Supporting Information

Nanostructured Li_2MnO_3 : a Disordered Rock Salt type structure for High Energy Density Li ion batteries

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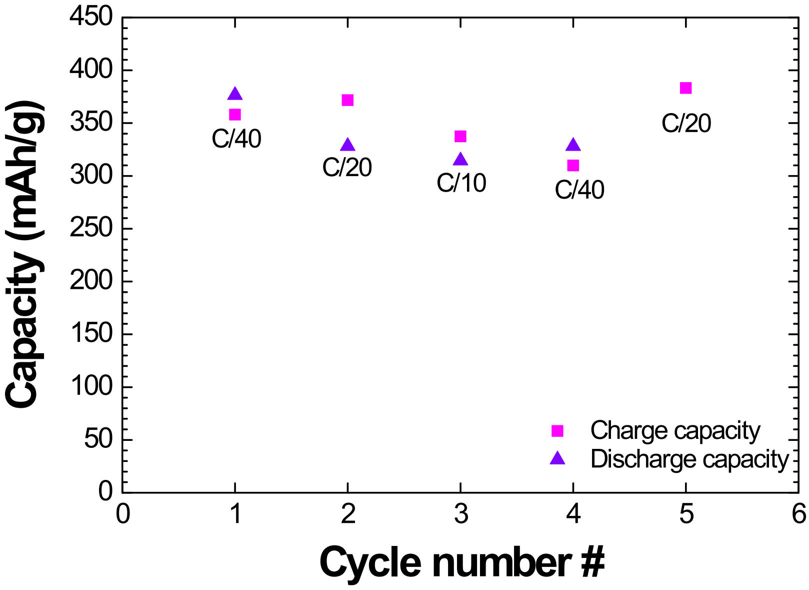

Figure S1: Evolution in cycling of the charge (up to 4.4V, 4.6V and 4.8V) and discharge (up to 1.2V) capacities of the Li_2MnO_3 material. The galvanostatic cycles have been realized using various rates. During the first cycle, the material has been charged to 4.4V and discharged to 1.2V, with a rate of $1Li^+$ in 20 hours (11.5 mA/g, C/40). For the second cycle, a rate of 1 Li^+ in 10 hours (23 mA/g, C/20) is used between 1.2V and 4.6V. The third cycle is characterized by a rate of $1Li^+$ in 5 hours (46 mA/g, C/10), between 1.2V and 4.8V. The fourth and the fifth cycle have been realized between 1.2V and 4.8V, with at C/40 and C/20 respectively).

This graph points out that the electrochemical performances of the five first cycles, at different rates between C/40 and C/5, are larger than 300 mAh/g. At higher rates, the electrochemical performances are not drastically decreased. Furthermore, a good stability and reversibility in cycling is denoted.

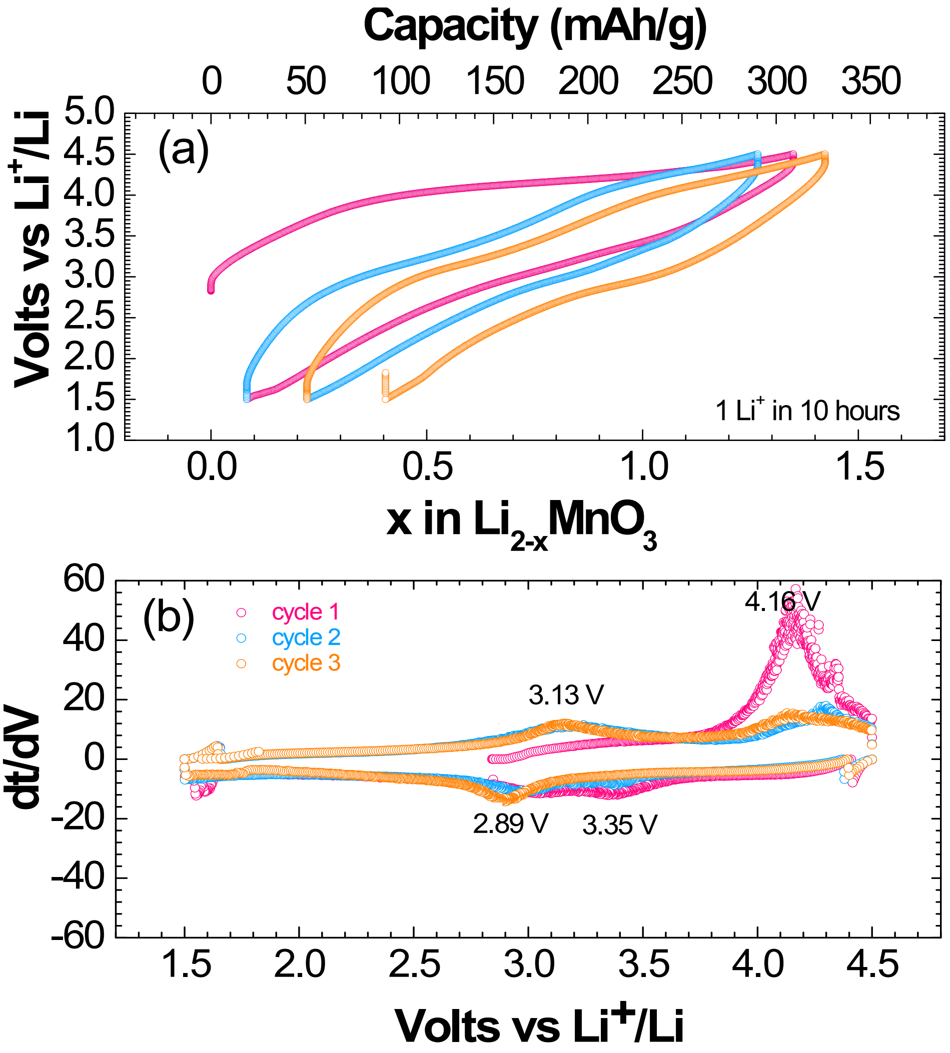

Figure S2. Electrochemical properties. (a) Galvanostatic curves of the Li_2MnO_3 material obtained with a rate of 1 Li^+ in 10 hours (23 mA/g) between 1.5 V and 4.5 V; (b) Derivative curves of the three first cycles.

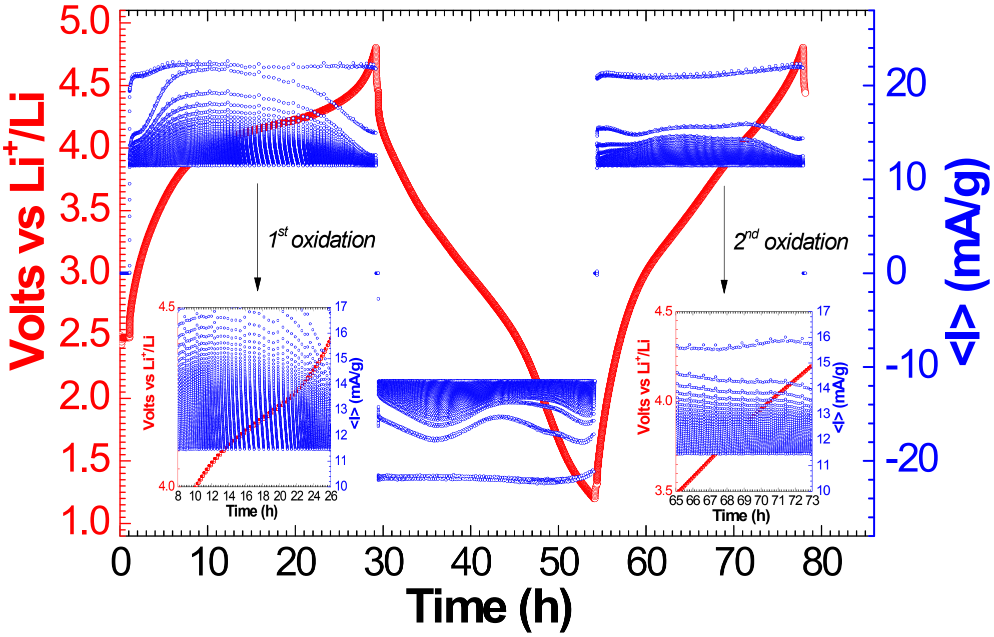

Figure S3: Potentiostatic Intermittent Titration Technique (PITT) curve of the first cycle and the second charge, for the Li_2MnO_3 material, at a rate of 1 Li$^+$ in 20 hours (11.5 mA/g). The material is charge directly to 4.8V and discharged to 1.2V. The enlargements are showing the two different galvanostatic processes occurring on the first and the second oxidations and evidence the structural transformation upon the first charge. On the second charge, a different exponential decay of the current is denoted, characterizing a solid solution process.

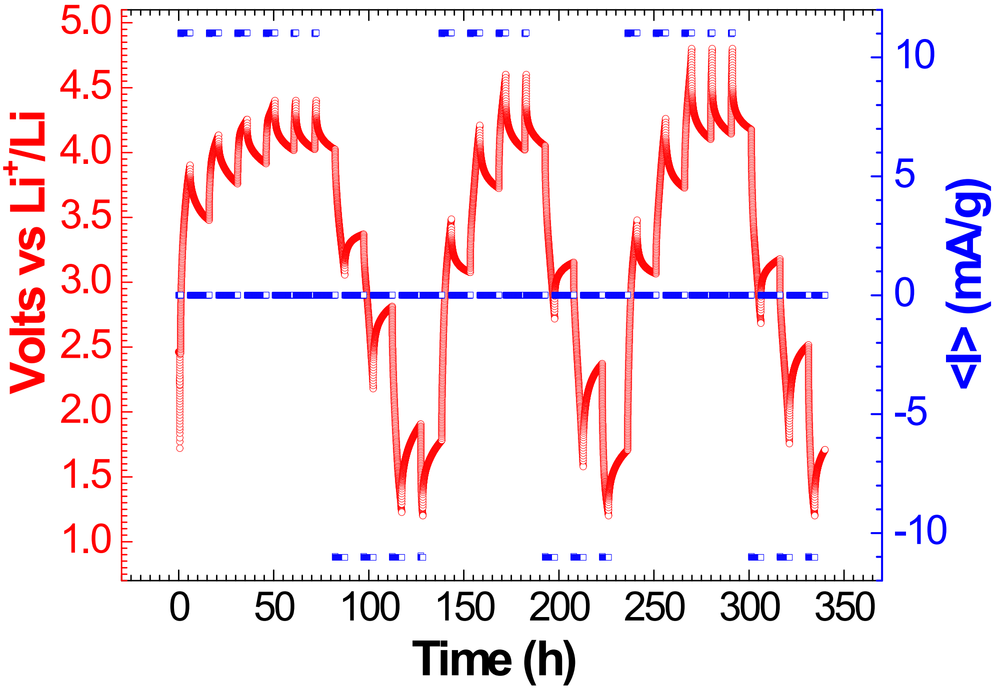

Figure S4: Galvanostatic Intermittent Titration Technique (GITT) curve of the three first cycles, obtained for a rate of 1 Li$^+$ in 20 hours (11.5 mA/g). Each step of current is hold during 5 hours and is followed by 10 hours relaxation. The first oxidation has been realized to a potential of 4.4V, the second and the third oxidations have been realized up to 4.6V and 4.8V, respectively.

We note an increase of the polarization at the end of each oxidation process. This behavior is exaggerated at potentials higher than 4.6V. Moreover, during the first charge no voltage plateau is observed.

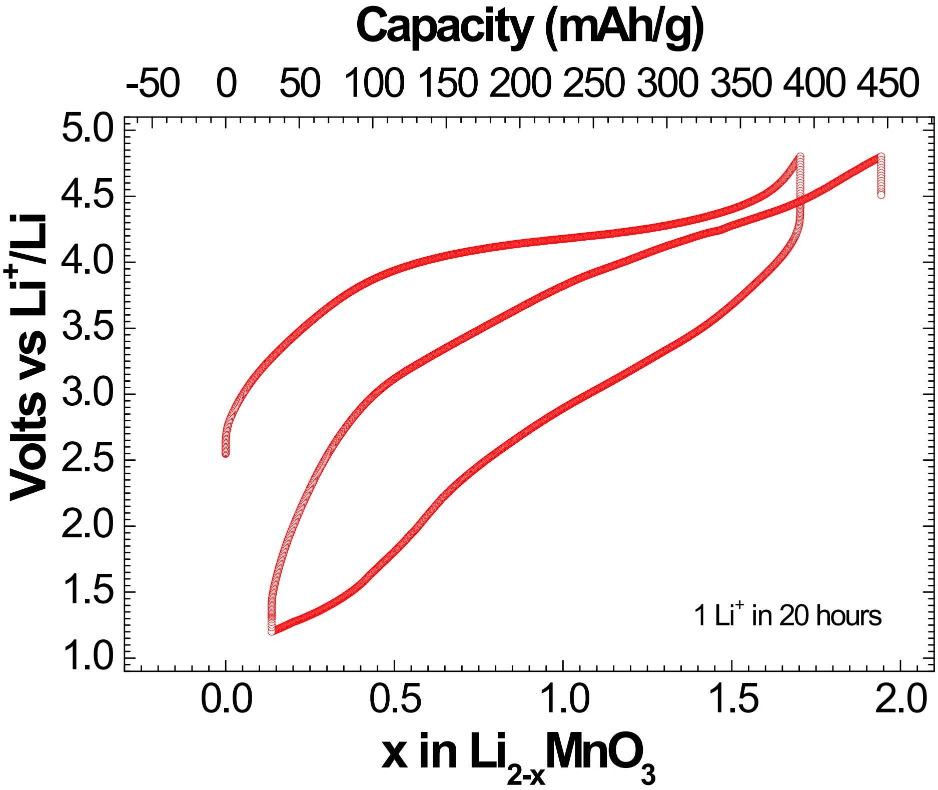

Figure S5: Galvanostatic curve of the Li_2MnO_3 material (first cycle and second charge), charging directly to 4.8V, obtained with a rate of 1 Li^+ in 20 hours (11.5 mA/g). The first oxidation to 4.8V allows to extract 1.7 Li^+ ion, providing a capacity of 390 mAh/g. In comparison to the batteries which are first oxidized to 4.4V (in the first charge), an irreversible capacity of 30 mAh/g is obtained after the first cycle, and no plateau voltage is denoted at 4.5V, as it is observed in the literature for the monoclinic Li_2MnO_3. The second cycle is characterized by a larger charge capacity equal to 415 mAh/g (1.8 Li^+ ion extracted), and by a larger polarization of about 700 mV.

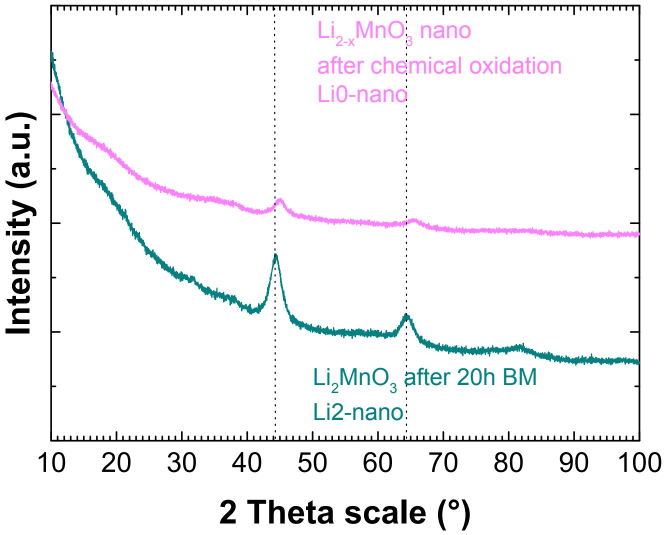

Figure S6: XRD patterns of the nano-structured Li_2MnO_3 materials: as-prepared (Li2-nano) and after chemical oxidation with NO_2BF_4 (Li0-nano). A shift to higher angles is observed between the as prepared Li2-nano and the Li0-nano. This result is in agreement with a decrease of the volume of the cell after the oxidation process, and consequently indicates a decrease of the cell parameter after the delithiation.