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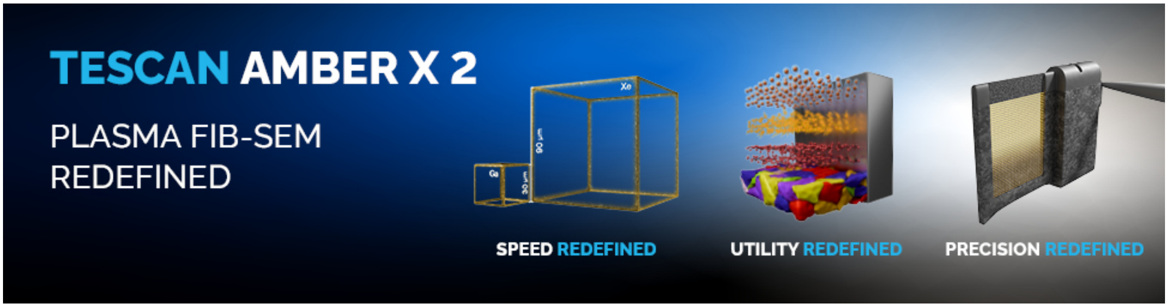

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Spatially Resolved Components in Battery Corrosion Films by 4D STEM

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Next generation batteries with high energy density beyond lithium-ion (Li^+) architectures largely look toward lithium (Li) metal designs, which stores energy electrochemically through reversible plating and striping of Li^+ upon charging and discharging [1]. The reversibility of this electrochemical cycling process governs the performance of Li metal batteries but is largely affected by the corrosion film, solid electrolyte interphase (SEI), as the ionic conductivities of the SEIs are closely related to the Li^+ migration. While it is well-established that the SEI functions as an ionically conductive yet electronically insulating layer, conformally passivating the Li metal surface from electrolyte degradation and governing Li^+ transport between electrode and electrolyte [2], its structure and chemistry remain mysterious [3, 4]. Thus, one of the most important yet unanswered questions in Li-based battery research still remains: how are components distributed across the SEI and how do they govern Li^+ transport? Direct imaging of local SEI structure would provide fundamental insight into Li^+ transport mechanism and unlock new design principles for electrolytes and batteries.

This work applies a multi-faceted imaging and diffraction technique, four-dimensional scanning transmission electron microscopy (4D STEM), to reveal the distribution of nanoscale components like lithium fluoride (LiF), lithium oxide (Li_2O), lithium carbonate (Li_2CO_3) lithium alkyl carbonates ($ROCO_2Li$) and other individual phases point-by-point across micron length-scales in the SEI, allowing previously a wide array of overlooked phases (Li_2O, $ROCO_2Li$, etc.) to be statistically compared with other prominent SEI constituents (LiF). Our understanding of the SEI is still incomplete despite being first proposed by Peled in 1979 [5]. To date, the designing strategy of electrolytes for Li metal anodes heavily relies on inorganic functionalization, with the goal of achieving high Coulombic efficiency (CE) primarily through the perceived advantages of LiF in the SEI [6]. However, the lack of direct experimental techniques capable of accurately quantifying the breakdown of SEI composition hinders thorough examination of other potentially significant phases. To demonstrate our proof-of-concept and impact on battery technology, we combine 4D STEM and cryogenic electron microscopy (cryo-EM) to investigate components distributions within the SEI which is correlated to battery performance. Specifically, we apply 4D STEM technique that can overcome two critical challenges in previous attempts to detect components in the SEI: (1) directly visualizing components distribution throughout the whole individual particle and (2) avoiding the electron beam damage on the beam sensitive materials, especially the SEI. Conventional cryo-EM that widely used in battery research [7, 8] can rapidly freeze air-sensitive battery materials to acquire high-resolution images and related electron diffraction, but only primarily through direct imaging with high-dose parallel beam to get the integrated information.

The 4D STEM technique merges a two-dimensional reciprocal space image associated with each scan point as the beam raster across a two-dimensional region in real space. Spatially-resolved control of diffraction is now possible and is a more straightforward approach for limiting electron beam exposure (Fig. 1a) [9]. Therefore, 4D STEM is a flexible and powerful approach to avoid damage the sample and elucidate structure at the probe-based resolution (down to sub-atomic level) rather than getting an integrated image without being able to distinguish specific substances. After exploring suitable 4D STEM imaging conditions for battery materials, we have developed related algorithm to analyze SEI structure and get virtual apertures of components distribution.

Our preliminary result captures the distribution of Li_2O in dendritic Li deposited in two different electrolytes. Virtual apertures of Li dendrites deposited in different electrolytes are shown in Fig. 1b. In contrast compared to baseline electrolyte (1M lithium hexafluorophosphate in ethylene carbonate/ diethyl carbonate, Fig. 1b left), good performing electrolyte (4M lithium bis(fluorosulfonyl)imide in dimethoxyethane, Fig. 1b right) demonstrates stark increased and uniformly distributed Li_2O particles as the decomposition product in the SEI. These direct visualized data not only show that high Li_2O content correlates with higher CE, but also emphasize that the benefits imparted to the SEI by high Li_2O content derive from its distribution and function. Similar to that LiF being widely regarded as the major desirable SEI phase, we highlight the importance of Li_2O functionality that possesses two times higher Li^+ conductivity than LiF. Thus, uniform distributed Li_2O can support more uniform Li^+ flux, rendering Li_2O more beneficial to SEI transport.

By measuring the distribution of effective components and chemically mapping them out within the SEI, we will be able to identify the dynamic structure and chemistry of the SEI and distinguish which type of SEI is more preferable corresponding to different electrolytes (Fig. 1c). We hypothesize that the uniformity of the SEI serves as the pivotal factor in promoting uniform Li^+ transport during plating and stripping, which emphasize the significance of the SEI's structure and distribution, surpassing mere differentiation between constituents of crystalline and amorphous as previously done. In high-performance electrolytes, we anticipate a more evenly distributed array of components to facilitate the rapid transfer of Li^+. Indeed, this is supported by our preliminary result using ether electrolyte, where Li_2O particles are smaller, more numerous, and more evenly distributed. Furthermore, the new methodologies developed here have broad impact for scientific discovery in diverse research fields beyond batteries, where the interfacial structure and chemistry govern processes in systems spanning electrochemistry [10].

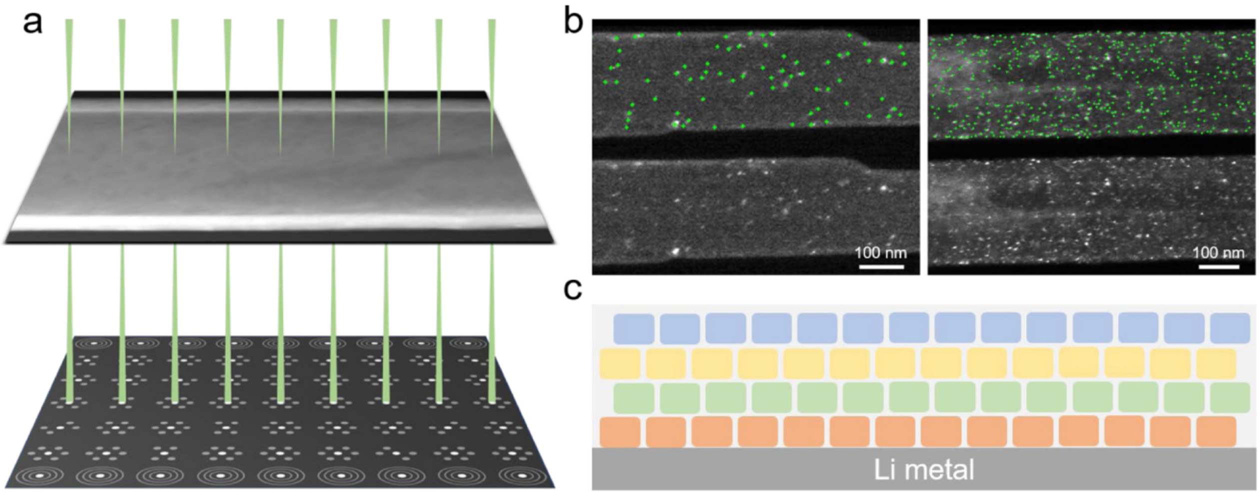

Fig. 1. (a) Schematic illustrating 4D STEM technique. A diffraction pattern is captured at each raster position on the region of interest. The beam positions are shown in green, the sample is where the beam is focused, and the diffraction patterns are shown below. (b) Preliminary data showing direct visualization of Li_2O distribution. The green points indicate the location of the oxide as determined from 4DSTEM. Different electrolytes show different distributions of Li_2O. (c) Schematic illustrating the research aim of mapping of all components in the SEI. Each color represents a different component.

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