doi:10.1017/S1431927622002082
Microsc. Microanal. 28 (Suppl 1), 2022

Cryogenic Electron Microscopy Combined with Energy-Dispersive X-ray Spectroscopy Tomography for Materials Science

Lin Jiang[1*], Yang He[2*‡], Chongmin Wang[3], Cedric Bouchet-Marquis[1], Lee Pullan[1], Brandon Van Leer[1], Liu Zhao[1], Yuri Rikers[1], Christian Maunders[1], David Foord[1], Richard G. White[1]

[1.] Materials & Structural Analysis Division, Thermo Fisher Scientific, Hillsboro, OR, USA
[2.] Beijing Advanced Innovation Center for Materials Genome Engineering, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, China
[3.] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA.
* Corresponding author: lin.jiang@thermofisher.com; yanghe@ustb.edu.cn
‡ Previously working at Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA

The discovery of fundamental mechanisms leading to the synthesis of next-generation materials, necessitates advanced electron microscopy (EM) techniques. Cryogenic EM (cryo-EM) was initially developed to provide levels of structural preservation at low or cryogenic temperatures that allows the architectural studies of biological samples (for example cells, viruses). Recently, cryo-EM has been extended into materials science to study beam sensitive samples, such as organic perovskites, metal-organic frameworks, and solid electrolyte interphases in battery materials [1-2]. It generally combines low-dose imaging techniques to acquire microstructure information using a minimal electron dose. In contrast, cutting-edge imaging techniques such as energy-dispersive X-ray spectroscopy (EDX) tomography normally require a significant amount of electron dose to determine the elemental distributions of materials samples in three dimensions (3D). Applying such high-dose methods to beam sensitive samples is therefore a challenging task. Here, combining cryo-EM with EDX tomography sets a new standard in the ability to study the structure and the atomic composition of chemically reactive and beam-sensitive materials in 3D, specifically battery materials.

Basic questions related to the use of the technique still need to be answered: How much irradiation can a beam sensitive material sustain while being “beam showered” under cryogenic conditions when preparing the sample for EDX quantification and tomography which is historically very damaging to the samples? How do we determine the optimal dose and minimize radiation damage of the sample under investigation during EDX acquisition while maintaining required counts for tomography reconstruction?

Here, the first case is successfully demonstrated in materials science where cryo-EM with EDX tomography was combined and allowed the extraction of structural and elemental information to help unravel fundamental battery aging mechanisms.

Solid-electrolyte interphases (SEI) play crucial roles in the performance and degradation of electrode materials in lithium batteries. The SEI forms between the Si electrode and the electrolyte solution. Resolving its composition and structure of SEI is essential for understanding how lithium ions move in and out of the Si electrode and hence how the capacity retention drops over battery cycling. However, the characterization of the 3D SEI structure has been challenging up until now because the dose required to acquire a single 2D image severely damages its native structure.

By combining cryo-EM with EDX tomography, 3D elemental distribution of the SEI in nano-sized Si electrode wires was explored for the first time in its native electrochemical state with its structural and chemical information preserved under cryogenic conditions. The beam damage usually associated with EDX tomography acquisition and EDX quantification was significantly reduced. At the post processing stage of this study, the benefits of using specific algorithms (expectation-maximization, etc.) in elevating the quality of the final reconstruction are discussed (Fig. 1).

Advantages of cryo-EDX over cryo-STEM (Fig. 2) and 3D-EDX over 2D-EDX (Fig. 3) were employed to show an inward growth of SEI facilitated by the internal structure deterioration of nanosized Si with cycling [3]. The Si-SEI configuration gradually evolves from the classical "core-shell" structure to a "plum-pudding" structure as the material progresses through charge and discharge cycles, rendering capacity loss by disrupting electron conduction pathways within the nanowire [3]. This model subverts the traditional SEI growth mechanism, in which SEI is believed to form primarily on the material surface in contact with the electrolyte. The new insights and knowledge obtained through this revolutionary method will benefit battery research and ultimately lead to an extended cycle life and better harnessing of the high capacity in advanced electrodes in lithium batteries.

Lastly, the potential of cryo-EDX tomography for enabling 3D chemical insights into beam-sensitive nanomaterials will be discussed, as well as revealing mechanisms that only happen under cryogenic conditions. This is only one example where one can foresee an increasing role of cryo-EM in characterizing and analyzing the morphology and chemical composition of nanomaterials [4].

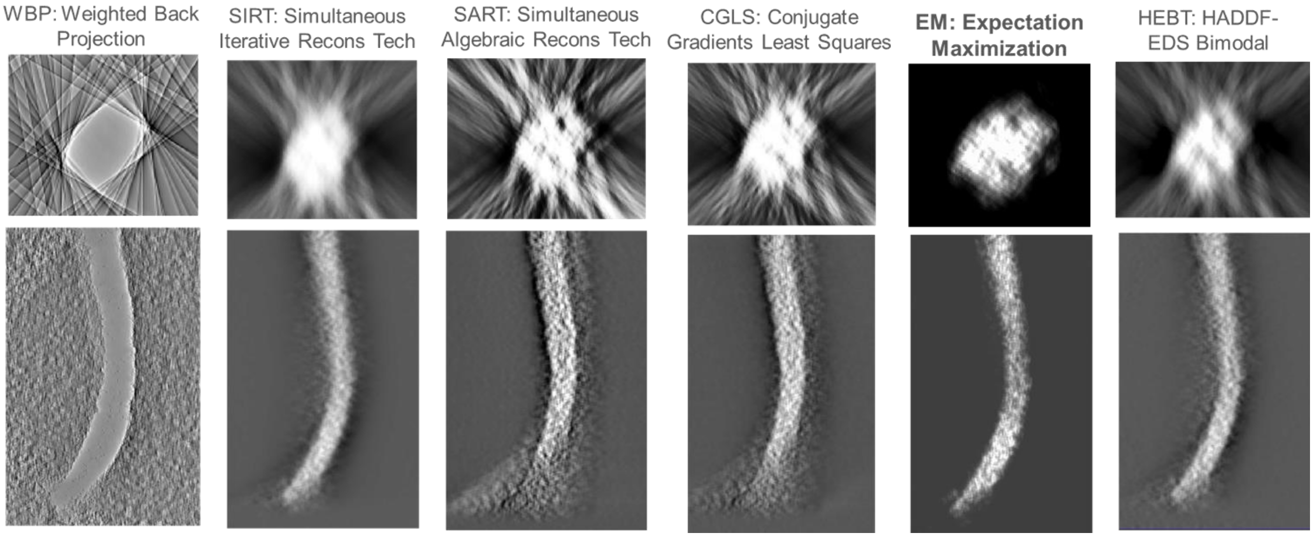

Figure 1. Comparison of Si (Net EDX counts) reconstruction slices using different algorithms in Inspect 3D. The advantage of using Expectation-Maximization is that it reduces the elongation of particles and dampens more missing wedge artifacts [3].

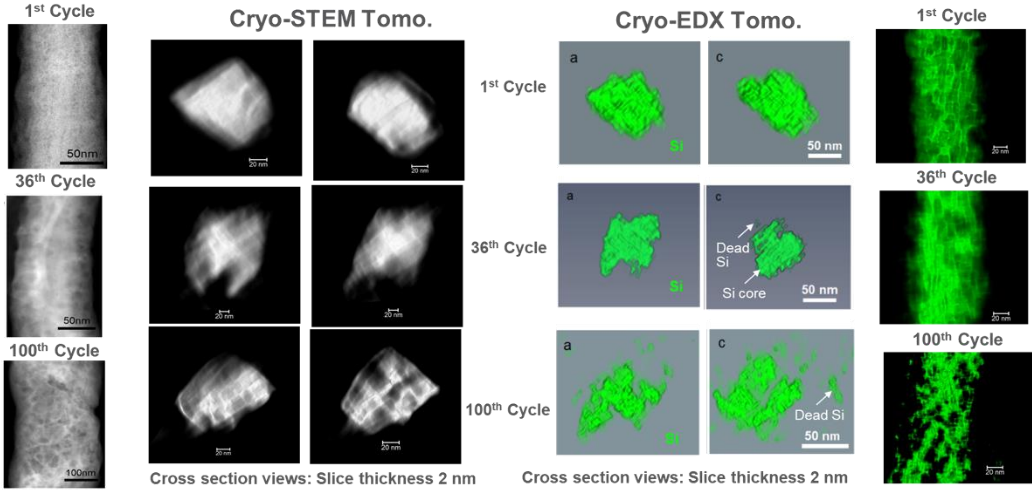

Figure 2. Comparison of Cryo-STEM tomography with Cryo-EDX tomography results after different battery cycles. Cryo-EDX provides better evidences on porous core structure with dead Si [3].

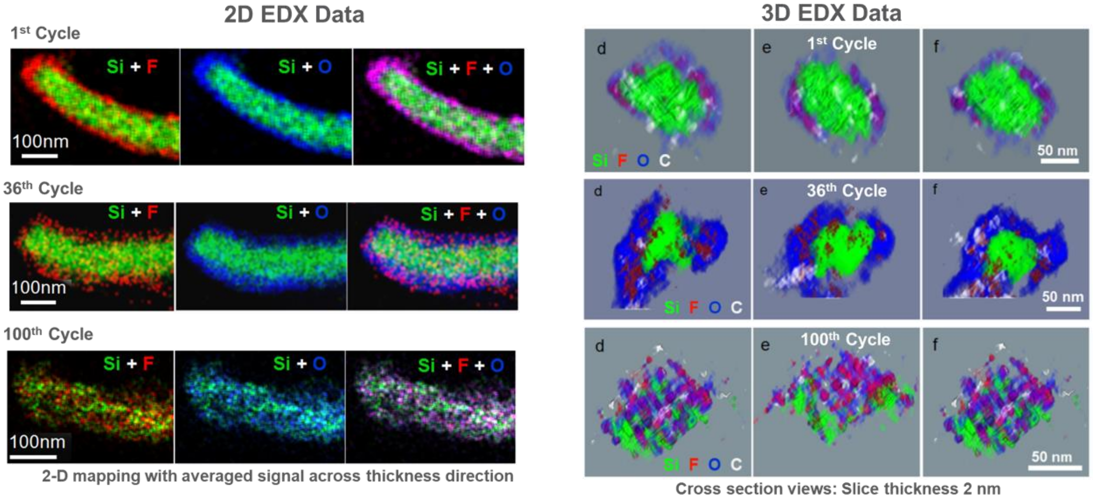

Figure 3. Comparison of 2D EDX with 3D EDX tomography results after different battery cycles. 3D EDX data provides better observation of SEI inward growth: from "core-shell" to "plum-pudding" [3].

References:

[1] Y Li, W. Huang, Y Li, W Chiu, Y Cui, Opportunities for Cryogenic Electron Microscopy in Materials Science and Nanoscience. ACS Nano **14** (2020), p. 9263. doi:10.1021/acsnano.0c05020.
[2] X Wang, Y Li and Y S Meng, Cryogenic Electron Microscopy for Characterizing and Diagnosing Batteries. Joule **2** (2018), p.1. doi:10.1016/j.joule.2018.10.005.
[3] Y. He, L. Jiang, H. Jia, R. Yi, Y. Xu, A. Genc, C. Bouchet-Marquis, R. Warran, L. Pullan, T. Tessner, J. Yoo, X. Li, J.G. Zhang, C.M. Wang. Progressive growth of the solid–electrolyte interphase towards the Si anode interior causes capacity fading. Nature Nanotechnology **16** (2021), p. 1113. doi:10.1038/s41565-021-00947-8.

[4] The authors acknowledge funding from the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy.