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# Correlated XRM and 3D FIB-SEM Workflow to Investigate the Structure-Property Relationship of Si-Based Battery Anode Materials

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Lithium (Li)-ion based batteries are one of the most used systems in decentralized storage systems, e-mobility or mobile electronic devices like headsets etc. However, an essential problem of state-of-the -art cells concerns the fast fading of the capacity during electrochemical cycling. The engineering of anode concepts beyond graphite-based Li-ion technology shall pave novel possibilities for more improved capacity properties. Here, the use of silicon (Si) as an active material in the anode provide promising prospects. A main advantage to use Si for the anode is the rather high theoretical specific capacity of silicon ($Li_{15}Si_4$ with 3578 mAh $g^{-1}$) [1]. This is about ten times larger than that of graphite ($LiC_6$ with 372 mAh $g^{-1}$) [1]. However, the major disadvantage of silicon is, that it undergoes high volumetric expansions upon lithiation (up to 300%) [1] which results into insufficient lifetime expectancy and strong capacity fading due to mechanically induced Si cracking and pulverization as well as emerging delamination at the Si/CBD interface [2].

Understanding the microstructure of silicon-based anodes and its change with electrochemical cycling in connection with the electrochemical properties is highly crucial to develop more advanced Li-ion batteries [2]. However, a big problem for the microstructure characterization concerns the complex hierarchical structures of the anode material going from μm- down to nm-scales. Here, multi-method approaches are essential to cover the different scales with respect to resolution, contrast, and the representative volume of interest to gain sufficient statistical information while maintaining the ability to extract the needed information at relevant scales and with appropriate contrast modalities. However, to setup and apply correlated workflows is highly demanding due the complexity of the Si-based anode material.

In this work we develop and apply a multiscale correlated workflow to investigate the microstructure of Si-based anodes in 2D as well as in 3D in correlation with chemical element information to gain a comprehensive, multiscale, representative picture of the intricate microstructure dictating the ultimate electrode performance (Fig.1). Specifically, we use XRM (ZEISS Xradia 620 Versa) to obtain a 3D non-destructive view of the Si-based anode microstructure across millimeters of material with micrometer-level resolution. We then use that information as a 3D map to guide further nanoscale investigations into the detailed material arrangements using 3D FIB-SEM tomography (ZEISS Crossbeam 550) supplemented with 2D elemental analysis using both energy dispersive x-ray spectroscopy (EDX) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Navigation to the specific representative site for the FIB-SEM tomography was accomplished using the ATLAS 5 connected software environment where the 3D XRM image was registered to the FIB-SEM instrument coordinate system so that known sub-surface locations in the XRM data could be targeted for further investigation.

A fs-laser mill attached to the load lock of the FIB-SEM instrument [3] allowed for rapid material ablation to expose the targeted sites prior to polishing and more detailed investigation using the $Ga^+$ beam to clean up the laser ablated surface and precisely mill the sample for 3D slice-and-view imaging and analytical measurement.

Figure 1(a) shows the same regions of the electrode surface in both XRM and scanning electron microscope (SEM) views correlated in the ATLAS 5 connected software environment. Figure 1c shows an example image of the correlated FIB-SEM pristine anode microstructure and the EDX data collected at the volume of interest (VOI) 1, also shown in Fig. 1a and b, with the graphite and composite Si/$FeSi_2$ particles clearly visible.

This workflow establishes a route to gain multi-scale 3D microstructural data on battery electrodes where the highest resolution information is extracted intentionally from representative sample volumes. The integration of ToF-SIMS into this workflow enables future studies of lithium distributions in cycled anodes of this type, as well as other battery components such as lithium metal oxide cathodes [4].

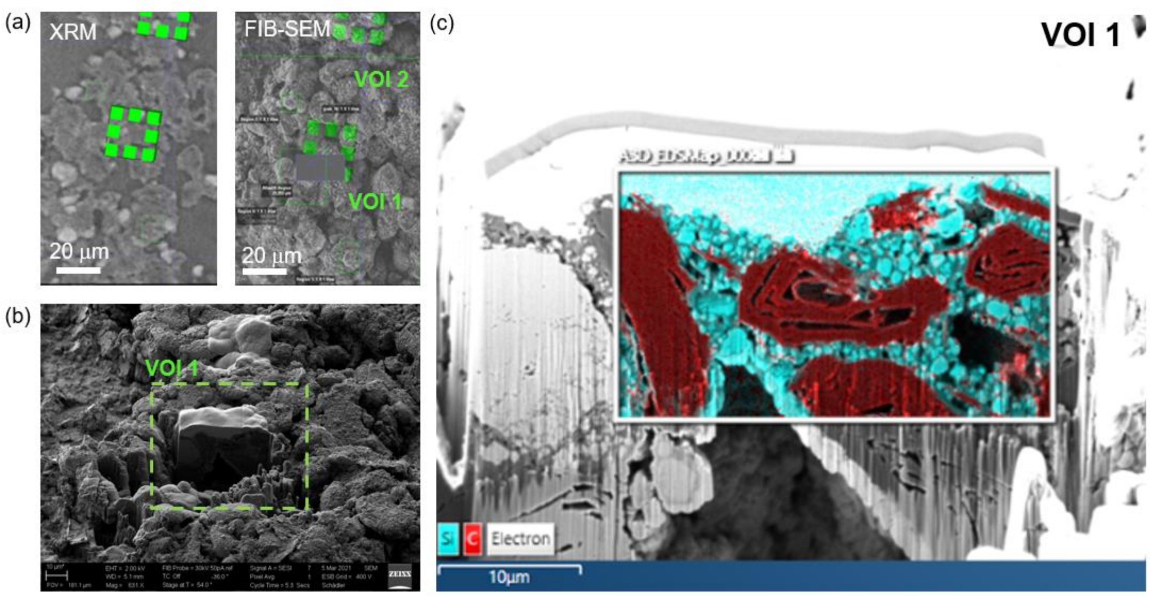


**Figure 1.** (a) ATLAS 5 connected software environment showing the 3D XRM (left) and FIB-SEM (right) data. Green Areas indicate the correlated volume of interests (VOIs). (b) FIB-SEM cut from VOI 1. (c) FIB-SEM cross section from the pristine anode with the correlated EDX image, illustrating the Si and C distribution within the anode microstructure.

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