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INFLUENCE OF THE MANGANESE SUBSTITUTION ON THE CATION DISTRIBUTION AND MAGNETIC STRUCTURE OF THE SPINEL-RELATED $\text{LiFe}_{1-x}\text{Mn}_{1+x}\text{O}_4$ ($x=0, 0.25, 0.50, 0.75$) SYSTEM

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ABSTRACT

We report a modified synthesis for lithium manganese ferrites $\text{LiFe}_{1-x}\text{Mn}_{1+x}\text{O}_4$ ($x=0, 0.25, 0.50, 0.75$) based on the thermal decomposition of nitrates which produces purer materials when compared to other synthesis methods. The different oxidation states of the various cations and their preferences for particular crystal sites within the spinel-related structure lead to a complex cation distribution and magnetic properties which depend strongly on the composition. The large, almost complete, lithium occupancy of the tetrahedral sites in the spinel structure for particular compositions and the concomitant occurrence of unusual oxidation states of iron show how the synthesis method can be tailored to obtain materials which can have promising applications in the field of lithium-containing batteries.

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1. Introduction

Spinel-related structures in the Li-Mn-O system are good candidates as host frameworks for electrodes in lithium-ion rechargeable batteries because the replacement of manganese ions ($3d^3/3d^4$) at the octahedral sites by other transition metal ions can be easily carried out giving rise to stable matrices with a variety of satisfactory properties for the lithium-ion insertion/extraction [1]. In designing these matrices, spinel-related manganese-lithium ferrites or iron-doped lithium manganites are of interest due to the abundance and benign environmental impact of iron and to the favourable electrochemical properties of the resulting materials [1-4]. Both the cation distribution and the manganese and iron oxidation states have a great influence on the electrochemical and magnetic properties of each single phase belonging to this system. Since the thermal and chemical stability, the cation distribution, the cation oxidation states, and the electrochemical behaviour in the lithium insertion/extraction reaction are not easily deducible from theory [2], these questions have been extensively studied from various experimental points of view [1-13].

In previous work we have carried out the bulk and surface characterization of the $\text{Li}_{1-0.5x}\text{Fe}_{1.5x+1}\text{Mn}_{1-x}\text{O}_4$ ($0.2 \leq x \leq 1$) series by X-ray Diffraction (XRD), Mössbauer spectroscopy, X-ray Photoelectron Spectroscopy (XPS) and Fe K-edge XANES/EXAFS [9,11] and we have also studied the electrocatalytic activity of these materials for the oxygen evolution reaction [9]. Our results [9,11] showed that: i) the Fe^{3+} occupancy ratio on the tetrahedral/octahedral sublattices does not change significantly along the series, ii) the Fe^{3+} ions exhibit canted spin structures on both octahedral and tetrahedral sites, iii) manganese, present as Mn^{3+} and Mn^{4+} ions, occupies only octahedral positions along the composition range examined, and iv) as the Li/Mn insertion progresses, the new inserted Li^+ ions enter on tetrahedral sites and also some of the Li^+ ions initially occupying octahedral sites are displaced onto tetrahedral positions. As the electrochemical properties of the Fe-doped lithium manganese oxides with composition next to that of the $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ oxide appear to be satisfactory for lithium batteries [1,3,4], we decided to turn into the Li-Mn-Fe-O system to carry out a study of a composition series similar to that studied in [1]. Therefore, the aim of the present work was to determine the cation distribution and the oxidation states of the manganese and iron ions along a series in which the lithium content of its first member, LiFeMnO_4 , is kept constant while the substitution of iron ions by manganese ions goes forward in the range of $0.5 \leq \text{Fe}/(\text{Fe}+\text{Mn}) \leq 0.125$. The study was conducted by carrying out XRD, XPS and ^{57}Fe -Mössbauer spectroscopy measurements. Since obtaining pure

specimens in this oxide family, especially in the case of LiFeMnO_4 , proved to be difficult (a first synthesis of this compound by conventional solid-state reaction techniques using Li_2CO_3 , Fe_2O_3 and MnO_2 as precursors and a sintering temperature of 800°C was not successful [9,11]), we resorted then to a procedure based on a modification of a nitrate thermal decomposition (NTD) synthesis with the objective of making pure compounds.

2. Experimental

Four compositions ($x=0.00$, 0.25 , 0.50 and 0.75) in the $\text{LiFe}_{1-x}\text{Mn}_{1+x}\text{O}_4$ series were synthesized in this work. These correspond to Fe/Fe+Mn ratios of 0.5 , 0.375 , 0.25 and 0.125 , which are within the suitable range to yield electrodes with satisfactory working conditions for the insertion/extraction of lithium ions [1,8]. A first synthesis attempt using the NTD method (see above) gave a nominal LiFeMnO_4 specimen whose X-ray diffractogram showed spurious peaks at 2θ diffraction angles of 37.06° and 44.75° (corresponding d-spacings: 24.26 nm and 20.25 nm , respectively). The presence of similar XRD peaks in a sample of LiFeMnO_4 , prepared from a starting mixture of lithium, iron and manganese hydroxides, was also observed by Ohzuku et al. [1] and was assigned to the lithium iron manganese oxide $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [4]. Finally, following the synthesis pathway described below, a LiFeMnO_4 sample was obtained which showed a satisfactory single-phase X-ray diffractogram. Very residual impurities were still detected in the XRD data recorded from the $x=0.25$ and $x=0.50$ samples. In this successful modified NTD route, pure LiNO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ powdered salts (Merck, refs. 1.12230.0250, 3883 and 1.05940.0500, respectively) were used. The powders were accurately weighed in the appropriate stoichiometric ratio, thoroughly mixed and heated at 90°C in open atmosphere to dissolve the nitrate salts into their self crystallization water. The heating was maintained until a dry solid residue was obtained. Further, this residue was slowly heated up to 350°C and kept at this temperature for nitrate decomposition until the emission of gaseous products was completely stopped. During the decomposition process, the ceramic capsule containing the reagent product was covered with a lid which allowed gas expulsion but which prevented sample spillage. The resulting product was ground and dried and finally calcined in a tubular furnace in air. The calcination treatment involved the slow rise of temperature up to 800°C , temperature which was maintained constant for 20 h , and a final cooling step to room temperature. The final product was ground once more and stored in a desiccator.

The X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer using Ni-filtered Cu K α radiation ($\lambda=0.154056$ nm) and a 99.99% pure Si powder as internal standard. The diffractometer, equipped with a copper anticathode, a graphite monochromator and a stepped detector (2θ increment= 0.05°), was operated at 40 kV and 20 mA, with a scanning range of $5 \leq 2\theta \leq 80^\circ$. The cubic spinel lattice parameter, a , was determined using the Lattice program [14].

XPS data were recorded with a triple channeltron CLAM-2 analyser using Al K α radiation, a constant analyser transmission energy of 20 eV and an operating vacuum better than 1×10^{-8} torr. The powdered samples were mounted on double-sided conductive carbon adhesive tape. Binding energy values were charge-corrected to the main C 1s contribution of the adventitious carbon layer which was set at 284.6 eV.

^{57}Fe Mössbauer data were recorded at 298 K and various temperatures between 298 K and 14 K with a conventional constant acceleration spectrometer equipped with a ^{57}Co (Rh) source and a closed-cycle He cryogenerator (Air Products Inc.). The spectra were computer-fitted to a sum of Lorentzian lines by applying the usual constraints of equal linewidth and area for the two peaks of doublets, and equal line width and areas in the 3:2:1:1:2:3 ratio for the six peaks of sextets. In some of the fits, the addition of a hyperfine magnetic field distribution was necessary to account for the broad magnetic components observed. The isomer shifts were referred to the centroid of the spectrum of α -iron at RT. The relative concentrations of the different iron sites were calculated from their corresponding spectral areas assuming equal recoil-free fractions, f factors, for all the iron components present in the spectrum.

3. Results

3.1 X-ray Diffraction

The X-ray powder diffraction patterns recorded from the $x=0.00$ to $x=0.75$ samples are shown in Figure 1. The diffractograms show as main lines the hkl peaks 111, 311, 220, 400, 440, and 511 characteristic of the spinel-related structure. The pattern of the $x=0.00$ sample can be assigned to LiFeMnO_4 [1,15]. The a -cell parameter obtained for LiFeMnO_4 (0.8292 nm) is consistent with published data [1,15]. The a values corresponding to the rest of the samples (Table 1) are lower than that of the first member of the series, similarly to that found

by other authors [1,3,5-7,12,13]. An additional small peak near the 400 reflection in the patterns of the $x=0.25$ and $x=0.50$ samples suggest the presence of traces of other oxides like $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (see above). The observed intensity increase of the 111 and 531 reflections and the decrease of the 220, 311, 440 and 422 reflections with increasing manganese content in the series are characteristic of the incorporation of manganese in the spinel structure as reported in refs. [1,5,6,12,13].

Inspection of Figure 1 shows that there exist differences among the diffractograms of the various samples. The most significant differences are between the one recorded from the $x=0.00$ sample and those of the other three samples ($x=0.25, 0.50, 0.75$), while the latter present fewer differences among them. It is worth noting that in the pattern of the $x=0.00$ sample the main line is the 311. With manganese incorporation, this peak diminishes in intensity in parallel with the intensity increase of the 111 peak, which grows to become the main line in the patterns of the $x=0.25, 0.50$, and 0.75 samples. In this respect, it is relevant to note that the intensity of the 111 peak is directly related with the amount of lithium occupying the tetrahedral A-sites [6,12]. When the Li^+ ions reside exclusively on the octahedral B-sites of the spinel lattice, the 111 reflection is not present in the diffractogram. According to that, it seems clear from our XRD data that the Li^+ ions are being progressively displaced into the tetrahedral sites as manganese content is increased through the series, suggesting that manganese ions enter predominantly into the octahedral sites of the spinel structure.

The decrease in the intensity of the 220 reflection in the diffractogram of the $x=0.25$ sample respect to the observed in that of the $x=0.00$ one together with the disappearance of this peak in the diffractograms of both $x=0.50$ and $x=0.75$ samples, indicate a diminution of the amount of Fe^{3+} ions located at the tetrahedral sites. In fact, in the two samples having the highest manganese content, all iron ions seem to be located only at the octahedral sites [5,15]. This can be explained taking into account that the intensity of the 220 reflection usually observed in the XRD powder pattern of spinels depends on the atomic scattering factors of the ions occupying the tetrahedral sites [12,16]. Therefore, the vanishing of the 220 peak in the XRD patterns of the last two samples would imply that, in these two cases, the tetrahedral positions are exclusively occupied by the light lithium atoms [16,17] which have a very low scattering factor.

3.2 X-ray photoelectron spectroscopy

Figure 2 shows the Mn 3s XPS spectra recorded from the different samples. It is well-known that the Mn 3s spectra are much more sensitive to the oxidation state of manganese than the more intense Mn 2p spectra [18]. Because of the occurrence of multiplet splitting, the Mn 3s spectrum, which should be a singlet, is constituted by two well separated peaks. The energy separation, ΔE_{3s} , between the two peaks in the Mn 3s spectrum is absolutely characteristic of the oxidation state of manganese. So, ΔE_{3s} 's of 4.5 eV, 5.3 eV and 6.0 eV are characteristic of Mn^{4+} , Mn^{3+} and Mn^{2+} , respectively [18]. The measurement of these energy differences has facilitated the determination of the oxidation state of manganese in various Mn-containing spinels [19,20]. The two peaks appearing at lower binding energy in Figure 2 correspond to the Mn 3s spectrum while the third one appearing at higher binding energy corresponds to the Fe 3s spectrum which overlaps slightly with the former. Table 2 contains the measured ΔE_{3s} in the different samples together with the average oxidation state calculated using the equation deduced by Beyreuther et al. [21]: $v_{Mn}=9.67-1.27\Delta E_{3s}$. Inspection of this table indicates that in the samples $x=0.25$, 0.50 and 0.75 manganese is predominantly present as Mn^{3+} while the $x=0$ sample contains both Mn^{3+} and Mn^{4+} .

3.3 Mössbauer spectroscopy

Figure 3 (left) depicts the 298 K Mössbauer spectra of the various samples. The spectrum recorded from $LiFeMnO_4$, which has the smallest manganese content of the series, is constituted by a well-developed magnetic component and a weak paramagnetic doublet. With increasing manganese content, the intensity of the magnetic component decreases significantly and disappears completely in the spectrum of the $x=0.75$ sample, which shows only an asymmetric doublet. The magnetic part in the $x=0.00$, $x=0.25$ and $x=0.50$ spectra was best fitted considering two magnetic sextets whose hyperfine parameters (Table 3) can be associated with the presence of both octahedral and tetrahedral Fe^{3+} components [11]. The Mössbauer parameters of the doublet present in the $x=0.00$ and 0.25 samples are characteristic of high spin Fe^{3+} in octahedral oxygen coordination and are identical to those previously reported [3,9,10,11] in other Li-Fe-Mn oxide spinel series. The doublet in the spectra of the $x=0.50$ and 0.75 samples, however, is clearly asymmetric and a fit to a unique doublet yielded unacceptable results. To obtain a better fit, a spectrum was recorded from the $x=0.75$ sample in a lower velocity range. The inset in Fig. 3 (left) depicts the results of

two different fits to the central part of the $x=0.75$ spectrum considering either one or two quadrupole doublets. Since the fit to two doublets gave, as expected, a much more satisfactory result, the high velocity $x=0.50$ and $x=0.75$ spectra were fitted considering two doublets. The obtained parameters are also collected in Table 3. While the parameters of the most intense doublet are typical of octahedral Fe^{3+} , the assignment of the minor doublet is not so clear. According to reference [3], the parameters of this doublet could be compatible with: i) tetrahedrally coordinated high spin Fe^{3+} , ii) Fe^{3+} on octahedral sites in either a Mn-rich or oxygen deficient environment or iii) octahedral Fe^{4+} [10]. As the isomer shift of this minor doublet is slightly higher than that typical of tetravalent iron, a mixed valence of iron, like $\text{Fe}^{3.5+}$, appears to be a more realistic scenario [3]. This might imply the existence of an electron-hopping mechanism between the Fe^{3+} and Fe^{4+} ions. Inspection of Fig. 3 shows, as mentioned above, that the intensity of the whole quadrupole absorption component increases as the amount of manganese increases. This increase of the doublet contribution to the spectrum with increasing manganese content has been previously reported [9,11] and suggests that the incorporation of manganese, mainly as Mn^{3+} , in the spinel-related structure weakens the magnetic interactions at a such extent that magnetic ordering collapses completely at room temperature for some compositions.

Figure 3, right, collects the Mössbauer spectra recorded at 14 K from all the samples. In general, they show very broad components. Even more, the higher the manganese content in the samples, the broader the magnetic components. Given the characteristics of the spectra is clear that they cannot be fitted using discrete sextets and that a fit considering several contributions including hyperfine magnetic distributions is necessary. It is known that in the absence of an applied magnetic field the assignment of the magnetic sextets in the low temperature Mössbauer spectra of ferrites is always difficult given the large overlap between the tetrahedral and octahedral Fe^{3+} components [11,22]. In the present case, the broadening of the spectra and the presence of several strongly overlapping magnetic contributions make this assignment even more difficult and, therefore, we have not attempted to do it. It is clear that the 14 K spectra of the $x=0.00$ and 0.25 samples are asymmetric: the depth of the peaks at *ca.* -7.5 mms^{-1} is much larger than the depth of the peaks at *ca.* $+8.0 \text{ mms}^{-1}$ while in the case of the $x=0.50$ and 0.75 samples the spectra are much more symmetric. In the former case, this strongly supports the existence of both Fe^{3+} tetrahedral and octahedral contributions similarly to what is usually observed in other ferrites [22,23] although their precise ratio cannot be deduced from the present Mössbauer spectra. However, in the latter case, this would imply the only contribution of octahedral Fe^{3+} , as the 298 K hyperfine

parameters already suggested. This agrees qualitatively with the XRD data which have shown the predominant occupation of tetrahedral sites by lithium ions in these two samples. Figure 4 shows the evolution with decreasing temperature of the Mössbauer spectra recorded from the samples with $x=0.50$ and $x=0.75$. In the first case, the spectra are composed by a well defined magnetic component in all the range of temperatures together with a broad component which starts developing just above 36 K and that is better defined at 12K. In the case of the $x=0.75$ sample, only the broad magnetic component is observed and it starts developing at a temperature slightly lower than for the $x=0.50$ sample. The results of the $x=0.50$ sample suggest a behaviour, that with all likelihood can be extended to the $x=0.00$ and 0.25 samples, in which the material contains two very different situations from the magnetic and structural point of view. The presence of a well defined magnetic component from 298 K to 14 K (note that the absorption of this component remains constant along all the temperature range) implies that there exist some regions in the crystal where the Fe^{3+} ions are within a neighbourhood rich in Fe^{3+} such that they are already ordered at room temperature. Clearly the proportion of these regions/clusters decreases as manganese is incorporated within the spinel-related structure.

4. Discussion

It is known that in the Mn-Li ferrite spinel system either tri- and/or tetravalent manganese ions can substitute the available ferric ions located at the octahedral sites, and also that, as the manganese content increases, lithium ions, which only occupy octahedral sites in the lithium ferrite $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, start to be progressively displaced to tetrahedral positions until they occupy exclusively tetrahedral sites in the last member of the series: the stoichiometric cubic spinel LiMn_2O_4 [2,5]. It has been also shown that lithium ions tend to occupy octahedral sites when the iron content exceeds 50% [5], and that in some Li-Mn-Fe oxide spinel solid solutions with high iron content and lithium content lower than that existing in the lithium ferrite, the average oxidation state number of manganese can be lower than 3 [12,13]. In this case Mn^{2+} and Mn^{3+} ions are located at tetrahedral and octahedral sites, respectively. In contrast to that, higher substitution percentages of lithium and manganese yield compounds with an average oxidation state of $\text{Mn} \geq 3+$, occupying both Mn^{3+} and Mn^{4+} ions octahedral positions, while the Li^+ ions prefer tetrahedral sites [12,13].

Our results agree, in general terms, with the above picture. In the present case, the Li concentration is constant along the series while the iron/manganese ratio decreases. In the

1 compound with the highest iron content, Fe^{3+} occupies both tetrahedral and octahedral sites,
2 Li^+ ions are distributed over the tetrahedral and octahedral sites and Mn^{3+} and Mn^{4+} occupy
3 the remaining octahedral sites. As the manganese/iron ratio increases, manganese enters the
4 spinel-related structure mainly as Mn^{3+} and the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio decreases concomitantly.
5 The Mn^{3+} ions occupy the octahedral sites and displace a significant fraction of the Li^+ ions
6 into the tetrahedral sites. Further incorporation of Mn^{3+} into the octahedral sites continues
7 displacing Li^+ ions into the tetrahedral sites to such extent that in the case of the $x=0.75$
8 sample all the lithium is located in the tetrahedral sites while iron and manganese are
9 distributed over the octahedral sites.

10 Particularly interesting is the displacement of all the lithium ions to the tetrahedral sites and
11 the likely presence of a small Fe^{4+} fraction in the last two samples because these two facts
12 can have implications in the possible application of these materials as electrodes in Li-
13 containing batteries. It has been postulated that the simultaneous occupancy of both
14 tetrahedral and octahedral sites by Fe^{3+} cations can affect negatively the diffusion of lithium
15 through the lattice during the Li^+ insertion/extraction electrochemical processes [1,24]. In
16 fact, as reported by Grygar et al. [8], in the Li-Mn-Fe-O series the electroactivity to the Li^+
17 insertion/extraction reaction is insignificant for spinel compositions with $\text{Fe}/(\text{Fe}+\text{Mn}) > 0.4$
18 because only the Li^+ ions located at tetrahedral positions can be electrochemically extracted.
19 As far as the redox reactions occurring in the Li / $\text{LiFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cell is concerned, Ohzuku
20 et al. [1] and Sakai et al. [25] have demonstrated the formation of tetravalent iron species at
21 30°C and operating voltages higher than 5 V. Shigemura et al. [3] confirmed this partial
22 oxidation of the trivalent iron at the 5 V plateau and also the oxidation of Mn^{3+} to Mn^{4+}
23 around 4 V. The existence of Fe^{3+} and Fe^{4+} ions as major and minor iron components,
24 respectively, both located at noncubic octahedral 16d positions, in a series of iron-doped
25 lithium manganites has been also reported [10]. The authors proposed the possible
26 substitution by Fe^{3+} and Fe^{4+} of Mn^{3+} and Mn^{4+} , respectively. This two-fold substitution
27 would explain the changes observed in the lattice constant depending on the Mn/Fe content
28 given the dissimilarities of the ionic radius of the various cations in different oxidation states
29 existing in the samples [10]. Therefore, the presence of Fe^{4+} in the present samples is not an
30 isolated fact and the synthesis route described in the paper shows how the composition of
31 the lithium manganese ferrites can be tailored to obtain materials which can have application
32 for energy storage.

33 The insertion, displacement and rearrangement of diamagnetic Li^+ and magnetic Mn^{3+} ,
34 Mn^{4+} , Fe^{3+} and Fe^{4+} ions over both the octahedral and tetrahedral sublattices of the spinel
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1 structure can yield many possible magnetic configurations which strongly complicate the
2 interpretation of the magnetic properties of the Li-Mn-Fe oxide spinel series [6,11]. Even
3 more, the system can show canted spin structures for some compositions [6,11,13] a fact
4 which has to be taken into account also to explain the magnetization behaviour of these
5 materials. The occurrence of clustering and the associated superparamagnetic-like behaviour
6 has been also reported for some of these materials [11].
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9 The present results indicate, as mentioned above, that the increase of the manganese content
10 which enters the spinel lattice mainly as Mn^{3+} at the octahedral positions, weakens the
11 magnetic interactions. This is likely due to the concomitant displacement of the diamagnetic
12 lithium ions into the tetrahedral sites. Since in spinels the octahedral-tetrahedral
13 superexchange interaction is the dominant, the almost complete occupation of the tetrahedral
14 sites by lithium ions eliminates this interaction leaving only the weaker octahedral-
15 octahedral interaction that starts developing magnetic ordering only at very low
16 temperatures, below 40 K. These materials also show the presence of isolated Fe^{3+} rich
17 clusters within the structure that are already magnetically ordered at room temperature, as
18 the Mössbauer data of the $x=0.00$, 0.25 and 0.50 samples have shown. The concentration of
19 these clusters decreases as the manganese concentration increases and lithium is driven into
20 the tetrahedral sites as Mn^{3+} ions replace the Fe^{3+} ions at the octahedral sites.
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33 34 35 **4. Conclusions**

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37 In the present work we have characterized samples comprising a series of Fe/Mn ratios of
38 the spinel-related compounds $\text{LiFe}_{1-x}\text{Mn}_{1+x}\text{O}_4$. They have been made by a modified thermal
39 decomposition of nitrates synthesis which has given pure materials. The combination of
40 XRD, XPS and Mössbauer spectroscopy has allowed us to determine the distribution of the
41 different cations over the tetrahedral and octahedral sites of the spinel structure as a function
42 of the Fe/Mn ratio. In particular, we have shown that for the Fe-rich samples the lithium
43 cations are located both in the octahedral and tetrahedral positions, while for the Mn-rich
44 samples they are located only at the tetrahedral sites. The introduction of manganese also
45 weakens the magnetic interactions reducing the magnetic ordering temperature in each
46 sample. We have also found Fe^{4+} in the Mn richest sample. The ability to tailor the lithium
47 site makes this family of spinel oxides very attractive for their use in battery electrodes.
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References

- [1] T. Ohzuku, K. Ariyoshi, S. Takeda, and Y. Sakai, *Electrochim. Acta*, **46** (2001) 2327-2336.
- [2] T. Grygar, P. Bezdička, P. Vorm, N. Jordanova and P. Krtil, *J. Solid State Chem.*, **161** (2001)152-160.
- [3] H. Shigemura, H. Sakaebe, H. Kageyama, H. Kobayashi, A.R. West, R. Kanno, S. Morimoto, S. Nasu, and M. Tabuchi, *J. Electrochem. Soc.*, **148** (2001) A730-A736.
- [4] C.J. Chen, M. Greenblatt and J.V. Waszczak, *J. Solid State Chem.*, **64** (1986) 240-248.
- [5] E. Wolska, K. Stempin and O. Krasnopwska-Hobbs, *Solid State Ionics*, **101-103** (1997) 527-531.
- [6] G. Bonsdorf, K. Schäffer and H. Langbein, *Eur. J. Solid State Inorg. Chem.*, **34** (1997) 1051-1062.
- [7] S.M. Woodley, C.R.A. Catlow, P. Piszora, K. Stempin, and E. Wolska, *J. Solid State Chem.*, **153** (2000) 310-316.
- [8] T. Grygar, P. Bezdička, P. Piszora, and E. Wolska, *J. Solid State Electrochem.*, **5** (2001) 487-494.
- [9] E. Ríos, Y.-Y. Chen, M. Gracia, J.F. Marco, J.R. Gancedo, and J.L. Gautier, *Electrochim. Acta*, **47** (2001) 559-566.
- [10] T. Tsuji, M. Nagao, Y. Yamamura, N.T. Tai, *Solid State Ionics*, **154-155** (2002) 381-386.
- [11] M.Gracia, J.F. Marco, J.R. Gancedo, J.L.Gautier, E.I. Ríos, N. Menéndez, and J. Tornero, *J. Mater. Chem.* **13** (2003) 844-851.
- [12] C. Wende and H. Langbein, *Cryst. Res. Technol.*, **41** (2006) 18-26.
- [13] C. Wende, Kh. Olimov, H. Modrow, F.E. Wagner, and H. Langbein, *Mat. Res. Bull.*, **41** (2006) 1530-1542.
- [14] M.H. Mueller, L. Heaton and K.T. Miller, *Acta Crystallogr.*, **13** (1960) 828.
- [15] Y.F. Liu, Q. Feng, and K. Ooi, *J. Coll. Inteface Sci.*, **163** (1994) 130-136.
- [16] D.G. Wickham and W.J. Croft, *J. Phys. Chem. Solids*, **7** (1958) 351-360.
- [17] Y.J. Wei, L.Y. Yan, C.Z. Wang, X.G. Xu, F. Wu, and G. Chen, *J. Phys. Chem. B*, **108** (2004) 18547-18551.
- [18] J.L. Gautier, E. Ríos, M. Gracia, J.F. Marco, and J.R. Gancedo, *Thin Solid Films*, **311** (1997) 51-57.
- [19] D. Alburquenque, L. Troncoso, J.C. Denardin, A. Butera, K.D. Padmasree, J. Ortiz, F. Herrera, J.F. Marco, J.L. Gautier, *J. Alloy Comp.*, **672** (2016) 307-316.
- [20] D. Alburquenque, J.C. Denardin, L. Troncoso, J.F. Marco and J.L. Gautier, *Ionics* **24** (2018) 977-987.
- [21] E. Beyreuther, S. Grafström, and L.M. Eng, *Phys. Rev. B*, **73**, (2006)155425 (1-9).
- [22] M. Sánchez-Arenillas, M. Oujja, F. Moutinho, J. de la Figuera, M.V. Cañamares, A. Quesada, M. Castillejo and J.F. Marco, *App. Surf. Sci.* **470** (2019) 917-922.
- [23] P. Prieto, J.F. Marco, J.E. Prieto, S. Ruiz-Gómez, L. Pérez, R.P. del Real, M. Vázquez and J. de la Figuera, *App. Surf. Sci.* **436** (2018) 1067-1074.
- [24] A.D. Robertson, H. Tukamoto and J.T.S. Irvine, *J. Electrochem Soc.*, **146** (1999) 3958-3962.
- [25] I. Sakai, K. Ariyoshi, , and Ohzuku, T., *Hyperfine Interact.*, **139/140** (2002) 67-76.

Table 1.- Lattice parameters of $\text{LiFe}_{1-x}\text{Mn}_{1+x}\text{O}_4$

x	Lattice constant, a (nm)
0.00	0.8292 ± 0.0007
0.25	0.8257 ± 0.0002
0.50	0.8230 ± 0.0011
0.75	0.8235 ± 0.0005

Tabla 2.- Binding energies of the Mn 3s XPS core level spectra measured in the different samples

Sample	BE Mn 3s(1) /eV	BE Mn 3s(2) /eV	ΔE_{3s} /eV	Mn valence ⁽¹⁾
x=0.00	83.3	88.2	4.9	3.45
x=0.25	83.3	88.6	5.3	2.94
x=0.50	83.2	88.4	5.2	3.07
x=0.75	83.4	88.6	5.2	3.07

⁽¹⁾Determined from the equation proposed by Bayreuther et al., see text.

Table 3.-Hyperfine parameters obtained from the fit of the 298 K Mössbauer spectra recorded from the different samples

	Sextet A					Sextet B					Doublet D			
	d_A (mm s ⁻¹)	$2e_A$ (mm s ⁻¹)	H_A (T)	G_A (mm s ⁻¹)	I_A (%)	d_B (mm s ⁻¹)	$2e_B$ (mm s ⁻¹)	H_B (T)	G_B (mm s ⁻¹)	I_B (%)	d_D (mm s ⁻¹)	D_D (mm s ⁻¹)	G_D (mm s ⁻¹)	I_D (%)
x=0	0.29(1)	-0.02(1)	47.0(1)	0.55(2)	36(3)	0.31(1)	-0.01(1)	49.4(2)	0.43(1)	47(2)	0.35 (1)	0.73(1)	0.31(1)	17(2)
x=0.25	0.27(1)	-0.02(1)	47.9(2)	0.52(2)	26(2)	0.32(1)	0.02(1)	49.8(2)	0.43*	29(2)	0.35 (1)	0.72(1)	0.32(1)	46(1)
x=0.50	0.31(3)	-0.02(2)	47.0(2)	0.55*	7(2)	0.32(3)	0.02(1)	49.4(2)	0.43*	7(2)	0.35 (1) 0.17 (1)	0.71(2) 0.43(2)	0.29(2) 0.29(2)	80(2) 6(1)
x=0.75	-	-	-	-	-	-	-	-	-	-	0.36 (1) 0.16 (1)	0.68(1) 0.44(1)	0.30(1) 0.30(1)	82(2) 18(2)

[d=Isomer shift (relative to α -Fe); 2e=Quadrupole shift; D=Quadrupole splitting; H=Magnetic hyperfine field; G=Full linewidth at half maximum; I=Relative spectral area; numbers in parentheses give the uncertainty in the last digit]

Figure captions

Figure 1.- X-ray powder diffraction patterns recorded from the $\text{LiFe}_{1-x}\text{Mn}_{1+x}\text{O}_4$ samples. The diffractograms have been normalized to the peak height of maximum intensity; that is, the 311 peak in the pattern of the LiFeMnO_4 sample and the 111 one for the other three samples.

Figure 2.- XPS Mn 3s spectra recorded from the different samples

Figure 3.- Mössbauer spectra recorded at 298 K (left) and 14 K (right) from all the samples.

Figure 4.- (Left) Mössbauer spectra recorded at different temperatures from the $x=0.50$ sample. (Right) Mössbauer spectra recorded at different temperatures from the $x=0.75$ sample.

Figure 1

Figure 2

Figure 3

Figure 4