

***In-Situ* Liquid/Bias Transmission Electron Microscopy to Visualize the Electrochemical Lithiation/Delithiation Behaviors of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$**

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Liquid cell electron microscopy (EM) is a developing technique that allows us to apply the powerful capabilities of the EM to image and analyze materials immersed in liquid. The liquid/ bias cell consists of silicon nitride window on silicon support called E-chip, which separate the liquid from the microscope vacuum. The importance of liquid cell microscopy in electrochemistry is that liquid cell experiments enable direct imaging of key phenomena during battery operation [1,2].

In our study we carried out *in-situ* liquid TEM studies of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ (LFMP) nanoplatelets synthesized with colloidal procedure, while are very promising for ingrate high rate batteries. The microscopic mechanism of the phase transition from LiMPO_4 to MPO_4 (M=Fe, Mn) and its dependence on particles size still under debate [3, 4]. The synthesized LFMP were studied using advanced TEM to find crystal structure and atomic distributions. HR-HAADF-STEM showed Li/(Fe, Mn) anti-site defects (fig1). EFTEM and EELS mapping show the coexistence and homogenous distribution of Fe, Mn, and P elements on single particle. For *in-situ* experiments LFMP nanomaterials based cathode deposited onto a glassy carbon working electrode in E-chip used to encapsulate conventional electrolyte LP30 ($\text{LiFP}_6/\text{EC}/\text{DMC}$), the assembly were followed with: HAADF-STEM, EELS, and EFTEM-EELS during cycling. A key mechanistic aspect in the performance of Li-ion battery electrodes is how Li ions intercalate and deintercalate from electrode during cycling. In this study, we probe in real time the evolution of individual grains of LFMP in the native environment of a battery in a liquid cell TEM. The *in-situ* electrochemistry reproduces well-established, we performed cyclic voltammetry and galvanostatic cyclic inside the TEM. Particles are seen to delithiate in EFTEM images during charging and discharging: we used 5eV EFTEM to obtain spectroscopic mapping of nanoparticles, where the rich and poor lithium particles appear with different contrast, brighter for FMP and darker for LMFP. HRTEM, EDX, and EELS were useful techniques to study the structural and compositions transformation of this nanomaterial (fig2). In this work we demonstrate the unique ability of a liquid cell in-situ TEM to shed the light on the progress of Li transport across individual particles during cycling of LMFP NPs using a conventional electrolyte.

References:

[1] FM Ross, Science **350** (2015), pp. 10-1126.

[2] ME Holtz, Y Yu and D Gunceler, Nano letters **14** (2014), pp. 1453-1459.

[3] AP Giovanni, BS Marras, E Dilena, Nano letters **14** (2014), pp. 6828-6835.

[4] D Burch *et al*, Chem Acta **B139** (2008), pp. 95-100.

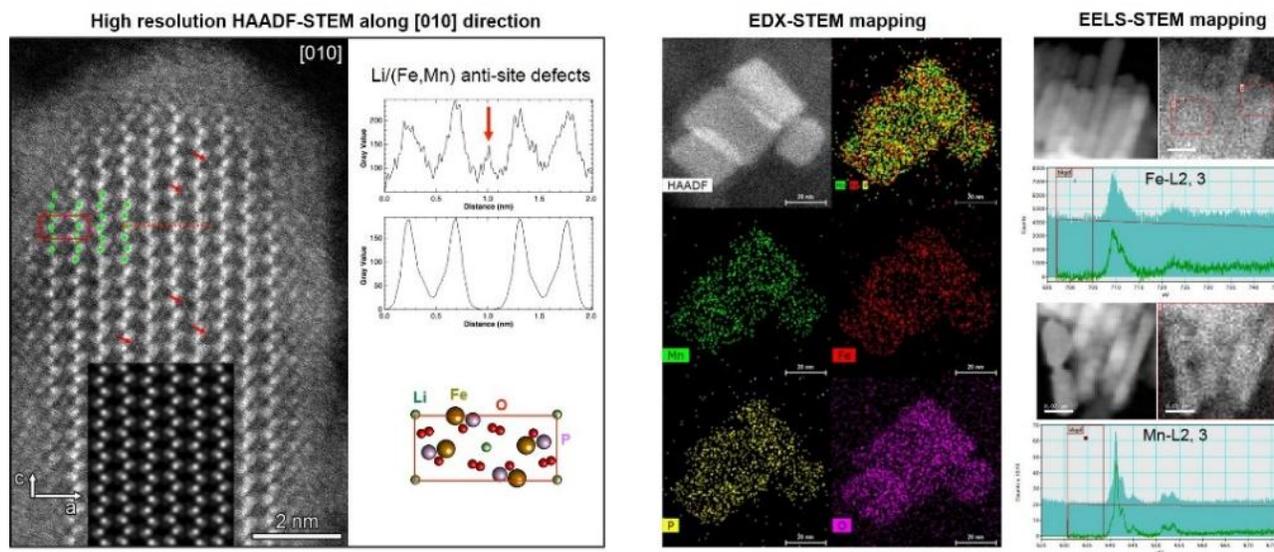


Figure 1. High resolution HAADF STEM with calculated image and profile plot and atomic structure model, EDX-STEM mapping of all element, and EELS-STEM mapping.

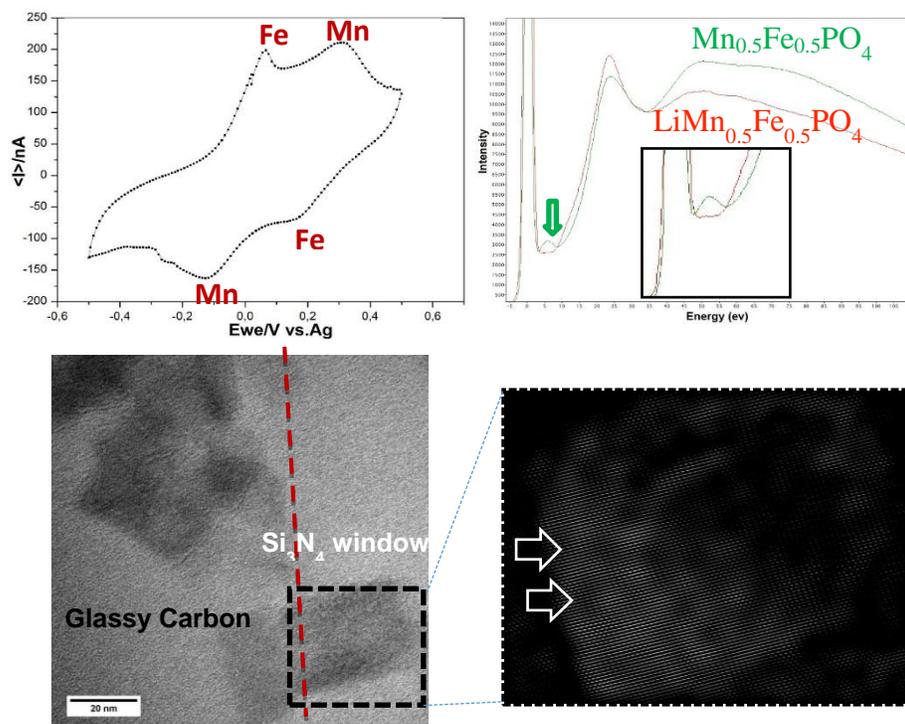


Figure 2. (a) Cyclic Voltammetry (Ag as reference electrode). (b) EELS spectrum of a single particle before (red) and after (green) in situ cycling (c) HRTEM image of LFMP NPs after *in-situ* cycling on top of glassy carbon. (d) filtered the noise HRTEM image of one particle showing local defects (white arrows).