

Li₈MnN_{5-y}O_y AS ANODE IN LITHIUM ION BATTERIES

M.R. Palacín*, J. Cabana*, G. Rousse[†]

* Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB E-08193 Bellaterra, Catalonia, SPAIN.
[†] Physique des Milieux Condensés UMR 7602 Université Pierre et Marie Curie. 4 Pl.Jussieu F-75252 Paris Cedex 05, FRANCE

The exponential growth in portable electronic devices has created an ever increasing demand for compact and light-weight power sources. Lithium based batteries are emerging as the prime power source for these applications due to their higher energy density compared to other rechargeable battery systems. It is now more than ten years after Li-ion batteries entered the market and a great deal of work has been devoted to the search on alternative materials with better performances from diverse points of view (e.g. capacity, cycle-life, safety or cost). The diversity of materials investigated to substitute carbon as the negative electrode includes intermetallic compounds, vanadates, tin composite oxides or, more recently, binary oxides.

One of the most “exotic” class of new anode materials proposed is lithium transition metal nitrides, the compound Li_{3-x}Co_xN, achieving a stable reversible capacity of 600 mAh/g.¹ In general, one of the major drawbacks to the practical use of lithium transition metal nitrides is their air and moisture sensitivity, that would hinder handling during manufacturing. The chemistry of lithium transition metal oxynitrides is even less explored than that of nitrides, but the few examples known seem to indicate that this compounds present higher ambient stability, as could be expected from the fact that they are already partly oxidized.

Within this scenario, the aim of our work was to survey the Li-Mn-N-O system trying to formulate new compounds that might present interesting redox properties taking into account crystal chemical parameters and analogies with other existing oxynitrides or nitrides such as Li₇MnN₄.^{2,3} This compound presents an ordered anti-fluorite structure and a reversible electrochemical capacity of about 310 mAh/g, with a capacity loss of 12% after 40 cycles.

Following a similar synthetic procedure, we have successfully obtained the first lithium manganese oxynitride: Li₈MnN_{5-y}O_y (y~1.5). This compound presents also an anti-fluorite type structure, but disordered, with space group Fm-3m and cell parameter $a = 4.73 \text{ \AA}$ (fig. 1) as determined by X-ray and neutron powder diffraction data.⁴ Its ambient stability is higher than for Li₇MnN₄ and the electrochemical performances are slightly better. When cycled between 1.9 and 0 V versus Li⁰-Li⁺, a reversible capacity of about 300 mAh/g ($\Delta x \approx 2.2$) (fig. 2) is obtained. The capacity loss upon cycling is small (less than 5 % after 40 cycles) (fig. 3). The structural evolution of this phase upon cycling has also been investigated by in situ X-ray powder diffraction and ex situ neutron powder diffraction data (D20 diffractometer at ILL, France)

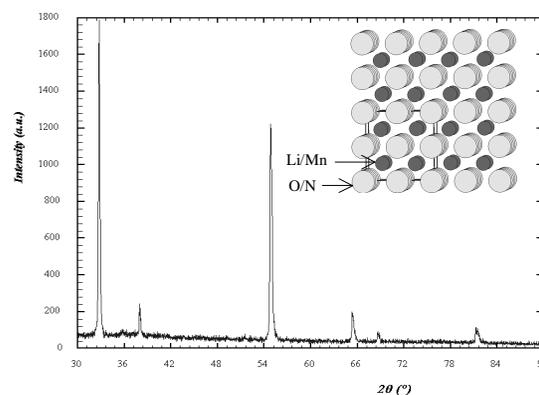


Fig. 1: X-Ray powder diffraction pattern and crystal structure of Li₈MnN_{5-y}O_y (y~1.5).

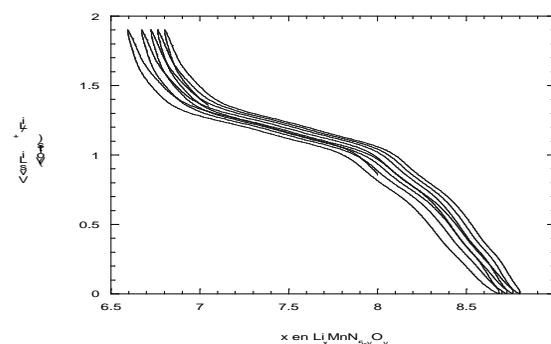


Fig. 2: Potential-composition profile for Li₈MnN_{5-y}O_y recorded in galvanostatic mode at C/10.

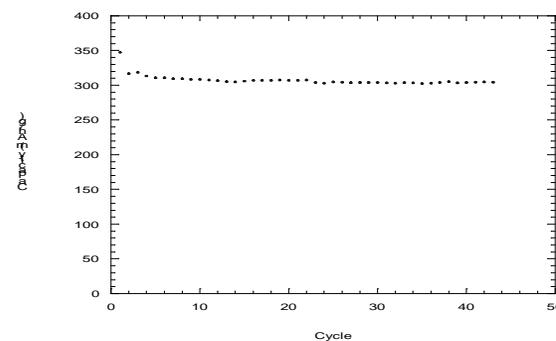


Fig. 3: Plot of the total discharge capacity between 0 and 1.9V versus cycle number for Li₈MnN_{5-y}O_y

References:

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4. J. Cabana, G. Rousse, A. Fuertes and M.R. Palacín. *Submitted for publication*.