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On the role of defects in decreasing the extra 3.3/3.95 and 4.5 V redox steps in Li–Mn–O spinels

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Abstract

LiMn₂O₄ spinels were studied with the aim of assessing the role of different types and amounts of defects in blocking the phase transition from spinel to double hexagonal that is associated with anomalous 4.5 and 3.3/3.95 V redox steps. The influence of the type of MnO₂ precursor (β or γ , both with diverse amounts of stacking faults), the effect of introducing defects in the final spinel by ball milling or of cationic substitutions on the spinel 16d sites (Al or Li) were examined. Electrochemical experiments performed on all these defective samples indicate that defects block the phase transition to a certain extent. The introduction of either Li or Al in spinel 16d sites proved to be the most effective to prevent the structural transformation, and thus eliminate the anomalous redox steps that are detrimental to the electrochemical performances of LiMn₂O₄. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electrochemical properties of LiMn₂O₄ are highly dependent on the synthesis route, the processing conditions and thermal history of the samples. Its typical potential-composition profile usually exhibits two large reversible plateaus at 4.05 and 4.1 V. However, two anomalous redox steps are known to appear at 4.5 and 3.3 V under specific synthesis conditions to the expense of the usual ones, leading to a decrease in the useful 4 V capacity and to poor cycling performances [1–4]. We recently performed a thorough study on diverse Li–Mn–O spinels that allowed us to: (i) determine the oxidation level at 3.95 V corresponding to the reduction observed at 3.3 V [5] and (ii) propose a general mechanism explaining the occurrence of both steps [6] based on the existence of a structural transformation from spinel to double hexagonal (DH) structure as determined by high resolution electron microscopy studies [7].

The additional steps observed at 3.95/3.3 and 4.5 V are associated with the formation/disappearance of DH layers upon oxidation/reduction to the expense/benefit of the spinel phase. The extent of capacity obtained at 3.3 V is clearly correlated with the amount of spinel phase involved in the structural transformation. We found that the amount of capacity on the 3.3 V reduction step is directly related to the spinel cell parameter, spinels with larger values transform more easily into the DH structure. However, other factors may affect the extent of the structural transformation as samples prepared from β -MnO₂ present much larger capacities at 3.3 V than what would be expected from the value of their cell parameters. Bearing in mind the importance of structural defects on the electrochemical performances of manganese oxides [8] we undertook a systematic study of their influence on the additional steps observed in defective LiMn₂O₄ spinels. The influence of the MnO₂ phase used to prepare the spinel (β -phase, γ -phases with diverse amounts of pyrolusite and microtwinning defects [8]) was analyzed as well as that of the defects induced by ball milling either the MnO₂ precursor or the final spinel. Additionally, Al substitution (Li[Mn_{2-x}Al_x]O₄) was performed and compared with Li substitution (Li[Mn_{2- δ} Li _{δ}]O₄) [3].

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2. Experimental

LiMn_2O_4 spinels were prepared by two successive solid-state reactions in air, each for 8 h at 1073 K, starting from Li_2CO_3 (Prolabo Rectapur 99%+) and various sources of MnO_2 (β -Aldrich 99%+ ground to various extents and several γ -phases from Guyomard's group [9]) in which the exact contents of manganese were carefully checked. Ball milling (shock in stainless steel containers) of either the β - MnO_2 starting material or the obtained LiMn_2O_4 was achieved with careful control of the (ball-mass)/(sample-mass) ratio (r) and of the milling time (t). $\text{Li}[\text{Mn}_{2-x}\text{Al}_x\text{O}_4]$ ($0 < x < 0.30$) spinels were also prepared using the same thermal procedure with Al_2O_3 as the Al source.

Electrochemical experiments were made using SwagelokTM type cells [10]. The positive electrode was prepared by mixing the LiMn_2O_4 sample with 15% (weight) carbon black (SP from MMM, Belgium). Two sheets of Whattman GF/D borosilicate glass fiber were used as a separator, soaked with 1 M LiPF_6 in EC/DMC 50:50 electrolyte (Merck), and the negative electrode consisted of a lithium metal foil. Cells were tested with a MacPile potentiostat/galvanostat (Bio-Logic Co., Claix, France). Galvanostatic cycling was usually performed at room temperature between 2.8 and 4.8 V at a rate of $C/20$. Stepwise potentiodynamic studies were made using the electrochemical potential spectroscopy (EPS) protocol of Thompson [11] with an amplitude of ± 5 mV and a limit current for potential stepping equivalent to a $C/250$ galvanostatic rate.

3. Results and discussion

The fact that LiMn_2O_4 prepared from β - MnO_2 , with exact stoichiometry [12], presented pretty large capacities on the anomalous redox steps ($\sim 13\%$) was the first indication that defects in the MnO_2 precursor may have an influence on the

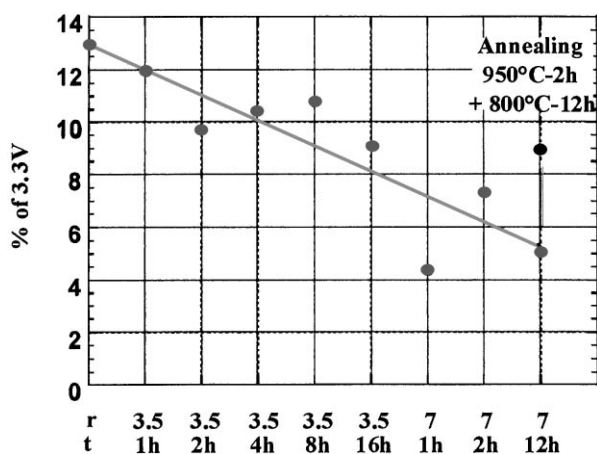


Fig. 1. Plot of the relative capacity at 3.3 V for LiMn_2O_4 prepared from ball milled β - MnO_2 vs. r and t . Annealing of a ball-milled precursor results in a decrease in the amount of defects and thus in an increase of the relative capacity at 3.3 V for the final spinel.

extent of the spinel to DH phase transition. β - MnO_2 has a perfect rutile structure whereas γ - MnO_2 is an intergrowth of rutile and ramsdellite-like block units with large amounts of microtwinning (Pr and Tw parameters, respectively) [8].

We thus prepared a first series of LiMn_2O_4 batches from seven different γ - MnO_2 precursors that had previously been characterized in terms of types and amounts of defects. Apart from the fact that the 3.3 V step is always smaller than for spinels prepared from β - MnO_2 , no definite correlation

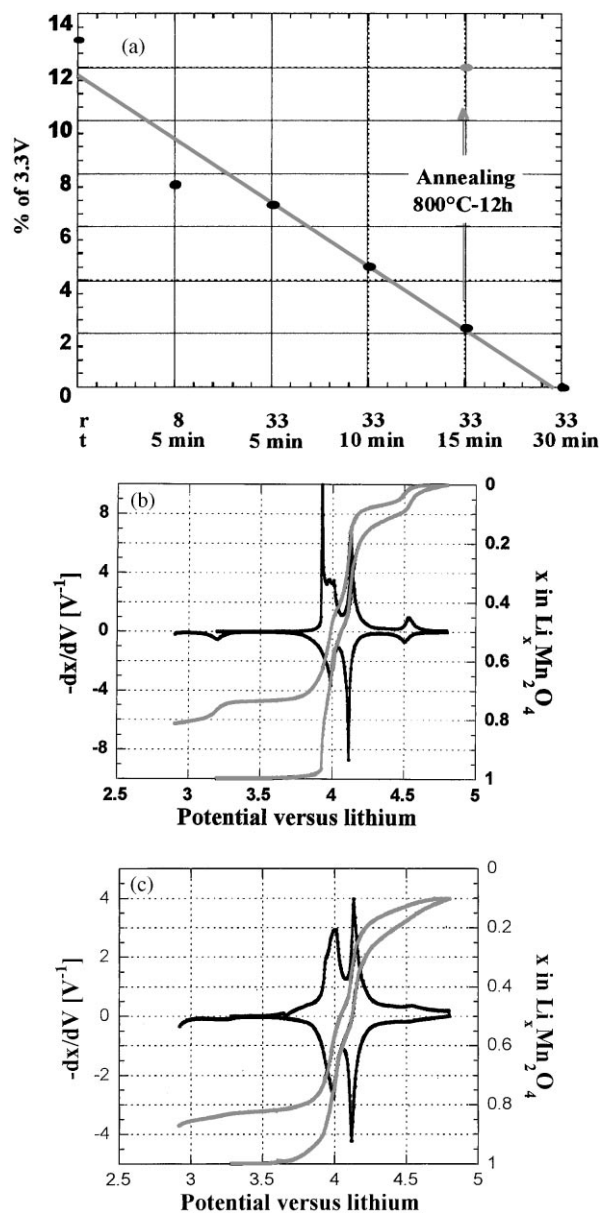


Fig. 2. (a) Plot of the relative capacity at 3.3 V for ball milled LiMn_2O_4 vs. milling parameters r (ratio of ball mass to sample powder mass) and time t . (b) Incremental capacity and voltage-composition plots for the initial non-milled LiMn_2O_4 where the sharp peak at 3.96 V upon oxidation corresponding to the reduction at 3.3 V can clearly be seen. (c) Incremental capacity and voltage-composition plots for LiMn_2O_4 after milling ($t = 15$ min., $r = 33$) where the peak at 3.96 V has almost disappeared.

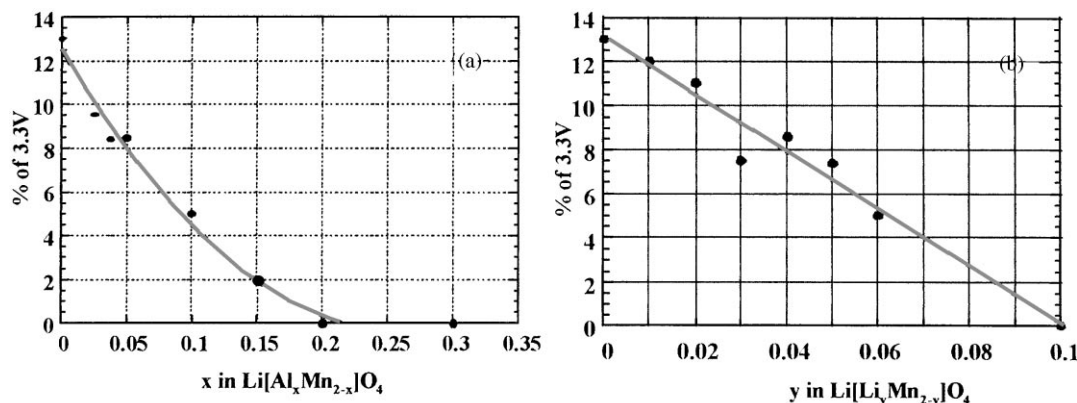


Fig. 3. Plot of the relative capacity at 3.3 V for $\text{Li}[\text{Al}_x\text{Mn}_{2-x}]\text{O}_4$ ($0 < x < 0.3$) and $\text{Li}[\text{Li}_y\text{Mn}_{2-y}]\text{O}_4$ ($0 < y < 0.1$) spinels as a function of x and y , respectively.

between the extent of the 3.3 V plateau in the final spinel and that of the “Pr” and “Tw” values of the precursor could be drawn.

A second series of batches was investigated after shock milling the pristine $\beta\text{-MnO}_2$ with various ball/sample ratios (r) and milling time (t), thus obtaining a series of MnO_2 precursors with different degrees of crystallinity and concentrations of defects such as dislocations. The obtained spinels (after thermal treatment at 800°C) look pretty similar at a first sight, with the exact same lattice parameter ($a = 8.248 \text{ \AA}$) [13], but the electrochemical tests clearly showed that the relative capacity at 3.3 V decreases with increasing t or r (Fig. 1). This indicates that the structural transformation from spinel to DH is partially blocked when structural defects are introduced in the $\beta\text{-MnO}_2$ precursor. Further confirmation of this trend came from the observation that annealing one of these spinels at 930°C for 2 h (hence with less defects) restored a large capacity at 3.3 V (Fig. 1).

A third series of experiments consisted in ball-milling a pristine LiMn_2O_4 to various r and t values. This led to spinels with decreasing particle sizes and degrees of crystallinity [13] and with higher concentrations of defects. Here again, the percent of capacity “wasted” at 3.3 V at the expense of the usual 4.05 and 4.1 V steps decreases when r or t are increased (Fig. 2a). This can be clearly seen on the curves obtained from PITT experiments, as the sharp peak at 3.95 V upon oxidation that is associated to the reduction at 3.3 V (Fig. 2b) has almost disappeared after 15 min of grinding with $r = 33$ (Fig. 2c). As for the previous case, annealing at 800°C to eliminate the defects introduced upon ball milling results in the recovery of the capacity at 3.3 V. This fact further confirms the role of defects in blocking the structural transformation from spinel to double hexagonal.

Finally, we further investigated the role of the defects on the extent of the 3.3 V reduction step by introducing foreign cations on the 16d sites of the spinel structure by doping with Al or Li to obtain the solid solutions $\text{Li}[\text{Al}_x\text{Mn}_{2-x}]\text{O}_4$ ($0 < x < 0.3$) and $\text{Li}[\text{Li}_y\text{Mn}_{2-y}]\text{O}_4$ ($0 < y < 0.1$). As clearly demonstrated in Fig. 3, the relative amount of the

3.3 V plateau decreases sharply upon the introduction of small amounts of foreign cations. These “foreign” cations play indeed the role of an obstacle against the migration of Mn atoms that is necessary for the spinel \rightarrow DH structural transformation.

4. Conclusion

Diverse types of defects were introduced by different means (changing the MnO_2 precursor, ball-milling, cationic substitution) that were shown to partially block the structural transformation from spinel to double hexagonal and thus decrease the electrochemical capacity on the anomalous 4.5 and 3.3/3.95 V redox steps. Among these, the substitution on the spinel 16d sites (Al or Li) proved to be the most effective, and is certainly a good direction to follow for designing good LiMn_2O_4 -based positive electrodes for battery applications.

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