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Application of FIB-TOF-SIMS for 3D high-resolution chemical characterization of Li-ion solid-state batteries

Agnieszka Priebe[1*], Abdessalem Aribia[2], Jordi Sastre[2], Moritz H. Futscher[2], Yaroslav E. Romanyuk[2] and Johann Michler[1]

[1] Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland
[2] Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Thin Films and Photovoltaics, Überlandstrasse 129, Dübendorf, CH-8600 Switzerland
[*] corresponding author email: agnieszka.priebe@empa.ch

The growing interest in Li-ion batteries (LIBs) is particularly driven by the vast need for electric vehicles (EVs), providing environment-friendly (i.e., renewable, clean and zero-emission) energy storage systems.[1] The development of new chemical systems, ensuring improved LIBs' capacity, power and efficiency as well as the reduction of production costs, was a great milestone. However, the safety issues as well as short lifetime are still the critical problems of the conventional LIBs. All-solid-state-batteries (ASSBs) using inorganic solid-state electrolytes (SSE) are great alternatives to commonly used LIBs based on highly flammable organic liquid electrolytes as they enable for operation in a wide range of temperatures.[2] Therefore, ASSBs are considered as one of the most promising future energy storage technologies. The characterization of ASSBs is demanding because they contain buried structures and heterogeneous interfaces. Furthermore, detection of Li and representing its 3D distribution with nanoscale resolution is attainable only to few analytical techniques. In this work, we exploit the outstanding potential of FIB-TOF-SIMS (focused ion beam time-of-flight secondary ion mass spectrometry, Figure 1) for comprehensive chemical characterization of novel Li-containing thin films, which are potential materials for the future generation batteries. This technique allows for parallel detection of all sample components with high spatial resolution (i.e., lateral resolution < 50 nm and depth resolution < 10 nm)[3–5] and high sensitivity (ppm). Our studies show that FIB-TOF-SIMS can reveal presence of 400±100 nm overlithiated grains and 100±30 nm nanoparticles with an increased $^{7}Li^{16}O^{+}$ ion content in the Li- and Ni-rich layered oxide with the composition of $Li_xNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (LR-NMC811, x>1) as well as monitor structural changes upon air exposure (both on the surface and in the bulk).[6] Furthermore, we demonstrate that simultaneous delivery of fluorine gas during FIB-TOF-SIMS can significantly improve the quality of acquired TOF-SIMS data.[7–11] The latter is proved using a novel $Au/Li_7La_3Zr_2O_{12}/Pt/MgO/Si$ multilayer. In this case, the enhanced TOF-SIMS data helped understand the operation of the system. The detection of Li within Au layer after the polarization measurements explained the previously observed formation of internal electric field.[12] Our studies prove that FIB-TOF-SIMS is a powerful technique delivering essential insights into the complex structure of novel

Li-based materials, which can help optimize the functionality of future energy storage technologies.

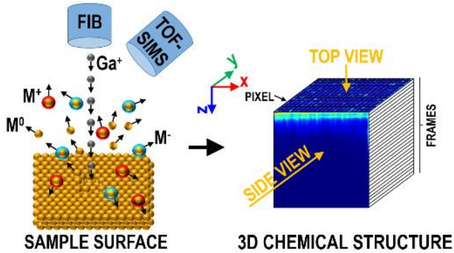

Fig. 1: FIB-TOF-SIMS is one of few analytical techniques allowing sample's 3D chemical structure to be assessed with nanoscale resolution.

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