

Synthesis of an efficient LiMn_2O_4 for lithium-ion cells

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Abstract

A technique is described which allows to obtain an LiMn_2O_4 cathode showing high material utilization and extended cycleability at high rates in Li or Li-ion cells. Basically, the precursors, e.g. chemical MnO_2 and LiOH , were ground together in the presence of a dispersing agent, e.g. alcohol, so to reduce the particle size to a few microns and to minimize the formation of side products during the synthesis. The spinel so obtained shows limited capacity fading at a current density of 6 mA/cm^2 (520 mA/g).

Keywords: Lithium-ion cells; Lithium; Manganese

1. Introduction

A major breakthrough in the realization of rechargeable non-aqueous batteries has occurred with the introduction of the lithium-ion concept [1,2]. Up to now, the cathode material of choice in these batteries has been LiCoO_2 by virtue of a good specific capacity ($0.12\text{--}0.13 \text{ Ah/g}$) which has a limited fade upon optimized cycling [1]. As is known, Co is rather expensive (2.5 times more than Ni and 7.5 times more than Mn) [3] and its compounds pose some environmental concerns. Furthermore, it is sensitive to overcharge insofar as its structure is adversely affected by an extended delithiation.

Possible alternatives are represented by LiNiO_2 and LiMn_2O_4 [4]. The latter has some distinct advantages over the other two oxides: it can be prepared from inexpensive precursors, it is non-toxic and can stand overcharge, as full delithiation leads to the stable $\lambda\text{-MnO}_2$. The theoretical specific capacity of the Mn spinel is lower than that of LiNiO_2 or LiCoO_2 , but optimized syntheses can afford capacities of $\sim 0.12 \text{ Ah/g}$ [5,6].

A further advantage of properly prepared spinels is a high rate capability. The D_{Li^+} values do not greatly differ in the three cathode materials, being around $10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ in a broad compositional range [7–9]. Nonetheless, LiMn_2O_4 shows a better rate capability as it can be prepared with particles having a good porosity (surface area $> 5 \text{ m}^2 \text{ g}^{-1}$), while LiNiO_2 and LiCoO_2 are formed by smooth, tiny particles of low surface area ($\sim 1 \text{ m}^2 \text{ g}^{-1}$).

We have developed a new synthesis enabling to obtain an Mn spinel with a homogeneous composition and a relatively high surface area ($\sim 10 \text{ m}^2 \text{ g}^{-1}$). This material shows remarkably high rate capabilities and retains a good fraction of its initial capacity when cycled in a tough regime.

2. Experimental

Stoichiometric amounts of the lithiating agent (anhydrous LiOH or LiNO_3) and Faradiser M MnO_2 (IBA 12 from Sedema, Tertre, Belgium) were pre-mixed and poured in a planetary micro mill (Fritsch, Pulverisette 7) with stainless-steel balls. A dispersing liquid, e.g. alcohol or cyclohexane, was added to form a slurry which was ground overnight through combined shaking/rotation actions. The slurry was dried at 80°C to evaporate the liquid and the resulting powder ($5\text{--}10 \text{ g}$) was kept at 730°C in the air for two days. The cubic a parameter of this spinel was, on average, 8.23 \AA . In a comparative test, Faradiser M was ground alone with the dispersing liquid and, then, reacted at 730°C with the Li salt. A third spinel was synthesized with IBA 21 MnO_2 (median particle diameter, 4 versus $38 \mu\text{m}$ for IBA 12).

The electrochemical tests were performed in laboratory coin cells using LiPF_6 -ethylene carbonate/dimethyl carbonate (2:1) as the solution, glass fiber (Whatman GF/A) as the separator and Li as the anode.

3. Results and discussion

A suitable Mn spinel to be used as a cathode is normally synthesized by a solid-state reaction between a lithiating

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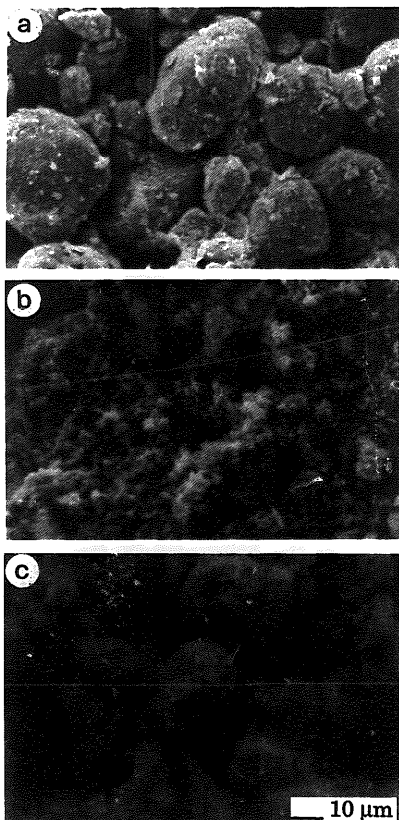


Fig. 1. SEM pictures of MnO_2 (CMD, Faradiser M): (a) original; (b) after grinding overnight with LiOH (the latter eliminated by washing), and (c) after grinding without LiOH .

agent (LiOH , LiNO_3 or Li_2CO_3 , all decomposing into Li_2O at high temperatures) and MnO_2 at 700–800 °C [5]. The initial morphology of MnO_2 is basically retained during the spinel formation, at least for temperatures below ~ 800 °C, while higher temperatures result in the formation of particles resembling those of $\text{LiNiO}_2/\text{LiCoO}_2$ [10]. Therefore, if one aims at obtaining LiMn_2O_4 with small and porous particles, so to enhance its cycleability and rate capability, the precursor MnO_2 has to be based on the same particles. Commercially available battery-grade MnO_2 's normally have median particle diameters above 30 μm [11]. An example is offered by CMD Faradiser M (IBA 12) (Fig. 1(a)) which has a medium size of 38 μm and a surface area of 105 $\text{m}^2 \text{g}^{-1}$ [11].

On the other hand, the lithiating agent is also formed by large particles. An example is given by the most widely used one, e.g. LiOH . As shown in Fig. 2(a), particles with diameters of some hundreds of microns exist in the untreated hydrated material. LiOH melts at 450 °C, but its limited amount in the reaction mixture ($\text{LiOH}:\text{MnO}_2 = 1:2$, molar and volumetric ratio) does not grant a homogeneous dispersion around the grains of the Mn oxide. So, a reduction of the particle size of both reactants may have a positive effect.

In order to simultaneously achieve a high degree of micronization for them, a slurry was made and ground as described above. The effect of this grinding procedure on the MnO_2 particles is shown in Fig. 1(b): a homogeneous reduction to few microns was obtained. The above procedure was repeated with Faradiser M, but without the lithiating agent. The micro mill proves to be more efficient than other devices in reducing the particle size (Fig. 1(c)). However, one can notice that the particles of Fig. 1(b) are smaller and more homogeneous.

In a separate experiment in which $\text{LiOH} \cdot \text{H}_2\text{O}$ was ground alone, this material too showed a remarkable reduction to small particles ($\sim 10 \mu\text{m}$) (Fig. 2(b)).

Grinding of the slurry also grants a thorough mixing of the two components. It is often experienced, in the solid-state synthesis of LiMn_2O_4 , the formation of side products coming from incomplete mixing. Zones where excess LiOH is present result in the formation of the rock-salt phase Li_2MnO_3 , whereas excess MnO_2 produces Mn_2O_3 (both electrochemi-

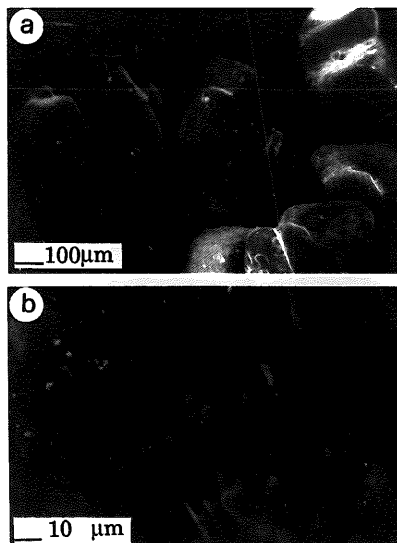


Fig. 2. SEM pictures of $\text{LiOH} \cdot \text{H}_2\text{O}$: (a) original, and (b) after grinding for 3 h.

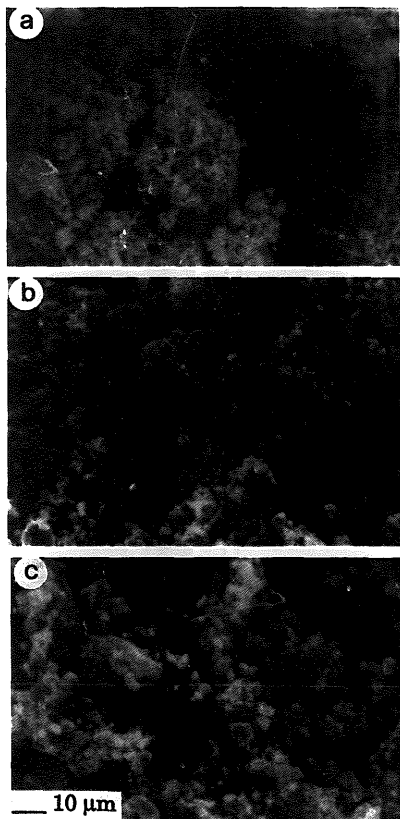


Fig. 3. SEM pictures of different LiMn_2O_4 : (a) from the slurry of LiOH and MnO_2 ; (b) from ground-alone MnO_2 , and (c) from IBA 21.

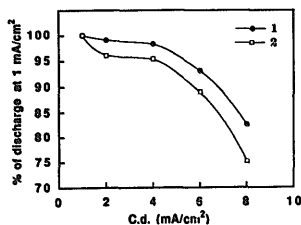


Fig. 4. Influence of current density on the capacity retention of LiMn_2O_4 : (1) from the slurry of LiOH and MnO_2 ; (2) from ground-alone MnO_2 .

cally inactive). This requires regrinding between annealing treatments for an improved performance [12].

As a matter of fact, small-particle battery-grade MnO_2 is also commercially available. IBA 21 is an EMD with a median particle diameter of $4 \mu\text{m}$ and a surface area of $40 \text{ m}^2 \text{ g}^{-1}$ [11]. We have used this material too in the synthesis of the spinel for the sake of comparison.

In Fig. 3(a), the spinel obtained with the present technique, after heating at 730°C for two days, is shown. It is formed by very fine grains of micron and submicron sizes as the synthesis itself has some grinding effect. In Fig. 3(b) and (c), the morphology of LiMn_2O_4 from ground-alone MnO_2 and from IBA 21 MnO_2 , respectively, is shown. Their larger particles are evident.

All spinels were tested as cathodes in laboratory coin cells. In these preliminary tests, a Li anode and a liquid electrolyte (see Section 2) were used. To evaluate the rate capability at different current densities, the cells were previously submitted to ten cycles at 1 mA cm^{-2} . In this way, a reasonably stable capacity was reached. In Fig. 4, the better performance of the spinel prepared by the slurry technique is shown. It has to be noted that at the medium rate of 1 mA cm^{-2} , the novel synthesis produces a specific capacity 7% higher with respect to that of the other spinel. This may be the sum of two factors: a lower amount of byproducts (Li_2MnO_3 , Mn_2O_3) and a better material utilization in small particles of high surface area. BET analysis of the spinels of Fig. 3 has given the following results: $4 \text{ m}^2 \text{ g}^{-1}$ for the spinel from IBA 21; $5 \text{ m}^2 \text{ g}^{-1}$ for the spinel from ground-alone Faradiser M, and 9–10 $\text{m}^2 \text{ g}^{-1}$ for the one prepared with the slurry technique.

The good performance brought about by this synthesis is more evident in Fig. 5, where the cycling behaviour at high rate is compared. In this experiment, also including the spinel from IBA 21, a discharge rate of 6 mA cm^{-2} (3.5 C or 520 mA g^{-1}) was chosen, while recharge was performed at 1 mA cm^{-2} (V limits: 3.40–4.35). To the best of the authors' knowledge, cycling at this rate has not been reported thus far in the literature. As cycling progresses, the capacity fades to a much more limited extent for the spinel of the slurry technique. Again, this comes from its being formed by highly porous, small particles. Fast Li uptake/removal is favoured by this morphology, whilst the larger and less porous particles

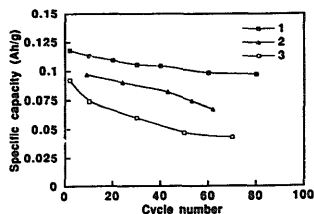


Fig. 5. Cycling of $\text{Li/LiMn}_2\text{O}_4$ cells at $I_d = 6 \text{ mA cm}^{-2}$ (3.5 C or 520 mA g^{-1}) and $I_c = 1 \text{ mA cm}^{-2}$: (1) from the slurry of LiOH and MnO_2 ; (2) from ground-alone MnO_2 ; (3) from IBA 21.

of the other spinels show decreasing charge/discharge efficiencies. Lithiation of these latter spinels preferentially occurs in the smaller particles and in the outer regions of the larger ones. These concentration gradients create overpotentials which reduce, cycle after cycle, the amount of Li^+ which can be inserted down to a pre-fixed voltage limit.

A surface area of $\sim 10 \text{ m}^2 \text{ g}^{-1}$ for the spinel might create some concern in terms of self-discharge, because it could favour electrolyte decomposition [13] or spinel dissolution [14]. We have recently undertaken self-discharge experiments with spinels of 0.7, 6 and $11 \text{ m}^2 \text{ g}^{-1}$ [15]. Surprisingly enough, self-discharge has proven to be inversely related to surface area. We are seeking the rationale for this.

The results presented clearly demonstrate that, with a proper grinding/mixing procedure of the precursors, LiMn_2O_4 can be obtained in a form affording cycling at high rates with a limited capacity fade in Li or Li-ion cells.

Acknowledgements

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