

A high performance Li_xMnO_y cathode material for rechargeable lithium cells

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Abstract

Lithiated $\alpha\text{-MnO}_2$ has been synthesized and used as cathode material for rechargeable lithium cells. Coin cells have been used to test the material cycleability and characteristics with 1 M $\text{LiCF}_3\text{SO}_3/\text{PC-EC-DME}$ electrolyte. Reversible capacity has been demonstrated for 130 cycles with 160 A h/kg with 3.6 to 2 V cycling cutoff voltages without important capacity loss. Pilot industrial batches have been used to realize prototype 'C'-size cells; their cycling leads to performances as high as 200 A h/kg of Li_xMnO_y (α) in the first cycles corresponding to 2.4 A h for a cell capacity with discharge voltage of 2.87 V. To date, 60 cycles have been achieved with an anode excess of 2.6, which corresponds to a lithium cycling efficiency > 95%.

Introduction

The growing tendency to utilize lithium in primary cells and storage batteries has its origin in three essential characteristics: (i) increased ratio of energy output to unit volume compared with other electrochemical power sources (two or three times higher than Ni/Cd cells) essentially coming from the high specific energy of Li (3860 A h/kg) and from the high working potentials of these systems; (ii) very low self-discharge during storage, about 5% per year at room temperature, and (iii) operation in a wide temperature zone.

Within this framework, the main metal oxides used as cathode materials are Li_xMnO_2 , V_2O_5 , Li_xNiO_2 , Li_xCoO_2 , Li_xCrO_x ; their utilization has been widely reported in the literature and reviewed by many authors [1-6]. Among these materials, Mn compounds have been widely used and studied for primary applications [7-11]. They have the advantage of potentially lower cost among all these oxides, and are less toxic (contrary to chromium or vanadium compounds, for example).

The present work deals with the development of secondary cells based on a cathode consisting of a lithiated manganese oxide (Li_xMnO_y): unlithiated materials showed high capacity in the first discharge but very small reversible capacity was found irrespective of the MnO_2 type used.

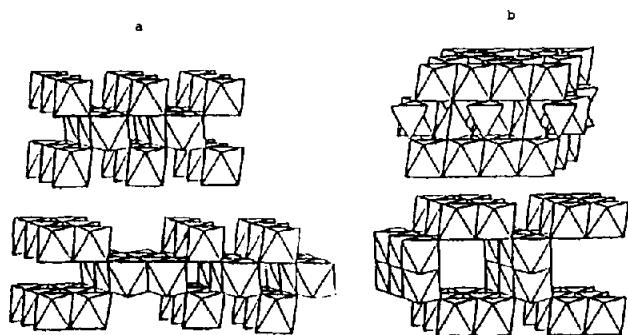
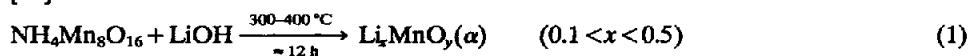


Fig. 1. Crystal structure of various MnO_2 types: (a) β - MnO_2 ; (b) λ - MnO_2 ; (c) γ - MnO_2 , and (d) α - MnO_2 .

Various MnO_2 types allow chemical lithiation: α -, β - and γ - MnO_2 [12–15]. Because of their crystallographic structure (presented in Fig. 1) which contains large channels, MnO_2 compounds may enable reversible insertion of lithium. Following preliminary studies, lithiated α - MnO_2 [15] was selected because of its reversibility and better capacity in comparison with other lithiated MnO_2 . An explanation may reside in the α - MnO_2 structure which is characterized by 2×2 tunnels formed by the MnO_2 octahedra: these tunnels represent a very privileged way for Li^+ migration and accommodation in the structure.

Synthesis and lithiation of α - MnO_2

α - MnO_2 is obtained by oxidation of MnSO_4 with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The hollandite $\text{NH}_4\text{Mn}_8\text{O}_{16}$ (α - MnO_2) thus obtained is characterized by the X-ray diffraction (XRD) pattern shown in Fig. 2. As said above, these materials have a very small reversible capacity (≈ 50 – 70 A h/kg). The lithiation of α - MnO_2 is realized as described above [15]:



Temperature and heat-treatment duration are chosen in such a way that the lithiated compound retains the crystal structure of the starting α - MnO_2 : the XRD patterns in Fig. 2 show the same peaks as the starting material. The content of Li inserted in the structure (x) varies from 0.1 to 0.5.

Active material obtained in this manner was the subject of electrochemical cycling tests: these were carried out in coin cells and the first validation tests have also been carried out in prototype spirally-wound cells ('C' size).

Electrochemical properties

Cyclic voltammetry has been experimented at low scanning rate (0.5 mV/min), as represented in Fig. 3 for the first three cycles. The wide reduction peaks observed are in accordance with a topotactic reaction. However, some irreversible phase transition is revealed by: (i) the existence of two peaks at 2.85 and 2.65 V in the first cycle,

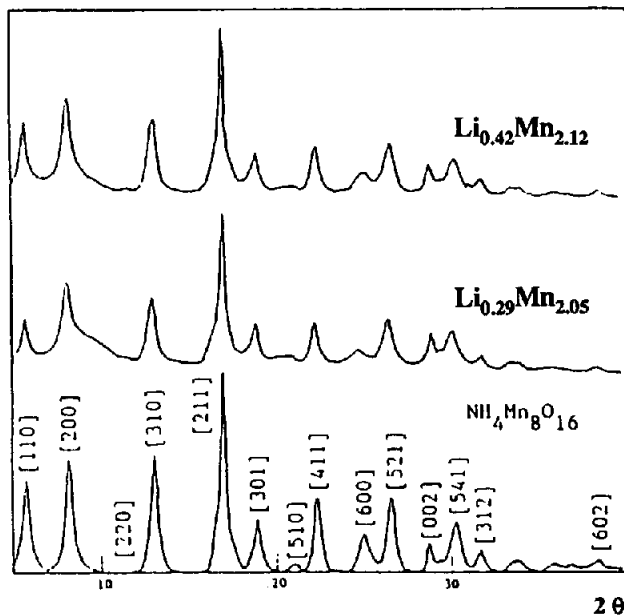


Fig. 2. Mo $K\alpha$ X-ray diffraction pattern of $\text{NH}_4\text{Mn}_8\text{O}_{16}(\alpha\text{-MnO}_2)$ and $\text{Li}_x\text{MnO}_y(\alpha)$.

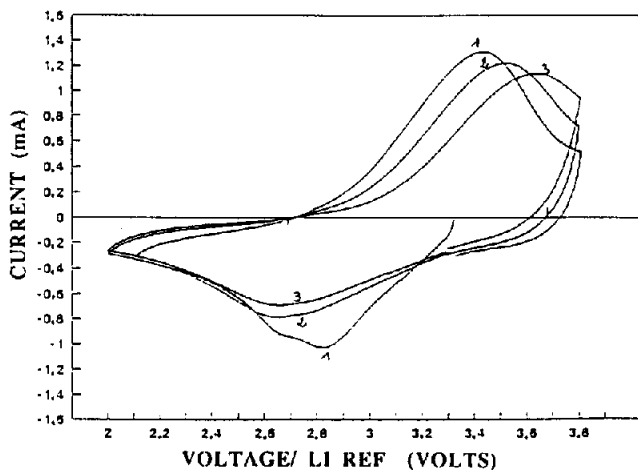


Fig. 3. Cyclic voltammety of $\text{Li}_x\text{MnO}_y(\alpha)$ for the first three cycles; scanning rate: 0.5 mV/min, reference electrode: Li/Li^+ .

and (ii) the clear difference between the first and the following cycles. This phase transition is somehow not clear since the XRD pattern is similar for charged and discharged compounds [16].

Coin cells were used to carry out tests with cathode materials. The cathode consists of a mixture of active material (80 wt.%), graphite (7.5 wt.%), carbon black (7.5 wt.%) and a binder, in general polytetrafluoroethylene (PTFE) (5 wt.%) pressed into an

aluminium grid from which the electrode (2 cm^2) is cut after drying. The anode consists of a Li disc (2 cm^2) in a large excess compared with the cathode. The two electrodes are separated by a polypropylene sheet and a felt serving as a reserve of the electrolyte. The electrolyte consists of a mixture of solvents PC-EC-DME in the proportion 1/1/2, respectively, by volume, to which one of the following salts is added: 1 M LiCF_3SO_3 , 1 M LiBF_4 or 1 M LiAsF_6 , respectively. Cycling is done under the following conditions: $I_c = I_d = 1 \text{ mA}$ (0.5 mA/cm^2) with various cycling voltages.

The presented results are obtained with the LiCF_3SO_3 salt. Typical charge/discharge curves are presented in Fig. 4.

The curves given in Fig. 5 show the evolution of capacity versus cycling for the best compounds $\text{Li}_{0.42}\text{MnO}_{2.12}$. An increase in the capacity is always observed during the first several cycles with the best materials. This 'formation' phase may reveal the same non-reversible structural modification of the material as described above. This formation is simultaneous (and probably due) to chemical Li^+ partial deinsertion, which results in an increase in the energy density: increase in specific capacity and

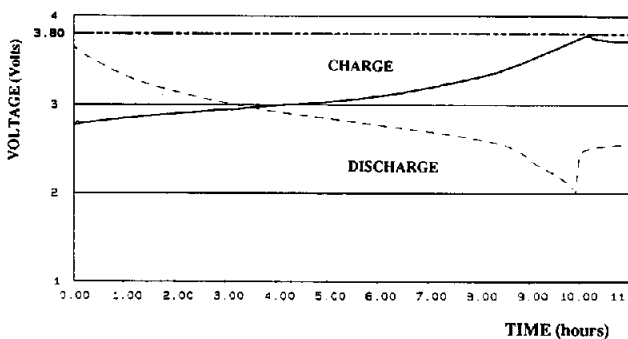


Fig. 4. Charge and discharge curves of $\text{Li/Li}_{0.42}\text{MnO}_{2.12}$ coin cell with 1 M LiCF_3SO_3 in PC-EC-DME (1/1/2) electrolyte; cycling conditions: 0.5 mA/cm^2 , cycling range: 3.8–2 V.

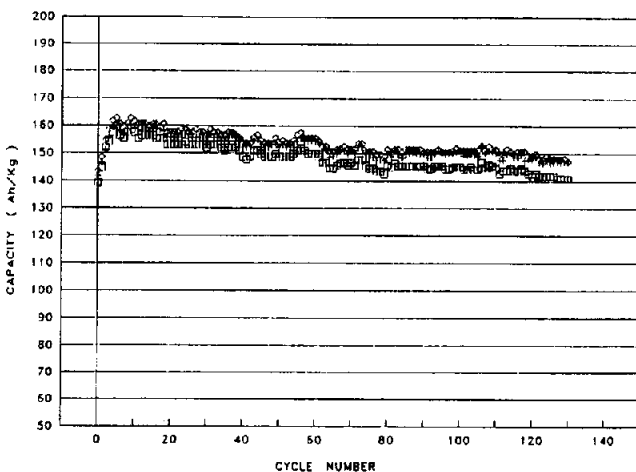
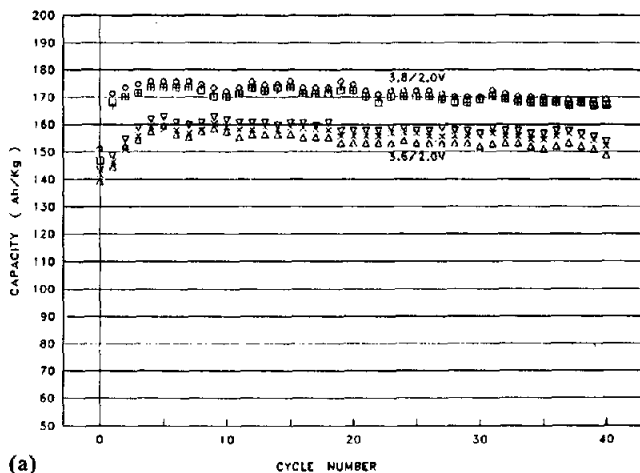


Fig. 5. Specific capacity vs. cycle number of $\text{Li/Li}_{0.42}\text{MnO}_{2.12}$ coin cells with 1 M LiCF_3SO_3 in PC-EC-DME (1/1/2) electrolyte; cycling conditions: 0.5 mA/cm^2 , cycling range 3.6–2 V.

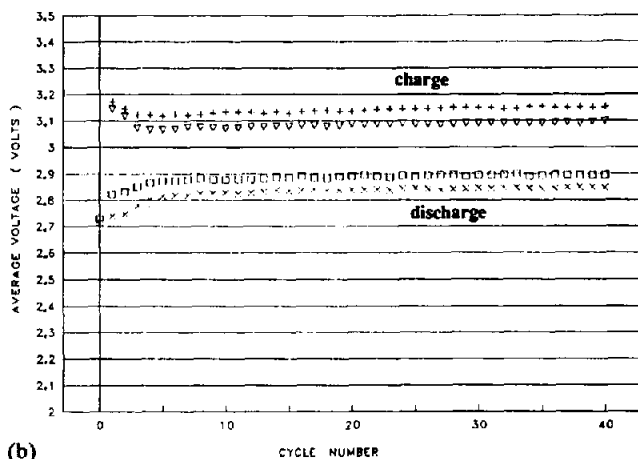
average voltage at the same time. The material structure is close to the initial ' α ' material and remains stable during cycling, as revealed by XRD.

The observed capacity is above 160 A h/kg for an average voltage of 2.85 V once the formation phase is completed (Fig. 5). This corresponds to an insertion of 0.53 Li/Mn. The reversibility of Li intercalation appears to be very good: after 130 cycles without failure the remaining capacity is still close to the initial one (i.e., 150 A h/kg) and the average voltage remains constant.

Two values of the maximum cutoff voltage, 3.6 and 3.8 V, have been investigated: a slight increase in capacity to 170 A h/kg and discharge voltage to 2.9 V is obtained with the 3.8 V cutoff (Fig. 6).



(a)



(b)

Fig. 6. Comparison of 3.6–2 V and 3.8–2 V cycling ranges of Li/Li_{1-x}MnO_x(α) coin cells with 1 M LiCF₃SO₃ in PC-EC-DME (1/1/2) electrolyte: (a) specific capacity, (b) average voltage ((\square) and (+) 3.8–2 V, (x) and (∇) 3.6–2 V); cycling conditions: 0.5 mA/cm² at room temperature.

The laboratory-size process for material synthesis has been scaled up to an industrial process by SEDEMA (Belgium). Similar performances were obtained with pilot batches of several kg. They were used to build cylindrical cells.

Prototype spirally-wound cells

Spirally-wound cells have also been manufactured with this cathode material. The electrochemical coil consists of a spiral of polypropylene separator between a Li foil and a cathode material coated on a steel or aluminium collector. The electrolyte is 1 M LiCF_3SO_3 , in PC-EC-DME (1/1/2), the starting lithium:cathode ratio is 2.6 and the theoretical capacity is 1.94 A h, based on a cathodic specific capacity of 160 A h/kg.

The first results obtained in prototype 'C'-size wound cells with $\text{Li}_x\text{MnO}_y(\alpha)$ are given in Fig. 7 ($I_c=100$ mA; $I_d=200$ mA ($C/20$ and $C/10$, 0.3 and 0.6 mA/cm²)) with cutoff voltages 2 and 3.8 V. The initial cells capacity is better than expected reaching 2.4 A h during the first cycles: this corresponds to 200 A h/kg of cathodic-active material. The higher capacity in 'C' cells may be due to: (i) mechanical compression of the cathode in spirally-wound cells, which does not exist in coin cells, and (ii) more homogeneous current distribution because in spiral cells the cathode is working on both faces. The average voltage (2.89 V) is the same as in coin cells. High rate discharges have been experimented at 1 A ($C/2$; 3 mA/cm²) and 2 A (C) as reported in Fig. 7. The cell polarization was rather limited, so that the decrease of the discharged capacity was quite acceptable. Good performances have also been obtained at 0 °C (0.2 A), with a 160 A h/kg discharged value as shown in Fig. 6.

Up to this day, about 60 cycles have been achieved with these 'C'-size cells, corresponding to a Li cycling efficiency >95% (or a figure-of-merit >22). After 60 cycles, the cell capacity is close to 2 A h, which corresponds to 165 A h/kg for $\text{Li}_x\text{MnO}_y(\alpha)$ and cycling is continuing. These excellent results (resumed in Table 1) also show the very good performance of LiCF_3SO_3 as electrolyte salt for Li rechargeable cells. The total starting energy of the cell is about 6.9 W h (that is 280 W h/l or 140 W h/kg) compared with 3 W h for a Ni/Cd cell.

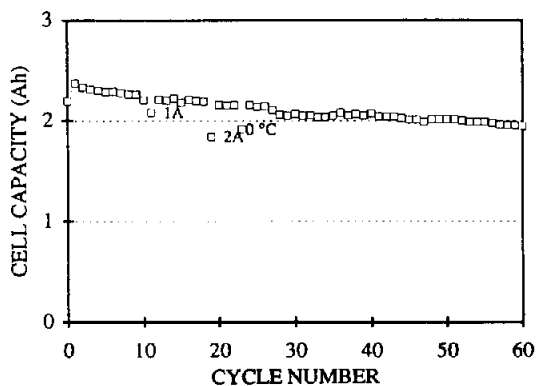


Fig. 7. Cell capacity vs. cycle number of $\text{Li}/\text{Li}_x\text{MnO}_y(\alpha)$ 'C'-size cell with 1 M LiCF_3SO_3 in PC-EC-DME (1/1/2) electrolyte; cycling conditions: $I_c=0.1$ A, $I_d=0.2$ A; cycling range: 3.8–2 V cutoff.

TABLE 1

Cycling efficiency of a Li_xMnO_y (α) cell^a

Q_0 (A h/kg)	$\langle U \rangle$ (V)	Q (A h)	Specific energy		Cycle	Lithium efficiency (%)
			(W h/kg)	(W h/l)		
200	2.9	2.4	140	280	> 60	> 95

^a0.05 kg and 0.025 l.

Conclusions

The results obtained allow to rank lithiated $\alpha\text{-MnO}_2$ among the most competitive cathodes for Li cells. High capacities have been obtained (up to 200 A h/kg in 'C'-size cells) and the electrochemical characteristics of these compounds are stable during cycling (capacity loss <6% after 130 cycles). Moreover, some of these results are obtained with products from an industrial process, which is still under improvement.

Acknowledgements

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