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$Li_2Mn_4O_9$ revisited: crystallographic and electrochemical studies

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Abstract

Three different cation-vacant spinels aiming at composition "$Li_2Mn_4O_9$" were prepared by (1) low-temperature solid state reaction, (2) chemical delithiation, (3) electrochemical delithiation. Products of routes (1) and (2) were studied by neutron diffraction. Rietveld refinements confirmed the double-vacancy scheme proposed by de Kock et al. [Mater. Res. Bull. 25 (1990) 657] in the former. The exact composition of both samples departed significantly from the expected stoichiometry. They also differed in their electrochemical behavior. Both can be cycled at 3 V with much better stability than stoichiometric $LiMn_2O_4$, probably due to the increased initial manganese valence with respect to $LiMn_2O_4$. Spinel with tetrahedral-vacancies only gives an additional reversible redox step ca. 150 mV above the main plateau. This feature is observed on both discharge (lithium insertion) and charge (extraction). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Li–Mn–O system; Spinel; Cation-vacancies

1. Introduction

The Li–Mn–O system gives rise to a rich crystal chemistry [1–3]. A range of stoichiometric spinels is known between compositions $LiMn_2O_4$ and $Li_4Mn_5O_{12}$, as well as phases containing tetrahedral-site-vacancies, such as λ-MnO_2, or even anionic-vacancies [4,5]. A very peculiar case in this system is $Li_2Mn_4O_9$, initially reported by de Kock et al. [6]. This compound is interesting, because (i) it contains tetravalent manganese only, (ii) its structure contains cation-vacancies on both tetrahedral- and octahedral-sites. From a neutron diffraction study, de Kock et al. indeed deduced the structural formula $(Li_{8/9}vac_{1/9})[Mn_{16/9}vac_{2/9}]O_4$ in spinel stoichiometry, where () and [] indicate the tetrahedral- and octahedral-site contents, respectively. Such a high cation-deficiency could lead to high lithium intercalation capacity, although the reversibility of intercalation in such sites is doubtful a priori.

The synthesis of $Li_2Mn_4O_9$, however, is difficult, and subsequent attempts by various groups [7,8] to reproduce de Kock's result yielded products with a manganese oxidation state v(Mn) never exceeding ca. +3.8. In this paper, we reconsider the $Li_2Mn_4O_9$ case, using three different preparation routes.

Indeed, the global composition "$Li_2Mn_4O_9$" can also be reached by lithium extraction from a stoichiometric spinel, the composition of which is determined by the simple condition $Mn/O = 4/9$. Along the stoichiometric spinel solid solution $Li_{1+\alpha}Mn_{2-\alpha}O_4$, this corresponds to $\alpha = 2/9$, i.e. a parent stoichiometric spinel $Li_{11/9}Mn_{16/9}O_4$. Upon delithiation, one expects vacancies to occur on tetrahedral-sites, yielding the compound $(Li_{6/9}vac_{3/9})[Mn_{16/9}Li_{2/9}]O_4$, i.e. a lithium manganese spinel with same global composition "$Li_2Mn_4O_9$" as de Kock's compound, but with different cation and vacancy distribution.

We describe here the crystallographic and electrochemical properties of these two "isomers", made by (1) de Kock's low-temperature solid state reaction procedure, (2) chemical, (3) electrochemical lithium extraction.

2. Experimental

Sample A was made by solid state reaction between β-MnO_2 and LiOH at 425–500°C in air, according to the procedure described previously [6]. For routes 2 and 3 above, the starting material was $Li_{1.22}Mn_{1.78}O_4$ powder. Chemical delithiation was carried out according to Hunter's procedure [9] using 0.1 M HCl, yielding sample B. Sample C was obtained by electrochemical delithiation, using galvanostatic charging up to 4.4 V in a lithium cell.

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Manganese oxidation states were determined by wet titrimetry using the oxalate-permanganate procedure. Samples were characterized by X-ray diffraction using a Siemens D-5000 diffractometer with Cu Kα radiation. Selected vacancy-containing samples were studied in the powder neutron diffractometer D2B of Institut Laue-Langevin, France, with a wavelength of 1.5938 Å. Structures were refined using the Fullprof program.

For electrochemical studies, the active material was mixed with 20% carbon black and 10% PTFE emulsion. Cathodic pellets were cut from the resulting paste and dried under vacuum at 120°C for 15 h before use. The electrolyte was 1 M $LiPF_6$ in EC–DMC (Merck), and the anode was lithium foil. Coin-type or Swagelok cells were assembled in a glove-box with <1 ppm H_2O. Batteries were tested using a MacPile controller.

3. Results and discussion

3.1. Crystal chemistry

X-ray diffraction showed that all samples belong to the spinel structure. Refined cell constants are given in Table 1. They vary widely between samples obtained by solid state reaction (de Kock's procedure) and by delithiation. The latter have a smaller cell parameter, especially sample B obtained by chemical lithium extraction (8.09 Å). This trend is in agreement with measured manganese oxidation states (see Table 1, last column). It should be pointed out that the solid state reaction procedure yielded products containing unreacted lithium carbonate and with v(Mn) $\leq +3.82$, i.e. far from the theoretical value +4 [10]. However, the cell parameter value for solid state reaction sample A (8.179 Å) agrees well with de Kock's data (8.174 Å).

Details of the neutron diffraction experiments will be reported elsewhere [10]. Full structure refinements, including cation site occupation and individual temperature parameters (19 variables), yielded R_{wp} values of 5.76 and 3.90 for samples A and B, respectively. This again reflects the poorer diffracting quality of low-temperature, solid state reaction products such as sample A.

The Rietveld refinement of cation occupations from neutron diffraction data confirms the double-vacancy scheme proposed by de Kock et al. [6]. Complete cation distributions are given in Table 1. As expected, the vacancy distribution depends on the synthesis procedure. The structure refinement on sample B showed no vacancies on octahedral-sites in this sample (see Table 1), as expected from the preparation route. Samples obtained by delithiation are closer to the ideal "$Li_2Mn_4O_9$" stoichiometry than those obtained by de Kock's procedure.

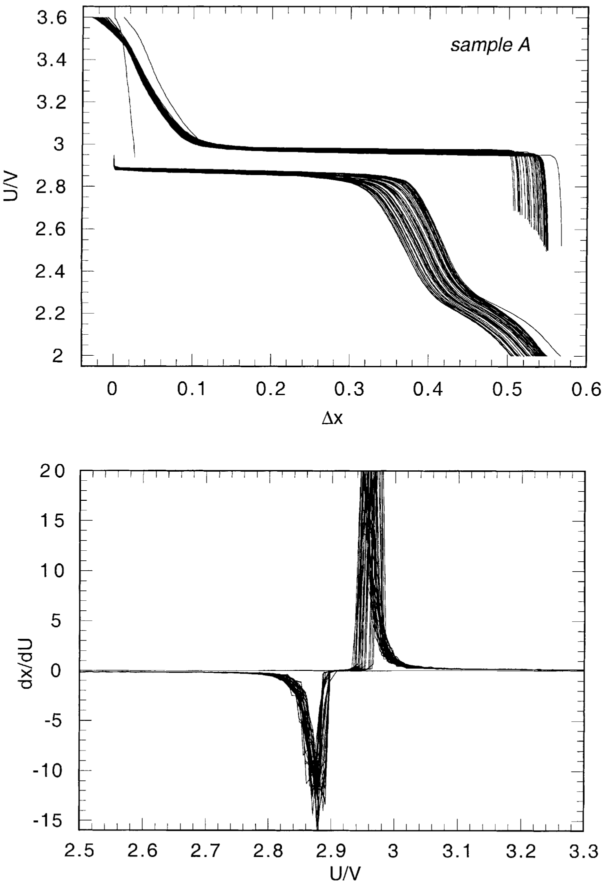

Fig. 1. Galvanostatic cycling (top) and incremental capacity curve (bottom) for the double-vacancy spinel A at C/10 regime.

3.2. Electrochemical properties

The electrochemical interest of these materials is two-fold.

1. They have manganese oxidation state v(Mn) close to +4, and can be expected to cycle on the 3 V plateau of the Li–Mn–O spinel system while staying away from the

Table 1
Crystallographic data for samples

Spinel	Synthesis procedure	a (Å)	Formula (from Rietveld refinement)	v(Mn)
[6]	Solid state 400°C	8.174	$(Li_{0.83}vac_{0.17})[Mn_{1.76}vac_{0.24}]O_4$	4.07 (?)[a]
A	Solid state 500°C	8.179 (3)	$(Li_{0.78}vac_{0.22})[Mn_{1.88}vac_{0.12}]O_4$	3.69
B	Chemical delithiation	8.091 (1)	$(Li_{0.62}vac_{0.38})[Mn_{1.80}Li_{0.20}]O_4$	3.97
C	Electrochemical delithiation	8.139–8.143	$(Li_{0.66}vac_{0.34})[Mn_{1.78}Li_{0.22}]O_4$[b]	4.00[b]

[a] From neutron refinement of site occupations.

[b] From electrochemical lithium extraction.

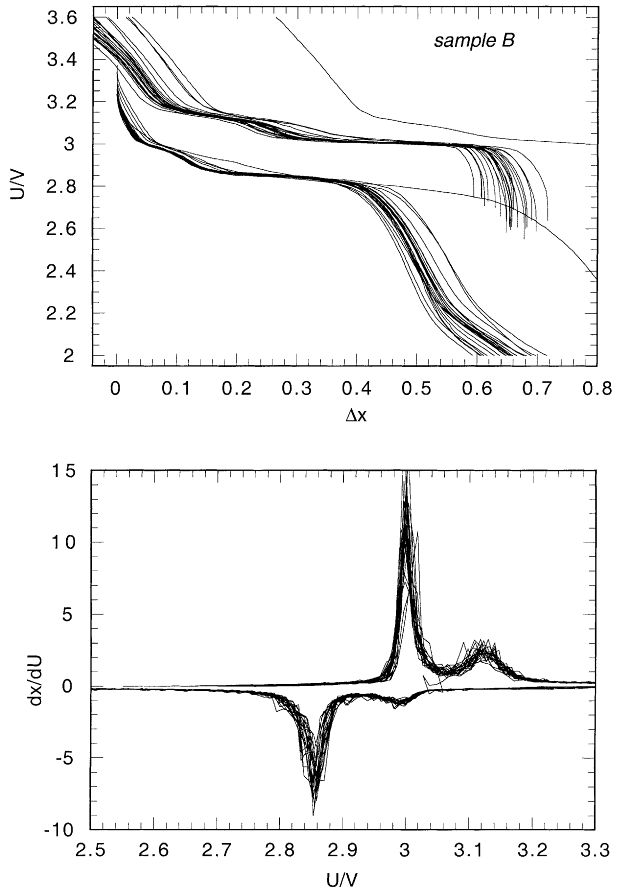

Fig. 2. Galvanostatic cycling (top) and incremental capacity curve (bottom) for the tetrahedral-vacancy spinel B at C/20 regime.

Jahn–Teller distorsion limit v(Mn) = +3.5 [1], unlike $LiMn_2O_4$.

2. An extra intercalation capacity is expected to occur because of the lithium-vacancies, and might show up as distinct steps in charge-discharge curves. However, the capacity associated with the filling of these vacancies is unlikely to be reversible in the 3 V range.

Figs. 1 and 2 show galvanostatic cycling at ≈C/10 for samples A (double-vacancy spinel) and B (tetrahedral-vacancies only). Both samples cycle on the “3 V plateau” clearly characteristic of a 2-phase system, at a slightly lower potential than stoichiometric $LiMn_2O_4$. In addition, sample B exhibits a prominent second current peak occurring ca. 150 mV above the main redox peak. As shown by the derivative curve (Fig. 2b), this feature is reversible, does not become smeared out on cycling and seems specific to this kind of sample. It is not observed on cycling either $LiMn_2O_4$ or $Li[Li_xMn_{2-x}]O_4$. The associated capacity is ≈0.20 Li/spinel formula unit, i.e. equal to the vacancy content in sample B (see formula in Table 1). However, lithium extraction from the 8a tetrahedral-sites usually occurs at 4 V, and the connection between this extra feature and the tetrahedral-vacancies remains to be confirmed.

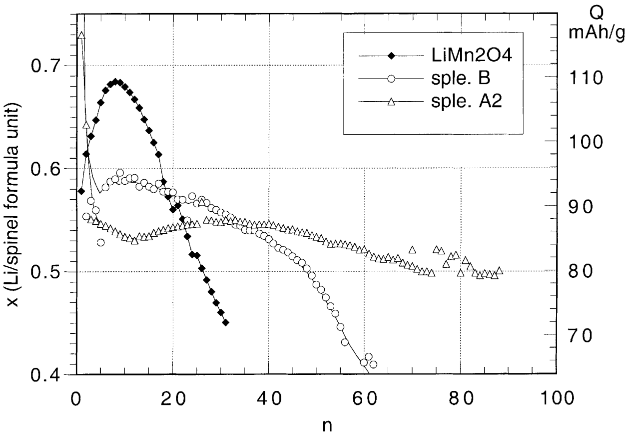

Fig. 3. Variation of the 3 V capacity on cycling at ≈C/10: sample B = tetrahedral-vacancy spinel, sample A2 = double-vacancy spinel obtained at 500°C.

The first discharge capacity is rather high (x ≈ 1 for both samples), but drops to ≈0.6 Li/spinel formula unit within 3–4 cycles. On further cycling, both cation-vacant spinels are much more stable than $LiMn_2O_4$ (see Fig. 3). The double-vacancy sample A is especially stable when cycled at C/10 over more than 80 cycles.

4. Conclusions

This study confirmed the double vacancy scheme for Li–Mn–O spinels prepared by low-temperature solid state reaction. It also showed remarkable differences between spinel-type compounds with compositions close to $Li_2Mn_4O_9$, depending on the distribution of cationic-vacancies in the lattice. These differences are also reflected in their electrochemical behavior in lithium batteries: whereas the capacity associated with vacancy filling is barely noticeable in the double-vacancy compound A, an extra lithium insertion/extraction step is clearly visible in sample B with tetrahedral-vacancies only; this sample is surprisingly stable.

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