**REPORT ON LiFePO4 SAMPLES M1 AND M2**

**Experimental**

Mössbauer data were recorded at room temperature using a conventional constant acceleration spectrometer. Absorbers were prepared to have approximately 5 mg Fe/cm2. The velocity scale was calibrated using a 6 μm thick natural iron foil. All the spectra were computer-fitted and the isomer shifts were referred to the centroid of the room temperature spectrum of α-Fe.

**Results**

Figure 1 shows the room temperature Mössbauer spectra recorded from LiFePO4 samples M1 and M2. They contain three contributions, two corresponding to Fe2+ and a third characteristic of Fe3+ (see Table 1). The respective spectral areas show small differences depending on the sample. The most intense quadrupole doublet is characteristic of the high spin octahedral Fe2+ in the LiFePO4 structure [1]. The second, minor paramagnetic Fe2+ doublet is also characteristic of octahedral Fe2+. Mössbauer parameters similar to those of this additional Fe2+ doublet have been found both in samples where the synthesis procedure has lead to incomplete lithiation of the final materials or in amorphous lithiated compounds [2]. Alternatively, Mössbauer parameters close to these have been reported for the impurity phase Fe2P2O7 [3]. Unless a such impurity has been detected in the corresponding XRD pattern, the assignment of this doublet remains uncertain. The identification of the remaining Fe3+ doublet needs of careful examination. In a first approximation one might think that this Fe3+ contribution would arise from Fe3+ within the structure of LiFePO4. In such a situation, there would be two possible scenarios [4]. The first one would contemplate the substitution of three Fe2+ ions by two Fe3+ ions leaving an iron vacancy in the M2 site, or the substitution of a Li+ Fe2+ pair by one Fe3+ ion leaving a vacancy of Li in the M1 site or Fe in the M2 site and Fe occupation of the M1 site. Since the ionic radius of Fe3+ in octahedral coordination (78.5 pm) is much smaller than that of Fe2+ (90 pm) this would be reflected in a large reduction of the lattice parameters of LiFePO4. The second scenario would consider the presence of amorphous impurities. The presence of amorphous FePO4 can be discarded as its hyperfine parameters do not match those of our Fe3+ component [2]. Although the presence of amorphous iron oxides cannot be discarded (low temperature Mössbauer data would be necessary) we think that this Fe3+ contribution could arise more likely from the ageing of LiFePO4 brought about by its exposure to the laboratory atmosphere. It has been reported [5] that exposure of lithium iron phosphate to the atmosphere can result in the formation of amorphous ferric phosphate phases whose concentration can amount to very large percentages depending on the exposure time and conditions, even at ambient temperature. The data indicate that the Fe3+ contribution is much more important in sample M2 than in sample M1.

**References**

[1] A.S. Anderson, B. Kalska, L. Haggstrom, J.O. Thomas, Solid State Ionics **130** (2000) 41-50.

[2] K. Galoustov, M. Anthonisen, D.H. Ryan, D.D. MacNeil, J. Power Sources **196** (2011) 6893-6897.

[3] F.B. Khan, K. Baruth-Ram, D.H. Ryan, D.D. MacNeil, Hyperfine Interact. **197** (2010) 317-323.

[4] B. Hannoyer, A.A.M. Prince, M. Jean, R.S. Liu, G.S. Wang, Hyperfine Interact. **167** (2006) 767-772.

[5] M. Cuisinier, J.F. Martin, N. Dupré, A. Yamada, R. Kanno, D. Guyomard, Electrochem. Comm. **12** (2010) 238-241.

Figure 1. Room temperature Mössbauer spectra.

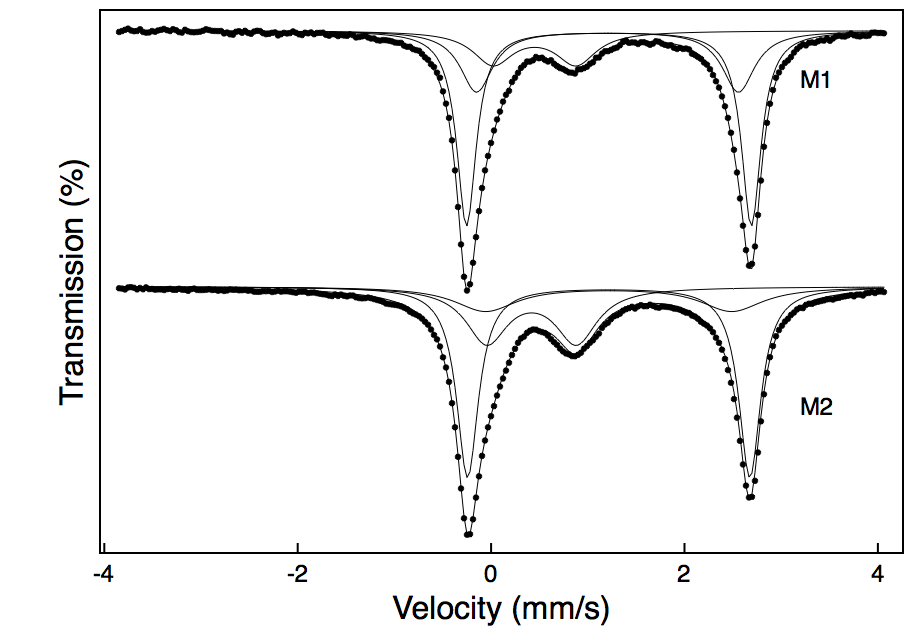


Table 1.- Mössbauer parameters and spectral areas obtained from the fit of the spectra

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Component | δ (mms-1) | Δ (mms-1) | Area (%) |
| M1 | Fe2+ | 1.22 | 2.94 | 54 |
|  | Fe2+ | 1.20 | 2.71 | 28 |
|  | Fe3+ | 0.45 | 0.86 | 18 |
| M2 | Fe2+ | 1.26 | 2.92 | 52 |
|  | Fe2+ | 1.26 | 2.55 | 19 |
|  | Fe3+ | 0.42 | 0.93 | 29 |