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Operando TEM Studies of the Structural Evolution of All-Solid-State Li-ion Battery

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Conventional lithium-ion batteries (LiB)[1] are the the most efficient energy storage devices that triggered the transformation of our lifestyle into a digital nomad with the revolution of portable electronics. Inorganic solid-state electrolytes (SSE) represent a promising alternative due to their nonflammable nature, broader temperature operating range and larger electrochemical window. Therefore, all-solid-state-batteries (ASSB) made an important step toward new-generation in electrochemical energy storage systems[2]. However, several limitations still impact the performances of ASSBs such as SSE ionic conductivity, chemical evolution of SSE/active-materials interface, lithium dendrite growth, grain boundary conductivity and solid/solid interfacial resistance[3].

To get a better insight into the limiting parameters of the performances of the ASSBs, a better quantification of the relationship between the structural and electrochemical properties is strongly required. In this study we propose an approach to carry out *Operando* TEM measurements[4] to study the structural and chemical modifications while operating the ASSB inside a TEM, focusing on the multiple solid/solid interfaces. For this study, several ASSBs will be investigated using different combinations of materials with specific SSE such as: $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$[5], Li_6PS_5Cl, $LiBH_4$ and Li_3PO_4.

A nanobattery is obtained using a FIB milling workstation and electrical contacts are realized on a microchip in order to cycle the ASSB inside of the TEM. The microchip with the nanobattery is characterized during the cycling using a holder which allows heating and biasing and information about the microstructure, the degree of oxidation and chemical composition are obtained.

[1] N. Recham *et al.*, "A 3.6 V lithium-based fluorosulphate insertion positive electrode for lithium-ion batteries," *Nat. Mater.*, vol. 9, no. 1, pp. 68–74, 2009.

[2] K. Takada, "Progress in solid electrolytes toward realizing solid-state lithium batteries," *J. Power Sources*, vol. 394, no. February, pp. 74–85, 2018.

[3] J. C. Bachman *et al.*, "Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction," *Chem. Rev.*, vol. 116, no. 1, pp. 140–162, 2016.

[4] Y. Nomura *et al.*, "Quantitative Operando Visualization of Electrochemical Reactions and Li Ions in All-Solid-State Batteries by STEM-EELS with Hyperspectral Image Analyses," 2018.

[5] A. Aboulaich *et al.*, "A new approach to develop safe all-inorganic monolithic li-ion batteries," *Adv. Energy Mater.*, vol. 1, no. 2, pp. 179–183, 2011.