

Ball-milled Li_7MnN_4 : a high rate negative electrode material for lithium-ion batteries

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In Li-ion batteries, graphite is used as negative electrode but it suffers of the formation of a solid electrolyte interphase (SEI) leading to low rate capability and moderate cycling performance. To circumvent this problem, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was proposed as rechargeable negative electrode with a working potential near 1.5 V, a high rate behavior, excellent cycling properties but with a limited specific capacity of 175 mAh g^{-1} . Therefore more competitive anode materials must be found allowing the benefits of enhanced safety. Within this framework, lithium transition metal nitrides have received considerable attention and especially 2D lithiated transition metal nitrides with a layered structure such as $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ and other compositions $\text{Li}_{3-2x}\text{Co}_x\text{N}$ ($0.1 \leq x \leq 0.44$) [1-4].

Some works also report that a 3D metallic nitride, Li_7MnN_4 exhibiting an antiferroite structure, is a good candidate anode material with a rechargeable specific capacity of 210 mAh g^{-1} at about 1.2 V [5]. However little effort has been spent to investigate its cycling properties. The major drawback of this material being its low rate capability with a capacity which does not exceed 100 mAh g^{-1} at a 1C rate [6].

With the aim of optimizing the rate performance of Li_7MnN_4 we demonstrate here the promoting effect of an appropriate ball-milling process of this ternary nitride. In order to completely understand its electrochemical properties we highlight its structural response upon the first Li extraction-insertion cycle using *in operando* XRD experiments. A 3-phases mechanism involving two wide biphasic regions (for $0.1 \leq x \leq 0.8$ and $0.8 \leq x \leq 1.2$) and a solid solution behaviour ($1.2 \leq x \leq 1.5$) for $\text{Li}_{7-x}\text{MnN}_4$ explains its electrochemical fingerprint and the excellent cycle life of this promising negative electrode for Li-ion batteries.

The rate capability of Li_7MnN_4 is examined as a function of ball-milling conditions. Electrochemical data are discussed in relation with SEM and XRD characterization of ball-milled samples. The high rate behavior of ball-milled Li_7MnN_4 at C rate and 5C rate is analyzed without any conditioning electrochemical step. At 1C the optimized experimental conditions are found at 500 rpm for 1h with the highest specific capacity of 240 mAh g^{-1} and the best cycle life characterized by a specific capacity retention of 97% after 50 cycles. This very high capacity value combined with a working potential of $\approx 1.2 \text{ V}$ instead of $\approx 1.5 \text{ V}$ for the best rechargeable Li intercalation anode material, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, makes Li_7MnN_4 a promising negative electrode without the drawback of the SEI formation in the 1.6V/1V potential range as cycling limits [7]. At 5C once again the ball-milling effect results in a stable capacity vs cycles, around 120 mAh g^{-1} , which compares very well with the behavior achieved for

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ while the pristine material is practically inactive.

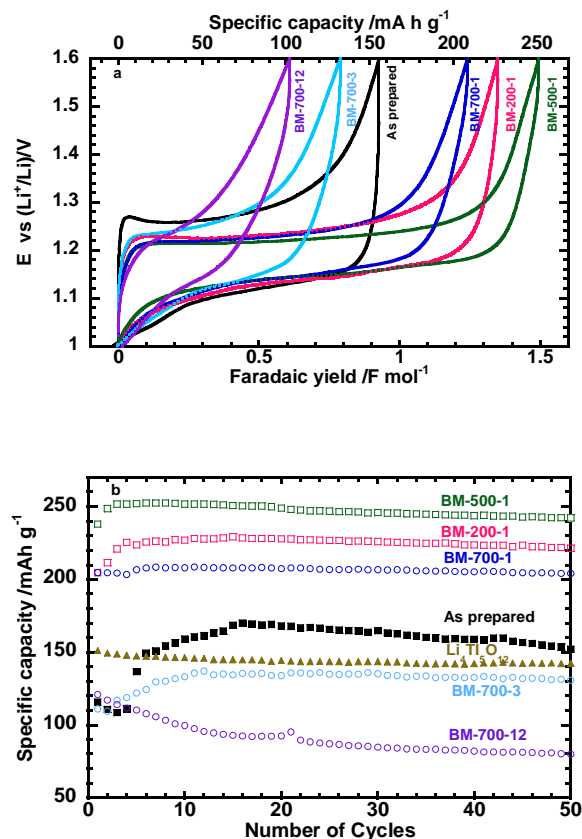


Figure 1: Influence of the ball-milling on the Li_7MnN_4 cycling behavior at C rate in the 1.6V-1V potential range: (a) charge-discharge curves for cycle 10; (b) evolution of specific capacity as a function of the number of cycles.

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