Structural and Electrochemical Studies of Li-ion Battery Cathode Single Particle by Using an *In-situ* FIB-SEM Setup and TXM Tomography

Arnaud Demortière[1,4,5], Martin Bettge[2], Vincent De Andrade[3], Jonathan Ando[4], Dean Miller[1]

[1]*Electron Microscopy Center,* [2]*Chemical Sciences & Engineering,* [3]*Advanced Photon Source,*
Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA
[4]*Réseau sur le Stockage Electrochimique de l'Energie (RS2E),* [5]*Laboratoire de Réactivité et Chimie des Solides (LRCS)*
CNRS, UMR7314, Univ. Picardie Jules Verne, 80039 Amiens Cedex, France

[*]arnaud.demortiere@u-picardie.fr; Téléphone : 0033 695760165

This last decade, fundamental studies of electrochemical phenomena have been slowed down by a lack of effective in-situ (and operando) experimental setup, which is able to clearly identify structural modifications inside and at the surface of electrode materials. Evolution of microstructures, the appearance of cracks and porosities, the formation of SEI at the electrode/electrolyte interface, and the transformation of crystal phases have to be properly investigated in order to get a better insight into the influence of charge/discharge processes in materials and the reaction mechanisms implied in electrochemical storage. Improving our understanding of the microstructural changes and crack formation in Li-ion electrode materials during electrochemical cycling can provide new insight into battery behavior. In order to monitor microstructural evolution dynamically during electrochemical cycling, we developed a micro-scale battery set-up implemented within a FIB/SEM instrument [1]. The single particle of cathode oxide (NCA and NMC) materials with a size of 5-10 µm is attached to a metal probe (W) via a bridge of carbon (GIC) that induces a good connection for electron conductivity. The micromanipulator allows moving the particle in the chamber and immersing in ionic liquid electrolyte (low vapor pressure), which is deposited on counter electrode, *i.e.* lithium metal. Electrochemical measurements are carried out using ultra low current instrument (biologic SP200) with two points connection configuration, external probe tip and SEM metal holder, respectively connected. After immersing into electrolyte and minimization of Li-metal/particle distance, the single particle of active materials is cycled in galvanostatic mode with a steady current around 1 nA, which corresponds to a C-rate of about 1 based on the particle volume and the theoretical capacity [2].

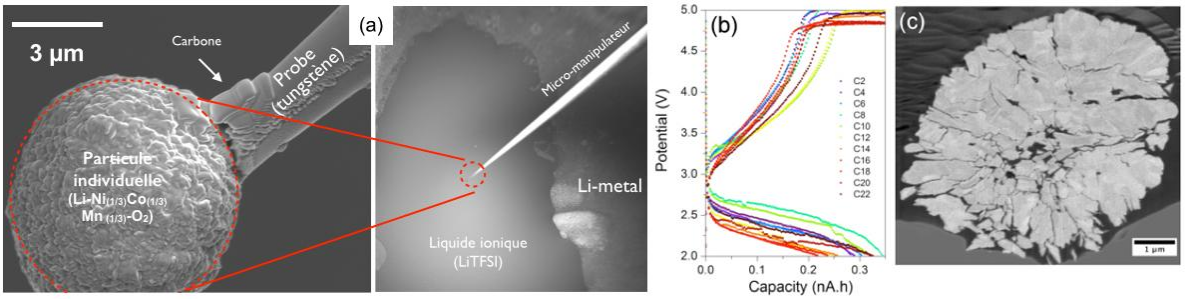

Figure – (a) Experimental setup allows electrochemical cycling of an individual particle of positive electrode active material (NMC) inside FIB/SEM microscope. Micromanipulator (W) connected to active particle (using carbon junction) permits the immersion into liquid electrolyte, which is directly deposited on lithium metal (anode). This *in-situ* setup forms a micro-battery system in which we can carry out electrochemical measurements (charge/discharge, impedance) on active particles or composite materials and analyze morphological and chemical modifications of active compounds. (b) Charge/discharge cycles obtained from this FIB/SEM setup in galvanostatic conditions for NMC materials. (c) SEM image of an individual particle of cathode material after 12 cycles and sectioned by FIB exhibiting a clearly presence of cracks and porosity.

Experimental setup was optimized, by mainly reducing particle/Li-metal distance, to minimize the over potential and get a proper charge/discharge curve. We studied structural modifications of individual particle after each charge/discharge cycle by FIB slicing and SEM imaging. Using specific FIJI plugins and AMIRA software, we quantified the formation of cracks as a function of cycle number and extracted 2D skeleton and tortuosity. Evolution of the discharge capacity was correlated with cracks and porosities appearance inside cathode materials. Impedance measurements suggested an increase of lithium diffusion inside the particle that is relied on the formation of cracks, which induces an enhancement of discharge capacity. On the other hand, the characterization of the 3D structure of these materials is crucial in order to gain a deeper insight into structural configuration and evolution of the discharge capacity. In this purpose, the reconstruction of 3D microstructures by FIB tomography methods was used [3]. The changes of structural parameters such as porosity, grain connectivity and crack propagation that are induced by cycling were extracted from 3D reconstruction and linked with electrochemical properties. Finally, 3D structural data was compared to that obtained from 3D TXM tomography [4], which is carried out in APS synchrotron at Argonne NL.

[1] Miller, D. J., Proff, C., Wen, J. G., Abraham, D. P., & Bareño, J. (2013). Observation of microstructural evolution in Li battery cathode oxide particles by in situ electron microscopy. *Advanced Energy Materials*, *3*(8), 1098-1103.

[2] Demortiere, A., Bettge, M., De Andrade, V., Ando, J., Miller, (2015). Study of microstructural evolution in Li-ion battery cathode single particle by in situ FIB-SEM setup and TXM tomography. *Advanced Energy Materials* (in submission)

[3] Chen-Wiegart, Y. C. K., Liu, Z., Faber, K. T., Barnett, S. A., & Wang, J. (2013). 3D analysis of a LiCoO 2–Li (Ni 1/3 Mn 1/3 Co 1/3) O 2 Li-ion battery positive electrode using x-ray nano-tomography. *Electrochemistry Communications*, *28*, 127-130.

[4] Tariq, F., Yufit, V., Kishimoto, M., Shearing, P. R., Menkin, S., Golodnitsky, D., ... & Brandon, N. P. (2014). Three-dimensional high resolution X-ray imaging and quantification of lithium ion battery mesocarbon microbead anodes. *Journal of Power Sources*, *248*, 1014-1020.