SUPPORTING INFORMATIONS

Atomic Layer Deposition of nanometer-thick Li_3PO_4 protective layer on $LiNi_{0.5}Mn_{1.5}O_4$ films: dream or reality for long term cycling?

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Highlighting the cathode electrolyte interface by X-Ray micro-diffraction analyses. We perform structural characterization of the LNMO film before and after 50 cycles. The results are reported in **figure S1e**. The evolution of the crystal structure upon charge / discharge cycling on the average atomic structure was studied by X-ray diffraction using the microdiffraction configuration (see experimental paragraph) on the same areas as reported previously for chemical mapping and corresponding to the film surface of pristine and after 1, 10 and 50 cycles-samples. These cycling zones being ~ 7 mm in diameter, to check the homogeneity (or not) of the analysis, we used a programmable X-Y table allowing translations and we realized a mapping of these zones decomposed into 16 distinct analyses in steps of 1 mm. On each analysis of 400 µm in lateral size (the longitudinal size depends on the incidence angle), all the power of the rotating anode is focused on the spot to achieve a beam brilliance remarkable for a laboratory machine, and allowing relatively fast acquisitions. The acquisition time is set to 15 min for Bragg angles between 15 and 70° with a step of 0.01°. **Figure S1e** shows the pristine zone diffractogram compared to the 50 cycles one. Note that in order to increase the statistics and the signal-to-noise ratio of the reported patterns, once we verified that the 16 measurements are indeed identical, and thus the homogeneity of the analysis zone, we summed the 16 measurements, which finally corresponds to a measurement time of 4h per zone. For the sake of clarity, the diffractogram after 1 cycle is not reported because it is completely superimposable to the pristine one. For the pristine LNMO sample, apart from the (111) platinum peak, the other peaks are easily attributable to the spinel structure of $LiNi_{0.5}Mn_{1.5}O_4$ (PDF file 01-080-2162), with a preferential orientation effect according to the [111] direction, in good agreement with previous studies [5,6] and what we observe by TEM analyses in **figure 1b**. On the other hand, the diffractogram after 50 cycles shows some additional

peaks, of low intensity, but clearly visible after summing the 16 measurements. A phase identification using PDXL 2 software [50] allows to attribute all the additional peaks to a LiCOOH formulation phase (PDF 00-014-0809). To explain the appearance of this lithium carboxylate phase, two hypotheses can be stated. Either it comes from the decomposition product issued from the electrolyte during cycling, suggesting one component of the well-known SEI (Solid-Electrolyte-Interface) or CEI (Cathode Electrolyte Interphase) [51], or a simple deposit of lithium salts issued from the organic electrolyte (1M $LiClO_4$ in EC / DMC), unrelated to charge / discharge cycling. To rule out this hypothesis, we deposited a drop of liquid electrolyte on a silicon substrate, let it dry for several days and recorded the diffractogram of the solid residue. Both the visual aspect is very different (see SEM and optical micrographs in supplementary materials **figure S2**), but also and especially the diffractogram (**figure S2**) is clearly different. Those figures show the appearance of an extremely well crystallized compound, easily identified as the lithium chloride salt $LiClO_4$ (PDF 00-008-0156). It can thus be proposed that the compound observed after 50 cycles (Lithium formate) would be a component of the SEI, as already observed on the anodic side (for a review, see [51]), but very rarely observed on the cathodic side by X-ray diffraction technique.

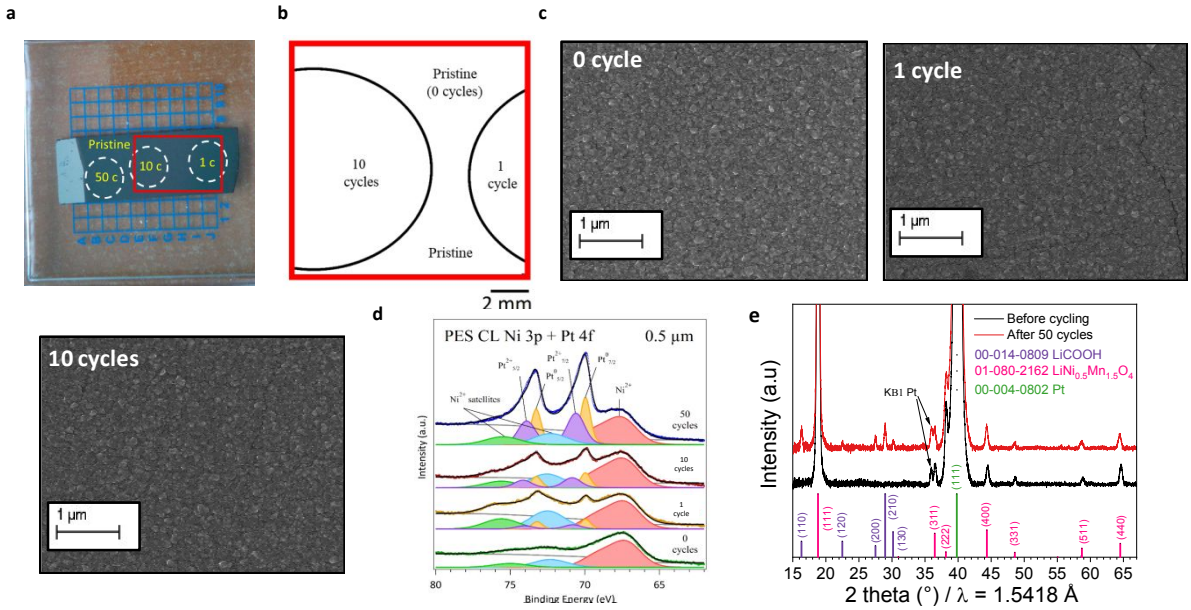

Fig. S1 | a. Optical image shows pristine (0 cycle) and areas with 1 cycle and 10 cycles. **b.** Sketch up of the optical image. **c.** Top view SEM analysis of 0.5 µm-thick LNMO films before and after 1 and 10 cycles respectively. **d.** Full PES spectra of Ni 3p core level of the sputtered 0.5 µm-thick LNMO film. The incident photon energy was 200 eV. **e.** X-Ray diffraction analyses of the Si / Al_2O_3 / Pt / LNMO films before and after 50 charge/discharge cycles at 1C highlighting the formation of the CEI layer (Cathode Electrolyte Interface) on the surface of the LNMO.

Table S1. Analysis of the electrolyte composition by ICP-AES (Inductively Coupled Plasma Auger Emission Spectroscopy) vs the number of charge / discharge of 500 nm-thick non protected LNMO film.

Number of cycles	***Amount of manganese in the electrolyte (ppm)***	***Amount of manganese in the electrolyte (ppm)***
1	< 0.3	< 0.3
5	< 0.3	< 0.3
15	< 0.3	< 0.3
50	18.9	6

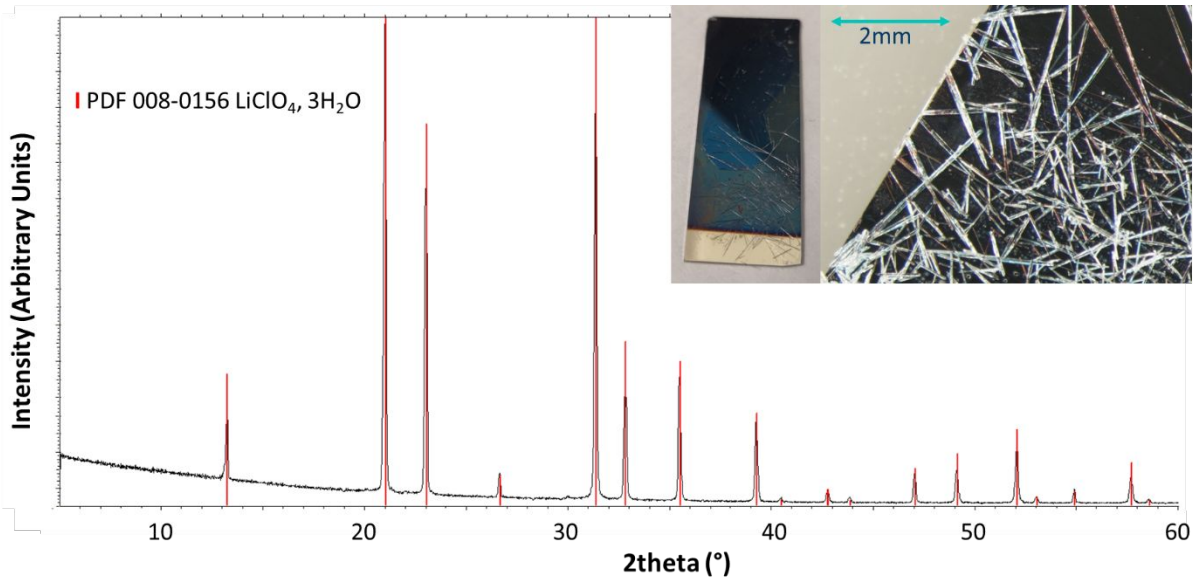

Fig. S2 | X-Ray diffraction analysis and optical images of the crystallized LiClO4 liquid electrolyte dried on the surface of the LNMO film.

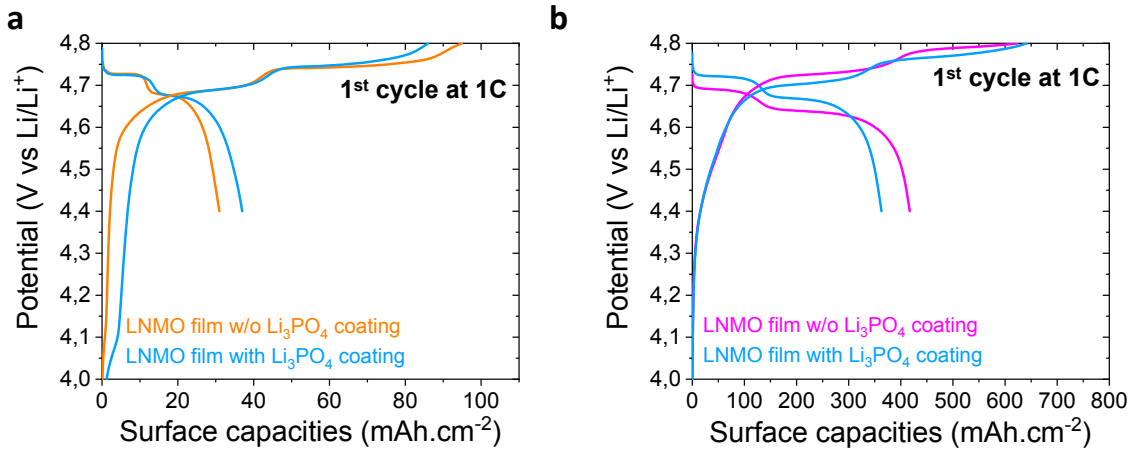

Fig. S3. Galvanostatic Charge and discharge plots of the 1st cycle at 1C of 500 nm-thick **(a)** and 7400 nm **(b)** LNMO electrodes.

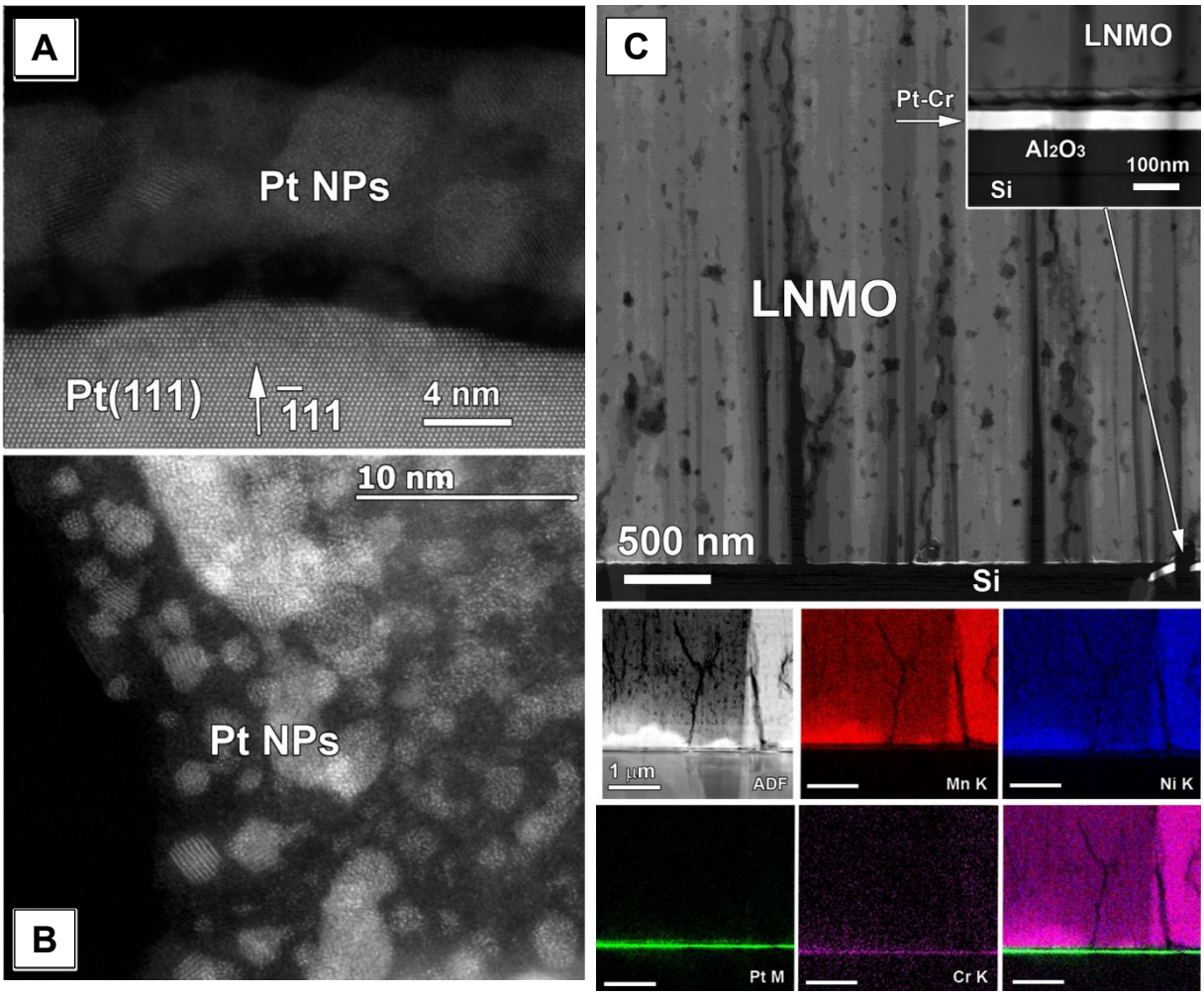

Fig. S4 | a. High resolution HAADF-STEM image of Pt (111) / LNMO nondestructive interface, **b.** High resolution HAADF-STEM image of destructive region of interface with Pt NPs deposited on Pt (111) surface. **c.** HAADF and EDX mapping from TEM analyses of the 7400 nm-thick LNMO film.