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Electrochemical and structural study of the 3.3 V reduction step in defective $Li_xMn_2O_4$ and $LiMn_2O_{(4-y)}F_y$ compounds

M.R. Palacín [a,*], G.G. Amatucci [b], M. Anne [c], Y. Chabre [d], L. Seguin [e], P. Strobel [c], J.M. Tarascon [e], G. Vaughan [f]

[a] *ICMAB (CSIC), Campus UAB, 08193 Bellaterra, Catalonia, Spain*
[b] *Bellcore, Red Bank, NJ, 07701, USA*
[c] *Laboratoire de Cristallographie, CNRS, BP 166, F-38042, Grenoble, France*
[d] *LSP, UJF-Grenoble and CNRS, BP 87, F-38402, St. Martin d'Hères, France*
[e] *LRCS, Université de Picardie and CNRS, 33 Rue St. Leu, F-80039, Amiens, France*
[f] *ESRF, BP 220, F-38043, Grenoble, France*

Abstract

Non-stoichiometric or fluorine-substituted $Li_xMn_2O_4$ are known to present a reversible redox step at 4.5 V as well as a reduction step at 3.3 V appearing to the expense of the usual 4.0–4.15 V. We present results of very slow stepwise potentiodynamic studies which allowed to localise the oxidation step associated to the 3.3 V reduction level close to 3.95 V. We propose the cubic spinel lattice parameter value as the key parameter for knowing a priori if these redox states will be present or not, with 8.215 Å as threshold value. In situ XRD studies performed across the 3.3 ↔ 3.95 V redox step indicate that these additional states are probably associated to structural features. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The $LiMn_2O_4$ spinel phase has been given intensive studies over the last years as positive electrode material for Li-ion batteries. Due to its 4.0 and 4.1 reversible redox states, it seems to be the best candidate to replace $LiCoO_2$ in commercial lithium-ion batteries, for cost and toxicity reasons. But when prepared with conditions which lead to non-stoichiometric compounds, this system was shown to present an additional reversible redox step at 4.5 V [1], as well as a reduction step at 3.3 V [2]. Although these states have attracted attention because they seem to be related to poor performance for batteries made with such compounds, their physico-chemical origin is still unclear. From studies of samples prepared in various conditions, Tarascon et al. [1] suggested that the 4.5 V step is related to Li–Mn cation mixing with Mn^{3+} on the spinel 8a tetrahedral sites, whereas Gao and Dahn [2] gave evidence that the presence of the 3.3 V reduction step is related to that of the 4.5 V redox one, and that their amplitudes are related to the amount of oxygen deficiency. Then, Amatucci et al.

[3] determined that these two steps have equal capacities, which tends to prove that they have a common cause.

We have done an extensive study of these anomalous states on a series of defective $Li_yMn_2O_4$ ($0.925 \leq y \leq 1.0$) and high temperature heat-treated samples, as well as on a partly fluorinated sample $LiMn_2O_{3.74}F_{0.26}$ [4], which all appear to show similar 4.5 and 3.3 V peaks [5]. Results are presented in this paper on a quenched $Li_{0.925}Mn_2O_4$ and the fluorinated compounds, determining the oxidation level corresponding to the 3.3 V reduction step which was previously said irreversible [2]. In situ XRD has been performed on these compounds in order to look for a possible structural signature of this step.

2. Experimental

$Li_yMn_2O_4$ ($0.925 \leq y \leq 1.075$) were prepared as reported elsewhere [1]. The fluorine-substituted sample $LiMn_2O_{4-z}F_z$ was synthesized according to Amatucci et al. [4]. From the determination of its Mn oxidation state, its formula was $LiMn_2O_{3.74}F_{0.26}$. For obtaining samples with a wide range of lithium deficit, some of the $Li_yMn_2O_4$ compounds were heat-treated at 1100°C for 24 h, cooled

* Corresponding author

down to 820°C, allowed to rest 15 h at this temperature and then quenched to room temperature.

Electrochemical studies were performed on Swagelok™ type cells, with a lithium metal foil as negative electrode, using 1 M $LiPF_6$ in EC/DMC as electrolyte. The positive electrode was usually prepared by mixing the $LiMn_2O_4$ compound with 30% w black carbon.

In situ XRD studies were performed in transmission mode on the BM16 line at ESRF (at 0.4 Å wavelength) on Bellcore's PLiON™ type batteries with a lithium reference electrode [6]. To allow the positive electrode material to cycle back to a fully intercalated state, the positive electrode films were electrochemically pre-lithiated before assembly by amounts large enough to compensate for the lithium used on the first charge in the formation of the SPE/passivation film on the negative graphite electrode.

Continuous and intermittent galvanostatic cycling as well stepwise potentiodynamic studies were made using a MacPile system (Bio-Logic, Claix, France).

3. Electrochemical studies

Fig. 1 shows the potential/composition curve obtained on the first galvanostatic cycling of a $Li_{0.925}Mn_2O_4$ sample performed at a nominal C/20 rate in the 4.8 V ↔ 2.8 V potential window. On first charge, the additional high potential oxidation step is well observed at 4.6 V after the usual 4.0 and 4.15 V plateaus. On first discharge, both additional states are observed at 4.5 V and 3.2 V. The plateaus at 2.8–3.0 V correspond to cycling partly on the cubic ↔ tetragonal transition, $Li_1Mn_2O_4 \leftrightarrow Li_2Mn_2O_4$. Note that, in such condition, no oxidation level is observed that could be quite obviously associated to the so called 3.3 V reduction step, neither on the first charge, nor on the second.

Fig. 2 shows a first cycle incremental capacity measurement performed on a Bellcore-type cell using the EPS protocol of Thompson [7], with very small potential step
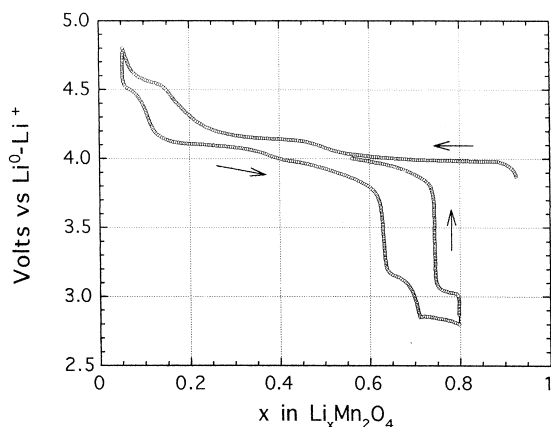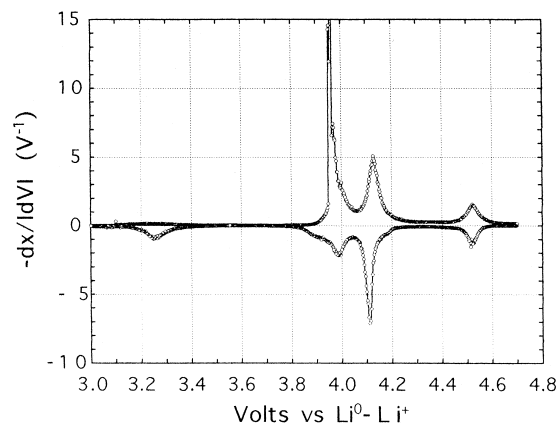
Fig. 2. Incremental capacity voltammogram of the quenched $Li_{0.925}$-Mn_2O_4 from a stepwise potentiodynamic cycling, with ±2.5 mV potential steps once the oxidation/reduction current is lower than an equivalent C/100 regime. $-dx/|dV|$ peaks to 33 V^{-1} at 3.96 V.

amplitude (±2.5 mV) and stepping once the redox current was lower than a C/100 equivalent galvanostatic rate. One can see an abrupt increase of $-dx/|dV|$ when reaching the 3.95 V level, which peaks at 33 V^{-1} for 3.960 V, whereas the peak corresponding to the usual first plateau is observed at 3.9675 V with amplitude 7.4 V^{-1}. The assignment of this first incremental capacity peak to a specific oxidation of the 3.3 V state was suggested by potentiodynamic experiments with limited oxidation, both in potential and in amount. For example, Fig. 3 presents the result of such a limited second cycle, performed on the fluorine-substituted compound: reaching 3.955 V with 5 mV steps and a C/250 final current condition and then keeping this potential applied, the current has decayed to almost 0.2 mA/g (an equivalent C/750 regime) after one day. Once a $\Delta x = 0.2$ oxidation amount was reached, the cell was turned to reduction, performed with -5 mV steps and C/250 final current condition. One can see that as much capacity was recovered in the 3.3 V step as above 3.6 V, the latter corresponding to the charge recovered from partial oxidation on the usual 4.0 V plateau. On the
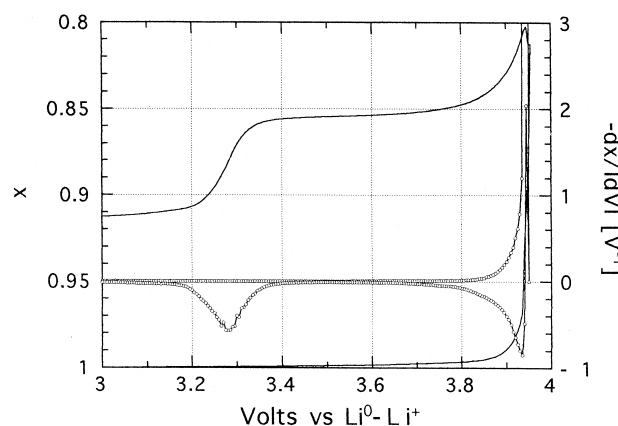
Fig. 1. Titration curve of a 1100°C heat-treated $Li_{0.925}Mn_2O_4$, from a galvanostatic cycling at a C/20 rate.

Fig. 3. Incremental capacity and corresponding titration of the $LiMn_2$-$O_{3.74}F_{0.26}$ compound in a first potentiodynamic cycling with oxidation limited to 3.955 V and $\Delta x = 0.2$ (see text).

contrary the 3.3 V reduction step is not observed if the first cycle is performed with oxidation limited to 3.90 V. Besides, upon further cycling the same behavior is observed, i.e., occurrence of the 3.3 V reduction step only if oxidation is driven above 3.95 V, although the corresponding incremental capacity peak upon oxidation is then much lower than in the first cycle.

These observations and additional PITT experiments indicate unambiguously that the oxidation of the 3.3 V reduction step occurs close to 3.95 V. However GITT experiments performed during the reduction of the 3.3 V state, with open circuit relaxation time as long as 24 h gave a quasi-equilibrium potential lower than 3.6 V. Thus this state can be cycled but with quite a large hysteresis, and it appears to have very low kinetics. This is contrary to what is observed for the 4.5 V state which was confirmed to be very reversible in both lithium defective, as shown in Ref. [1], and fluorine substituted compounds, and with the same capacity as that of the 3.3 V state.

4. In situ XRD studies of the 3.3 V step

We looked for a possible structural signature of this 3.3–3.95 redox state during a extensive in situ study of
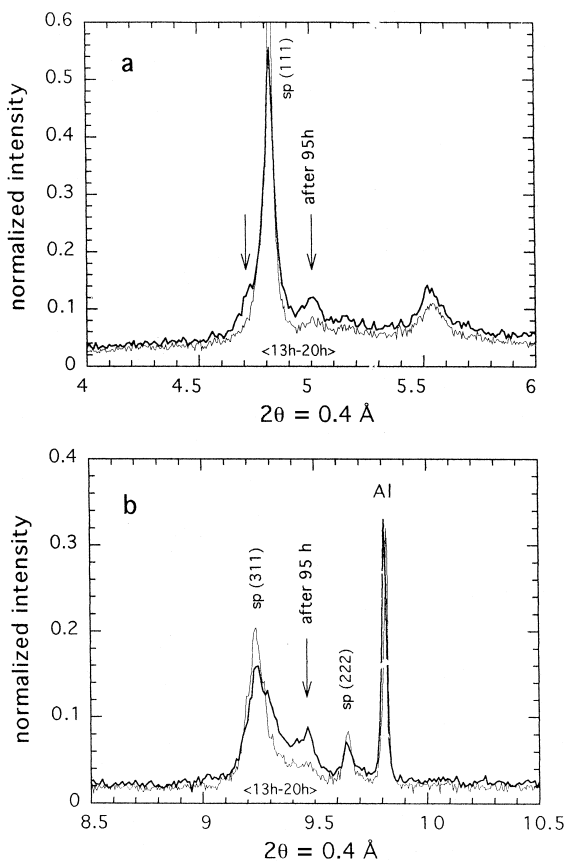

Fig. 4. Some of the new small lines (arrows) appearing in the in situ XRD study of a $LiMn_2O_4$ compound, during a 4-day first oxidation at 3.96 V constant potential.

these spinel systems [8,9]. Several XRD patterns were recorded at given intervals over a 4-day oxidation at 3.96 V constant potential. The as-prepared fluorinated compound shows a splitting of all reflections except the (hhh) ones into three which seems to exist also for $Li_yMn_2O_4$ ($y < 1$) compounds, though in a much lesser extent. This splitting can be assigned to a small fraction of a second phase with a slight orthorhombic distortion [9]. The amplitude of the corresponding satellite lines progressively decreased at the beginning of the oxidation at 3.98 V, without change of the splitting value, and disappeared at $x = 0.82$ [9]. At the same time, a new set of small lines appeared in the course of the oxidation process at 3.96 V, in the vicinity of some of the spinel lines, as shown in Fig. 4 for a $LiMn_2O_4$ sample. These new lines, whose assignment is an open question yet, disappeared on the following reduction. On the contrary, the satellites of the initially split lines of the fluorinated sample did not reappear in the reduction following the 3.98 V limited oxidation.

5. Discussion

The most intriguing question at the beginning of this study was the fact that both cation defective spinels (as samples of nominal formula $Li_yMn_2O_4$ with $y < 1$) and anion defective ones (i.e., $LiMn_2O_{3.74}F_{0.26}$) show the additional 4.5 V and 3.3 V redox steps. Cation-defective compounds present these states when the oxidation states are lower than 3.53 [2,3], which is also the case for the fluorinated sample. Recent investigations [10] are in agreement with this trend, but they determined a maximum Mn oxidation state of 3.60 for the observation of these additional redox steps. However, the analysis of the manganese oxidation state in the spinel for quenched samples is hindered by the fact that they contain Li_2MnO_3 impurities; thus, we considered the cell parameter as a better parameter, as it is specific of the spinel phase and can be determined for all samples. The cell parameter is directly related to the manganese oxidation state (it decreases with increasing manganese oxidation state) but also to the site occupation [11–13] and, as most of the samples studied presented vacancies, we considered that this could be a clue factor relying the results obtained for all samples. Indeed, when the relative capacity on the 3.3 V reduction step for both the samples we studied and those taken from the work of Gao and Dahn [2] are plotted against the cell parameter, linear relations are observed (see Fig. 5). There appear to be two families of samples: those that have been post-treated at high temperature and thus contain a certain amount of lithium and/or oxygen vacancies, and those annealed at $T < 820°C$ which, in principle, should not contain vacancies. Thus, the cell parameter appears to be the key parameter for knowing a priori if a lithium manganese spinel compound will or will not present the additional redox steps at 4.5 V and 3.3 V, which is of high
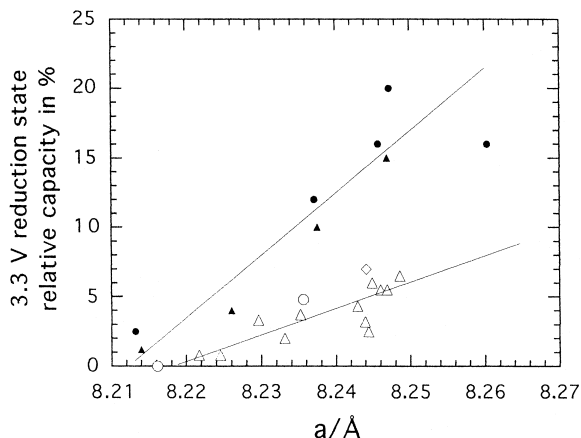
Fig. 5. Relative capacity of the 3.3 V step observed on reduction as a function of the cubic spinel lattice parameter for various compounds. $Li_yMn_2O_4$: O, this work; Δ, from Gao and Dahn [2]. $LiMn_2O_{3.74}F_{0.26}$: $\diamond$. Closed symbols: high temperature heat-treated samples.

practical interest. The upper limit value beyond which these redox steps appear is close to 8.215 Å.

Besides, all the samples we studied showing the 4.5 V and 3.3 V steps also present the Jahn–Teller transition first observed by Yamada and Tanaka [14]: both the $Li_yMn_2O_4$ series with $0.925 \leq y \leq 1.0$, as previously observed by Amatucci et al. [3] and Tabuchi et al. [10], and our high temperature heat-treated samples, and also the fluorine substituted one. This Jahn–Teller transition has recently been shown to be from cubic to orthorhombic symmetry [15,16] and not from cubic to tetragonal as previously proposed. Thus, the disappearance of the satellite lines on the fluorinated sample at the beginning of the first oxidation, can be attributed to the transition of the orthorhombic part of the sample back to the cubic spinel phase, due to the increase in the Mn oxidation state. The fact that these satellite lines do not reappear when cycling back to 3.0 V is most likely related to the irreversible capacity, which is high in these samples (as can be observed in Fig. 1). This prevents coming back to a Mn oxidation state low enough for the occurrence of the cubic $\rightarrow$ orthorhombic transition and explains the lower amplitude of the 3.95 V oxidation peak associated to the 3.3 reduction step on the second and further cycles.

The set of small additional lines which appear close to some of the spinel lines upon oxidation above 3.95 V and disappear when crossing the 3.3 V reduction state are thus directly linked to this anomalous redox state. However, the structural feature responsible for these additional lines is still unclear. Recently, Sugiyama et al. [17] showed that the Jahn–Teller transition is related to the oxygen deficiency δ in $LiMn_2O_{4-\delta}$. The same group proposed a model of cluster involving strong interaction between oxygen defects to explain results of thermogravimetric measurements on their non-stoichiometric compounds [18]. We are presently working in this direction, looking if such

clusters could be the cause of these additional lines and thus of the 3.3 V $\leftrightarrow$ 3.95 V and 4.5 V additional redox steps.

6. Conclusion

An extensive study was performed on the additional 4.5 V and 3.3 V redox states that can be observed in some non-stoichiometric $Li_yMn_2O_4$ spinels as well as in fluorine substituted ones. We have first determined the oxidation potential of the 3.3 V reduction step which is close to 3.95 V. Two linear relationships have been found between the amplitude of these redox states and the spinel lattice parameter value, for low temperature and high temperature treated samples respectively. The cubic spinel lattice parameter thus appears as the key parameter for predicting observation of the 4.5 V and 3.3–3.95 V redox states, with 8.215 Å as the threshold value of occurrence. From in-situ XRD observations when cycling on the 3.3–3.95 V redox state, we propose that these additional redox states which appear at the expense of the usual ones, origin in distorted domains, the nature of which is still under study.

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