From design to « operando » experiments in the SEM: application to battery studies

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In batteries, electrochemical reactions take place at the interfaces (electrodes-electrolyte, etc.), inducing more or less reversible change such as poor ion transport, dendrite formation, electrochemical degradation and chemo-mechanical degradation[1]. Among the new-generation systems under development, all-solid-state batteries (ASSBs) are no exception to this rule. Understanding the phenomena at interfaces that lead to premature battery ageing is therefore crucial to understanding and finding ways of improving the battery. Thanks to the emergence of in-situ and operando techniques, these complex, constantly evolving interfaces can now be studied by live, battery-scale observations using SEM[2].

To carry out this type of study, we have developed a simple electrochemical cell (Figure 1) that can be used to operate all-solid state lithium metal batteries inside the SEM. The use of lithium metal, which is an air-sensitive compound, led us to fabricate a sealed box enabling the battery to be transferred between the glovebox and the SEM (and vice versa). Morphological (secondary and backscattered electron imaging) and chemical (X-ray energy dispersive spectroscopy) changes at solid-state interfaces could thus be monitored in real time and during battery operation.

In this study, we focused on sulfide-based solid electrolyte (SE) particle size distribution and its impact on electrochemical performance. A batch of Argyrodite (Li6PS5Cl (LPSCl)) was sieved to obtain two batches of particles range (0,5-20µm and 50-150µm). The AASBs were prepared using the two particles size distribution while keeping the anode (lithium metal), cathode (active material: NMC) composite formation and the fabrication process constant. From the two particles sized distribution, the one with the large particles have better electrochemical performance. From morphological point of view at the cathode composite electrode, the formation of a cathode electrolyte interface is visible in the different batteries but is more developed in the case of small sized particles. In the solid electrolyte, the type of cracks differs with relatively strait feature for small particles and sinuous one for large one. At the anodic interface, a lost in contact between the SE separator and the lithium is observed and increased with the cycling process with a higher impact for the small particles (Figure 2.a and b). By investigating further, the formation of dendrites with different morphologies are visible at the anodic interfaces (Figure2.c).

We categorized the observed changes into three modes: (i) electrical failure by the formation of lithium dendrites of different morphologies following the ES going up to short circuit in the case of small particles, (ii) mechanical failure by the formation of cracks in the electrolyte whose shape and propagation strongly depend on the distribution particles size and (iii) electrochemical failure with the formation of solid electrolyte interphases on the surface of the active material. The main obstacles for the use of lithium metal are related to the propagation of lithium dendrites and thus to the mechanical instability of solid electrolytes.

Graphic:

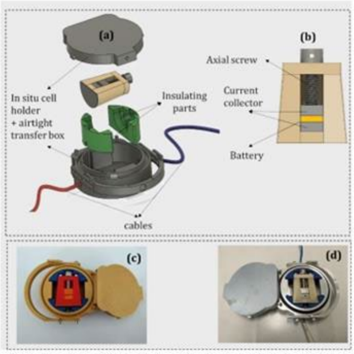

Figure 1: development step of the electrochemical cell for SEM "operando" studies

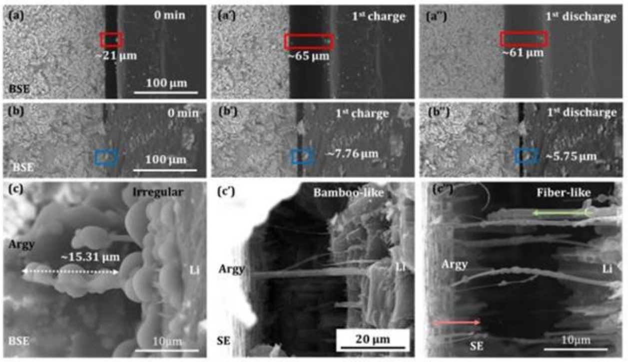

Figure 2: The depiction of loss of contact in small SE particles at (a) 0 min (a') 1st charge and (a") 1st discharge in large SE particles at (b) o min (b') 1st charge and (b") 1st discharge. Morphologies observed for large particles: These are at the end of the 10th cycle. (c) Irregular shape (c') Bamboo-like (c") fibre-like.

Keywords:

SEM, operando cycling, battery

Reference:

[1] S. Wang, H. Xu, W. Li, A. Dolocan, and A. Manthiram, "Interfacial Chemistry in Solid-State Batteries: Formation of Interphase and Its Consequences," J. Am. Chem. Soc., vol. 140, no. 1, pp. 250–257, 2018.
[2] M. Nagao, A. Hayashi, M. Tatsumisago, T. Kanetsuku, T. Tsuda, and S. Kuwabata, "In situ SEM study of a lithium deposition and dissolution mechanism in a bulk-type solid-state cell with a Li_2S–P_2S_5 solid electrolyte," Phys. Chem. Chem. Phys., vol. 15, pp. 18600–18606, 2013.