# In situ electro-chemical liquid TEM experiments to study LiFe0.5Mn0.5PO4 Nanoplatelets

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Liquid cell electron microscopy is a developing technique that allows us to apply the powerful capabilities of the electron microscope to image and analyze materials immersed in liquid. We are thus able to examine liquid based processes in materials science and physics that are traditionally inaccessible with conventional TEM. The liquid/bias sealed cell (Protochips Poseidon 510) consists of two designed silicon echips having $Si_3N_4$ windows and microelectrodes fabricated by lithography technique (**figure 1**). Electrochemical echips separate the liquid from the microscope vacuum also confining it into a layer that is thin enough for imaging with transmitted electron. The importance of liquid cell TEM in electrochemistry is that liquid cell experiments enable direct imaging of key phenomena during battery operation and relate the structural and compositional changes **[1]** to electrochemical signature **[2,3]**.
In this work, we carried out *in situ* liquid TEM studies of $LiFe_{0.5}Mn_{0.5}PO_4$ (LMFP) nanoplatelets synthesized with a colloidal procedure **[4]**, while are very promising nano-objects for high-rate batteries**.** The synthesized nanoplatelets LMFP were studied using advanced TEM: high angle annular dark field STEM (HAADF-STEM), EDX-STEM mapping, and EELS-STEM mapping to find crystal structure and atomic distributions. The figure 2 shows high-resolution HAADF-STEM image of single LMFP nanocrystal oriented along [010] direction in which Li/(Fe, Mn) anti-site defects is observed (see plot profile). EFTEM and EELS mapping show the coexistence and homogenous distribution of Fe, Mn, P elements in single nanoplatelets. For *in situ* liquid experiments, this cathode material was deposited onto glassy carbon (on silicon nitride membrane) of the top echip used to encapsulate conventional liquid electrolyte LP30 ($LiFP_6$/EC/DMC). A gap of 500 nm between both echips and a flow mode introduction were used for the liquid medium. The assembly was followed with TEM/STEM imaging and spectroscopy (EELS, EDX) during electrochemical cycling so as to monitor in real time the delithiation process of LMFP single nanocrystals.
We succeed to follow by TEM imaging in real time the structural and chemical changes taking place on positive electrode materials during the electrochemical cycling. Figure 3 shows electrochemical cyclic voltammetry (25mV/s) corresponding to LFMP in LP30 measured in three-contact mode with silver as reference electrode. Using EELS, it was possible to follow the transition between LFMP and FMP during extraction and insertion of lithium from $LiFe_{0.5}Mn_{0.5}PO_4$ showed by the appearance a peak at 5 eV (in figure 3), also confirmed by EFTEM. The structural changes due to the lithiation/delithiation processes during electrochemical cycling were imaged by high-resolution TEM showing local structural distortion.
[1] A. Demortière et al. Micro&Microanal 2014
[2] Frances M. Ross Science 2015
[3] Megan E. Holtz et al. Nano letters 2014
[4] Andrea Paolella et al. Nano letters 2014

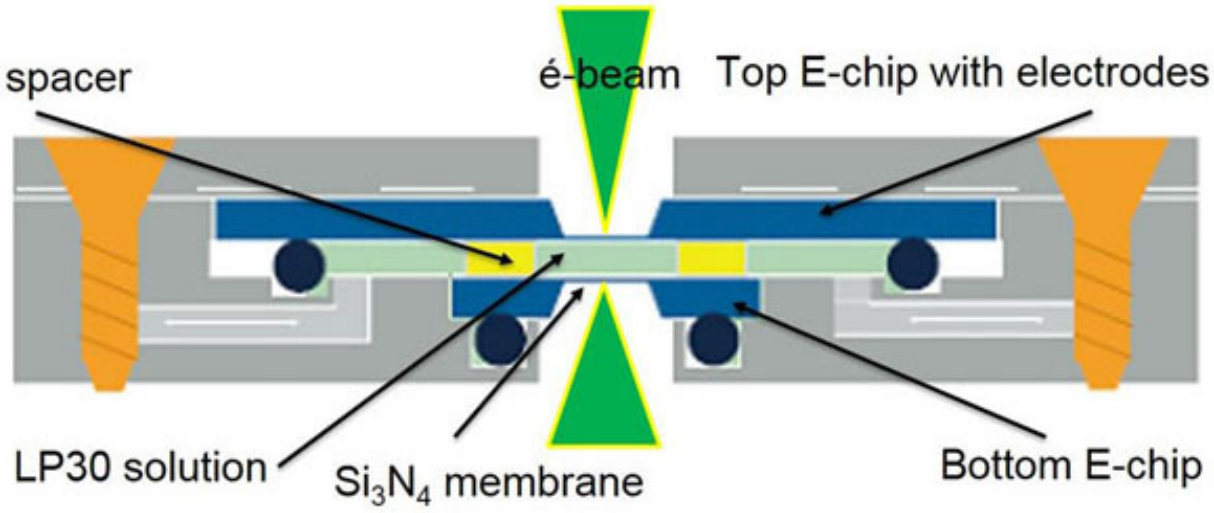


Figure1: Shematic presentation of sealed liquid cell

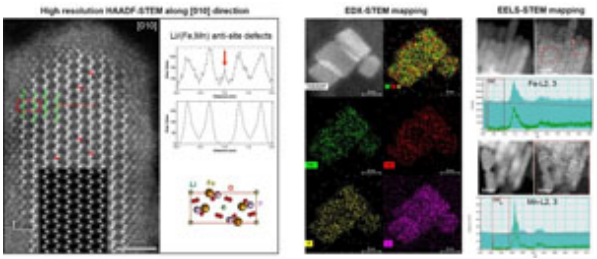

Figure2: Advanced STEM (high resoltution, EFTEM, EELS) analyses of nanoplatelets LFMP

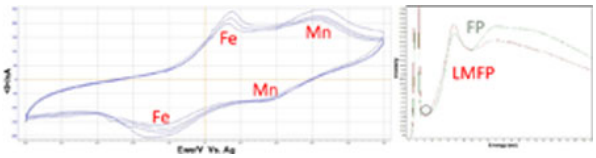


Figure3: Cyclic Voltammetry(Ag as reference electrode) and EELS-STEM spectrums of single particles