PhD Thesis

Dynamic Study of the 3D Morphological Evolution of All-Solid Li-ion Batteries during their Manufacture and Cycling

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Candidate profile: All-solid-state battery, X-ray tomography, *operando* experiments, image processing, computer vision, deep learning
Skills: Chemical-physics, Dynamical process, Imaging, Python coding, AI

PhD topics:

The objective of the DynaMoBat research project is the analysis and quantification of the evolution of the 3D morphology of all-solid Li-ion batteries, on the one hand during the sintering manufacturing stage and on the other hand, during their operation in electrochemical cycling. The dynamic study in morphology will be based on the use of X-ray tomography imaging techniques at different scales (µ and nano) [1,3] and from different sources (laboratory and synchrotron). The non-destructive aspect, the possibility of coupling between imaging and spectroscopy and the recent improvements in terms of spatial resolution and rapid acquisition make X-ray tomography an ideal tool to follow operando the morphological modifications within batteries all-solid Li-ion [4].

The project will be based on the optimization of electrochemical cells and compression cells (and temperature annealing) dedicated to X-ray tomography and already developed in the MATEIS and LRCS laboratories. During cycling, these morphological modifications can lead to degradation up to the loss of electrochemical performance of all-solid-state batteries. Indeed, the wide variety of solid/solid interfaces in these devices generates many chemical and mechanical instabilities that can evolve such as, for example, the formation of lithium dendrites (Li-metal/electrolyte interface), the propagation of cracks, local loss of electrolyte/active material contact and formation of resistant species. During the pressure or annealing manufacturing stages, the optimization of the 3D architecture via the sintering and percolation processes is fundamental. The electrolyte/active material interfaces are crucial for electrochemical performance because they define the amount of charge transfer within the electrode. In addition, the ionic and electronic percolation paths, tortuous in the electrode, will define the properties of diffusion and effective conductivity directly impacting the cyclability and the aging of all-solid-state batteries. Finally, the presence and appearance of inhomogeneities in the volume of the electrode can induce large variations in current density leading to the over-stressing of certain areas and to a loss of capacity of other areas induced by their disconnection. to the percolating network.

The 3D data will be segmented to identify the different materials and analyzed using deep learning networks. The 4D dynamic data will be used to calculate 3D displacement maps allowing to follow the sintering phenomena and the propagations of cracks according to the experimental parameters (Mines-Paris-Tech). The quantification of these mechanical properties will be correlated with the evolution of electrochemical performances, to detect the primary origins of polarizations and capacitance losses. Thus, the 3D analysis and quantification of the morphological evolution of the different constituents, depending on the state of charge in operation and the pressure (and temperature) applied for manufacturing, is the heart of this DynaMoBat project. Its ambition is to provide 4D quantitative data, making it possible to improve our understanding of limiting phenomena, and to open new way for optimization in the manufacture of these all-solid devices, which has an essential need to quickly acquire greater technological maturity.

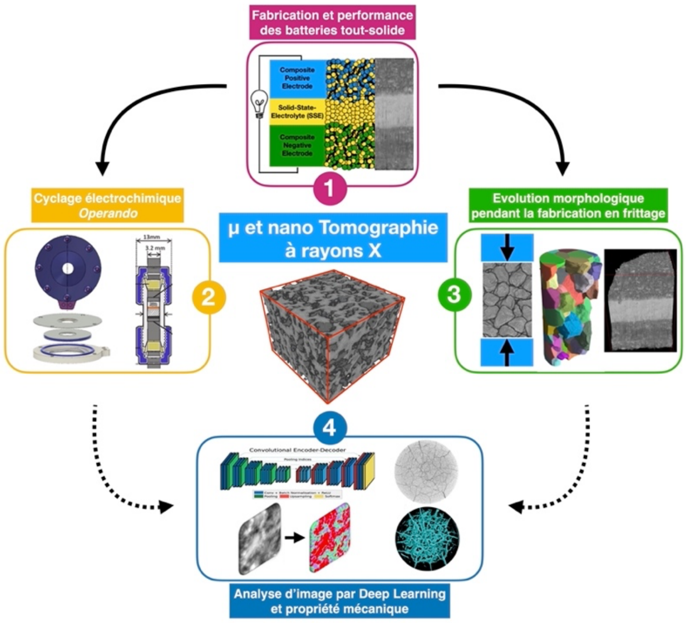

Figure 1. Schematic summarizing the approach of the DynaMoBat project on the study of the evolution of the 3D morphological properties of all-solid-state batteries during electrochemical cycling and during the manufacturing states. Based on the use of electrochemical and pressurized *operando* cells, we will quantify the morphological transformations in real time. The analysis of the images and their segmentation by deep learning approach will allow a detailed understanding of the dynamic processes and the evolution of the mechanical properties.

The state of the subject in the host laboratory.

For 3 years, in the LRCS Imaging and Diffraction (I&D) team, developments have been carried out around the monitoring of the lithiation dynamics in Li-ion batteries and all-solid-state batteries using the 3D nano-XCT coupled with different techniques, such as XANES spectroscopy, Zernike phase contrast and Holography, with convincing results (figure 1). These results were made possible by the development and use of "home-made" electrochemical operando cells, but also by the mastery of image processing tools via AI algorithms (CNN deep learning) [9]. The use of "home-made" AI software and algorithms allowing the 3D analysis will be an important asset.

Publications :

[1] Nguyen, T. T., Villanova, J., Su, Z., Tucoulou, R., Fleutot, B., Delobel, B.,& Demortière, A. 3D Quantification of Microstructural Properties of LiNi0. 5Mn0. 3Co0. 2O2 High-Energy Density Electrodes by X-Ray Holographic Nano-Tomography. *Advanced Energy Materials*, *11*(8), 2003529 **2021**

[2] Su, Z., De Andrade, V., Cretu, S., Yin, Y., Wojcik, M. J., Franco, A. A., Demortière, A. (2020). X-ray nanocomputed tomography in zernike phase contrast for studying 3D morphology of Li–O2 battery electrode. *ACS Applied Energy Materials*, *3*(5), 4093-4102. **2020**

[3] Su, Z., Nguyen, T. T., Le Bourlot, C., Cadiou, F., Jamali, A., De Andrade, V., Franco, A. A. Demortière, A. Towards a Local In situ X-ray Nano Computed Tomography under Realistic Cycling Conditions for Battery Research. *Chemistry‐Methods*, e202100051. **2022**

[4] Lewis, J. A., Cortes, F. J. Q., Liu, Y., Miers, J. C., Verma, A., Vishnugopi, B. S.,& McDowell, M. T.. Linking void and interphase evolution to electrochemistry in solid-state batteries using operando X-ray tomography. *Nature Materials*, *20*(4), 503-510. **2021**

[5] Nguyen,T-T., Xu, J., Andrade,V., Su, Z., Delobel, B., Delacourt, C. Demortière, A., 3D *operando* Monitoring of lithiation spatial composition in NMC cathode electrode by X-ray nano-CT & XANES techniques (in reviewing) **2022**

[6] Su, Z., Decencière, E., Nguyen, T. T., El-Amiry, K., De Andrade, V., Franco, A. A., Demortière, A. (2022). Artificial neural network approach for multiphase segmentation of battery electrode nano-CT images. *npj Computational Materials*, *8*(1), 1-11. **2022**