

Synthesis of Mn spinels from different polymorphs of MnO_2

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Abstract

Four polymorphs of MnO_2 , i.e., α , β , ϵ and ramsdellite, have been lithiated with LiI solutions to give Li_xMnO_2 ($0.4 < x < 0.7$). Heating of these phases always results in spinel formation. β - and ϵ - MnO_2 are more easily converted into spinels, whereas the larger tunnels of α - and ramsdellite- MnO_2 allow limitation of the Li–Mn repulsion causing the structural change. The formation of such by-products as Mn_2O_3 and Li_2MnO_3 has been demonstrated by X-ray and thermogravimetric and differential thermal analyses. Solid-state reactions of these polymorphs (with LiOH) also give rise to Mn_2O_3 -contaminated spinels, in spite of the stoichiometric ratios. The electrochemical characteristics, as determined mainly by potential step voltammetry in the 4 V range, are similar to those of conventionally prepared spinels but the presence of by-products limits the available capacity.

Keywords: Manganese dioxide; Manganese spinels

1. Introduction

The growing interest in lithium-ion batteries has stimulated the search of high-voltage, high-capacity cathode materials. Particular attention has been devoted to the cubic spinel LiMn_2O_4 which has distinct advantages over the layered phases LiMO_2 ($M = \text{Co}$ or Ni) in terms of cost, safety and rate capability.

A number of papers has lately appeared on the synthesis conditions enabling the best performance with LiMn_2O_4 to be achieved [1,2]. Most of them use chemical manganese dioxide (CMD) or electrochemical manganese dioxide (EMD) as the Mn source, with a few exceptions such as γ - MnOOH [3] or $\text{Mn}(\text{CH}_3\text{COO})_2$ [4,5]. Both CMD and EMD are γ - MnO_2 , disordered structures formed of pyrolusite and ramsdellite domains.

Thus far, very little attention has been devoted to aspects of spinel formation from well-defined MnO_2 structures. Thackeray et al. [6] have reported the synthesis of $\text{Li}_{0.5}\text{MnO}_2$ from ramsdellite lithiated with LiI and its transformation into Mn spinel at 300 °C. In the above-mentioned paper, no attempts were made to investigate, with respect to the spinel formation: (i) the effect of different Li contents in Li_xMnO_2 ; (ii) the possible formation of by-products, and (iii) the electrochemical characteristics of the material obtained.

In recent papers, the reduction of different MnO_2 polymorphs in either alkaline [7] or Li-containing solutions [8] has been reported. The voltage–composition curves show rather distinctive features, e.g. for Li^+ -inserted ramsdellite and rutile [8], this testifying to the influence of the crystalline sites on the insertion thermodynamics.

The basic idea which has prompted this investigation was to lithiate some structurally different MnO_2 's at low temperature and to follow the transformation, upon heating, of these phases into spinel. In this way, we aimed at observing: (i) the ease of spinel formation; (ii) the occurrence of side reactions, and (iii) the structural and electrochemical features of the final products.

The four polymorphs chosen were: α -, β -, ϵ - and ramsdellite- MnO_2 .

2. Experimental

2.1. Synthesis of MnO_2 polymorphs

(i) α - MnO_2 . $\text{Li}_2\text{Mn}_2\text{O}_3$ was treated at 90 °C with 3 M H_2SO_4 , to extract Li_2O [9]. The material so-obtained contained, after drying at 100 °C, some Li^+ and H^+ . However, heating at 300 °C was effective in obtaining α - MnO_2 with negligible amounts of foreign ions [9].

(ii) β - MnO_2 . By heating γ - MnO_2 at 400 °C, the transformation into a β -like structure was induced.

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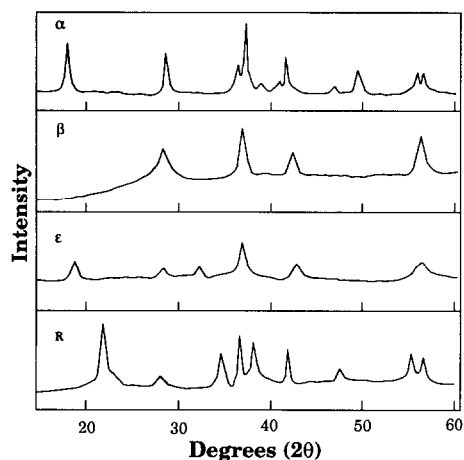


Fig. 1. X-ray patterns of different MnO_2 's, $\text{Cu K}\alpha$ radiation.

(iii) ϵ - MnO . This material, which basically has the γ - MnO_2 structure, was synthesized from λ - MnO_2 heated at 230°C [10].

(iv) Ramsdellite- MnO_2 (R- MnO_2). LiMn_2O_4 or $\text{Li}_2\text{Mn}_4\text{O}_9$ can be leached free of Li or Li_2O by reaction with H_2SO_4 at 95°C for 24 h [6].

After drying at 200°C (300°C for α - MnO_2), the MnO_2 's were submitted to X-ray analysis in order to compare them with literature data [6,9–11]. The patterns reported in Fig. 1 for the four materials are in close agreement with those previously described.

2.2. Lithiation with LiI

The MnO_2 's were lithiated with a LiI solution in acetonitrile [6]. The slurry was heated to 70°C and kept under reflux for 5 h. Two sets of conditions were chosen in terms of the LiI content: (i) a 0.55:1 ratio of LiI to MnO_2 , and (ii) an LiI excess (about 3 times). With the first condition, a composition approaching $\text{Li}_{0.5}\text{MnO}_2$ was expected, whereas, also in view of electrochemical results [6], compositions $\text{Li}_{>0.8}\text{MnO}_2$ were expected when using an excess of LiI.

The real Li^+ content was determined by chemical titration. Basically, all the Mn in Li_xMnO_2 was reduced to Mn^{2+} by a solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$. The excess of Fe^{2+} used was back-titrated with a KMnO_4 solution [12]. Some Mn oxides with a known Mn oxidation state, e.g., MnO_2 and LiMnO_2 , were also used to check the method.

2.3. Transformation of Li_xMnO_2 phases into spinels

The lithiated samples were heated under vacuum at 200, 300 and 400°C for 1 day. X-ray analysis was done after each thermal treatment. A final heating at 750°C in the air allowed well-defined spinel patterns to be obtained in all cases.

In a few experiments, Li_xMnO_2 were obtained from α -, β - and R- MnO_2 by thermal lithiation. LiOH and the appropriate MnO_2 were reacted at 380°C for 1 day and, then, heating at 750°C enabled spinels to be obtained.

The evolution of the Li_xMnO_2 phases formed with LiI with temperature was also followed by thermogravimetric and differential thermal analysis (TGA and DTA) under N_2 atmosphere ($5^\circ\text{C}/\text{min}$ to $\sim 900^\circ\text{C}$).

Potential step voltammetry ($10\text{ mV}/1\text{ h}$) was applied to all spinels obtained at 750°C . In this way, a characterization of the first charge/discharge cycle was sought. In these tests, and in prolonged cycling tests, an $\text{LiPF}_6/\text{EC}-\text{DMC}$ solution was used. The cells were of the coin-type with an Li rod reference electrode.

3. Results and discussion

The different arrangements of the MnO_6 octahedra in the four polymorphs are represented in Fig. 2. Table 1 summarizes the main crystallographic features. As anticipated in Section 2, ϵ - MnO_2 has basically the γ -structure (where domains of rutile exist in a ramsdellite network). However, ϵ - MnO_2 has a higher degree of disorder and tends to show an oriented texture [7,13].

Accommodation of Li^+ in sites of different size and energy results in the formation of Li_xMnO_2 phases with variable x and with a different thermal behaviour. Table 2 shows the Li^+ content of the 8 Li_xMnO_2 samples, together with the amount of unreacted MnO_2 for the samples prepared with stoichiometric LiI.

As shown in Table 2, x in Li_xMnO_2 remains below 0.5 when using 0.55 mol LiI/1 mol MnO_2 . In Ref. [6], R- $\text{Li}_{0.3}\text{MnO}_2$ and R- $\text{Li}_{0.5}\text{MnO}_2$ were reported to be prepared with the stoichiometric amount of LiI. The lithium deficiency entails the formation, upon heating, of Mn_2O_3 resulting from the decomposition of MnO_2 , according to the reactions:

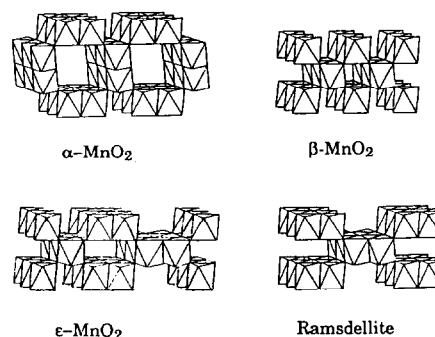


Fig. 2. Crystal structures of MnO_2 polymorphs showing the connection of the MnO_2 octahedra and tunnels shape.

Table 1
Crystallographic characteristics of different forms of MnO_2

MnO_2 -type	Structure-type	Symmetry	Tunnel shape
α - MnO_2	Hollandite	Tetragonal	(1×1) and (2×2)
β - MnO_2	Rutile	Tetragonal	(1×1)
ϵ - MnO_2	Ramsdellite/ rutile intergrowth	Hexagonal	(1×1) and (2×1)
R- MnO_2	Ramsdellite	Orthorhombic	(2×1)

Table 2
Li⁺ content in Li_xMnO₂ and unreacted MnO₂ (for the samples made with s-LiI)

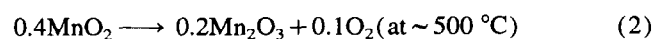
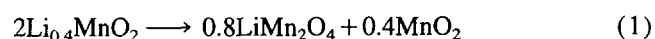
Li _x MnO ₂	x (s-LiI) ^a	x (e-LiI) ^b	%MnO ₂ ^c (chemical titration)	%MnO ₂ ^d (TGA)
α-Li _x MnO ₂	0.40	0.59	20	22
β-Li _x MnO ₂	0.40	0.45	20	28
ε-Li _x MnO ₂	0.46	0.69	9	9
R-Li _x MnO ₂	0.40	0.64	20	23

^a Stoichiometric LiI (0.55 mol/1 mol MnO₂).

^b Excess LiI (about 3 times).

^c As determined from the Mn oxidation state and from Eq. (1) (see below).

^d As determined from the weight loss at ~ 500 °C in the TGA curve due to the reaction MnO₂ → 0.5Mn₂O₃ + 0.25O₂.



In Eq. (1), it is assumed that, at 750 °C, a spinel with an Li⁺ content close to unity is formed. This assumption will be discussed later.

The formation of Mn₂O₃ is confirmed by the X-ray patterns of the spinels obtained at 750 °C (Fig. 3). The main peak of Mn₂O₃, at 2θ at 33 °C, is evident in the spinels derived from α-, β- and R-MnO₂. In contrast, the lower amount present in the spinel derived from ε-MnO₂ is barely visible. The TGA curves (Fig. 4) also show that, at ~ 500 °C, a step is present. From the weight loss corresponding to Eq. (2) (9.2%) and from the loss measured in the step (reported in Fig. 4), the amount of MnO₂ present in Li_xMnO₂ could be determined. There is a good agreement between the values obtained by chemical titration and TGA. Only for β-Li_xMnO₂ is the difference significant.

If the X-ray patterns of Fig. 3 are considered again, some features are worth noting. First, the MnO₂ which most easily converts into spinel is ε-MnO₂. Unlike the three other forms, ε-MnO₂ shows a spinel-like character already at 200 °C. β-MnO₂ starts showing spinel structure at 300 °C. These results are in agreement with previous observations of a greater tendency to form spinels in γ-MnO₂ containing a significant β-MnO₂ component [6]. In our case, the stoichiometry of ε-Li_xMnO₂, with x closer to 0.5, may have favoured this material over β-Li_xMnO₂ (x = 0.4).

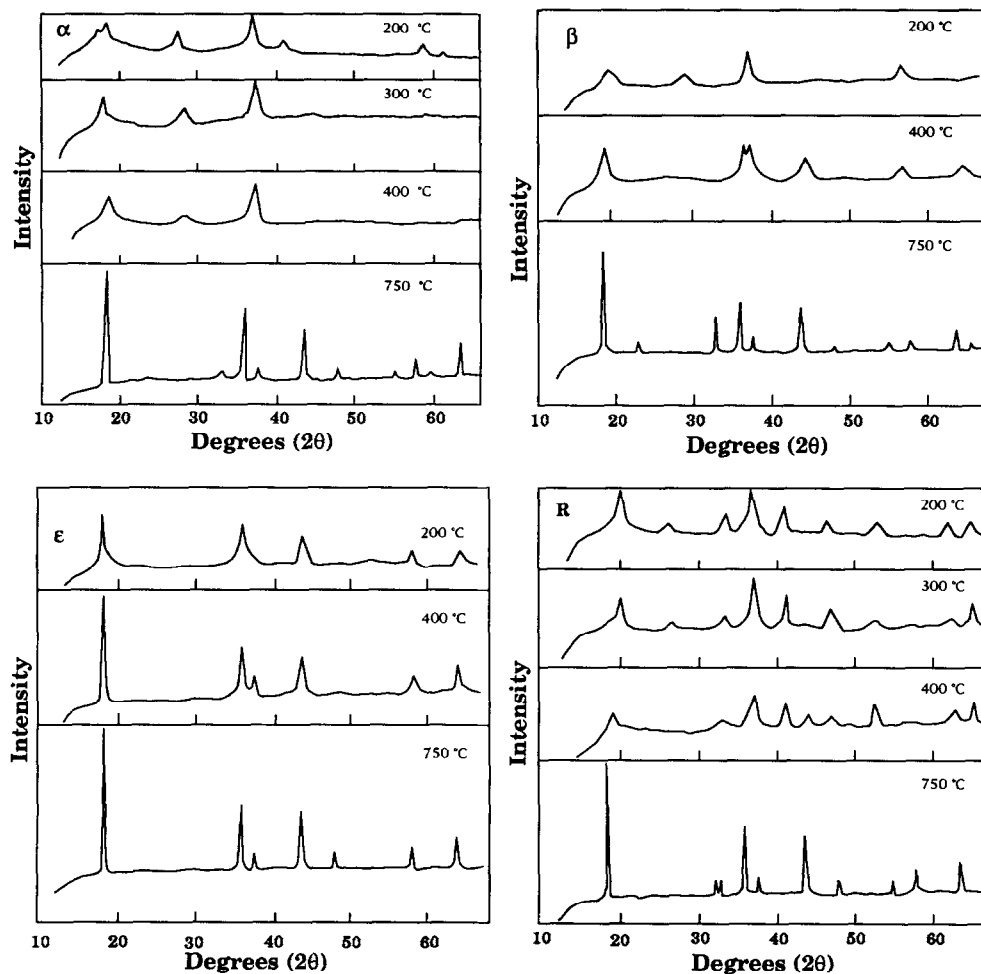


Fig. 3. X-ray patterns of the compounds obtained by lithiating the MnO₂'s with 0.55 mol LiI/1 mol MnO₂.

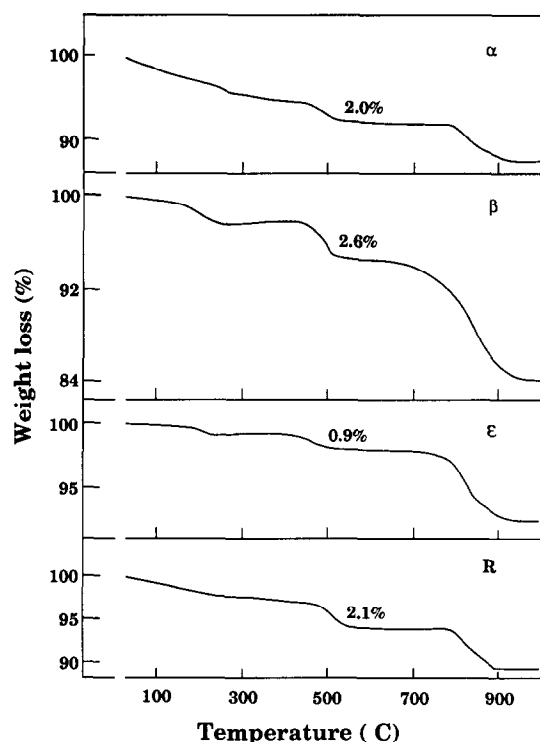


Fig. 4. TGA curves for Li_xMnO_2 obtained with 0.55 mol LiI/1 mol MnO_2 ; 5 °C/min and N_2 atmosphere.

Table 3

Values of the cubic parameter a of the spinels obtained from different MnO_2 's treated with stoichiometric or excess LiI, or synthesized by solid-state reaction (SSR). Average values from the (311), (400) and (440) peaks are given

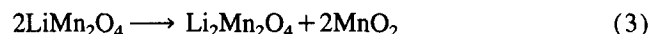
MnO_2 -type	a (Å)		
	s-LiI	e-LiI	SSR
α - MnO_2	8.272	8.218	8.265
β - MnO_2	8.260	8.233	8.298
ϵ - MnO_2	8.268	8.241	
R- MnO_2	8.270	8.228	8.318

As pointed out by Thackeray et al. [6], the driving force for the transformation of lithiated MnO_2 into spinel is the electrostatic interaction between inserted Li^+ and Mn ions in neighbouring face-shared octahedra (Fig. 2). On the basis of this model, it is very likely that in the structures endowed with larger channels, i.e. α - and R- MnO_2 , such interactions are not so strong as the average $\text{Li}^+-\text{Mn}^{+(4-x)}$ distances are greater than in β - or ϵ - MnO_2 . As a result of the $\text{Li}^+-\text{Mn}^{+(4-x)}$ interaction, the latter ions are cooperatively displaced into empty interstitial sites, thus resulting, through a shear mechanism, in the building-up of the cubic close-packed oxygen array [6].

In Table 3, the cubic parameter a of the different spinels is reported. With almost stoichiometric LiI, a values of 8.26–8.27 Å are obtained. Spinel synthesized at 750–900 °C have a of 8.23–8.245 Å [14–16]. It is also known that Li^+ extraction leads to lower a values [14,15]. So, the possibility of

formation of Li^+ -deficient spinels seems rather remote. Values higher than those of conventionally prepared spinels have also been measured in the spinels obtained by solid-state reaction (SSR). Later in the text, this will be further commented upon.

The transformation of the Li_xMnO_2 's into spinels as well as other structural changes are evident in the TGA curves given in Fig. 4. After an initial weight loss (probable desorption of acetonitrile and water), there is a pseudo-plateau during which the spinel formation starts. At ~ 500 °C, unreacted MnO_2 gives rise to Mn_2O_3 . At ~ 800 °C, there is another weight loss which accounts for the reaction:



Of course, newly formed MnO_2 is immediately decomposed into Mn_2O_3 . This weight loss corresponds to 4.4% (48% MnO_2 is present in Eq. (3)) and this is in fair agreement with the values observed (see also Fig. 8). Tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ has been reported to form from LiMn_2O_4 upon heating in air at ~ 900 °C [2]. The easier O_2 loss in an N_2 atmosphere explains the lower temperature here observed. The behaviour of the spinel derived from β - MnO_2 is peculiar, as a remarkable weight loss starting at ~ 700 °C is observed. It seems that this spinel loses a good fraction of O_2 before transforming into $\text{Li}_2\text{Mn}_2\text{O}_4$.

The electrochemical behaviour of the spinels obtained with almost stoichiometric LiI has been evaluated by potential step voltammetry tests. The results are shown in Fig. 5. The following features may be noted: (i) there is a good agreement between the MnO_2 present (see Table 2) and the minimum x attainable when oxidizing $\text{Li}_x\text{Mn}_2\text{O}_4$ ($x = 0.22, 0.29, 0.07$ and 0.25 for the spinels from α -, β -, ϵ - and R- MnO_2 , respectively); (ii) the highest reduction capacity is shown by the spinel from ϵ - MnO_2 ($x = 0.70$), and (iii) the lowest Δx and ΔE (charge/discharge) are shown by LiMn_2O_4 from β - MnO_2 .

On the basis of these results, LiMn_2O_4 from β - and ϵ - MnO_2 were submitted to cycling tests at 1 mA/cm². The

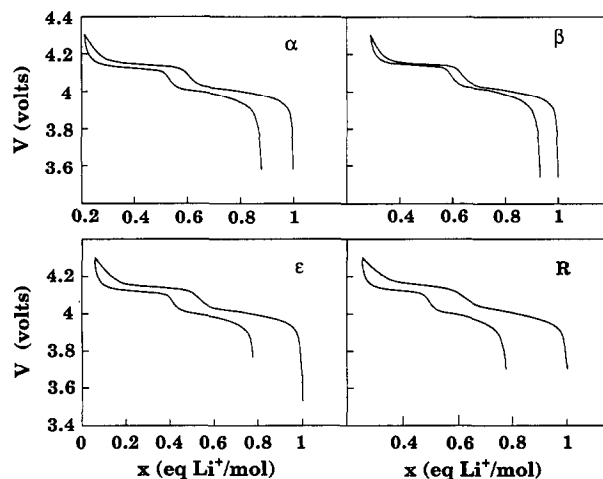


Fig. 5. Potential step voltammetry (10 mV/1 h) for spinels obtained with 0.55 mol LiI/1 mol MnO_2 .

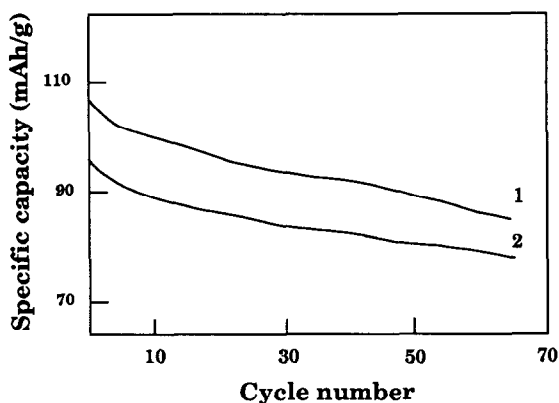


Fig. 6. Cycling tests for spinels obtained from (1) ϵ - and (2) β - MnO_2 , reacted with 0.55 mol $\text{LiI}/1$ mol MnO_2 .

results, shown in Fig. 6, do not compare favourably with those of optimized spinels [1,2] as relatively low and decreasing specific capacities have been measured.

Lithiation of the MnO_2 's with excess LiI also leads to spinel formation, but with some distinctive features. The X-ray patterns of Fig. 7 again show the easier formation of LiMn_2O_4 from ϵ - and β - MnO_2 . In this case, both show a spinel-like pattern at 200 °C. For α - and R- MnO_2 , one might place the onset of spinel formation at 300 to 400 °C. The a values (see Table 3) for the spinels from β -, ϵ - and R- MnO_2 are rather in agreement with values previously found at 750 °C [14]. Only for the material derived from α - MnO_2 , is a a little lower.

From the x values of Table 2 for $\text{Li}_x\text{Mn}_2\text{O}_4$ prepared with excess LiI , one may anticipate that spinel formation from α -, β - and R- $\text{Li}_x\text{Mn}_2\text{O}_4$ entails the elimination of Li^+ in excess of 0.5. First of all, we have to observe that all x is well below 1. For R- $\text{Li}_x\text{Mn}_2\text{O}_4$ prepared with the same technique, an $x=0.9$ had been found by atomic adsorption spectroscopy [6]. We have no explanation for this discrepancy.

The course of the reaction leading to spinel was again followed by TGA and DTA. As shown in Fig. 8, the trend of

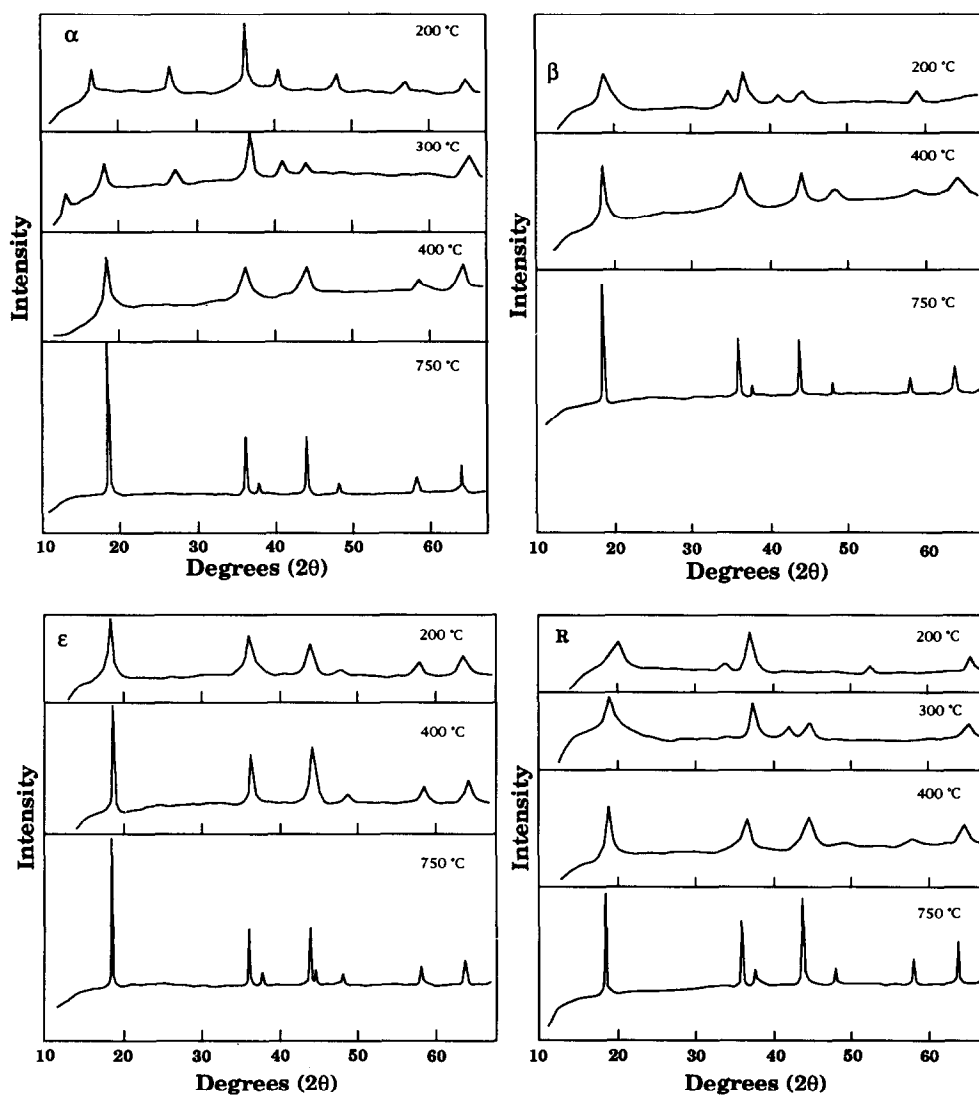


Fig. 7. X-ray patterns of the compounds obtained by lithiating MnO_2 compounds with excess LiI .

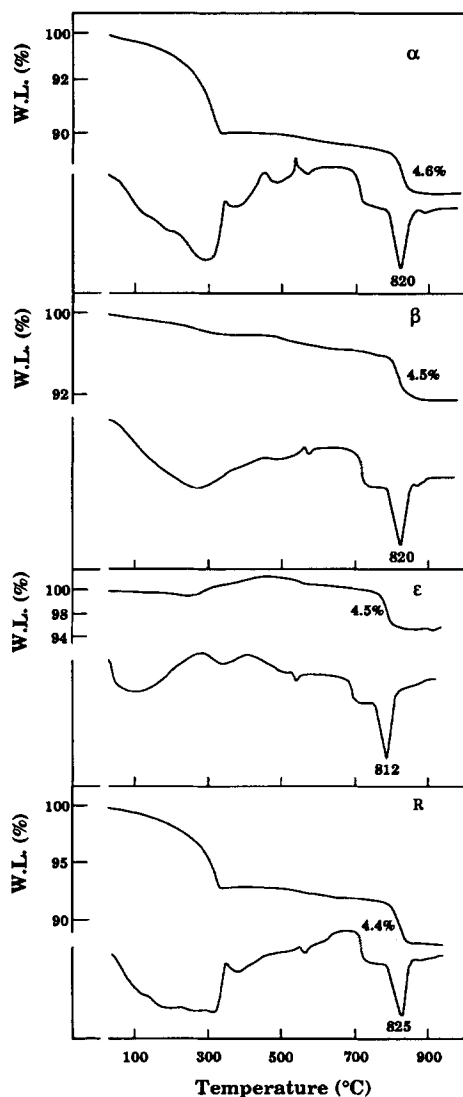


Fig. 8. TGA (upper) and DTA (lower) curves for Li_xMnO_2 obtained with excess LiI.

the TGA curves are qualitatively similar to those given in Fig. 3. However, α - and R- Li_xMnO_2 have a remarkable weight loss (9.0% and 7.7%, respectively) when heated up to $\sim 300^\circ\text{C}$. The possibility cannot be excluded that in their (2×2) and (2×1) large tunnels, Li^+ may be accommodated in a solvated state. Solvent molecules would be completely removed only upon heating to relatively high temperatures.

For ϵ - Li_xMnO_2 only, a peculiar weight gain was observed between ~ 280 and 550°C . The possible formation, in the

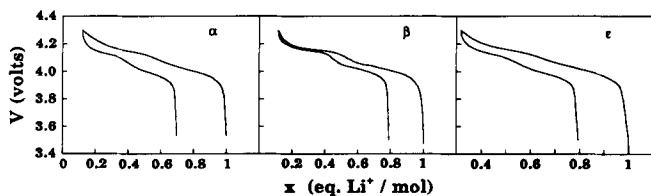
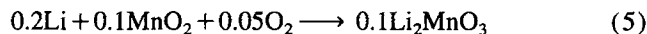
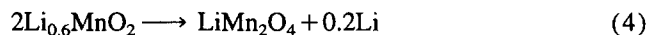


Fig. 9. Potential step voltammetry (10 mV/1 h) for spinels obtained with excess LiI.

N_2 atmosphere, of a compound like Li_3N was ruled out by repeating the experiment in an Ar atmosphere: the same trend was observed.

The formation of LiMn_2O_4 from compounds of the general formula $\text{Li}_{0.5+x}\text{MnO}_2$ leads us to suppose that an excess of Li is extruded and, in an inert atmosphere, combines with some unreacted MnO_2 :



O_2 in Eq. (5) is likely to come from the decomposition of MnO_2 . In all TGA curves given in Fig. 8, one may notice a small inflection near 500°C , possibly due to the reaction of Eq. (2). Li_2MnO_3 is known to accompany LiMn_2O_4 when excess LiOH (or LiNO_3) is used in the synthesis [2]. We have obtained evidence of its formation in the spinel derived from ϵ - Li_xMnO_2 , i.e., the material with the highest Li^+ content. As shown in Fig. 7, a peak at $2\theta = 44.6^\circ$ ($d = 2.028 \text{ \AA}$) appears. By using the x values in Table 2 and Eqs. (4) and (5), we have calculated the following contents of Li_2MnO_3 : 6, 11 and 8.3% in the spinels derived from α -, ϵ - and R- Li_xMnO_2 , respectively.

All TGA curves in Fig. 8 again show the formation of tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ at 812 to 825°C . The weight loss ($\sim 4.5\%$) confirms this transition. The DTA curves have a large and broad endothermic peak corresponding to the initial weight loss. It is remarkable that the temperature of the peak decreases as the ease of spinel formation increases (see Fig. 7). For the spinel derived from ϵ - MnO_2 , this temperature is below 100°C . The features around 500°C are probably connected with O_2 evolution from MnO_2 . Finally, the clear endothermic peak above 800°C marks the formation of $\text{Li}_2\text{Mn}_2\text{O}_4$. The lowest temperature (812°C) is for the spinel from ϵ - MnO_2 .

For three of the spinels obtained with excess LiI, potential step voltammetry tests were run (Fig. 9). For LiMn_2O_4 from α - and β - MnO_2 , an extraction of 0.9 Li^+ is possible, together with a discharge capacity corresponding to $x = 0.58$ and $x = 0.66$, respectively. The spinel from ϵ - MnO_2 , containing the highest amount of Li_2MnO_3 , has $x = 0.68$ in charge and $x = 0.43$ in discharge conditions. These capacities are lower than those of the spinels from stoichiometric LiI (equal only for the spinel from β - MnO_2). One therefore cannot foresee a good performance in an extended cycling.

Given the difficulty to synthesize Li_xMnO_2 compounds with the exact composition $x = 0.5$, we have tried to prepare them starting from α -, β - and R- MnO_2 lithiated at 380°C with the stoichiometric amount of LiOH (real LiOH: MnO_2 ratio, 1.02:2). Then, the Li_xMnO_2 compounds were heated at 750°C to convert them into spinels. In all cases, a remarkable formation of Mn_2O_3 was observed with the following scale: $\text{R} > \beta > \alpha$. Only when using excess LiOH (1.2:2), a limited amount of Mn_2O_3 was detected, but, of course, the presence of lithiated by-products (Li_2O , Li_2MnO_3), which are electrochemically inactive, does not allow a good electrode perform-

ance to be achieved. In Table 3, the cubic parameter a of the spinels synthesized by SSR is also reported. The values are quite high and, surprisingly, follow the order of Mn_2O_3 content. As the values obtained with the samples prepared with stoichiometric LiI are also high (first column of Table 3), the obvious conclusion is that Mn_2O_3 influences the spinel structure. However, we cannot say how this happens and why the a values in the samples obtained with LiI do not strictly follow the order of Mn_2O_3 content.

4. Conclusions

The lithiation of MnO_2 polymorphs always gives rise to products from which, upon heating, spinels are formed regardless of the initial Li^+ content. β - and ϵ - MnO_2 show a spinel-like structure at lower temperatures with respect to α - and R- MnO_2 , possibly because of the narrower tunnels of the former. In other words, the $\text{Li}^+ - \text{Mn}^{(4-x)+}$ repulsion would be stronger for β - and ϵ - MnO_2 , this facilitating the cooperative displacement of Mn ions into empty interstitial sites.

The spinels obtained with excess LiI show cubic parameters a rather similar to those reported for the classical syntheses with γ - MnO_2 , whilst with stoichiometric LiI and with the solid-state reactions higher values were obtained. The by-product Mn_2O_3 has certainly a role in this respect, not yet elucidated.

As all spinels formed by the polymorphs studied here contain different amounts of Mn_2O_3 and/or Li_2MnO_3 , their electrochemical behaviour is accordingly impaired.

Acknowledgement

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