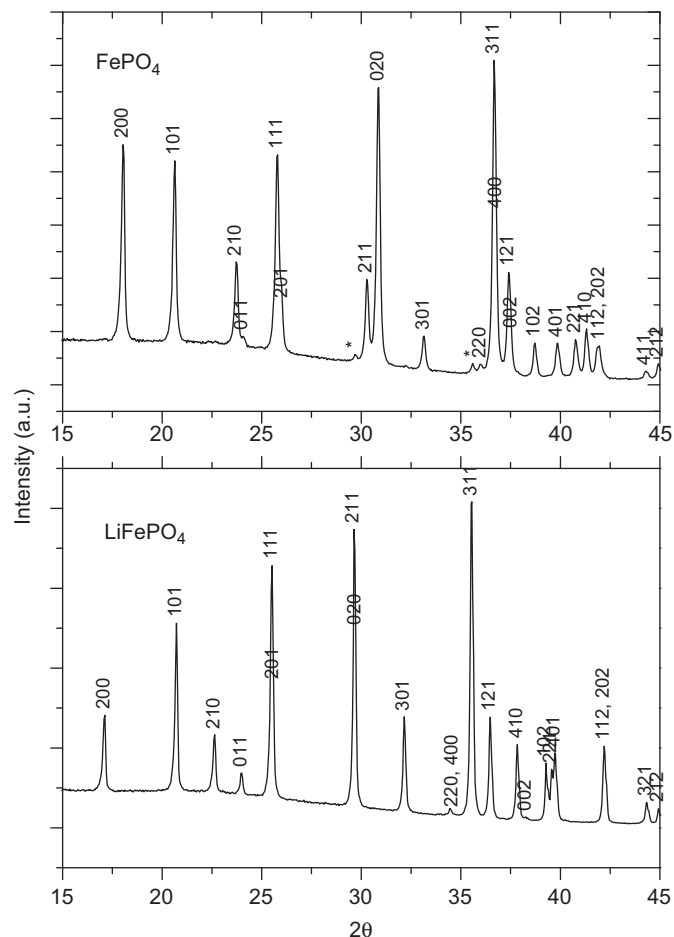


Fig. 1. X-ray diffraction patterns of both LiFePO₄ and FePO₄ compounds recorded at room temperature. Both phases have been indexed in the orthorhombic $Pnma$ space group. Main peaks of unreacted LiFePO₄ in FePO₄ sample are shown with a star (*).

corresponds to the temperature dependence of the absorption or spectral intensity which is given by :

$$d(\ln A(T))/dT = -3E_0^2/M_{\text{eff}}c^2k_B\theta_M^2$$

From this latter expression it is possible to determine both Debye temperature θ_M and Lamb-Mössbauer f -factor. For ⁵⁷Fe, $f(T)$ can be obtained from $f(T) = \exp(-136.38T/\theta_M^2)$.

Andersson et al. [17] have reported lithium extraction/insertion in LiFePO₄ from X-ray and Mössbauer spectroscopy investigation. They assume that Mössbauer spectral intensities are proportional to the product of the mole fraction of the phases and the recoil-free factor f which is both temperature dependant and different for each Fe site. They first assume the two f -factors to be identical. It can be noted, however, that there is a small indication that the isotropic temperature factors deduced from X-ray diffraction of the FePO₄ phase are slightly smaller and hence f Lamb-Mössbauer factor is expected to be larger.

⁵⁷Fe Mössbauer spectra have been recorded over the temperature range from 120 to 300 K. Examples of spectra are given for LiFePO₄ in Fig. 2 and for FePO₄ in Fig. 3 at low and room temperatures. The spectra are mainly composed of a doublet with isomer shift, IS \sim 1.2 mm/s and quadrupole splitting, QS \sim 3 mm/s suggesting Fe^{II} (high spin configuration) in octahedral coordination in the case of LiFePO₄. For FePO₄, we observed IS \sim 0.40 mm/s and QS \sim 1.5 mm/s attributed to Fe^{III} (high spin configuration) in octahedral co-ordination as expected from the

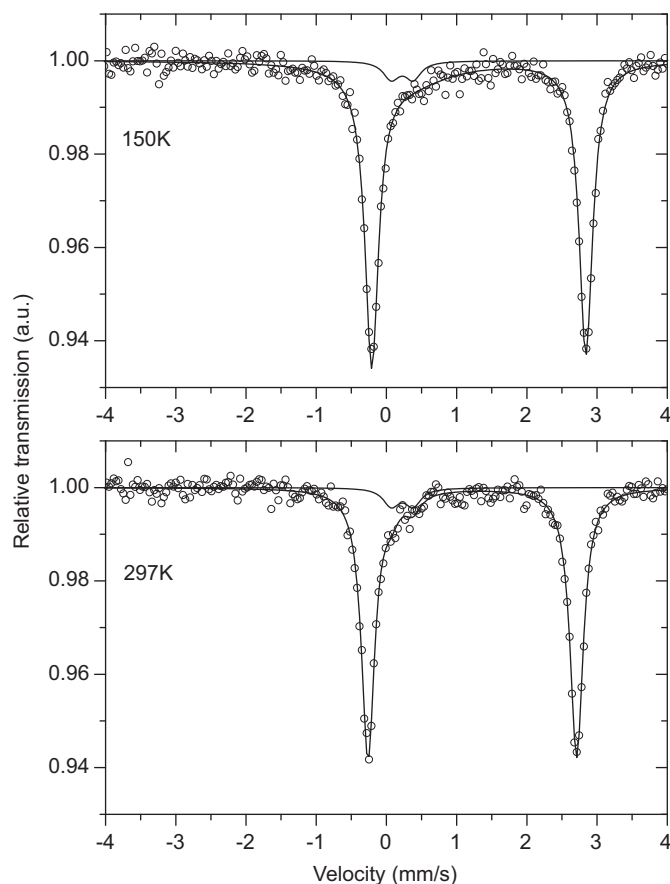


Fig. 2. ^{57}Fe Mössbauer spectra of LiFePO_4 (Triphylite), recorded at 150 and 297 K. Experimental (open circle) and calculated spectra (solid line) are represented. A small contribution due to Fe^{III} impurity (see text for explanation) is also shown for clarity.

crystal structure [18]. Table 1 gives hyperfine parameters deduced from the fitting procedure.

In the case of LiFePO_4 sample, we also observed a small contribution ($\sim 7\%$) due to unidentified species with $\text{IS} \sim 0.2$ mm/s and $\text{QS} \sim 0.3$ mm/s. The presence of this doublet affects the lineshape at low velocity. The strategy of refinement using the fitting procedure [19] was to first simulate the doublet with two singlets. Then we have extracted the linewidth of the singlet at high velocity. This value was used and fixed of the linewidth of the doublet in the final run of the fit, including the doublet due to the impurity.

The nature of the unidentified contribution which is currently the object of a controversial discussion in the literature [20,21,22], is beyond the scope of the present paper. Nevertheless this small contribution is often describe as Lithium deficient phase $\text{Li}_{1-x}\text{Fe}^{\text{II}}_{1-x}\text{Fe}^{\text{III}}\text{PO}_4$ or a partial reduction under Ar/H_2 atmosphere of LiFePO_4 leading to Fe_2P as impurity.

Concerning FePO_4 , we still observed the previous contribution of the un-identified species ($\sim 7\%$) but also a contribution of about 4% of unreacted LiFePO_4 since we start from this compound to prepare FePO_4 . The unidentified specie, not detected by XRD, is still present after oxidation by bromine. Our Mössbauer measurements at room temperature are in a good agreement with those found in the literature [23].

Fig. 4 shows the temperature dependence of both the isomer shift (IS) and the absorption logarithm ($\ln A$). We have determined the slopes from linear regression and the results are summarized in Table 2.

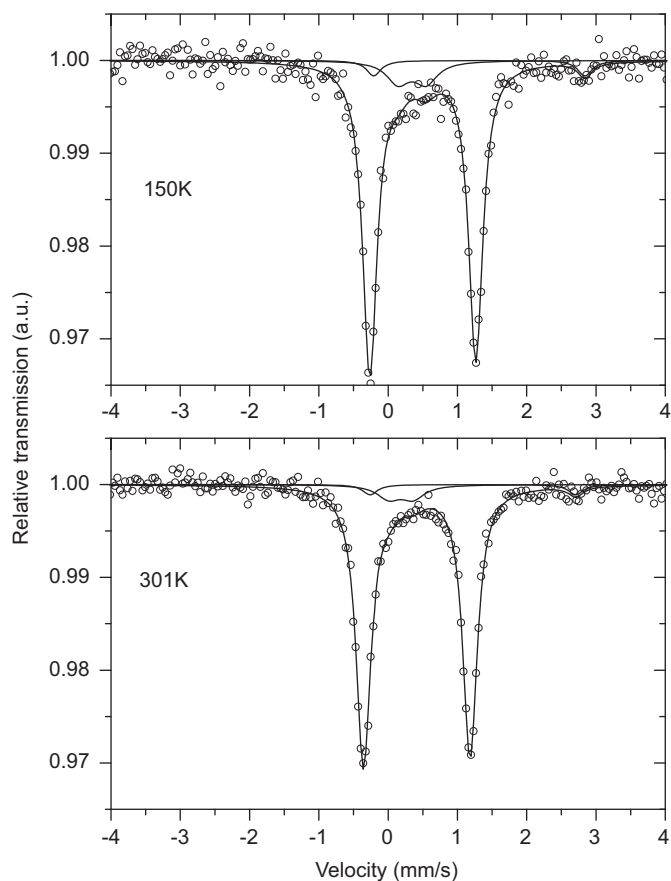


Fig. 3. ^{57}Fe Mössbauer spectra of FePO_4 (Heterosite) recorded at 150 and 301 K. Experimental (open circle) and calculated spectra (solid line) are represented. Small contributions are due to unreacted LiFePO_4 (Triphylite) and the previously detected Fe^{III} .

Table 1

Hyperfine parameters obtained for $\text{LiFe}^{\text{II}}\text{PO}_4$ and $\text{Fe}^{\text{III}}\text{PO}_4$ at various temperatures. IS, QS, Γ and $\ln A$ correspond respectively the isomer shift, the quadrupole splitting, the linewidth and the logarithm of the absorption.

Compound	T (K)	IS (mm/s)	QS (mm/s)	Γ (mm/s)	$\ln A$
LiFePO_4	131	1.330(4)	3.052(8)	0.232(5)	-1.893
	150	1.316(4)	3.048(8)	0.233(5)	-1.875
	180	1.298(4)	3.044(8)	0.235(5)	-1.956
	210	1.279(4)	3.027(8)	0.233(5)	-1.965
	240	1.260(4)	3.011(8)	0.232(5)	-1.986
	270	1.239(4)	2.992(8)	0.230(5)	-1.998
	297	1.224(4)	2.970(8)	0.228(5)	-2.083
FePO_4	141	0.489(4)	1.526(8)	0.245(5)	-2.6015
	150	0.499(4)	1.530(8)	0.263(5)	-2.5878
	166	0.498(4)	1.528(8)	0.257(5)	-2.6213
	175	0.488(4)	1.538(8)	0.242(5)	-2.5954
	200	0.470(4)	1.533(8)	0.259(5)	-2.6739
	250	0.444(4)	1.538(8)	0.254(5)	-2.6800
	301	0.412(4)	1.540(8)	0.254(5)	-2.7273

The effective vibrating mass was determined from the linear dependence of $\text{IS}(T)$: $M_{\text{eff}} = 65.3(0.3)$ a.m.u. and $69.3(1.4)$ for LiFePO_4 and FePO_4 , respectively. These values suggest that ^{57}Fe atom is involved in the Fe–O chemical bond with a more covalent character in the case of FePO_4 than in LiFePO_4 .

From the second set of slopes (Fig. 4, top), the Debye temperatures have been calculated $\theta_M = 336(15)$ K and $359(9)$ K for LiFePO_4 and FePO_4 , respectively. Here again, these values give valuable information on the nature of the bonding. Since Debye

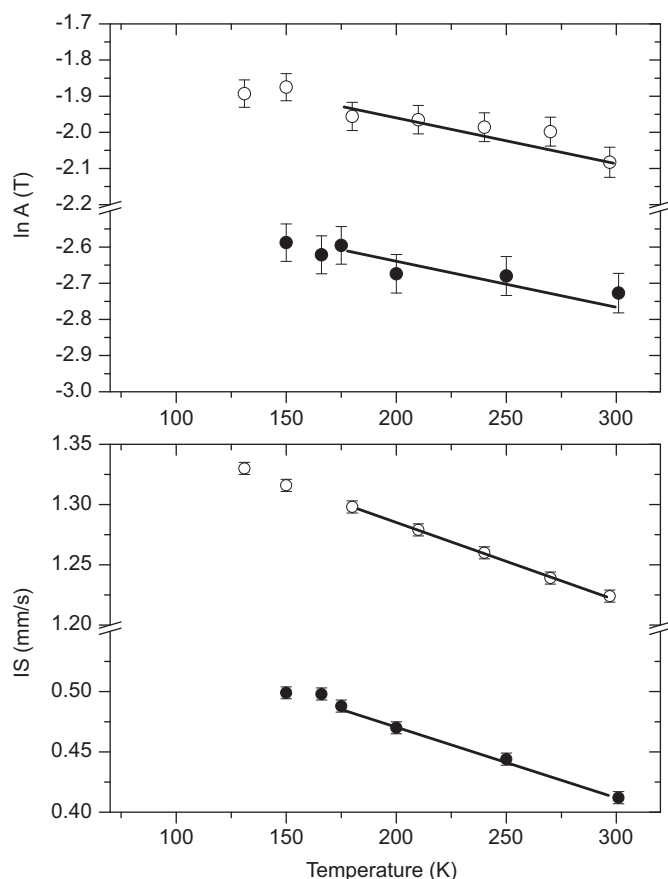


Fig. 4. Temperature dependence of the isomer shift (IS, bottom) and the logarithm of the absorption ($\ln A$, top) of both studied samples LiFePO₄ (open circle) and FePO₄ (filled circle). Straight lines from linear fit using values in the temperature range [180–300 K] are shown.

Table 2

Values of the slopes determined from linear regression of both isomer shift and absorption logarithm. M_{eff} is the effective vibrating mass, θ_M Mössbauer temperature and estimated Lamb-Mössbauer factors are given for 77 and 300 K for FePO₄ and LiFePO₄, respectively.

Compound	$d(\text{IS})/dT$	$d(\ln A)/dT$	M_{eff}	θ_M	$f_{77\text{K}}$	$f_{300\text{K}}$
LiFePO ₄	-6.38×10^{-4}	-10.5×10^{-4}	65.3(0.3)	336(15)	0.922(6)	0.729(19)
FePO ₄	-6.01×10^{-4}	-8.71×10^{-4}	69.3(1.4)	359(9)	0.935(2)	0.770(6)

temperature is higher for FePO₄ than for LiFePO₄, we conclude on a more covalent bonding. These values are within those observed for some matrices : ⁵⁷Fe in metals (162 K in Au [24], 210 K in Al [25], 253 K in Ag [26], 406 K in W [26], 420 K in a-Fe [27], 450 K in Fe–Cr alloys [28]), in oxides (251 K in Al₂O₃ [29], 344 K in SiO₂ [29], 288 K for octahedral and 677 K for tetrahedral sites in CuCr_{0.1}Fe_{1.9}O₄ [30]).

The values of f -factors have been calculated and are reported in Table 2. Furthermore these values have been employed for the determination of the real contribution of the Fe^{II} and Fe^{III} species observed during the charge/discharge processes in the LiFePO₄/FePO₄ system followed by Andersson et al. [17] For this the already reported relative contribution of species (Table 4 in Ref. [13]) have been corrected using the f -factors and good agreement between the electrochemical compositions of delithiated samples and Mössbauer data is obtained as observed in Fig. 5.

Moreover, other experimental techniques like Raman or Infrared [31] spectroscopies give local information of the nature of Fe–O bonding. For instance, a band located at 631 cm⁻¹ for

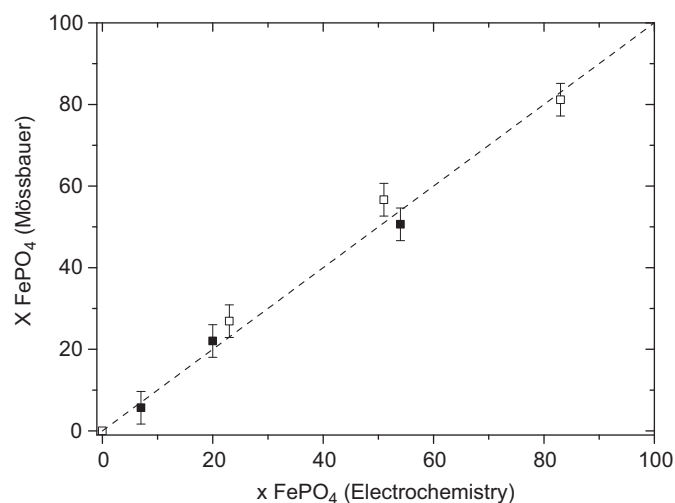


Fig. 5. Relative amount of FePO₄ obtained by Mössbauer and electrochemical data from Ref. [17]. We have corrected Mössbauer spectral intensities with our f -factors of both LiFePO₄ and FePO₄. Open (filled) squares correspond to values obtained during charging (discharging) process. The dashed line, given as a guideline for the eye, corresponds to the ideal case. Amounts deduced from different experimental measurements are equal.

LiFePO₄ is shifted to 640 cm⁻¹ for FePO₄ [32]. This band is attributed to FeO₆ coupled to PO₄ units. The frequency is in a first approximation given by:

$$\nu = 1/2\pi(k/m)^{1/2}$$

where k is the force constant reflecting the bond strength (or covalent character), and m the mass of the oscillator. If we assume that the mass correspond to the effective vibrating mass, the increase in frequency is in agreement with an increase of the bond strength of about $(69.3/65.3) \times (640/631)^2$ i.e. about 9%. This variation in bond strengthening is in agreement with our f -factors determination, from $f_{300\text{K}}=0.73$ for LiFePO₄ to $f_{300\text{K}}=0.77$ for FePO₄.

4. Conclusions

Finally, from the Debye temperature determination, we have access to the Lamb-Mössbauer factor of these two compounds in order to determine the effective fractions of both FePO₄/LiFePO₄ during electrochemical lithiation/delithiation by ⁵⁷Fe Mössbauer *in situ* and *operando* measurements. Our experimental data (effective vibrating masses, Debye temperatures and f -factors) are in agreement and could be correlated with those obtained by i) XRD [17] resulting in a shortening of the Fe–O bond (2.08–2.27 Å from Fe²⁺ in LiFePO₄ to 1.92–2.15 Å from Fe³⁺ in FePO₄), ii) infrared spectroscopy [31,32].

Extrapolated Lamb-Mössbauer factors are about 0.70 for LiFePO₄ and 0.75 for FePO₄ at a temperature of 60 °C [33] at which some electrochemical performance tests coupled with Mössbauer spectroscopy *in situ* measurements will be carried out in the near future. Then we will pay attention to the relative amount of species deduced from Mössbauer spectra, in order to avoid an overestimation of the FePO₄ contribution as compared to LiFePO₄ in a Mössbauer spectrum.

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References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] J.L. Tirado, *Mater. Sci. Eng.* 40 (2003) 103.
- [3] C.V. Ramana, A. Mauger, F. Gendron, C.M. Julien, K. Zaghib, *J. Power Sources* 187 (2009) 555.
- [4] A. Ibarra-Palos, C. Darie, O. Proux, J.L. Hazemann, L. Aldon, J.C. Jumas, M. Morcrette, P. Strobel, *Chem. Mater.* 14 (2002) 1166.
- [5] J.-C. Jumas, F. Robert, L. Aldon, E.J. Skordeva, *J. Optoelectronics Adv. Mater.* 7 (2005) 177.
- [6] R. Patrice, L. Dupont, L. Aldon, J.C. Jumas, E. Wang, J.M. Tarascon, *Chem. Mater.* 16 (2004) 2772.
- [7] S. Boyanov, J. Bernardi, F. Gillot, L. Dupont, M. Womes, J.-M. Tarascon, L. Monconduit, M.-L. Doublet, *Chem. Mater.* 18 (2006) 3531.
- [8] F. Robert, P.E. Lippens, J. Olivier-Fourcade, J.-C. Jumas, F. Gillot, M. Morcrette, J.-M. Tarascon, *J. Solid State Chem.* 180 (2007) 339.
- [9] F. Robert, F. Morato, J. Chouvin, L. Aldon, P.E. Lippens, J. Olivier-Fourcade, J.-C. Jumas, B. Simon, P. Biensan, *J. Power Sources* 119 (2003) 581.
- [10] A. Yamada, Y. Kudo, K.-Y. Liu, *J. Electrochem. Soc.* 148 (2001) A747.
- [11] A. Yamada, Y. Kudo, K.-Y. Liu, *J. Electrochem. Soc.* 148 (2001) A1153.
- [12] J. Molenda, W. Ojczyk, K. Swierczek, W. Zajac, F. Krok, J. Dygas, R.-S. Liu, *Solid State Ionics* 177 (2006) 2617.
- [13] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55–69.
- [14] V. Streltsov, E.L. Bclokoneva, V.G. Tsirelson, M.K. Hansen, *Acta Crystallogr. B* 49 (1993) 147.
- [15] R.H. Herber, A.E. Smelkinson, M.J. Sienko, L.F. Schneemeyer, *J. Chem. Phys.* 68 (1978) 3705.
- [16] R.H. Herber, *Phys. Rev. B* 27 (1983) 4013.
- [17] A.S. Andersson, B. Kalska, L. Häggström, J.O. Thomas, *Solid State Ionics* 130 (2000) 41.
- [18] Y. Sundarayya, K.C. Kumara Swamy, C.S. Sunandana, *Mater. Res. Bull.* 42 (2007) 1942.
- [19] K. Ruebenbauer, T. Birchall, *Hyperfine Interact.* 7 (1975) 125.
- [20] M. Maccario, L. Croguennec, A. Wattiaux, E. Suard, F. Le Cras, C. Delmas, *Solid State Ionics* 179 (2008) 2020.
- [21] M.-S. Song, D.-Y. Kim, Y.-M. Kang, Y.-I. Kim, J.-Y. Lee, H.-S. Kwon, *J. Power Sources* 180 (2008) 546.
- [22] X. Xia, Z. Wang, L. Chen, *Electrochem. Commun.* 10 (2008) 1442.
- [23] S. Okada, T. Yamamoto, Y. Okazaki, J.-I. Yamaki, M. Tokunaga, T. Nishida, *J. Power Sources* 146 (2005) 570.
- [24] P.K. Sharma, N. Singh, *Phys. Rev. B* 1 (1970) 4635.
- [25] K. Sorensen, G. Trumpy, *Phys. Rev. B* 7 (1973) 1791.
- [26] J.W. Burton, R.P. Godwin, *Phys. Rev.* 158 (1967) 218.
- [27] D.L. Williamson, S. Bukshpan, R. Ingalls, *Phys. Rev. B* 6 (1972) 4194.
- [28] J. Cieslak, S.M. Dubiel, J. Zukrowski, M. Reissner, W. Steiner, *Phys. Rev. B* 65 (2002) 212301.
- [29] J.R. Childress, C.L. Chien, M.Y. Zhou, P. Sheng, *Phys. Rev. B* 44 (1991) 11689.
- [30] H.N. Ok, Y.K. Kim, *Phys. Rev. B* 36 (1987) 5120.
- [31] A. Ait Salah, P. Jozwiak, K. Zaghib, J. Garbarczyk, F. Gendron, A. Mauger, C.M. Julien, *Spectrochim. Acta A* 65 (2006) 1007.
- [32] P. Jozwiak, J. Garbarczyk, F. Gendron, A. Mauger, C.M. Julien, *J. Non-Cryst. Solids* 354 (2008) 1915.
- [33] K. Zaghib, N. Ravet, M. Gauthier, F. Gendron, A. Mauger, J.B. Goodenough, C.M. Julien, *J. Power Sources* 163 (2006) 560.