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ELECTROCHEMICAL AND NEUTRON DIFFRACTION STUDY OF A PRELITHIATED HOLLANDITE-TYPE Li_xMnO_2 PHASE :

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Abstract Prelithiated αMnO_2 exhibits two types of electrochemical behavior previously correlated to different possible sites for both chemically and electrochemically inserted lithium ions. This work presents preliminary results concerning lithium localization in the material, in the light of a neutron diffraction study.

INTRODUCTION

For several years, secondary batteries, with lithium as anode or, most recently "rocking chair" systems[1], have been the subject of intense and important research with the aim to improve energy storage efficiency. Within this field of application, "MnO_2" has been well tested, but irreversible reactions occurring during discharge[2,3] made it difficult to operate secondary systems. Despite its promising behavior, the αMnO_2 variety has been the subject of only few experiments[4-7]. The αMnO_2 structure, built up from MnX_6 octahedra sharing edges and corners to form a double chain along the c axis, is represented in figure 1. Preliminary cycling on a chemically prelithiated αMnO_2 by Lecerf[8] yielded promising data, with energy density around 490 Wh/kg per cycle over a hundred cycles. Li+ localization in the hollandite lattice, before and after cycling seems to have a preponderant effect and will be discussed here from electrochemical and neutron diffraction results.

SAMPLE PREPARATION AND GLOBAL FORMULATION

Prelithiated αMnO_2 was obtained by solid phase reaction between $NH_4Mn_8O_{16}$ and $LiOH,H_2O$ at 300/400°C. $NH_4Mn_8O_{16}$ itself was synthesized by precipitation from a reaction between a $MnSO_4$ solution and $(NH_4)_2S_2O_8$ as oxidizing agent[8]. Two types of samples (labelled I and II) obtained under different syntheses conditions have been studied.

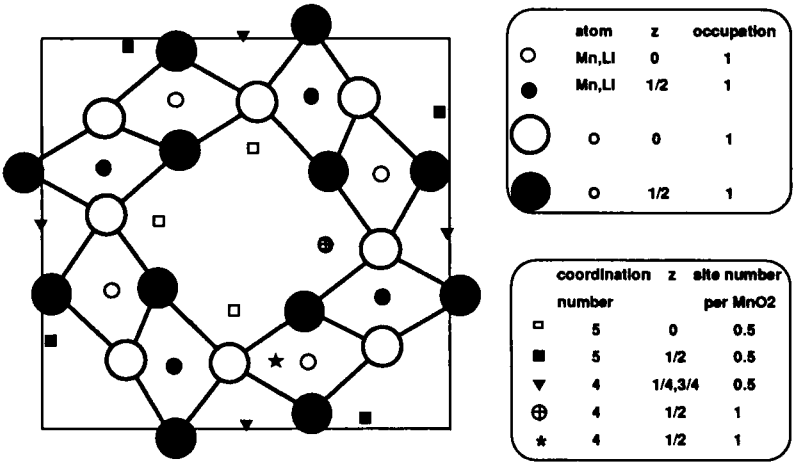

Figure1. Structure projection along the tunnel axis. For clarity, the equivalent positions of the last two tetrahedral sites are not drawn.

Their average formula was determined by chemical analysis whereas a redox procedure was used for manganese oxidation state determination[9]. The global formulation is the same for the two types of materials :

$$Li^{+}_{0.26}[Li^{+}_{0.08}Mn^{+3.9}_{0.93}]Oh[O^{--}_{1.92}(OH)^{-}_{0.08}](H_2O)_{0.06}(SO_4)^{2-}_{0.025}$$

STRUCTURE AND AVAILABLE SITES FOR LITHIUM

The above formulation shows that 0.07 lithium substitute manganese in the "MnO_6" octahedra. The 0.26 left lithium ions can be localized either in the pentahedral sites (□, ■) or in the three tetrahedra sites, to be found in the small tunnels (▼) or in the large ones (⊕, *), at the tunnel edge (Figure 1).

Both pristine $NH_4Mn_8O_{16}$ and chemically intercalated materials have been characterized by X-ray diffraction using $Cu_{k\alpha}$ radiation and an energy discrimination detector eliminating manganese fluorescence. The $NH_4Mn_8O_{16}$ quadratic parameters (a = 9.8647(8) Å, c = 2.8490(3) Å, symmetry I4/m) are in good agreement with those obtained by neutron diffraction time of flight technique (vide infra Table I). The prelithiated compounds exhibit a monoclinic distortion leading to an I2/m symmetry (a = 9.976(3) Å, b = 2.8429(9) Å, c = 10.058(2) Å, β = 90.41° and a larger cell volume of V = 285.24 Å^3). Their line widths are more important than for the pristine compound due to higher disorder and/or smaller particle size.

ELECTROCHEMICAL STUDY

Li/[1M $LiCF_3SO_3$ in PC/EC/DME (1/1/2)]/"αMnO_2" electrochemical button cells were used for all experiments. "αMnO_2" cathodes consisted of a mass of 80% prelithiated αMnO_2, 15% carbon and 5% Teflon binder. Cycling were done under constant current at a c/10 rate from 2 to 3.8 V[9].

The samples I and II presented differences in cycling capacities : 0.55 Faraday per "MnO_2" for compound I and only 0.45 Faraday for sample II. Such a difference is surprising since the two compounds global formulations are similar.

A careful analysis of the incremental capacity curves during discharge allowed to detect the occurrence of a shoulder between 3.1 and 3.7 volts only for the type I compound. This shoulder area corresponds to a difference between compounds I and II capacity of about 0.1 Faraday, i.e. the capacity difference of a whole cycle. This shoulder disappears around 200 cycles. However, the two types of compounds lead to a negative charge balance at the end of each charge (figure 2) previously attributed to electrolyte oxidation and possible chemically pre-inserted lithium ions[9] removal.

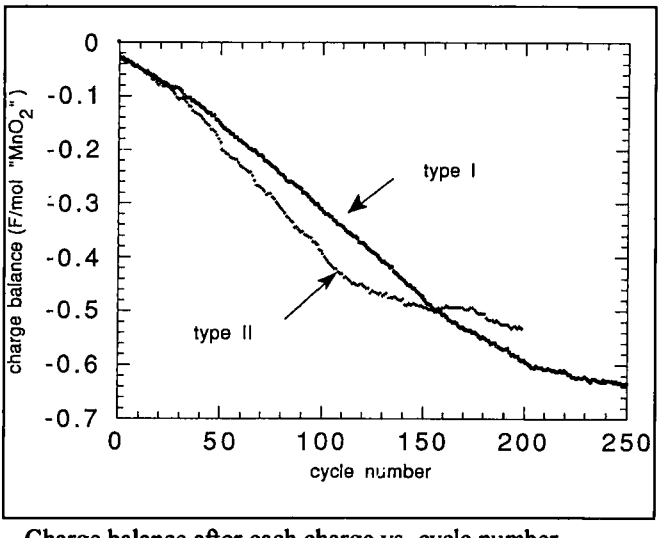

Figure 2. Charge balance after each charge vs. cycle number

In this figure, a slope modification appears around the 200th cycles for the type I material whereas it takes place before (≈ 120th cycle) for the type II compounds. For both materials, the break of the slope can be correlated to a stronger decrease of the cycling capacity versus cycle number (figure 3). From all these electrochemical observations, the

following hypotheses could be put forward : i) two kinds of pre-inserted lithium ions exist in the structure (in addition to the lithium in substitution of manganese).

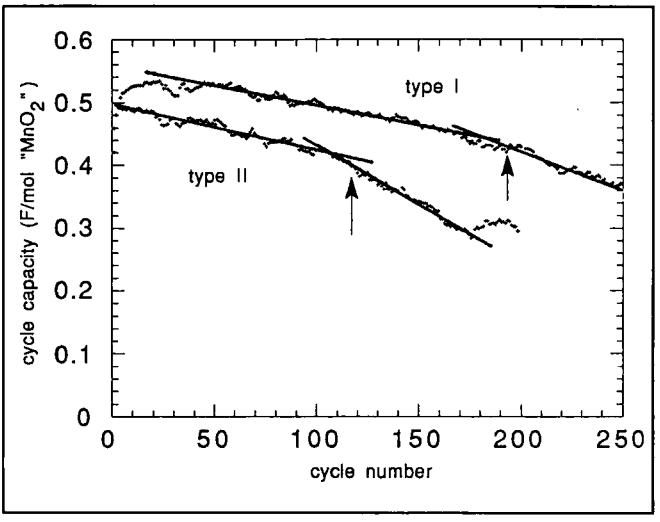

Figure 3. Cycle capacity vs. cycle number

The first will be called "normal" and the second "pillar" in the following. ii) Electrochemical lithium intercalation in the vicinity of these pre-inserted Li^+, leads to two incremental capacity peaks. One at 2.8 V corresponds to the presence of "normal" lithium, whereas the 3.1 to 3.7 V shoulder is linked to "pillar" lithium. iii) The progressive extraction of both "normal" and "pillar" lithium causes a capacity loss beyond a threshold cycle number. "Pillar" lithium in the material, when it exists, stabilizes the structure and pushes the capacity loss increase at a higher cycle number.

All these hypotheses had to be tested by a technique allowing lithium localization in the structure, as neutron diffraction experiments.

NEUTRON DIFFRACTION

Study of $NH_4Mn_8O_{16}$

Time of flight neutron experiments where done at Los Alamos Laboratories using detectors setting at +39, -39,+90 and 153° from direct beam.

The neutron study of $NH_4Mn_8O_{16}$ was necessary to calibrate the peak profiles for Rietveld refinements and to be the starting point for lithium containing compounds.

Refinement results are gathered in Table I. Fourier map calculations did not evidence any scattering residual in the large tunnels. The refinement used only U_{iso}.

Table I Atom positions for $NH_4Mn_8O_{16}$

Atom	x	y	z	frac	U_{iso}
Mn	0.343(1)	0.1862(8)	0	1	0.00594
N	0	0	0.5	1	0.0103
O(1)	0.1429(7)	0.1953(6)	0	1	0.0118
O(2)	0.5413(4)	0.1494(4)	0	1	-0.00612

Space Group I4/m, (a=9.8737(2) Å, c=2.8519(6) Å), cell volume : 278.03 Å^3
$R_p = 3.95$, $R_{wp} = 5.06$, $\chi^2 = 2.32$ for 64 variables and 13373 observations.

Study of chemically pre-inserted Mn_8O_{16}

As a large amount of prelithiated compound was necessary to perform neutron diffraction experiments, a new batch was prepared. Curiously, this material led to bad electrochemical behavior.

The following results were obtained, taking into account the manganese and oxygen atoms only . This may explain the negative values observed for U_{iso}. We plotted a Fourier map to try to localize lithium ions in the structure. The maps were ill defined and lithium could not be localized (figure 4) whereas no oxygen could be found in the compounds large tunnels, contrary to the acid phase prepared by Rossouw[7]. One finds the same overall distribution as in $NH_4Mn_8O_{16}$, with however a manganese deficiency (83% filling) (site occupancy for manganese was refined to check a possible substitution by lithium) and an increased distortion of the MnO_6 groups. In the large tunnels, the oxygen closest to manganese (a and a') present strongly different positive scattering density from the others (b and b').

Table II Atom positions for chemically inserted Mn_8O_{16}

Atom	x	y	z	frac	U_{iso}
Mn(1)	0.363(1)	0	0.1910(9)	0.83(1)	-0.0280
Mn(2)	0.8278(9)	0	0.358(1)	0.83(1)	-0.0369
O(1)	0.1510(8)	0	0.2061(7)	1	0.0116
O(2)	0.7839(8)	0	0.1458(8)	1	0.0275
O(3)	0.5405(6)	0	0.1692(6)	1	-0.0215
O(4)	0.8279(7)	0	0.5412(9)	1	-0.0084

Space Group I2/m, (a=9.834(1),b = 2.7846(5), c=10.191(1) Å, $\beta = 92.27°$)
cell volume : 278.88 Å^3, $R_p = 3.24$, $R_{wp} = 4.69$
$\chi^2 = 14.02$ for 58 variables and 7245 observations.

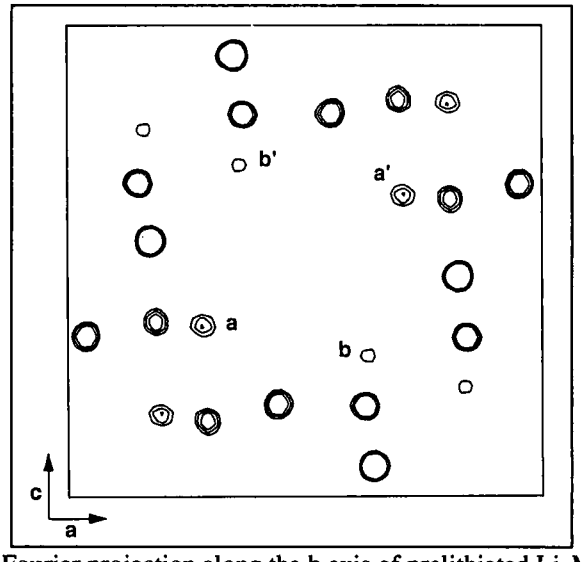

Figure 4. Fourier projection along the b axis of prelithiated Li_xMnO_2

One can notice that cell parameters are substantially different from those obtained from X-ray diffraction experiments on a different batch of compound having a good cycling capacity. Clearly, other classical monochromated neutron diffraction studies will have to be done to localize Li^+ in the pristine αMnO_2 and its cycled derivatives.

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