Operando HAXPES Study of Solid Electrolyte Interphase Formation in Anode-Free Solid-State Batteries with PEO:LiDFOB

Yi-Chen Weng[1], Edvin Andersson[2], Helena Wagner[1], Mohammad Baghban Shemirani[2], Zora Chalkley[3,4], Elmar Kataev[3,4], Andreas Lindblad[1], Maria Hahlin[1,2]

[1]*Division of X-ray Photon Science, Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden*

[2]*Structural Chemistry, Department of Chemistry - Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden*

[3]*Department of Interface Design, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), D-12489 Berlin, Germany*

[4]*Energy Materials In-Situ Laboratory Berlin (EMIL), HZB, D-12489 Berlin, Germany*

Anode-free solid-state batteries (AFSSBs) show improved capacities and safety compared to conventional Li-ion cells. However, the development of stable electrolytes is needed for achieving better cyclability. Our recent study has demonstrated the potential of polyethylene oxide (PEO)-based solid polymer electrolyte containing lithium difluoro(oxalate)-borate (LiDFOB) in AFSSB, showing promising capacity retention.[1] In this work, we applied *operando* hard X-ray photoelectron spectroscopy (HAXPES) to investigate the solid electrolyte interphase (SEI) at the anode|SPE interface in AFSSB with PEO:LiDFOB, as illustrated in Figure 1a. Specifically, we applied voltages in steps from 3.4 V to -0.1 V vs Li/Li$^+$, covering the SEI formation potentials, while simultaneously probing decomposition and lithium plating at the interface. In the Li 1s and C 1s spectra (Figure 1b and 1c), a relative shift in binding energy between the components in the SEI and the current collector at different potential steps is observed, which is caused by the formation of double-layer at the interface. This approach allows us to determine the potential at which PEO:LiDFOB begins to degrade and to identify the decomposition products. Our results indicate the correlation between the SEI formation and the improved capacity retention, which is benefit to the understanding of electrolyte stabilty and further development of AFSSBs.

[1]Andersson, E.K., et al. "*Initial SEI formation in LiBOB-, LiDFOB-and LiBF$_4$-containing PEO electrolytes*", Journal of Materials Chemistry A, 12(15), pp.9184-9199 (2024).

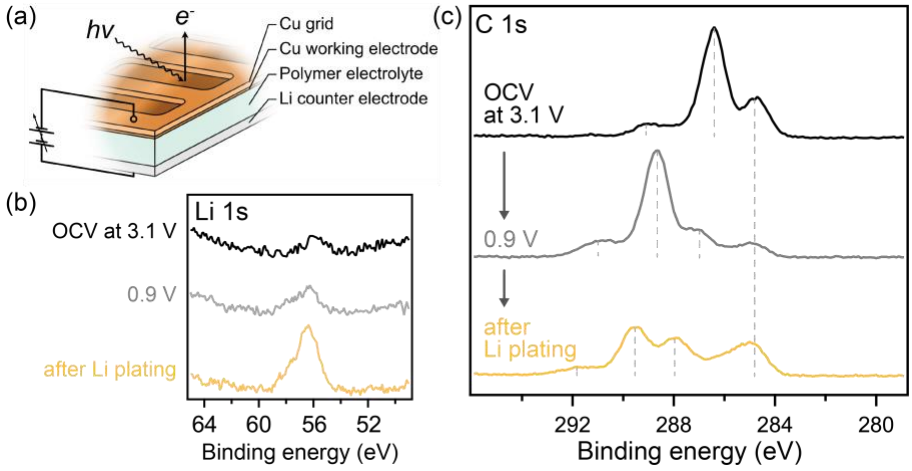

Figure 1. (a) Illustration of *operando* measurements. (b) Li 1s and (c) C 1s spectra at different potentials.