Operando analysis and monitoring of lithium in Li-ion batteries using nuclear microanalysis

S. Surblé[1], C. Paireau[1,2], M. Gauthier[1], H. Khodja[1], J-F. Martin[3]

[1] *Université Paris-Saclay, CEA, CNRS, NIMBE, LEEL 91191, Gif-sur-Yvette, France*
[2] *ARMOR, 44105, Nantes, France*
[3] *CEA / LITEN / DEHT / L2MB, 17 rue des Martyrs, 38054, Grenoble cedex 9, France*

Suzy.surble@cea.fr

Lithium-ion technology holds a prominent place in the battery's area. Although its energy densities increased and the number of cycles raised as high as thousands, it still needs vast improvements to meet ever-greater demands regarding autonomy, lifespan, safety and miniaturization. Capacity fading during cycling remains a major problem limiting battery lifetime. It is therefore necessary to understand the origin of aging phenomena leading to loss of electrochemical performance in order to guide research towards new materials. For this, many *in situ / operando* studies have been developed (XPS, MET, NMR, XRD, ...)[1]. However, none of the techniques mentioned can directly detect the lithium element, which makes the visualization and quantification of all the lithium present in an electrode or a battery impossible. Nuclear microanalysis is a technique capable of giving quantitative and qualitative information on spatial distributions of light elements such as lithium [2]. It is therefore a tool with great potential for understanding the mechanisms in lithium insertion materials.

In previous *ex situ* studies, we showed immobilization of lithium in the $LiFePO_4$ electrode during the first charge / discharge cycles[3]. We further developed an electrochemical cell coupled to the nuclear microprobe to perform *in situ / operando* analyzes[4].The cell is capable of providing electrochemical performances comparable to those obtained with conventional electrochemical cells on the first two cycles. We thus observed *operando* the formation of a SEI layer at the electrode / electrolyte interface and the trapping of lithium in a $LiFePO_4$ // $LiPF_6$ in EC-DEC // graphite assembly. The use of a liquid electrolyte creates complications for the analyses: it flows from the assembly to the cell window, rendering the interpretation of results difficult. The use of solid electrolyte in all solid-state batteries should give more information about the parasite electrochemical reaction (composition and thickness).

References:
1. Lu, J.; Wu, T.; Amine, K. State-of-the-Art Characterization Techniques for Advanced Lithium-Ion Batteries. *Nat Energy*, *2*, 1–13 (2017)
2. Habrioux, A.; Surblé, S.; Berger, P.; Khodja, H.; D'Affroux, A.; Mailley, S.; Gutel, T.; Patoux, S. Nuclear Microanalysis of Lithium Dispersion in $LiFePO_4$ Based Cathode Materials for Li-Ion Batteries. *Nucl. Instrum. Methods Phys. Res. B*, *290*, 13–18 (2012)
3. Surblé, S.; Habrioux, A.; Paireau, C.; Berger, P.; Khodja, H.; Neff, D.; Gosset, D.; Mailley, S.; Patoux, S. Complementary Ion Beam Analysis and Raman Studies for Investigation of the Carbon Coating Impact on Li Insertion/Deinsertion Process at $LiFePO_4$/C Electrodes. *J. Electrochem. Soc. 164*, A3538–A3544 (2017)
4. Surblé, S.; Paireau, C.; Martin, J.-F.; Tarnopolskiy, V.; Gauthier, M.; Khodja, H.; Daniel, L.; Patoux, S. Operando Analysis of Lithium Profiles in Li-Ion Batteries Using Nuclear Microanalysis, *J. Power Sources 393*, 37–42 (2018)