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## FIB-SEM: Emerging Multimodal/Multiscale Characterization **Techniques for Advanced Battery Development**

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ABSTRACT: The advancement of battery technology necessitates a profound understanding of the physical, chemical, and electrochemical processes at various scales. Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) has emerged as an indispensable tool for battery research, enabling high-resolution imaging and multiscale analysis from macroscopic structures to nanoscale features at multiple dimensions. This review starts with introducing the fundamentals of focused beam and matter interaction under the framework of FIB-SEM instrumentation and then explores the application of FIB-SEM characterization on rechargeable batteries (lithium-ion batteries and beyond), with a focus on cathode and anode materials, as well as solid-state batteries. Analytical techniques such as Energy Dispersive X-ray Spectroscopy, Electron Backscatter Diffraction, and Secondary Ion



Mass Spectrometry are discussed in the context of their ability to provide detailed morphological, crystallographic, and chemical insights. The review also highlights several emerging applications in FIB-SEM including workflow to maintain sample integrity, inoperando characterization, and correlative microscopy. The integration of Artificial Intelligence for enhanced data analysis and predictive modeling, which significantly improves the accuracy and efficiency of material characterization, is also discussed. Through comprehensive multimodal and multiscale analysis, FIB-SEM is poised to significantly advance the understanding and development of high-performance battery materials, paving the way for future innovations in battery technology.

## CONTENTS

1. Introduction	E
2. Overview of FIB-SEM and Its Associated Techni-	
ques	B
2.1. Specimen Interaction Fundamentals and	
Instrumentation	B
2.1.1. Electron Sources	C
2.1.2. Liquid Metal vs Plasma Ion Sources	D
2.1.3. Ultrashort Pulsed Laser Source	F
2.1.4. Focused Beam Configurations	F
2.2. Analytical Tools, Detectors and Accessories	
in FIB-SEM	F
2.2.1. SEM and FIB Imaging and Detection	F
2.2.2. EDS Analytics	F
2.2.3. EBSD Analytics	
2.2.4. FIB-SIMS Analytics	-
2.2.5. FIB-SEM In Situ Accessory	L
2.3. Cryogenic FIB-SEM	N
2.4. FIB-SEM Techniques: 2D Imaging, 3D To-	
mography, and TEM Lamella Preparation	N
2.4.1. 2D Sample Preparation	Ν
2.4.2. 3D Serial Sectioning Tomography	Ç

2.4.3. TEM Lamella Preparation	R
3. Application of FIB-SEM on Characterizations of	
Battery Materials	U
3.1. FIB-SEM Characterizations for Cathode Ma-	
terials	U
3.1.1. Morphological Analysis Techniques	U
3.1.2. Crystallographic Analysis Techniques	V
3.1.3. Chemical Analysis Techniques	W
3.1.4. Outlook on FIB-SEM Applications for	
Cathode Materials	W
3.2. FIB-SEM Characterizations for Anode Materi-	
als	Х
3.2.1. FIB-SEM for Alkali Metal Anode	Х
3.2.2. FIB-SEM for Other Types of Anodes	AB

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3.2.3. Outlook on FIB-SEM Application for	
Anode Materials	AC
3.3. FIB-SEM Characterizations for Solid State	
Battery	AD
3.3.1. FIB-SEM for Solid Electrolyte Separators	AD
3.3.2. FIB-SEM for Cathode/Electrolyte Com-	
posites	AF
3.3.3. FIB-SEM for Interfaces and Interphases	
of ASSBs with Metal Anodes	AG
3.3.4. FIB-SEM for Interfaces and Interphases	
of ASSBS with Alloy Anodes	AH
3.3.5. OUTIOOK ON FIB-SEM FOR SOLID STATE	
Ddlleries	AI
Future Perspective	۵١
4.1 Strategy to Preserve Battery Sample Integ-	R)
rity: Challenges and Opportunities	AJ
4.2. In-Operando Characterization of Battery in	
FIB-SEM	AM
4.3. Correlative Microscopy for Battery Applica-	
tion	AN
4.4. The Role of Artificial Intelligence for FIB-SEM	
Data Analysis and Modeling	AO
5. Conclusion	AP
Author Information	AQ
Corresponding Authors	AQ
Authors	AQ
Author Contributions	AQ
Notes	AQ
Biographies	AQ
Acknowledgments	AR
	AS AC
	AS

#### 1. INTRODUCTION

Since Sony's first commercialization of them in the early 1990s,<sup>1</sup> lithium-ion battery (LIB) technology has become widely used in consumer electronics, transportation electrification, and stationary grid storage.<sup>2</sup> Despite the incredible progress made in the past decades for battery development, the increasing demand for applications such as long-distance electric vehicles, long-duration grid energy storage, and electric aviation requires further development for more advanced battery technology directions, such as a high-energy Ni-rich layered cathode,<sup>3,4</sup> high-capacity silicon anodes,<sup>5,6</sup> solid-state batteries (SSBs),<sup>7,8</sup> and rechargeable lithium metal batteries.<sup>9,10</sup> This development must be driven not only by advancements in engineering and cell design but also by the synergistic enhancement of the battery through improvements in battery materials (active materials, conductive carbon and binder, electrolyte), electrode-electrolyte interfaces, and electrode architecture. To facilitate these improvements, a comprehensive understanding of the battery microstructure across different length scales and dimensions, utilizing multimodal information, is essential.<sup>11</sup>

First commercialized in 1992, the Focused Ion Beam– Scanning Electron Microscope (FIB-SEM), also call DualBeam, serves as an in situ, site-specific sample preparation and microstructural characterization technique to enable structural, chemical and failure analysis in various scientific fields.<sup>12</sup> It has been widely utilized in materials science, life sciences, and the semiconductor industry to provide visualization and analysis of micro- and macro-structures at multidimensions with nanometer scale resolution. For battery application, FIB-SEM provides unique capability to access the battery structure from the nanoscopic solid-electrolyte interface (SEI), microcracks,<sup>13-16</sup> to the full three-dimensional (3D) volume of the battery electrode structure up to sub-mm<sup>3</sup> scale,<sup>17</sup> linking multiscale battery structural characteristics and chemical information to their electrochemical performance and failure mechanism.<sup>18</sup> Recently, the integration of cryogenic capabilities has greatly expanded the functionality of FIB-SEM, enabling scientists to more effectively study reactive battery materials, including solid-state electrolytes, solid-electrolyte interfaces, and reactive alkali metals, which facilitates the development of a range of next-generation battery systems.<sup>19–29</sup>

As FIB-SEM emerges as a crucial characterization technique for battery development, this review presents an overview of FIB-SEM technology and its applications in battery research, with a particular emphasis on rechargeable LIBs and beyond. The aim is to offer a comprehensive guide for scientists and engineers interested in this analytical characterization method for battery applications. It begins by introducing the fundamentals of focused ion beam and matter interaction, the instrumentation, and the analytical capabilities of FIB-SEM. This is followed by application use cases of FIB-SEM on battery cathodes, anodes, and SSBs, highlighting how the findings support advancements in battery technology. In conclusion, we discuss emerging workflows and future directions of the FIB-SEM technique, emphasizing its expanding capabilities to meet future needs in battery development.

## 2. OVERVIEW OF FIB-SEM AND ITS ASSOCIATED TECHNIQUES

## 2.1. Specimen Interaction Fundamentals and Instrumentation

Focused beams are intricate and compact systems designed to emit, accelerate, deflect, and raster a narrow stream of either (i) negatively charged particles, specifically electrons, (ii) positively charged particles, known as ions, or (iii) photons as an ultrashort pulse laser (USPL). In the fields of materials science and battery research, these beams are commonly utilized for six primary purposes: imaging ( $e^-$ , ion), detection ( $e^-$ , ion, photon), deposition ( $e^-$ , ion and/or photon assisted), implantation (ion), milling/ablation (ion, photon), and polishing (ion, photon).

Depending on various parameters of the beams, different modes of interactions are dominant. In general, we can distinguish two dominant modes of operations: signal detection/imaging at low currents (electrons, ions)/low fluence (photons), and material removal at high currents (ions)/high fluence (ions).

When electrons, ions, or photons interact with a volume matter, they excite a variety of signals (Figure 1a) that can be detected, quantified, postprocessed, and visualized. The interaction volume and location of collected signals depends on the energy of the primary beam of electrons, the elemental composition and crystallographic orientation, and thickness of the specimen. For a bulk specimen, the size of the interaction volume is proportional to the energy of the electrons, and the signals are emitted back and detected. The electrons can penetrate deep into the material; for example, for silicon and normal incidence at 30 keV, electrons can reach depths of 9.3  $\mu$ m.<sup>29</sup> Small, nanometer size internation volume can be achieved by reducing the energy of electrons or by probing thin film, foil,

В



Figure 1. Schematics showing a variety of signals excited by interacting electrons (a), ions (b) and ultrashort pulsed photons (c) with matter.

and lamella specimens. In these electron transparent materials, transmitted signals are also detected and analyzed.

The primary electron beam interacting with superficial surface layers commonly generates signals such as secondary electrons (SE), which provide topographical information. Backscattered electrons (BSE) provide qualitative information about atomic number, phase differences, lattice channeling contrast, and elastically scattered electrons in techniques such as Electron Backscattered Diffraction (EBSD) or transmitted EBSD. Excited continuum and characteristic X-ray signals are analyzed and quantified by Energy Dispersive X-ray Spectroscopy (EDS) or Wavelength Dispersive X-ray Spectroscopy (WDS). These techniques are used to determine the elemental composition of a material. Photons are also generated that bring composition, structure, and optical properties information by a method called cathodoluminescence (CL). Inelastic scattering of transmitted electrons gives information about material composition and bond states by the Electron Energy Loss Spectroscopy (EELS) method. The less common analytical technique is Auger Electron Spectroscopy. This method is a surface analysis technique used to determine the elemental composition of a material and study its surface chemistry.

For the interaction of the primary ion with matter, a variety of primary ion focused beams are used, the most common are Gallium (Ga<sup>+</sup>), Helium (He<sup>+</sup>), Neon (Ne<sup>+</sup>), Argon (Ar<sup>+</sup>), Xenon ( $Xe^+$ ), and Oxygen ( $O^+$ ). Small and light ions, e.g.  $He^+$ , are mainly used for imaging, while the large and heavy Ga<sup>+</sup>, Ar<sup>+</sup>, Xe<sup>+</sup> and O<sup>+</sup> allow precise material removal. It is worth noting that an uncommon ion source, such as the photoionization of laser-cooled lithium atoms, has also been utilized in developing a scanning ion microscope to demonstrate nondestructive imaging of the nanoimprint lithography process.<sup>30</sup> When the primary ion beam irradiates matter, a variety of phenomena occur (Figure 1b). A range of secondary electron signals are generated by ions, similar to those generated by the primary electrons. Some primary ions are back sputtered; others are implemented in the superficial surface layers after undergoing collision cascades. The primary ions penetration depth depends on the type of ion, its energy, the incidence angle, the matter, and its crystallographic orientation. The small ions can penetrate deeper into material; for example, for silicon and normal incidence at 30 kV, He<sup>+</sup> ions can reach depths of about 400 nm,

while heavy Xe<sup>+</sup> only can reach depths of about 50 nm.<sup>31</sup> The primary ions also sputter the matter atoms and ions. These sputtered ions of the substrate can be detected and quantified using Secondary Ion Mass Spectroscopy (SIMS).

As previously mentioned, a focused beam of photons also interacts with matter. Here we are mainly discussing an USPL (duration <1 ps) with the beam intensities  $10^4 - 10^7 \text{ W/cm}^{2.17}$ The high pulse rate of femtosecond  $(10^{-15} \text{ s})$  laser ablation results in carrier excitation or material removal on a time-scale which is much faster than thermalization or phonon transfer rates of picoseconds  $(10^{-12} \text{ s})$ .<sup>32</sup> As a result, this ablation process offers the potential for removing large volumes of material with relatively low damage and largely avoiding high temperatures, melting and other thermal damage mechanisms.<sup>33</sup> The femtosecond laser (fs-laser) beam vaporizes and ionizes the material, creating a plasma plume. The plasma emits light as it rapidly cools down, and this emitted light is collected and analyzed using a spectroscopic method, called Laser-Induced Breakdown Spectroscopy (LIBS).<sup>34</sup> The emitted light contains characteristic spectral lines that correspond to the elements present in the sample.

The distinguishing factor of the various types of focused beams lies in the source utilized during their assembly. Various types of electron sources<sup>35</sup> are used both in Scanning Electron Microscopes (SEM) and Transmission Electron Microscopes (TEM). There are several types of focused ion sources,<sup>36</sup> where the most common are liquid metal ion source (LMIS), Inductively Coupled Plasma Ion Sources (ICP) and Electron Cyclotron Resonance (ECR) ion source.<sup>37,38</sup> ICP and ECR sources create a high-temperature plasma from a gas source. The plasma produces ions that can be extracted and focused for materials removal and analysis. A fs-laser beam is generated using a mode-locked laser system<sup>39,40</sup> equipped with a solidstate crystal or a fiber doped with rare-earth ions such as titanium, erbium, or ytterbium. Mode-locking is a technique that allows the laser to emit ultrashort pulses. The following sections will discuss the various types of focused beams used in current FIB-SEM systems.

**2.1.1. Electron Sources.** In the early stages,<sup>35</sup> electrons were generated from a resistively heated tungsten filament located at the tip of a device known as the electron gun. These guns can be categorized into two types: thermionic, which

employ sources such as tungsten,  $LaB_6$ , and  $CeB_6$ , and field emission guns (FEG). The former utilizes a tungsten crystal, where electrons are extracted from the cold filament through a strong electrostatic field known as an extraction voltage. Figure 2



**Figure 2.** Schematic of an electron gun with different types of electron emitters. Reproduced with permission from ref 41. Copyright under CC BY-SA 4.0, https://creativecommons.org/licenses/by-sa/4.0/.

provides a schematic of an electron gun illustrating different types of electron emitters. The choice of emitter depends on the intended application and experimental technique, with key parameters including the diameter of the electron source, its brightness, and the energy spread. A comparison of electron sources is presented in Table 1. For clarity, we have listed only LaB<sub>6</sub> as a representative electron source. While CeB<sub>6</sub> offers superior brightness, stability, and lifespan, its higher cost makes LaB<sub>6</sub> more popular due to its good performance and affordability.

2.1.2. Liquid Metal vs Plasma Ion Sources. The most common commercial source of ions for FIB-SEMs is LMIS with liquid Ga<sup>+</sup> metal ions source. Gallium, in its liquid metal state, is compatible with high vacuum conditions and generates a large mass ion for physical sputtering. While various elements and alloys have been utilized in LMIS, gallium is the preferred choice for 99% of FIB systems worldwide due to its extensive liquid range (from 29.8 to 2175 °C), enabling room temperature operation. Furthermore, gallium predominantly ionizes to the +1 state, which minimizes focusing issues, as the impact of focusing elements correlates with the charge of the particles traversing them. This characteristic makes gallium ion beams ideal for imaging and for SIMS chemical analysis,<sup>42</sup> as they prevent the creation of double images caused by multipole changes. The technology as we know it today dates back to the 1970s.<sup>43</sup> It opened new possibilities in ion beam technology and led to various applications in fields such as materials science, including batteries, surface analysis, and semiconductor manufacturing.44

To date, the ion beam enables operating at accelerating voltage lower than 1 kV to 30 kV, with the fine probe size and nm precision ion beam that is less than 10 nm (5 to 7 nm of full width at half-maximum current). It excels in producing high-quality small size cross-section and 3D tomography data for cathode or anode, typically providing a cut width of around 20 to 50  $\mu$ m, as well as in preparing a high quality of TEM specimen or Atomic Probe Tomography (APT) samples for material science applications including battery materials.<sup>13,45–48</sup> However, the use of the Ga<sup>+</sup> FIB column has two drawbacks:

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- a) LMIS is a divergent ion source (Figure 3a) emitting a beam shaped and focused to a spot by a FIB column.<sup>49</sup> This limits the optimal beam shape and the maximum current density that is achieved by a FIB column. Therefore, usable beam shapes, beam spot sizes, and beam current densities are limited to beams having currents <65 nA;<sup>50</sup> see Figure 3b. These constrain the maximum material removal rate (e.g., 17.6  $\mu$ m<sup>3</sup>/s for Si<sup>51</sup>) and the maximum volume of material (for most of the materials <50 × 50 × 50  $\mu$ m<sup>3</sup>) that is removed within a reasonable amount of time (~2 h). The maximum analyzable volume is smaller than the representative volume of certain battery systems, limiting its ability to fully capture the correlations between battery structure and performance.<sup>14,18,52</sup>
- b) Gallium can create low temperature eutectic alloys during ion matter interaction and implantation, particularly present along grain boundaries<sup>53</sup> (Figure 3d). Therefore, some aluminum, copper, iron and nickel alloys are prone to liquid metal embrittlement<sup>54</sup> during FIB irradiation. For battery materials, gallium will react with Lithium metal to form alloy at room temperature, which limits its application for analyzing certain battery material.<sup>47</sup>

The drawbacks of Ga<sup>+</sup> FIB, particularly ion implantation and matter amorphization, result in sample preparation challenges for LIB morphology and chemical analysis. Maintaining the representation of the original sample's volume is crucial to ensure representative analysis and reliable insights into the battery's chemistry and performance. This issue can be pronounced in TEM lamella preparation and APT tip preparation. It is also essential to avoid introducing artifacts or altering the microstructure or solute distribution, which can be influenced by the type of ion sources used.

In 2012, a different FIB source and column technology, known as plasma Xe ions, was introduced commercially<sup>55</sup> to address the limitations of small material volume removal and avoid Ga<sup>+</sup> contamination. Xe<sup>+</sup> are nonmetallic and originate from noble xenon gas. The plasma Xe ion source serves as a broad-area source with higher angular intensity, providing a well-defined beam profile at high currents of up 3  $\mu$ A, and

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I able	1.	Com	parison	<b>UI</b>	Different	Liechon	Sources	

Emission (kind of gun)	Thermionic Emission		Field Emission	Schottky
	W Tungsten hairpin	LaB <sub>6</sub> Single/multicrystal	Tungsten	Tungsten/zirconium oxide (single crystal)
Diameter of Electron Source (nm)	30,000	10,000	5	20
Brightness (A/cm <sup>2</sup> ·sr)	106	107	109	108
Energy Spread (eV)	1-5 (~2)	0.5-3.0 (~1.5)	0.2-0.3	0.3-1.0
Operating Lifetime (h/months)	~50 h	~1000 h	$\geq 12$ months	$\sim 9$ months
Vacuum (torr)	$10^{-4} - 10^{-5}$	$10^{-6} - 10^{-7}$	$10^{-9} - 10^{-10}$	$10^{-8} - 10^{-9}$
Temperature of cathode (°C)	~2330	~1530	~25 (room temperature)	~1430-1530



**Figure 3.** (a) Schematics of liquid metal ion source. Reproduced with permission from ref 49. Copyright under CC BY-SA 4.0, https:// creativecommons.org/licenses/by-sa/4.0/. (b) Comparison of the beam diameter versus the ion beam current for LIMS and ICP based FIB columns. Adapted with permission from ref 50. Copyright 2016 Elsevier under CC BY 4.0, https://creativecommons.org/licenses/by/4.0/. (c) Schematics of inductively coupled plasma source. Adapted with permission from ref 57. Copyright 2020 Springer Nature. Bottom row illustrates TEM specimens prepared from Al thin film on Si.<sup>53</sup> A gallium forming intermetallic compound with aluminum in aluminum/silicon interface: Al thin-film deposited on Si. HAADF Z-contrast, (d) Gallium FIB, (e) PFIB Xenon prepared specimen.



**Figure 4.** Depicts various types of ions simulations of ion implant depth for He<sup>+</sup>, Ne<sup>+</sup>, Ar<sup>+</sup>, Ga<sup>+</sup>, Xe<sup>+</sup> ions and electrons at 0-degree incident angle to single crystal Si at 30 keV. SRIM Monte Carlo simulation<sup>60</sup> for ions and CASINO Win X-ray Monte Carlo simulations<sup>61</sup> for electrons. Graphically, it clearly illustrates that electrons and low-mass ions penetrate deeply into the sample but produce very low Sputter Yield (SY), such as He<sup>+</sup>.

processes a long lifetime and source stability suitable for large volume material milling (Figure 3b). In addition, Xe<sup>+</sup> come from a noble gas; consequently, any implanted Xe atom is unlikely to form metallic bonding compounds (Figure 3e). For battery applications, unlike Ga<sup>+</sup>, Xe<sup>+</sup> is not reactive with metallic lithium at room temperature, providing a wide materials processing window for characterization.<sup>47,56</sup>

Commercial PFIB-columns currently utilize ECR<sup>38</sup> or ICP<sup>37</sup> ion sources to ignite noble gases (Xe and Ar) or reactive gases (O, N) and generate ion beams. Xe<sup>+</sup>, being a heavy element relative to lighter element ions like He<sup>+</sup>, Ne<sup>+</sup> and Ga<sup>+</sup>, penetrates a shallower implant depth and produces an increased sputter yield (Figure 4). These plasma sources overcome the drawbacks of LMIS FIB-based instruments by producing broad, parallel

beams of heavy and inert Xe<sup>+</sup> and Ar<sup>+</sup> ions. The PFIB optics at a wide range of acceleration voltages (30 kV to 500 V) shape and focus these beams to achieve spot sizes in the tens of nanometers range with pA beam currents suitable for ion beam polishing and imaging. Although PFIB's imaging resolution may be inferior to that of FIB or scanning helium ion microscopy (SHIM), its beam profile and spot size can be precisely controlled, even at very high beam currents<sup>50</sup> (e.g., Xe<sup>+</sup>: 2500 nA, Ar<sup>+</sup>: 3800 nA) and current densities. As a result, Xe<sup>+</sup> PFIB significantly enhances the maximum material removal rate, such as achieving a rate of 675  $\mu$ m<sup>3</sup>/s for Si.<sup>51</sup> This rate is 38 times faster than that of FIB, while maintaining a pristine surface similar to that of Ga<sup>+</sup> FIB. It also allows for the removal of larger volumes of material within a reasonable time frame, typically around  $\sim 200 \times 200 \times$ 200  $\mu$ m<sup>3</sup> for most materials. For example, using the maximum material removal rate, it takes approximately 25 min to remove a Si cube measuring  $(100 \ \mu m)^3$ . Argon ion sources, either provided by the PFIB or broad ion beam (BIB) milling system, <sup>58,59</sup> are well suited for battery materials' large (hundreds of microns to > mm) cross-section preparation and for the final polishing TEM specimens.<sup>16</sup> As a result, the adoption of plasma FIB (PFIB) in battery applications is beneficial, not only for LIB materials' development but also for investigating capacity fading on a large scale.<sup>16,18,56</sup>

**2.1.3. Ultrashort Pulsed Laser Source.** An USPL serves as an important source for battery sample processing. The evolution of USPL traces back several decades, encompassing a dynamic journey of technological advancement.<sup>39,40,62</sup> A fs-laser beam is generated using a mode-locked laser system<sup>39,40</sup> (Figure 5) equipped with a solid-state crystal (titanium-phaedite



**Figure 5.** Schematic of a mode-locked laser system based on Cr-doped colquiriite crystal (Cr: LiSAF,  $Cr^{3+}$ : LiSrAlF<sub>6</sub>).

sapphire or Cr-doped colquiriite crystal) or a fiber doped with rare-earth ions such as erbium, or ytterbium. Mode-locking is a technique that allows the laser to emit ultrashort pulses.

These lasers possess the remarkable capability to emit pulses of light with durations much shorter than 1 ps, enabling interactions with matter that mitigate thermal effects.<sup>33</sup> As a result, USPLs can ablate or remove materials without causing thermal damage, preserving the original microstructure of the remaining materials.<sup>17</sup> The impact of USPLs extends to various domains of science and technology,<sup>63</sup> driving revolutionary advancements in fundamental research, medicine, telecommunications, industrial manufacturing, and, more recently, battery research, especially for large volume analysis.<sup>51,64–66</sup>

When combined with laser optics paths and motorized mirrors, USPLs can generate tightly focused laser beams with diameters as small as  $15 \,\mu m$ .<sup>50</sup> This level of precision allows the beam to raster cross-sectional side-surfaces, similar to those applied in FIB instruments, enabling intricate material processing and manipulation at the microscale. It is important to note that the laser optics referred to are not designed for

imaging through the focused laser path but rather for ultrafast removal/ablation of materials. In TriBeam systems, SEM is used for precise positioning of the laser on the specimen surface. USPLs can remove significantly larger volumes of material compared to plasma FIB ( $500 \times -1000 \times$ ), for example, in the case of silicon, it can remove approximately 40,000  $\mu$ m<sup>3</sup>/s. Furthermore, the ablated surfaces remain pristine, as the laser interacts with the specimen surface at a glancing angle, and the laser parameters are carefully selected for the specific material.<sup>17</sup> Similar to ion optics, laser optics can be configured for either coarse larger volume removal or finer gentle removal. Laser processed cross-sectional surfaces often have damage layers below 20 nm.<sup>67</sup>

**2.1.4. Focused Beam Configurations.** Initially, instruments with focused beam configurations included standalone analog TEM,  $^{68,69}$  SEM,  $^{70,71}$  scanning ion microscopes (SIM) utilizing Ga<sup>+</sup> LMIS,  $^{43,72}$  and low-power, pulsed lasers (<10 W, <1 ns),  $^{73,74}$  alongside short pulse laser optics systems.  $^{75}$  Presently, these microscopes operate on digital circuits. Improvements in TEMs and SEMs include enhanced electron sources, optics, aberration correctors, and detection systems.  $^{76,77}$  SIM platforms expanded with commercial introduction of SHIM in 2008,  $^{78}$  and Xe<sup>+</sup> PFIB systems in 2011.  $^{79}$  Experimental FIB sources include liquid metal alloy ion sources (LMAIS), gas field ion sources (GFIS), low-temperature ion sources (MOTIS).  $^{80-82}$ 

Since the mid-2000s, pulsed lasers and optics for rapid submillimeter-scale micromachining and in situ laser-based characterization techniques transitioned to USPL (<1 ps pulse duration, typically  $\sim$ 50–300 fs). These lasers offer a thermal and nearly damage-free ablation with spot sizes of dozens of micrometers.<sup>83</sup> Figure 6 shows the widely used focused beam systems.

The first dual-column systems emerged commercially in the early 1990s,<sup>85</sup> combining SEM and FIB columns (utilizing Ga<sup>+</sup> LMIS) into a single microscope with two beams intersecting at a coincidence point. This configuration integrates high-resolution electron imaging and qualitative detection modes of SEM (SE and BSE detection) with FIB's implantation and milling/ polishing capabilities. As a result, it enables site-specific micrometer-scale operations such as cross-sectioning and serial sectioning tomography (SST).<sup>86</sup> Over time, FIB-SEMs have been enhanced by adding analytical functionalities like EDS, EBSD, and TOF-SIMS (Figure 7a).

Compared to Ga<sup>+</sup> LMIS as focused ion column, as discussed in Section 2.1.2, Xenon plasma FIB-SEM addressed the limitations of small material volume removal by using utilize ECR or ICP sources to generate Xenon noble gas Xe<sup>+</sup> ion beams.<sup>55</sup> These sources overcome drawbacks of LMIS FIBbased instruments by producing broad, high current (hundreds to thousands of nA) parallel beams of heavy and inert Xe<sup>+</sup> ions. Most recently, the enhancements to Xe<sup>+</sup> plasma FIB-SEM systems included correlative microscopy (CM) holder kits/ workflows,<sup>87</sup> negative tilts for the stage, and the incorporation of three additional primary ion species (Ar, O, and N) into the PFIB column.<sup>87</sup> The CM holder kits enable multiscale, multimodal studies and accurate tracking of volumes of interest from X-ray microCT to DualBeams. Such correlative analysis is critical for battery failure identification and starts with nondestructive CT on a cell level sample to pinpoint battery failure and then in-depth analysis via FIB-SEM.<sup>88</sup> Negative tilts facilitate mimicking the BIB polishing action at glancing angles



Figure 6. Schematics of standalone focused beam systems. Graphics of TEM, SEM, (P) FIB. Adapted with permission from ref 84. Copyright 2020 Technology Networks.



**Figure 7.** Schematics of a dual-column (a), tribeam (b), and dual-column with external laser beam (c) systems. Note that configurations b) and c) also can be equipped with EBSD, TOF-SIMS, and EDS detectors, which here are omitted for clarity of the diagrams.





while spinning the irradiated surface, introducing a new technique called PFIB spin milling, enabling sequential removal of sub-mm surface areas with nanometer precision and recording with SEM qualitative and quantitative imaging modes.<sup>89</sup> Large area two-dimensional (2D) sample preparation can provide structural characteristics with more statistics. The inclusion of noble (Xe and Ar) and reactive (O and N) ion

species broadens the range of applications in materials science and life science for the plasma FIB-SEM microscope,<sup>90,91</sup> and for battery samples specifically, Ar will minimize milling defects during 2D cross-section analysis and TEM lamella sample preparation.<sup>16</sup>

TriBeam systems, based on FIB-SEM platforms (Figure 7b), fs-laser and laser optics benches were independently tested to

enable three columns in the same systems in the early 2010s and fully commercialized in 2019.<sup>67</sup> These systems converged SEM, FIB, and fs-laser beams onto a coincidence point within the main vacuum chamber. Another design of FIB-SEM systems that have three focused beams has separate vacuum chambers (Figure 7c).<sup>92</sup> The addition of the fs-laser expands the application of the FIB-SEM systems to application scope to mm scale, especially for 3D large column materials' characterization.<sup>67</sup>

### 2.2. Analytical Tools, Detectors and Accessories in FIB-SEM

2.2.1. SEM and FIB Imaging and Detection. In SEM, SHIM, and FIB-SEM microscopes, a focused beam of electrons or ions is used to scan or raster the surface of a specimen. The movement of the beam is paused for a short period of time known as the dwell time, which typically ranges from 50 ns to a few microseconds per point. The scanning is performed in a rectangular area referred to as the field of view (FOV), usually line by line starting from the top of the FOV and progressing downward (Figure 8). Concurrently, for each point, the excited signal due to the interaction of the volume matter (as described in section 2.1) is collected and postprocessed, and an image is generated on the monitor screen. Throughout the scanning process, various detectors can simultaneously collect the excited electrons and X-rays. The standard and basic detector, side mounted in a microscope vacuum chamber, is an Everhart-Thornley Detector (ETD) that captures SE emitted from the sample when it is bombarded with a primary electron beam. The ETD can detect low-energy secondary electrons, making it very sensitive to the topography and surface details of the sample. The ETD detector also can operate in a BSE collection mode but is not optimized for this purpose. Electron detectors can also be positioned inside the SEM column, such as the Through Lens Detector (TLD) that detects SE and BSE, or placed beneath the pole piece, like retractable detectors such as the Concentric Backscattered (CBS) detectors. BSE units detect elastically scattered electrons, providing valuable compositional and topographical information. They excel in compositional contrast, with heavier elements appearing brighter, allowing differentiation between materials of different atomic masses. BSE images also offer some topographical insights and can penetrate deeper into samples than SEs, making them useful for imaging bulk materials and subsurface features. BSE imaging is less affected by charging issues, which is beneficial for nonconductive samples. However, BSE images have lower resolution than SE images due to a larger interaction volume, resulting in less detailed surface information. Their higher energy and deeper penetration make them less sensitive to surface details and fine features. Interpreting BSE images can be complex, influenced by factors like surface topography, sample orientation, and detector settings. Additionally, BSE detectors are less sensitive to low atomic number materials, leading to reduced contrast in samples composed of lighter elements. It is worth pointing out that CBS is designed to detect BSE more efficiently and to provide compositional contrast across the sample. It typically consists of concentric rings or segmented annular regions that surround the area of electron beam impact. These segments are designed to detect BSE at various angles. Application of segmented and pixelated electron detectors is on the rise in SEM microscopes.

**2.2.2. EDS Analytics.** Energy Dispersive Spectroscopy, commonly used in SEM or FIB/SEM, is the most accessible technique for elemental composition analysis in battery applications within an electron microscope. It works by using

a beam of electrons to hit the material, knocking out other electrons from the material's atoms. The atoms then relax by emitting characteristic X-rays with specific energies, allowing the identification of the elements and the composition present in the material.<sup>76</sup> The advancement of EDS systems has been closely linked with the development of silicon drift detectors and significant progress in computer technology over the past 20 years. This has resulted in high output count rates, exceeding several thousand counts per second, and the ability to acquire a complete spectrum at every pixel within an image. For battery application, this method is particularly suitable for detecting transition metal elements in the cathode<sup>93-97</sup> and for detecting carbon (C), silicon (Si), nitrogen (N), fluorine (F), and oxygen (O) elements in the anode.  $^{98-102}$  In addition, the F distribution in the electrode can be the indicator of the binder distribution, and Zirconium (Zr) or Copper (Cu) in cathode raw materials' quality assurance analysis indicates impurity.<sup>103</sup> The technique offers high spatial resolution, enabling the characterization of features on a submicron length scale, with minimum detection limits around 0.1 wt % in the best cases.

However, while EDS is commonly used for elemental analysis of battery materials, detecting lithium in cathode oxide materials poses challenges, especially given the increasing demand for accurate lithium detection due to its critical role in battery performance. A standard EDS detector with a window completely absorbs ultrasoft X-rays around 54 eV, including the Li K $\alpha$  emission at 54.3 eV, before they can reach the detector. As a result, detecting lithium via EDS is only feasible using a windowless EDS detector. Recently, a study demonstrated the success of detection of Li K $\alpha$  X-ray emission via a windowless silicon drift detector in various compounds.<sup>104</sup> One of the major challenges of windowless EDS for lithium detection in battery materials analysis is the lack of sufficient energy resolution ( $\sim$ 50 eV) when detecting lithium. For example, achieving a zero-peak width of <30 eV and distinguishing a 54 eV energy event involve analysis complexity when the L-lines of Al (70 eV), Mn (64 eV), Co (78 eV), Ni (85 eV), and Mg (40 eV) contribute to a bump centered around 50 eV (the Li K $\alpha$  line is located at 54.3 eV).

Soft X-ray Emission Spectroscopy (SXES), on the other hand, overcomes these energy resolution limitations by using a gratings-based spectrometer and charge-coupled device camera or X-ray detector. The higher energy resolution (up to 0.1 eV) enhances its lithium detection capability more than a windowless EDS detector. In addition, it provides an energy shift measurement that reflects chemical bonding.<sup>105</sup> However, low photon energy in SXES necessitates high electron currents and extended times for data acquisition, which present several challenges. Prolonged data collection at high currents hinders efficient acquisition, rendering SXES impractical for mapping applications. High electron currents in spot mode can potentially either damage sensitive battery materials or induce chemical changes during the analysis. Overall, although both windowless EDS and SXES can detect lithium in the battery materials, there are still challenges. Li K $\alpha$  X-rays emission is much weaker compared to that of heavier elements, and the exact processes involved in Li X-ray emission are not fully understood, making quantification difficult. Furthermore, the ultrasoft nature of Li K $\alpha$  X-rays makes them highly susceptible to absorption by the sample itself, especially in the top surface layer.

When analyzing battery materials via EDS, EDS mapping is a widely used technique to investigate the elemental distribution



**Figure 9.** (a) and (b) Quant mapping analysis NMC cathode particles identifies atomic composition of Nickel–Manganese–Cobalt (NMC) ratios as Nickel: 0.81, Manganese: 0.07, and Cobalt: 0.12. Phase mapping analysis of the same area (c) and (d), that distinguishes Nickel variation within NMC single crystal particles and detects impurities (such as Aluminum (Al), Tungsten (W) and Phosphor (P)).

within a sample, offering an intuitive way to interpret its elemental composition and arrangement. There are three different approaches for EDS mapping, namely gross count mapping, quantitative mapping, and phase mapping. The gross count mapping is the most basic approach, which involves mapping the total X-ray counts with corresponding elements present within the sample above the minimum detection limit. It provides a qualitative analysis, a general idea of the element density distribution within the materials, while there is a lack of quantitative information on each element in the materials. Quantitative mapping, also known as live chemical imaging, represents a more advanced technique. This method involves a step known as background removal and deconvolution to accurately identify and quantify the elements present, associating characteristic X-rays emitted by the sample with corresponding elements present. Figure 9a and 9b show quantitative mapping analysis of nickel manganese cobalt oxide (NMC) cathode particles to collect maps of Nickel (Ni), Manganese (Mn) and Cobalt (Co) with quantification. This method offers immediate visual feedback on the elemental composition, allowing for quick assessments and adjustments during analysis. It also provides precise elemental concentrations, expressed either as Wt.% or atomic percent (At.%).

If additional information, such as identifying phases due to variations in element concentration, is required, phase mapping is necessary. The phase mapping involves grouping pixels with similar compositions to identify unique chemical phases, contrasting with the other two mapping methods targeting pure elements. It uses Principal Component Analysis, a statistical method used for analyzing spectral data, and examines each pixel and the spectra it belongs to, aiding in understanding the complex sample because each pixel is assigned to a single phase. In the same area that analyzed NMC particles with quantitative mapping, phase mapping is performed for comparison, as shown in Figure 9c and 9d. Besides most materials showing as NMC with a ratio of  $Ni_{0.81}Mn_{0.07}Co_{0.12}$ , materials with low Ni concentration  $Ni_{0.67} Mn_{0.17}Co_{0.17}$  and other impurities are also observed. This method allows for a more comprehensive understanding of sample composition and can be routinely applied in the materials quality control process for impurity identification.

**2.2.3. EBSD Analytics.** Electron Backscatter Diffraction is widely used to characterize metals and alloys, measuring grain size, orientation, misorientation, and crystallographic texture. The technique relies on backscattered electron diffraction signals from shallow surface layers, typically a few tens of nanometers deep, requiring perfect sample surface finishing. In recent years, EBSD has also been applied for battery materials characterization to understand the performance and degradation of different battery systems.<sup>106–108</sup> For the development of cathodes, materials like NMC are typically synthesized into polycrystalline particles with varying sizes and crystal orientations. The grain orientation is connected with its lithium transport property and accounts for the intergrain lithiation barrier; therefore, it is critical to understand and quantify the



**Figure 10.** (a) Modeled backscattered electron yield and depth of lithium, NMC811, and nickel, with angles of incidence set to 70 and 0 degrees at 10 keV. (b) Electron backscattered diffraction (EBSD) of lithium metal. (c) Example Kikuchi pattern imaged by EBSD detector. (d) Inverse pole figure for shown map showing orientation of crystal lattice for points in the map. Reproduced with permission from ref 109, Copyright 2022 Elsevier.

grain property via the EBSD method for materials' diagnosis and development.<sup>107</sup>

For anode development, certain materials, such as lithium metal, pose practical challenges for EBSD characterization for two main reasons. The highly chemical reactivity of these materials results in challenges in sample handling that require careful protection, where the chemical reactions and passivation layer thickness are pivotal factors that influence the EBSD results. In addition, an intrinsically low backscattered electron coefficient and spatial resolution limitation due to the BSE surface radius with the depth of the BSE signals suggest that low index rate of lithium metal EBSD results are expected with challenges for grain boundary analysis.<sup>109</sup>

Figure 10a shows the results of using the Monte Carlo method to model the backscattered electron yield and depth across various battery related materials including lithium, NMC811, and nickel, via the software CASINO 2.5.<sup>110</sup> The results demonstrate that the backscattered electron signal of lithium metal has the deepest penetration depth, nearly 40 times deeper than that of nickel metal. This difference highlights significant variations in material properties and how electrons interact. It is noteworthy that while the backscattered electron coefficient between Nickel and NMC is similar in value, the coefficient for lithium is less than 50% of that for NMC or Nickel (Table 2).

Table 2. BSE Coefficient of Lithium Metal, NMC 811, and Nickel Metal at 0 Degree and 70 Degree with 10 kV Acceleration Voltage

	Lithium metal	NMC811	Nickel metal
BSE Coefficient	0.016	0.16	0.24
0 degree, 10 kV			
BSE Coefficient	0.21	0.50	0.56
70 degrees, 10 kV			

This discrepancy suggests that lithium metal requires a higher beam current for effective EBSD analysis, highlighting the unique challenges associated with characterizing this material at the nanoscale. Figure 10b–10d shows the EBSD results of the lithium metal prepared by the microtome method.<sup>109</sup> 78% of 29400 total points were indexed successfully, where the points around the cross-section rarely resolved, which is aligned with the simulation results where lithium has a low BSE coefficient and low-contrast diffraction poses challenges to gaining high quality EBSD data.

The intrinsic reactivity of alkali metals such as lithium or sodium poses challenges to performing EBSD analysis on them. Strategies from sample handling to site preparation to data collection in FIB-SEM need to be employed that lead to a successful experiment.<sup>106,108</sup> First of all, all stages from sample handling to data acquisition must be conducted in a rigorously controlled environment, such as a high vacuum or an inert atmosphere (e.g., argon backfilled) to prevent surface contamination and degradation of the highly reactive alkali metals. During the FIB milling process, milling parameters such as temperature, accelerating voltage, and protective coating layers selection are the parameters that can be tuned for experiment optimization. Operating the milling process at cryogenic temperature can reduce thermal damage to the highly reactive alkali metals. In addition, reducing the ion beam energy (e.g., lower acceleration voltages from 30 kV to 16 kV or 8 kV) during FIB milling helps reduce the ion range into the materials, minimizing the extent of ion-beam-induced damage within the alkali metal. To further mitigate potential damage, leveraging the current collector as the capping layer in battery samples (e.g., copper current collector in studying Li-metal battery) instead of using a Gas Injection System (GIS) process to generate a capping layer is recommended. In the EBSD data acquisition process, conducting the analysis at cryogenic temperatures is also beneficial together with a lower acceleration voltage (e.g., 10 kV is generally preferable to 20 kV) to minimize electron beaminduced damage.

In summary, the above protocols are designed to minimize sample alteration during preparation and analysis by preventing heating and surface damage, reducing ion range and electron penetration depth, which ensures the accurate measurement of the true grain size and crystallographic orientation of the alkali metals. It is worth noting that some protocols have trade-offs. For example, cryogenic FIB-SEM adds experimental complexity (details discussed in Section 2.3); lower ion or electron beam energy will extend the experimental time and reduce the signalto-noise ratio. Carefully selecting which strategy to adopt is critical in experimental design and can optimize the specific experimental condition for each sample.

**2.2.4. FIB-SIMS Analytics.** Secondary Ion Mass Spectroscopy is a major experimental technique used for materials chemical analysis. It operates by collecting and separating ions based on their mass-to-charge ratio (m/z) from secondary ions detected. These secondary ions are emitted from solid material surfaces as a small fraction of charged particles among sputtering particles by bombardment with a primary ion beam. SIMS instruments are typically dedicated instruments housed in ultrahigh vacuum (UHV) environments, featuring various



Figure 11. A schematic diagram illustrating the fundamental principles of ToF-SIMS. Reproduced with permission from ref 111. Copyright 2021 American Chemical Society.

configurations with multi-ion sources that separate the function of sputtering and SIMS analysis. The classification of these instruments is primarily determined by the type of mass analyzer integrated into them.<sup>42</sup>

Integrating a compact time-of-flight (TOF) SIMS, into a DualBeam FIB/SEM microscope not only enhances its capacities for imaging and sample preparation but also transforms focused ion beam (FIB) into an analytical tool. The combined system is often referred to as "FIB-SIMS" to distinguish it from dedicated SIMS instruments, as shown in Figure 11.11<sup>111</sup> The compact TOF-SIMS analyzer utilizes orthogonal extraction design to pulse the secondary ion beam, allowing for continuous sputtering of the sample surface by the primary FIB beam, and collect and separate all detected secondary ions in parallel.<sup>112</sup>

As an important materials chemical analysis technique, TOF-SIMS is critical for battery research, as it can efficiently detect lithium because lithium has a low ionization energy compared to other elements in the periodic table. This energy generally increases throughout a period, reaching its peak for noble gases, which have closed electron shells.

 $Li^0 + 5.39 \text{ eV/atom} \rightarrow Li^+ + e^-$ 

The low ionization energy of lithium means that FIB-TOF-SIMS can easily detect lithium as [<sup>7</sup>Li<sup>+</sup>] and [<sup>6</sup>Li<sup>+</sup>], making it well-suited for efficiently analyzing lithium in various lithium ion battery materials.<sup>113,114</sup> Figure 12a-12b present the lithium distribution within the cross-section of cathode materials in both discharged and charged states, with [7Li<sup>+</sup>] ion SIMS maps obtained using a PFIB-SEM Xe<sup>+</sup> TOF-SIMS. During SIMS data acquisition, the ion beam is directed perpendicular to the cut face of the cross-section. The obtained FIB TOF-SIMS results offer several insights: In the charged cathode (when external voltage is applied), most cathode particles exhibit minimal lithium signal, while some lithium ions are trapped at specific locations within the cathode materials. Upon discharge, lithium ions uniformly return to the cathode oxide material as a general pattern. The difference in SIMS lithium signal between charged and discharged states is approximately 5-fold (Figure 12c).<sup>115</sup> In



**Figure 12.** (a) and (b) TOF-SIMS [<sup>7</sup>Li<sup>+</sup>] maps of discharged and charged cathode cross sections, displaying the lithium distribution. (c) Normalized signal comparison of (a) and (b). (d) 3D distribution of <sup>7</sup>Li<sup>+</sup> in the cathode. (e) and (f) A cross-section of the lithium battery cathode and corresponding <sup>19</sup>F<sup>-</sup> distribution; scale bar:  $5 \mu m$ ; (a)-(c) data collected via PFIB TOF-SIMS, (d)-(f) data collected via Ga<sup>+</sup> FIB TOF-SIMS.

addition to 2D analysis of lithium, 3D TOF-SIMS can enable analysis of the lithium distribution within the electrode as shown in Figure 12d. In addition to lithium detection, FIB-SIMS can also detect other elements that are critical to the battery, such as fluorine (F), which is an important element for binder indication as well as the SEI component. SIMS simplifies the detection of fluorine in negative ions. For instance, when a fluorine atom gains an electron to become F<sup>-</sup> ion, it releases energy (-1.4 eV). In Figure 12f, the presence of a [<sup>19</sup>F<sup>-</sup>] SIMS image around active material particles indicates a high concentration, suggesting a binder layer approximately 250 nm thick by measurement of the location of fluorine. Traditional techniques like SEM-EDS lack the required lateral resolution for accurate measurement of the binding layer thickness from SEM-EDS fluorine elemental mapping, while TEM-EDS is limited to very small field widths.

Overall, the integration of TOF-SIMS into the DualBeam SEM/FIB system enables the ion beam to serve not only for sample preparation but also as an analytical tool. The technique boasts a high capability for detecting lithium, making it suitable for 2D/3D TOF-SIMS work in LIB research. However,

#### Table 3. Advantages, Disadvantages and Mitigation Strategies in FIB-TOF-SIMS Analysis of Battery Materials

Advantages	Challenges	Mitigation the weakness
Detection of Li and other light elements, C, O, F.	Relative low signal from transitional metals: Co, Mn, Ni.	Transition metal is better to use SEM-EDS.
High signal from some battery materials elements, Li, Na, K, F, O.	In the same area-of-interest (AOI), positive and negative ions are collected separately and subsequently undergo destructive analysis.	Run SEM-EDS before FIB- SIMS.
Lateral resolution better than SEM-EDS and XPS.		
High depth resolution similar to XPS depth profiling.	Preliminary knowledge of the composition of battery samples is essential for effective data analysis.	
Parallel collection all type of ions better than magnetic sector SIMS.	Even at low mass, the presence of mass interference introduces uncertainty when assigning mass peaks to small molecular ions.	
Analysis area better than APT and TEM: Area: $10^2 - 10^4$ um <sup>2</sup> .	Sensitive to topography and FIB milling curtains.	

#### Table 4. Comparison of Chemical Analytical Techniques<sup>a</sup>

	SEM/EDS	TEM/EDS	Atom Probe Tomography	XPS	SEM/FIB-SIMS
Probe Beam (In)	Electrons	Electrons	Photons	Photons	Ions
Analysis Beam (Out)	Photons	Photons	Ion	Electrons	Ions
Lateral Resolution	$1 \ \mu m$	0.5-1 nm	0.3–0.5 nm	5 to 500 µm	<50 nm
Depth Resolution	$1 \mu m$	2-10 nm	0.1–0.3 nm	1-10 nm	10-20 nm
Detection Limit	1000 ppm	1000 ppm	5–10 ppm	1000 ppm	100s ppm
Lightest Element	Li ( <sup>b</sup> )	В	Н	Li	Н
Depth Profiling	n/a ( <sup>d</sup> )	n/a	Yes	Yes	Yes
Quantification	Good	Good	Good	Excellent	Very Poor
Vacuum	10 <sup>-4</sup> Pa	10 <sup>-5</sup> Pa	$10^{-7} - 10^{-10}$ Pa	$10^{-7}$ -10 <sup>-10</sup> Pa	10 <sup>-4</sup> Pa
Information	Elemental	Elemental	Elemental	Elemental, Bonding	Elemental <sup>c</sup>
				Chemical State	Isotopes

"Note: The listed values are achievable using commonly available instruments and materials. <sup>b</sup>Requires windowless EDX detector and operating at well-defined beam and sample conditions without quantification. <sup>c</sup>Small molecule ions are possible. <sup>d</sup>Available in FIB-SEM, where FIB is used to remove material layers.

challenges such as the reliance on ionization of sputtering atoms resulting in removing materials, ionization chemical matrix effects, and the presence of mass interference can lead to uncertainties in the interpretation of molecular ions. These challenges can be mitigated through careful sample preparation techniques, optimization of FIB parameters, and the use of advanced data analysis algorithms aimed at reducing noise and improving peak assignment accuracy. Table 3 summarizes the guidance of using TOF-SIMS for battery research.

Given the wide range of chemical analytical techniques used for battery analysis, Table 4 summarizes these techniques to assist in selecting the appropriate method for analyzing battery materials. Notably, SEM/FIB-SIMS and SEM-EDS are two techniques that can be integrated into FIB-SEM. Comparing SIMS to EDS, SIMS stands out for superior spatial resolution, lower detection limits, especially on light elements (e.g., lithium), and capability for depth profiling and isotopic analysis. However, quantification is challenging with SIMS, and the measurements are destructive to the sample.

X-ray Photoelectron Spectroscopy (XPS) serves as a reliable average chemical analytical method for batteries, capable of detecting Li, chemical states, and bonding, and of providing quantification results. However, one of the main drawbacks of XPS is its spatial resolution as each 'pixel' or X-ray spot size representing the size of the smallest analysis area, which is typically around  $400-500 \,\mu\text{m}$  in standard operation, with recent advancement to resolution as low as  $10 \,\mu\text{m}$ . APT enables high-resolution and high-sensitivity imaging with isotope selectivity, providing quantified information. However, its applicability is limited due to limited sample size, labor intensive sample preparation process, and chance of introducing artifacts.

**2.2.5. FIB-SEM In Situ Accessory.** In addition to the detectors and analytical techniques mentioned in the above sections that are commonly equipped in FIB-SEM as accessories, in situ accessories such as GIS and nano manipulators are critical components for FIB-SEM. These accessories, along with other tools like nanogrippers, nano-indenters, and scanning atom probes, greatly extend the functionalities of FIB-SEM systems.<sup>12</sup> By using these in situ accessories, battery researchers can conduct dynamic experiments, make real-time sample modifications, and achieve precise manipulation of nanoscale objects.<sup>116–119</sup>

GIS enables the introduction of gases or gaseous metal precursors into the specimen chamber during FIB-SEM operations. This capability is particularly valuable for conducting in situ experiments and modifying the surface properties of the sample. The injected gases can serve various purposes, including enhancing imaging contrast, facilitating material deposition or etching processes, and improving FIB milling surface quality.<sup>116</sup>

Another valuable accessory is the tungsten needle nano manipulator. This device provides precise control over the positioning and manipulation of nanoscale objects within the FIB-SEM system. With the nano manipulator, researchers can easily move, rotate, and lift nanoscale structures, battery particles for in situ experiments, TEM lamellas for nanoscale characterization, or material chunks for FIB serial sectioning tomography.<sup>117–119</sup> The precise and repeatable control offered by the nano manipulator enables delicate operations with high accuracy, making it an essential tool for nanoscale research and manipulation within the FIB-SEM environment.



Figure 13. (a) A schematic overview of the Cryo-FIB setup. (b) Fully rotatable Cryo-stage. (c) Inert gas sample transfer system. (d) Sample preparation pot for Cryo-FIB. (e) EasyLift Nanomanipulator for Cryo-FIB-lift-out.

#### 2.3. Cryogenic FIB-SEM

Over the past 20 years, cryogenic FIB (Cryo-FIB) has emerged as a powerful technique for preparing and characterizing samples that are beam-/temperature-sensitive or contain liquid phases in both the biological and materials science communities. In the biological science field, the key benefit of adopting a cryogenic technique is the preservation of the natural structure of biological samples in their hydrated state, which is crucial for accurate imaging with electron microscopy. Cryo-FIB started serving as a sample preparation tool to apply Cryo lift-out on frozen-hydrated specimens for cryogenic electron tomography,<sup>120–122</sup> on-the-grid lamella preparation for TEM analysis of vitrified cell,<sup>123–125</sup> or Cryo-FIB lift-out sample preparation for thicker samples that went through high pressure freezing sample preparation.<sup>126</sup>

On the other hand, materials scientists started adopting Cryo-FIB by leveraging its advantage in reducing beam damage and reaction rate between ion and matter. The early success of Cryo-FIB has been widely demonstrated in characterizing various beam or temperature sensitive materials, including compound semiconductors,<sup>127</sup> soft and porous membrane electrode assemblies,<sup>128</sup> thin-film solar cells,<sup>129</sup> metal-organic frameworks crystals,<sup>130</sup> and low melting point metals such as indium.<sup>131</sup> Furthermore, this technique's capabilities extended to conducting reaction limited experiments, successfully preventing hydrogen pickup during TEM sample preparation of Ti alloys, <sup>132</sup> and suppressing surface nanodroplets formation on group III-V semiconductors.<sup>133,134</sup> Most recently, the application of Cryo-FIB has been further advanced to characterize samples with a liquid phase, including enabling character-ization of the solid–liquid interface,  $^{135-137}$  and for analysis of devices containing patterned functional liquids, maintaining the integrity of both phases throughout the characterization process.<sup>138</sup>

In terms of starting to adopt Cryo-FIB for battery research, this is mainly due to increasing demand in studying temperature sensitive, beam reactive, and liquid phase-containing systems for next generation battery development, such as lithium metal, sodium metal, solid-state electrolytes (SSE), and the SEI.<sup>22,139,140</sup> The past success and knowledge gained from other fields make Cryo-FIB a well-suited and powerful technique in battery or energy material research. To date, numerous

studies have highlighted the use of Cryo-FIB, which allows for the preservation of materials in their native state, with integration of various analytical techniques such as EDS, EBSD, TEM, and APT for advancing battery development (refs 20, 23, 24, 45, 47, 136, 137, and 141–146).

Figure 13 shows a typical Cryo-FIB setup with key components including Cryo-stage, sample transfer device, sample preparation station, and micromanipulator. The schematic diagram (Figure 13a) illustrates that the Cryo-stage and anticontaminator are cooled by nitrogen gas, which is sent through a heat exchanger in an offline dewar containing cold liquid nitrogen. This process maintains the stage down to liquid nitrogen temperature. The gas flow is adjustable to minimize vibrations and nitrogen consumption. Cooling can also be achieved via copper conduction bands, which are less prone to vibrations compared with the gas-cooling method, but the cooling rate is slower, as it relies on passive conduction rather than active cooling. Recent innovation in stage designs enables the fully rotatable Cryo-stage as shown in Figure 13b, which provides greater flexibility to access samples in different geometries. It is also equipped with a temperature control system by heating elements so that temperatures between 30 °C and -180 °C can be achieved. The wider temperature range allows dynamic experiments or phase transformation study.

Another important consideration for cryogenic setup is the sample transfer. Depending on the battery materials type, either inert gas transfer at room temperature or full Cryo-transfer at liquid nitrogen condition will be selected. Nevertheless, if samples are neither air/environmentally sensitive nor contains liquid component, and are only beam sensitive, they can be directly loaded onto the Cryo-stage before cooling down the stage to start the experiments. Figure 13c shows the sample transfer unit that enables inert gas sample transfer capability attached to the microscope chamber and can exchange sample between the glovebox and microscope. For samples that contain liquid, then the sample transfer needs more careful consideration, as samples need to be cooled down under liquid nitrogen before loading into the microscope, where a sample preparation station (Figure 13d) is needed to combine with the corresponding sample transfer unit to enable a full Cryo-transfer process.

There are other critical accessories that could be added onto the Cryo-FIB workflow. For TEM sample preparation, to minimize any heat transfer between the sample and nanomanipulator, a Cryo-compatible nanomanipulator is required. As shown in Figure 13e, the probe shaft has been assembled with a thermally isolated probe tip that is passively cooled via a direct connection via using a clamp to the cryogenic system's anticontaminator. In addition, considering that the electrical conductivity typically goes down at lower temperature, proper coating capability such as a microsputter coater or magnetron sputter coater is needed to minimize charging that is a challenge during both milling and imaging within FIB-SEM.

# 2.4. FIB-SEM Techniques: 2D Imaging, 3D Tomography, and TEM Lamella Preparation

As a versatile and powerful tool in materials research, FIB-SEM enables detailed microstructural analysis in multidimensions at multilength scale. For battery development, there are three major techniques that are widely used, namely 2D sample preparation and analysis, 3D tomography, and TEM lamella preparation (Figure 14). 2D sample preparation enables access



Figure 14. Schematic of different techniques in FIB-SEM for battery characterization.

to the internal microstructure of battery samples, to gain knowledge beyond the surface. 3D tomography provides more quantitative understanding of the battery structure and performance correlation. For high-resolution nanoscale characterization, TEM lamella preparation is an essential technique to enable a high quality sample for TEM analysis. The following sections will provide detailed insights into each technique and their contributions to battery development.

**2.4.1. 2D Sample Preparation.** The FIB technique provides exceptional flexibility in terms of specimen geometry and substrate materials for material sputtering for 2D sample preparation. This localized and direct approach allows for precise realization of desired geometries. Moreover, FIB processing can be conveniently monitored in real-time using SEM, enabling direct alignment and quality control during the operation.

In FIB-SEM characterization, implementing effective imaging and milling strategies and adhering to standard sample handling procedures are crucial for obtaining high-quality data. When preparing samples for FIB-SEM characterizations, several common defects and artifacts can occur, such as curtaining, charging effect, surface contamination, and beam damage effects, causing potentially misleading images. Curtaining appears as vertical streaks in the image at the FIB-milled area, caused by uneven milling due to variations in material hardness

or improper FIB settings. To mitigate this, one can apply a thick protective layer or use the rocking-polish method (see Section 2.4.1.2). Sample charging leads to distorted or bright regions in SEM images due to charge accumulation on nonconductive samples. This issue can be addressed by coating the sample with a conductive layer or using a low-vacuum mode. Contamination presents as unwanted deposits or particles on the sample surface, often resulting from contaminants in the vacuum chamber or improper sample handling. This can be mitigated by thorough cleaning and adhering to cleanroom protocols. Beam damage, resulting from prolonged exposure to photon, ion, or electron beams, alters the sample's microstructure or composition. A common beam damage effect in FIB-SEM characterization is amorphization, which occurs when ion beam interactions cause the crystalline structure of the sample to become amorphous. To mitigate this, it is necessary to minimize exposure time and use lower beam currents, energies, and doses. Overall, by understanding and addressing these common defects and artifacts, researchers can improve the accuracy and quality of their FIB-SEM characterizations.

Besides reducing image defects via appropriate imaging and FIB polishing strategies, users also need to follow standard procedures for sample handling in electron microscopy to ensure high-quality data. FIB-SEM manufacturers impose sample size and weight restrictions: specimens are typically fixed to 12 mm diameter stubs and should be a few millimeters in size. Use of a diamond saw or precision cutting tools to trim the sample to the desired size and shape followed by polishing it for a smooth finish can minimize topographical artifacts. In addition, sample cleaning is mandatory to remove contaminants or debris that could interfere with imaging. Solvents like isopropanol or acetone, followed by drying with nitrogen gas, should be used to obtain pristine samples. To reduce sample charging artifacts during handling, it is essential to fix specimens rigidly on a suitable holder or stub using conductive adhesive or doublesided metal tape to ensure they are well-grounded and prevent charging during imaging. Nonconductive samples should be coated with a thin layer (dozens of nanometers) of conductive material (e.g., gold, platinum, or carbon) to prevent charging and improve image quality. A sputter coater or evaporator is critical for a uniform coating. Finally, it is critical to always handle samples using protective gloves and dedicated tweezers.

2.4.1.1. Sputtering Mechanism. Ion sputtering occurs when a sample atom is ejected by the bombarding ion from the sample surface (see Figure 1b). A single ion can sputter several sample atoms; thus, sputtering yield is parameter that quantifies the number of sputtered atoms per number of incident atoms. Only atoms near the sample surface are potential candidates for sputtering. The more collisions that occur on the sample surface, the more likely that sputtering occurs. Atoms that are located deeper within the sample are less likely to be sputtered because the ion beam loses energy as it penetrates the specimen.

Sputtering yield is predominantly influenced by the ion element (Figure 4) and the initial ion energy (acceleration voltage), the incidence angle, the surface binding energy (atoms of the specimen), and the crystallographic orientation of the sample (ions channeling vs collision cascade). Figure 15 shows the influence of various factors on the sputter yield.

2.4.1.2. 2D Cross-Section Preparation. Focused ion beam cross-sectioning is a site-specific technique used in material science, life sciences and the semiconductor sector to prepare samples for further ex-situ and in situ imaging<sup>147</sup> and/or other analysis such as EDS and EBSD.<sup>148</sup> This technique combines the

Review



Figure 15. Influence of various factors on the sputter yield. These factors include the ion type and its energy (a), the incident angle (b), crystallographic orientation (c-d), and sample geometry (e).



**Figure 16.** Typical cross-section prepared with a FIB-SEM: (a) the cross-section preparation and analysis process steps. (b) FIB image; (c) SEM secondary electron image; (d) side-view schematics of top-down milled cross-section geometry,  $\alpha$  is typically 52°; (e) and (f) schematics of top-down milling with FIB or fs-laser beam (the protective layer is not needed for the laser) and rocking-polish for plasma FIB; (g) curtains created on NMC cathode cross-section by top-down milling with Xe<sup>+</sup> PFIB, 30 kV @ 200 nA; SEM and FIB Images in (b) and (c) are adapted with permission from ref 149. Copyright 2025 Analytical Answers.

advantages of precision milling using a focused ion beam and imaging with SEM to collect high-resolution images of cross sections of materials. Figure 16a shows typical cross-section preparation and analysis process steps.

The process begins by selecting the area of interest in the sample, which could be a specific feature, defect, or interface. The FIB-SEM then uses a beam of charged ions and GIS to gradually deposit a protective layer (typically Platinum (Pt) or Tungsten (W) several microns thick) over the region of interest. Later the focused ion beam ( $Ga^+$ ,  $Xe^+$ ,  $Ar^+$  or  $O^+$ ) or femtosecond pulsed laser focused beam (for TriBeam systems)

is used to gradually mill away material to create a cross-section. The ion beam or focused laser beam can be precisely controlled to remove material with high accuracy, allowing for cross sections with nanoscale resolution. Ga<sup>+</sup> FIB typically makes pristine cross sections (Figure 16c) by top-down milling (as depicted in Figure 16e), while plasma FIB in a similar milling manner creates surface topographic periodic vertical hills and valleys, known as curtains (Figure 16g). These curtains can be mitigated by applying a thicker protective layer (~10  $\mu$ m thick) and/or the so-called rocking-polish method.<sup>50</sup> Here the cross-section is created by periodic milling and advancing the beam at



Figure 17. Comparison of typical cross-section dimensions prepared by Ga<sup>+</sup> FIB, plasma FIB and fs-laser beam. Arrows indicate the milling direction.



**Figure 18.** (a) Schematic of the spin milling geometries. (b) Stage and detector positions for various steps of spin milling, e.g. on-axis and off-axis polishing, SEM imaging and EDS mapping positions, and EBSD data collection geometries. (c) Maps software collected tiles of high-resolution SEM image of two regions of interest spin milled using Xe<sup>+</sup> plasma FIB; SEM-SE image (d) and SEM-BSE image (e) of zoom in to microstructural detail of polished region; (f) the spin milling preparation, execution and analysis process steps.

two stationary angular positions (typically  $\pm$  <6 deg), as shown in Figure 16f. The type of focused beam used depends mainly on the size of the region of interest and the desired size of the crosssection that needs to be created. Due to its milling rate limits, Ga + FIB is used to make small cross sections with a width of less than 50  $\mu$ m and a depth of less than 20  $\mu$ m<sup>50</sup> (for example in Figure 16b and 16c). Plasma FIB allows creating much bigger cross sections having a width of hundreds of microns and a depth in a similar range as the width, while a femtosecond pulsed laser focused beam opens over a mm wide and deep cross-section. Figure 17 compares the sizes of cross sections of a NMC cathode prepared by Ga<sup>+</sup> FIB, Xe<sup>+</sup> PFIB and a fs-laser beam.

During the milling process, the SEM column also provides fast imaging using SE or BSE. This allows for monitoring the progress and making adjustments as necessary. The imaging capability of the FIB-SEM instrument provides valuable information about the sample's structure and helps in selecting the correct area for cross-sectioning. Once the desired depth is achieved, the cross-sectioned sample can be further analyzed using various characterization techniques (see Sections 2.2.2 to 2.2.4 for details on EDS, EBSD, FIB-SIMS techniques). Later the collected images and data are postprocessed, for example to remove noise from SEM images, segment microstructural features, create elemental EDS maps or crystallographic orientation maps, etc. Often machine learning (ML) algorithms are employed at the postprocessing step, e.g. image denoising and image segmentation.<sup>150</sup> Data quantification and reporting concludes the data collection and analysis procedure.

2.4.1.3. Spin Milling. Plasma focused ion beam spin milling (PFIB-SM)<sup>89,151</sup> is a relatively new FIB application. This technique, as shown in the schematic diagram in Figure 18a, replicates the milling geometry used in BIB polishing systems. In PFIB-SM, low glancing angles, typically less than 5 degrees, are employed against a flat surface. The focused ion beam is rapidly milling within a defined area, which can be either rectangular or oval in shape. To achieve spin milling, several stationary stage rotation positions are set instead of continuously spinning the stage. The typically accessed area in FIB-SM ranges from 300  $\mu$ m in diameter, but it is also possible to increase the area to ~1 mm. This method allows access to both on-axis and off-axis locations of the stage (Figure 18b).

During the spin milling process, the SEM is utilized to capture fast imaging at oblique angles using secondary electrons or backscattered electrons. This enables near real-time monitoring



**Figure 19.** (a) Serial cross-section preparation and analysis process steps, where darker green marks step that are authorized by the serial sectioning software. (b) FIB image with description of characteristic features of the serial cross-section site; (c) SEM secondary electron image; (d) side-view schematic of serial cross-sectioning geometry, where  $\alpha$  is typically 52 degrees.



Figure 20. Comparison of typical serial cross-section accessed volumes as prepared by FIB, plasma FIB and fs-laser beam.

of the polishing progress and allows for adjustments as needed. Once the spin milling is completed, the polished area can be further analyzed using in situ and ex situ characterization techniques. Figure 18b illustrates the in-chamber setups for acquiring SEM, EDS, and EBSD data. The subsequent data handling steps for spin milling are similar to FIB crosssectioning. Figure 18c-18e show the results of the SEM images of the PFIB-SM polished NMC cathode surface. Compared to the 2D cross-sectional analysis method, spin milling offers a high-throughput, large area (sub mm) surface polishing capability for electrode surface analysis to gain statistics for sample representativeness. The extensive high-quality polished area allows for detailed analysis of structural characteristics, including statistical evaluation, facilitating an in-depth examination of structural-performance correlations in battery studies, such as crack analysis and defect distribution.

**2.4.2. 3D Serial Sectioning Tomography.** Focused ion beam 3D serial cross-sectioning tomography is an in situ site-specific technique. This technique extends the capability of 2D cross-sectioning by adding the third dimension of the imaged and analyzed region of interest through continuous slicing in the third dimension. It combines the benefits of precision milling using both Ga<sup>+</sup> FIB and plasma FIB, femtosecond focused laser beam, and imaging with SEM along with analytical methods like EDS and/or EBSD to collect high-resolution data from serial cross sections of materials. The serial cross-sectioning and data

collection process is automatized by dedicated software, that ensures repeatability, precision, and unattended data acquisition.<sup>50</sup> Figure 19 shows the typical cross-section preparation and analysis process steps, where darker green marks steps that are authorized by the serial sectioning software for FIB and PFIB. In the case of serial cross-sectioning with the focused fslaser beam, the site needs to be prepared manually with the laser beam, whereas the automation is realized with the user interface of the laser unit.<sup>17</sup>

A specimen of typical size, a few millimeters, will first be fixed on a SEM stub. The in situ process starts by selecting the area of interest in the sample. Site preparation can be done manually or with automated serial cross-sectioning software. During this step, the FIB column deposits a protective layer (typically Pt or W) over the region of interest (ROI) and a smaller pad behind it. A tracking fiducial is milled on the pad for precise positioning of the serial cross-sectioning beam (Figure 19b). Side and front trenches are then milled, setting the conditions for serial crosssectioning, such as beam energy and current, slice thickness and depth, number of slices, and rocking-polish conditions for the plasma FIB instrument. Additionally, SEM imaging and/or EDS/EBSD mapping parameters are being defined. Once all the parameters for the FIB and SEM columns are set, the automated procedure is activated for 3D data collection. The focused fslaser beam, SEM column, sample stage, and peripherals of the TriBeam system are controlled by an automated routine defined

in the laser user interface or by custom Python scripts. The type of focused beam used depends mainly on the depth location and size of the ROI. Ga<sup>+</sup> FIB, due to its milling rate limits,<sup>148</sup> is used to access near-surface volumes of about 20 × 20 × 20  $\mu$ m<sup>3</sup>. Plasma FIBs allow for accessing much deeper into the surface and 3D mapping volumes of about 200 × 200 × 200  $\mu$ m<sup>3</sup>.<sup>50</sup> Meanwhile, the focused fs-laser beam can access deeply buried ROIs in the millimeter range, even under cryogenic conditions<sup>64–66</sup> and perform serial sectioning of material volumes close to 1 mm<sup>3</sup>.<sup>17</sup> Figure 20 compares the sizes of volumes prepared by Ga<sup>+</sup> FIB, Xe<sup>+</sup> PFIB, and fs-laser TriBeam beam for an NMC cathode and an electrode stack (fs-laser). The results indicate that, depending on the length scale of the feature of interest, the FIB-SEM technique must be carefully chosen to obtain representative information from the sample.

Once the 3D data set is collected, appropriate post processing is required to enable accurate microstructural characteristic extraction and modeling can be achieved during the data analysis stage.<sup>14,59,152</sup> First, aligning the slice is necessary using 3D rendering software to align the coordinates of each image. This process is necessary to correct errors caused by image drift, beam shift, and stage offset that may occur during data acquisition. The alignment can be done using various methods like translation, rigid transformation, anisotropic scaling, and affine transformation. The next process requires a shear transformation process. FIB cuts the specimen vertically, and the cross section is imaged at an angle of 52 degrees through SEM. As a result, the ROI area in SEM moves to the y-axis, changing the data structure when creating a 3D volume. Shear transformation is applied to restore this deformed structure. Once the 3D volume is corrected via slice alignment and shear transformation, image analysis and segmentation need to be performed before further quantification and modeling. Figure 21 shows the workflow from data collection to the final segmentation process.<sup>153</sup> After the slice and view process



**Figure 21.** Workflow of SEM-FIB serial section and digital processing on a single NMC particle. (a) SEM surface image of a ROI position. (b) Cross section image of serial section structure. (c) Backscatter electron (BSE) image obtained from the FIB cross-sectioning workflow. (d) Vertical stripe contrast artifacts in all the acquired BSE images were removed using FFT filters before constructing the image stack. (e) Statistical noise background in all the acquired BSE images were removed using Gaussian filters before constructing the image stack. (f) Experimental BSE image stack with a cropped size of  $256 \times 256$  pixels. Pore image prepared as segmentation data sets after applying Thresholding and Top hat. Adapted with permission from ref 153. Copyright 2023 Springer Nature.

(Figure 21a and 21b), the uneven and rough surface of the specimen normally creates vertical stripe pattern artifacts, namely the curtaining effect, in the SEM image (Figure 21c). To remove such artifacts, fast Fourier transform (FFT) will normally be applied on the entire SEM image stack. In the frequency domain, the stripes manifest as a strong directional component, which can be effectively removed with a wedgeshaped filter as shown in Figure 21d.<sup>50</sup> Following the FFT filtering, Gaussian filters were employed on the BSE images to remove the high frequency noise with minimal impact on the data (Figure 21e).<sup>154</sup> Finally, thresholding methods to well segment the phases with different gray scale values with Top Hat that enable Crisper object boundaries are essential to enable high segmentation accuracy (Figure 21f). It can be noted that the high raw images quality, namely good image contrast among phases and minimum artifacts due to milling or imaging, is always the most important factor to determine the final segmentation accuracy, as each image process operation will always introduce errors while removing the artifacts.

After the data set is processed with different phases well segmented, structural quantification will be performed on the 3D data set to develop an in-depth understanding of the analyzed structure. Using the battery electrode as an example, structural parameters such as the volume fraction of each phase (pore, active materials, carbon and binder domain), particle size distribution, surface area, curvature, connectivity and tortuosity can all be extracted to link to the battery performance and degradation mechanism explanation.<sup>14,59,155</sup> It is noted that microstructures, such as connectivity and tortuosity that strongly correlate with the battery transport property, can only be achieved via a 3D data set. Furthermore, the as acquired 3D data set can be used as the template with the real battery 3D structure to enable computational modeling on calculating the mechanical and electrochemical performance of the battery electrode.18,156

2.4.3. TEM Lamella Preparation. While TEM is an indispensable tool for investigating nanoscale microstructures, achieving accurate TEM analysis hinges on the high-quality TEM lamella sample.<sup>157</sup> Conventional sample preparation techniques such as polishing and ion milling suffer from inherent drawbacks, including a high propensity for specimen damage and limited fabrication precision.<sup>158</sup> Furthermore, challenges arise in efficiently locating and extracting the desired ROI in the specimen. FIB technology offers a compelling solution, effectively addressing these limitations. FIB utilizes a precisely controlled ion beam to achieve high-resolution sample preparation, minimizing specimen damage and significantly expediting the process compared to traditional methods. This enhanced capability allows for the effective analysis of even intricate structures. Owing to its superior efficiency, FIB has become a widely adopted sample preparation technique across diverse fields, encompassing materials science, biology, and the semiconductor industry.<sup>15</sup>

As shown in Figure 22 using an NMC cathode as an example, the general TEM sample preparation process via FIB-SEM consists of major steps including ROI position allocation, protective layer deposition, bulk milling, under cutting, lift-out, welding to the grid, and thinning. To ensure high quality samples, there are certain steps that need special attention. The protective deposition layer (Figure 22b) is essential if surface information on the specimen is critical, as directly performing milling without a protection layer will result in 25–40 nm damage on the surface. For the final thinning step, which



**Figure 22.** Workflow of TEM sample preparation on a NMC cathode sample. (a) SEM image of a ROI position. (b) Protective layer deposition with carbon precursor gas. (c) Bulk milling excluding target area for lift-out process. (d) Under cut of the specimen for the lift-out process. (e) Lift-out process with the specimen attached to the needle. (f) The process of welding a specimen to a grid for thinning. (g) Thinning to electron transparency. (h) SEM-STEM imaging and analysis of structure after thinning process.



**Figure 23.** Automated TEM sample preparation. (a) Bulk milling excluding target area using fiducial. (b) Lift-out process with the specimen attached to the needle. (c) The process of welding a specimen to a grid. (d) Thinning with thinning fiducial. (e) Automated TEM lamella preparation on an NMC cathode.

determines the quality of the lamella, the low-kV cleaning process is essential. During the initial, high-kV FIB process (e.g., 30 kV Ga<sup>+</sup> Ion), an amorphous layer, roughly 20 nm thick, inevitably forms on the exposed surface due to Ga<sup>+</sup> ion bombardment. This unwanted layer becomes even more substantial (around 40 nm total) for 100 nm thick specimens prepared with 30 kV Ga<sup>+</sup> FIB, significantly hindering highresolution TEM analysis. The low-kV FIB cleaning process effectively mitigates this issue. Using a lower acceleration voltage, such as 5 kV or 2 kV, reduces the thickness of the induced amorphous layer to about 6 and 3 nm, respectively. This reduction is crucial for achieving high-quality TEM analysis.

Although FIB techniques are well-established in producing TEM specimens, some obstacles still require special strategies to address. Damage caused by Ga ion beam bombardment and implantation complicates the structural analysis; therefore, inert ion-based specimen preparation methods should be employed.<sup>160</sup> In addition, fabricating specimens with a focused ion beam may result in heat damage on the sample where Cryo-FIB sample preparation needs to be implemented.<sup>132,161</sup> One



**Figure 24.** A schematic demonstrating some of the most useful FIB based characterization techniques and methods for cathode characterization as well as the most common forms of morphology found among cathode active materials. Working clockwise from the top: TEM-lift out, EDS, FIB-SIMS, Cryo-FIB, EBSD, Kintsugi, Tomography, with the coral morphology being seen in the EDS and FIB-SIMS sections, flower petal morphologies being seen in Cryo-FIB and Tomography, the agglomerated crystallite morphology being seen in the EBSD section, and the agglomerated sphere morphology being seen in the Kintsugi section.<sup>172</sup>

unique challenge in preparing TEM lamella from battery samples is working with battery electrodes, which are composites consisting of particles weakly bound by a binder, with voids present in between. During the TEM specimen thinning process, the binder, which has a higher milling rate, is removed first, or the voids hinder uniform thinning, making the specimen prone to breaking. A recently developed all-around deposition method, utilizing a deposition-based frame, effectively prevents the sample from breaking apart during the lamella thinning process.<sup>119</sup>

For the preparation of beam-sensitive materials, such as lithium metal, it presents unique challenges due to its high chemical reactivity with air and moisture, rapid oxidation potential, and susceptibility to electron beam damage;<sup>144,162</sup> therefore, specialized approaches are required to preserve the natural structure and chemical properties of the specimen. In this context, Cryo-FIB lift-out technology is needed to maintain Li-metal sample integrity throughout the preparation process.<sup>22,47</sup> Using Li-metal lamella preparation as an example, the representative Cryo-FIB process begins with initial trenching at

higher beam currents (10–20 nA) while maintaining temperatures below –180 °C, followed by intermediate thinning using reduced beam currents (1–5 nA) to minimize damage. The final thinning stage is conducted at low beam currents (10–500 pA) with reduced acceleration voltages.<sup>163</sup> Throughout this entire process, reduced dwell times and overlap percentages are employed to minimize local heating and beam damage, along with protective measures including metallic coating layers and sacrificial protection layers.<sup>164</sup>

In addition, driven by the demand for reducing human labor and error while increasing the throughput, automated TEM sample preparation is becoming increasingly essential for efficient and consistent results.<sup>165</sup> Traditionally, TEM sample preparation involves a multistep process that exceeds 50 individual steps.<sup>166</sup> Automation software revolutionizes this workflow by streamlining it into a three-step process: template selection, region of interest designation, and grid position specification. The creation of fiducial markers is the key enabling complete process automation.<sup>167</sup> As illustrated in Figure 23a–23d, these fiducial markers facilitate automated bulk

#### **Chemical Reviews**

milling, followed by the sequential execution of lift-out and welding processes. To date, even the thinning process can be automated using fiducial markers, ensuring specimens with the desired, consistent thickness. Consequently, automation software significantly enhances the ease and consistency of TEM sample production, minimizing variations in the final product and streamlining research workflows. Figure 23e shows a process of preparing 9 TEM lamella samples on a NMC cathode via the automated TEM sample preparation workflow.

## 3. APPLICATION OF FIB-SEM ON CHARACTERIZATIONS OF BATTERY MATERIALS

The design of the battery materials requires both the development of new chemistries and the fundamental understanding of the physical, chemical and electrochemical processes that occur in these complex systems. Although some significant advances have been made to prepare and utilize new materials, efforts toward the understanding of the mechanisms have waned. Batteries are inherently complex and dynamic systems, and their electrochemistry, phase transformations, and transport processes often vary throughout their lifetime. Their lifetime and characteristics are not only impacted by the chemistry occurring but also by the mechanical stresses caused by the volume changes in the individual crystallites and in the overall electrode structure.

Long-term battery stability requires control of chemistry across various temporal and structural length scales. FIB-SEM enables multiscale analysis, from the macroscopic electrode structure down to individual nanoparticles. FIB-SEM allows for high-resolution imaging of battery materials, enabling researchers to observe how individual crystallites and the overall electrode structure change during charge and discharge cycles. FIB-SEM combined with techniques like EDS can provide detailed elemental maps, showing how chemical composition changes in response to structure changes and transport processes. By examining the surfaces and cross sections of electrodes, FIB-SEM helps identify regions where interphase formation and chemical degradation occurs. This section provides an overview of how FIB-SEM is applied to the study of cathode, solid electrolyte, and anode materials for nextgeneration battery development.

#### 3.1. FIB-SEM Characterizations for Cathode Materials

Cathode materials are the primary drivers of cost and increased energy density in contemporary batteries.<sup>168,169</sup> They are the result of decades of work from the initial discovery of intercalation type cathodes such as LiCoO<sub>2</sub> (LCO) that led to the successor materials of high energy (NMC), with the formula of Li[Ni<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>]O<sub>2</sub> where x + y + z = 1, and the materials are referred to as NMC-xyz, and eventually phase change materials such as lithium ferrophosphate (LFP), with the formula of LiFePO<sub>4</sub>.<sup>170,171</sup> These electrochemically active particles are the primary source of lithium-ions within contemporary LIBs, and because of this their performance is a direct reflection of the wider battery's performance.

However, these cathode particles do not exist in isolation, as the larger cathode electrode not only consists of these electrochemically active particles but also includes the critical components of conductive media, usually porous carbons, a polymeric binder to provide mechanical strength and hold the components of the overall cathode electrode together, and counterintuitively empty space/porosity that allows the electrolyte to diffuse throughout the electrode. Therefore, when

evaluating the performance of the cathode, one must consider the morphological, crystallographic, and chemical changes in both the electrochemically active cathode material and the overall electrode system. As seen in Figure 24, FIB has maintained its essential role in the preparation of samples for high resolution TEM, while simultaneously gaining numerous other capabilities. For elemental analysis, FIB techniques have been able to leverage both EDS for heavier elements such as Ni and FIB-SIMS for the analysis of lighter elements such as Li. The trove of crystallographic and morphological techniques has also been greatly expanded to include methods such as EBSD, for analysis of crystal orientation, Kintsugi, for increasing phase and pore contrast,<sup>116</sup> and tomography, enabling 3D reconstructions of full cathode particles and electrodes.<sup>18</sup> Advances in FIB stage and transfer configurations have also been significant, with techniques such as Cryo-FIB expanding the base of FIBcompatible samples to include even the most reactive and delicate samples.<sup>17</sup>

**3.1.1. Morphological Analysis Techniques.** The morphology of a cathode is vitally important to its electrochemical performance, and to achieve high performance, cathode materials optimization of the cathode morphology is required at length scales ranging from the submicron primary particle(s) to the hundreds of micron thick electrode composite. The primary considerations for morphological evaluation are the electrochemically active particles and the composition and structures present within the overall electrode system.

The morphology of the electrochemically active cathode particles is dominated by the relationship between primary and secondary particles, e.g. their size, shape(s), and homogeneity. A useful example is the commonly used coprecipitation method where particles of cathode precursors nucleate in the solution before agglomerating to form the secondary particles. Cathodes made in this way can display several morphologies, for example all morphologies seen in Figure 24 could be seen from coprecipitation methods. Cathode electrochemically active particles made this way have gaps between primary particles which are referred to as pores. High performance material must find the optimal ratio of pore to primary particles as an increase porosity means reduced secondary particle density and more surface area for cathode/electrolyte reactions, which both reduces diffusion lengths and increases the number of sites for parasitic reactions. The connectivity and uniformity of these pores is also essential as the more uniform the pore distribution, the more homogeneous the lithiation is across secondary particles. These relationships are essential, as through the process of electrochemical cycling, cathode particles, such as NMC, undergo changes in volume as a function of lithiation and heterogeneities can result in mechanical stress and cracking in and or around primary particles that drive collapse of secondary particles and overall particle degradation.<sup>174–17</sup>

These effects directly scale to the level of the entire cathode electrode. Here the morphologies are dominated by the relationships between the components instead of primary and secondary particles. Electrodes resemble composite gels with the dense and large active particles serving as the dispersant phase and a mixture of the polymeric binder and conductive phase coating the active particles and serving as the matrix, with pores ultimately forming as a result of gaps in the dispersion. Since each component of an electrode serves a specific purpose whether it be electrochemical, electrical, or mechanical, the homogeneity of the electrode is the single most important feature for determining quality. Agglomeration of each pubs.acs.org/CR



**Figure 25.** Examples of how a combination of FIB and new software can allow for the reconstruction and classification of cathode materials at an electrode level. Adapted with permission from ref 18. Copyright 2023 Elsevier. (a) Demonstration of how FIB slices are reconstructed into a 3D image. (b) Demonstration of how Avizo software can be used to classify and segment the previous 3D reconstruction. (c) Chart demonstrating the makeup of the segmented 3D reconstruction using the Avizo software.

component can negatively impact the performance of the overall battery with increased mechanical stress, charge heterogeneity, material loss, and delamination as a nonexhaustive list of possible failure mechanisms from a heterogeneous electrode. Another critical metric for assessing the performance of an electrode is the tortuosity, which is a measure of how far an ion must travel through the pores of the electrode vs the overall electrode thickness.<sup>177,178</sup> This factor is critical for understanding how the electrolyte diffuses through the electrode, and therefore, it is directly related to the porosity and pore structure of the electrode.

Morphological evaluation of cathodes at all levels requires an accurate method to evaluate the size, shape, and distribution of multiple components across multiple length scales. FIB-tomography when paired with segmentation analysis software, such as Avizo, is naturally suited to this, as it allows the reconstruction of particle or entire electrode areas by knitting together FIB images to build accurate 3D reconstructions of their materials.<sup>18,50</sup> As shown in Figure 25, these reconstructions can then be segmented and used to build accurate models for the study of electrolyte diffusion across whole electrodes, or even individual particles.<sup>18</sup>

However, in many cases the contrast between different components of these systems is low, particularly in cases where pores are shallow, which can make classification difficult because of the pore back effects. The Kintsugi method has been developed to help resolve these contrast issues by filling these pores with depositions of conductive metal, thereby greatly increasing the contrast among active cathode materials, carbon and binder domain, and the now filled-in pores (Figure 26).<sup>116</sup> By filling these poreous structures with a known amount of metal, the pore depth and connectivity between FIB sections can be



**Figure 26.** An example of the Kintsugi method being applied on an electrode scale to better highlight the differences between pores and carbon-rich areas. Adapted with permission of ref 116. Copyright 2022 IOP Science. (a) FIB cross section of cathode that has undergone the Kintsugi method, where the deposited Pt fills the pores increasing the contrast of the images. (b) The EDS of the micrograph from (a) demonstrating how the Kintsugi method also aids in EDS analysis.

better understood, while also allowing the delicate porous samples to stay more cohesive when conducting TEM sectioning or lift-outs. Finally, by choosing the metal for deposition in the Kintsugi method to have minimal characteristic X-ray overlap with the elements of interest in the sample, elemental analysis can also be conducted more accurately across each 2D slice.

**3.1.2. Crystallographic Analysis Techniques.** Crystallography of cathodes is also a critical concern for the evaluation of performance, with the crystallographic orientation and crystallographic phases present being the highest concern. Of these factors, the relative orientation of the primary particles within the secondary particles has been demonstrated to provide critical information about the efficacy of lithium diffusion through the active cathode material, the interparticle diffusion barriers, as well as the lattice strain and defect distribution within cathode materials.<sup>107</sup> As seen in Figure 27, a combination of FIB



Figure 27. An example of how a cathode particle is sectioned in FIB before EBSD mapping is employed for the identification of the individual grains before mapping their individual orientations. (a) an SEM image of a FIB cross sectioned NMC532 cathode particle. (b) The corresponding IQ map of the same crystal. (c) An EBSD map of the NMC cathode particle grains with a pole map in the upper right to demonstrate the orientation of each grain. Adapted with permission from ref 107. Copyright 2020 Elsevier.

techniques to mill the particle to a flat surface allows for the employment of EBSD methods on the sectioned particle to elucidate the relationships between the particle orientation and the transport of lithium within the cathode materials. The particle in Figure 27 is an example of a mosaic style secondary cathode particle; as seen in Figure 27c, the use of EBSD greatly increases the visibility of the primary particles and further provides information that not all of these primary particles are single-grain, information which might have otherwise been lost from pure SEM based imaging.<sup>107</sup> The use of IQ mapping, a technique that measures Kikuchi diffraction with brighter grains having sharper Kikuchi patterns, seen in Figure 27b when paired

with the EBSD results, also provides clear boundaries between each grain, as well as a relative amount of strain or other lattice defects which would reduce the intensity of Kikuchi patterns behind the IQ mapping.<sup>107</sup> When cross referencing the SEM, IQ, and EBSD data from Figure 27 the boundaries between the primary particle and the grains within some of the primary particles become more clear, allowing for more accurate determination of primary particle size and morphology than with either method done independently. In this case the EBSD data reveals that the grain orientations within this cathode are not correlated or preferentially aligned, while the use of the IQ mapping reveals the abundance of grain boundaries in the system.

Crystallographic analysis of phases is particularly important at the delicate interfaces of cycled cathodes where the reactions between the electrolyte and the cathode components cause the formation of the cathode electrolyte interphase, or CEI. In order for these delicate phases to be accurately captured, one must account for their beam sensitivity using Cryo-FIB to reduce the kinetics of the beam/sample interactions, facilitating the preservation of CEI and other sensitive structures during TEM lift out procedures, which enables further crystallographic analysis.<sup>18</sup> Additionally, as shown in Figure 28, cycled cathode



**Figure 28.** Images of TEM lift preparations in a FIB and corresponding TEM of the sample surfaces demonstrating how many samples' relevant surface information could be lost without cryogenic techniques. Adapted with the permission from ref 18. Copyright 2023 Elsevier. (a) FIB used for the TEM lift-out of pristine cathode samples. (b) TEM of the pristine cathode sample surface, demonstrating how the pristine structure's surface can still have slight variations. (c) The lift-out preparation for TEM of a cycled cathode material. (d) The TEM of the cycled material, with the thin delicate antisite layer highlighted; note that this layer being 2 nm makes it highly beam sensitive.

materials have delicate surface layers which could be lost without careful preparation or imaging methods. Therefore, FIB techniques that minimize interactions between the sample and the beam, such as PFIB and Cryo-FIB, are essential in these cases. Cryo-preparation of samples with these delicate surface crystalline phases is essential to preserve them be preserved for later Cryo-TEM or conduct any other number of FIB based analysis techniques.

**3.1.3. Chemical Analysis Techniques.** Few elements and their compounds are suitable as battery cathode materials, and even fewer are viable when cost is considered.<sup>179–181</sup> The subset of elements that make up contemporary cathode materials are lithium, oxygen, nickel, iron, manganese, cobalt, aluminum, and phosphorus. Currently the dominant cathode chemistries form crystalline solids that will follow one of two stoichiometries: the oxides of the formula Li[TM]O<sub>2</sub>, where TM is typically Ni, Mn,

and Co but can also include Al; and the phosphates with  $LiFePO_4$ , where Mn can also be substituted in for the Fe. For both sets of cathode material, the electrochemical performance is reliant on the composition and chemical homogeneity.<sup>182–184</sup> For this reason, elemental analysis techniques such as EDS and FIB-SIMs are essential tools for the characterization of cathode materials.

In EDS the acceleration voltage of the electron beam is the primary determinate of the elements which can be detected. The resultant emission of characteristic X-rays from the cathode is also important to consider, particularly when emission spectra of many of the key elements in cathode materials are similar, which requires careful calibration and longer exposure time for increased accuracy, particularly for quantification. Despite this, as previously mentioned, EDS's primary disadvantage is the extreme difficulty in quantifying lighter elements, particularly lithium; however, some newer techniques such as windowless EDS or Soft X-ray emission spectroscopy are currently in development to facilitate the quantification of Li, which would greatly increase the relevance of the technique for all lithium-ion cathode materials. Currently, the detection of lighter elements requires another technique, FIB-SIMS.

As mentioned earlier, FIB-SIMS methods are unique to the FIB environment due to how they rely on a primary-ion to ablate the sample surface to generate the relevant analytically relevant ions. As illustrated in Figure 12 these FIB-SIMS methods can provide invaluable information about the lithiation and delithiation behaviors of cathode materials, as well information about the possible sources of irreversible lithium loss within the cathode materials themselves or about the formation of the CEI.

When conducting elemental analysis of cathode materials in the FIB environment, it is important to remember how both the EDS and FIB-SIMS methodologies rely on the interactions between the relevant source beam and the sample, which are inherently damaging. Therefore, it is critical to understand the beam tolerances of specific electrode components such as the conductive carbon, polymeric binder or specific samples, such as cycled cathode materials. The CEI formed on already cycled cathodes is notoriously fragile, as it is likely comprised of a delicate mixture of organic and inorganic components which are generally less beam tolerant than base active cathode materials.

3.1.4. Outlook on FIB-SEM Applications for Cathode Materials. FIB-SEM has proven to be a research multiplier when analyzing cathode materials and electrodes. The unique ability of FIB-SEM to explore multiple length scales and probe multiple types of information within a single sample provides invaluable information in the evolution of structural and chemical degradation of the complex cathode systems. The ability to analyze a sample across the primary particle and full electrode length scales can provide information about the impact of particle morphologies on the distribution and dispersion of carbon in the electrode, which is crucial for understanding the limiting factors in a system's conductivity and cathode utilization. Similarly, understanding the dissolution of transition metals from cathode particles requires a combination of crystallographic information from EBSD and chemical information provided by EDS and FIB-SIMS. Additionally, the use of Cryo-stages enables these investigations for sensitive samples. The multimodal capabilities of FIB-SEM have made the technique essential for understanding cathode systems, and while these techniques see more widespread adoption, the only limit to FIB-SEM's ability to accelerate new discoveries will be the number of ports.

#### 3.2. FIB-SEM Characterizations for Anode Materials

The anode materials, as another essential electrode material, affect the electrochemical performance of batteries as much as the cathode materials. They store active metal (e.g. Lithium or Sodium) during the charged state of the battery either in its cation or metal form. Hence, understanding their redox mechanisms, degradation behavior, and the SEI formed at the anode material surface is critical to improve the cycling performance in battery applications. FIB-SEM, with its characterization and sample preparation capability, is an indispensable method for anode research. Figure 29 summarizes



Figure 29. Summary of FIB-SEM characterization techniques for anode materials. From top-left and going counterclockwise, several representative FIB-SEM techniques are shown in the schematic for anode material characterization. Chemically sensitive, alkali metal anodes are well-known for high reactivity and moisture/air sensitivity, as are most lithiated/sodiated anode materials. Thus, airtight sample transfer and/or a cryogenic environment during measurement are essential for characterizing the aforementioned anode materials. The morphology of the anodes can be monitored by the cross-sectional images obtained by FIB-SEM, visualizing the internal morphology buried under the surface. EDS and EBSD can unravel the crystal orientations and lattice distribution for anode materials. TEM lamella lift out, requiring FIB-SEM milling, is a sample preparation process for interfacial study using TEM. Lastly, 3D tomography employing the slicing capability of FIB-SEM provides in-depth information on 3D microstructure and enables quantitative structural analysis of anode materials.

the five main perspectives for FIB-SEM application for battery anode material study. Due to the chemical sensitivity of the alkali metal anodes and most of the cycled anode materials, airtight transfer or Cryo-environment is essential to mitigate any contamination, decomposition, or beam damage. For microstructure and morphology, FIB-SEM cross-section images provide in-depth information. Meanwhile, 3D tomography sheds insights into quantitative analysis of the internal structure. FIB-SEM is also critical for the preparation of TEM lamella for interfacial studies. Lastly, utilizing EDS and EBSD, the chemical distribution and crystalline orientation of the anode materials can be further deciphered. In this section, we explore the main challenges for characterizing anode materials that can be resolved and probed by FIB-SEM. Finally, we provide some perspectives on the future direction of FIB-SEM applications on battery anode materials.

3.2.1. FIB-SEM for Alkali Metal Anode. Alkali metal anodes such as Li and Na, commonly recognized as the holy grail for metal-based batteries, can maximize the cell operating voltage and energy density due to their low reduction potential. However, realizing high Coulombic efficiency (CE) is always challenging. This is due to the inhomogeneous deposition and stripping of the metal anode that leads to dendrite/inactive metal formation during cycling, posing safety hazards and causing poor cyclability. To mitigate side reactions and dendrite formations, researchers have been eagerly developing various approaches. Given that, characterizing the metallic anodes becomes crucial as we move beyond 99.9% CE.<sup>185</sup> For the FIB-SEM-related characterization techniques for anode material study, we discuss the challenges of characterizing alkali metal and cycled anodes due to their chemical sensitivity and the suggested standard protocols. Using FIB-SEM, the morphology and microstructure of the deposited/stripped metallic anode can be visualized and studied. With 3D tomography and reconstruction, quantitative structural analysis can be realized, such as porosity, particle size distribution, and volume fraction of different components. Moreover, the (electro)chemomechanical properties of SEI play critical roles in the performance of anode materials, either suppressing dendrite formation, facilitating Li<sup>+</sup> ion transport, or mitigating electrolyte decomposition. With TEM lamella lift-out leveraging the milling and deposition functions of FIB-SEM, the interfacial properties of the as-formed SEI can also be investigated through TEM.

3.2.1.1. Chemical and Beam Sensitivity of Alkali Metal Anode. Due to its intrinsic chemical reactivity and beam sensitivity, examining reactive alkali metal morphology in a wider length scale imposed huge challenges to the field along with the elucidation of progressive change in the interface study. Li, as the second lightest element, is very active to air and moisture and cannot be easily detected through X-rays. As discussed in the previous paragraph, SEI formation and its characteristics are critical to anode materials' electrochemical performance. In general, SEI is composed of both organic- and inorganic-based compounds. However, the organic compoundcontaining SEIs are mostly considered more susceptible to beam-induced heating and local melting. To address these issues, techniques to preserve the sample properties are required, such as transferring samples using an airtight transfer arm from the glovebox to the FIB chamber, reducing the beam current during milling. Cooling the stage and sample to cryogenic temperature during the entire session is an effective approach to mitigate FIB-induced damage and contamination to the sample surface.<sup>23,24,47,141,144,146</sup>

Previous research has shown that under room temperature, lithium metal can be easily damaged chemically and morphologically due to Ga<sup>+</sup> implantation and local Joule heating, while these reactions can be well-prevented at cryogenic conditions (Figure 30). Moreover, recent research proves that Xe<sup>+</sup> probe can reduce the morphology damage at room temperature, even though the contamination on the sample surface is inevitable, featuring the minimum oxygen level under vacuum of the FIB chamber. It should be noted that lithium metal could experience phase change to the rhombohedral structure (hR9) when the temperature goes below 77 K near ambient pressure,<sup>186</sup> which is close to the liquid nitrogen



**Figure 30.** SEM and EDS mapping of cross sections of commercial lithium metal foil. (a-c) Cross-sectioned and cleaned at room temperature, (d-f) cross-sectioned at room temperature and cleaned at cryogenic temperature, and (g-i) cross-sectioned and cleaned at cryogenic temperature. Reproduced with the permission from ref 47. Copyright 2019 American Chemical Society.

condition. But considering that the temperature maintenance during the cryogenic session is always higher than 77 K due to thermal exchange, this phase change is unlikely to occur.

3.2.1.2. Morphology and Microstructure of the Alkali Metal Anode. While top-view SEM images display surface morphologies, cross-sectional images are crucial for directly observing the internal microstructure and morphology of samples. In the past, cross sections were primarily observed by cutting or slicing samples using tools such as scissors and blades. However, crosssectional morphology can be easily damaged and altered during traditional cutting, leading to unrealistic and misleading results. Conversely, with FIB-SEM, precise milling and polishing down to the nanometer scale ensure that cross-sectional morphology and structural details are well-preserved. This subsection discusses the application of FIB-SEM for visualizing the morphology and microstructure of representative alkali anode materials in batteries.

As the holy grail of anode material, metallic lithium anode suffers from unregulated growth, leading to dendrite and inactive lithium formation that cause low CE and safety hazards. Ideally, large granular lithium deposits with column structure aligning densely side-by-side are preferred. Hence, deciphering the morphology and microstructure of lithium upon both deposition and dissolution is crucial to validate and guide the strategies for improving the reversibility of lithium deposition/ stripping. However, due to the aforementioned ion-beam damage and Ga<sup>+</sup> implantation at room temperature, a cryogenic environment is required for FIB-SEM images of the lithium metal anode to preserve its structural and morphological details. In 2019, the surface morphology of lithium metal was systematically compared under room temperature and cryogenic conditions during the sample milling and cleaning process. This provided visible evidence reinforcing the importance of operating Ga<sup>+</sup> FIB at cryogenic temperature for characterizing lithium metal anodes.<sup>47</sup> With the implementation of Cryo-FIB, studying the dependency of deposited lithium morphologies with different parameters became feasible for metallic lithium anode.

Electrolytes hold an important role in altering lithium morphology upon metallic lithium anode cycling, thus leading to different microstructure of lithium dendrite and inactive lithium. In 2019, lithium deposit morphology and inactive lithium microstructure were investigated in different organic electrolytes using Cryo-FIB, with inactive lithium quantified by the titration gas chromatography (TGC) method. The results provided insightful information on the formation mechanism of inactive lithium and identified inactive lithium as the dominant source of capacity loss in the metallic lithium anode.<sup>187</sup> Later, the same group realized uniform and dense lithium deposition by fluoromethane-based liquified gas electrolytes, maintaining the large particle size and compacted morphology of lithium even after 100 cycles, as evidenced by Cryo-FIB-SEM.<sup>188</sup> Follow-on work demonstrated that the dense lithium deposition and ideal Li-substrate contact could be achieved even at -60 °C with the addition of acetonitrile cosolvent.<sup>1</sup>

Besides electrolyte formulation, other critical factors could also affect the morphology of lithium deposition and stripping



**Figure 31.** Cross-sectional images of alkali metal anodes taken using FIB-SEM. Cryo-FIB cross-sectional images of lithium deposited under (a) 70 kPa, (b) 140 kPa, (c) 210 kPa, and (d) 350 kPa at 2 mA cm<sup>-2</sup> for 1 h (2 mAh cm<sup>-2</sup>). Scale bars, 2  $\mu$ m. Note that the actual cross-sectional thickness should be divided by sin 52° due to the FIB-SEM stage rotation. Adapted with permission from ref 190. Copyright 2021 Springer Nature. Cross-sectional Cryo-FIB images of the plated sodium at optimal pressures in (e) 1 M NaPF<sub>6</sub> in DME (180 kPa) and in (f) 1 M NaPF<sub>6</sub> in EC:DMC (1:1) (250 kPa). The scale bars are 5 mm. Adapted with permission from ref 192. Copyright 2024 Royal Society of Chemistry. Cross-sectional images showing Li/Li cell failure within two stacked Celgard 2325 separators: (g) after 1st lithium stripping and (h) after the 101st plating step. Red regions indicate lithium, blue regions indicate separator and gray regions indicate SEI/electrolyte. Adapted with permission from ref 65. Copyright 2021 American Chemical Society.



upon cycling, such as depth of stripping and stack pressure. It was reported that large pressures promoted short circuits and cell failure instead of suppressing them, as evidence that with the increasing pressure to 1 MPa, a large quantity of lithium metal grew into the separators and accumulated between separator sheets upon cycling.<sup>64,65</sup> In another report, a dense lithium deposition with column structures could be achieved under 350 kPa stack pressure. Using Cryo-FIB to examine the deposited lithium cross-sectional morphology from 0 to 350 kPa stack pressure at 2 mA cm<sup>-2</sup> for 1 h (2 mAh cm<sup>-2</sup>), the morphological evolution made it clear that lithium deposits changed from the whisker-like porous structure into a close-packed columnar structure (Figure 31a-31d). Moreover, the strategy of not fully stripping the lithium and partially maintaining it as a lithium reservoir was proposed; this could lead to the preservation of the columnar morphology of lithium deposits during the extended cycles. This work highlighted the importance of stack pressure and depth of stripping on lithium deposition morphology and provided insights into the design rules for practical lithium metal batteries.<sup>190</sup> Later, another work studied the quantitative relationship between chemical corrosion rate and lithium deposition morphology by combining the TGC method and Cryo-FIB. Through the visualization of Cryo-FIB, the authors elucidated that the critical parameter determining the corrosion rate of lithium is the contact area with electrolyte, namely the porosity of the deposited Li. The integration of advanced electrolyte (Localized High Concentration Electrolyte, LHCE) and optimized stack pressure (350 kPa) enabled the ultralow porosity lithium deposition, which stabilized the dense lithium in liquid electrolyte with only 0.8% active mass loss after 10 days.

Similar to lithium metal anode, Na metal anode's practical application is also limited by high electrochemical and chemical reactivity, posing significant challenges to safety concerns and long-term cyclability. The impact of uniaxial pressure on the Na metal growth in carbonate- and ether-based electrolytes was quantitatively studied. With the cross-sectional visualization of Na morphology using Cryo-FIB and quantification of Na inventory by the TGC method, the optimal pressure for each system was identified, whereas the carbonate-based system requires a higher pressure of 250 kPa compared to 180 kPa for the ether-based system (Figure 31e and 31f). It was found that, in contrast to metallic lithium anode, the major sodium loss (irreversible CE) originated from the SEI Na<sup>+</sup>. This work highlighted two essential parameters: 1) uniaxial pressure and 2) the nature of the solvent and salt, to the uniformity and thickness

of Na deposition and the chemical composition of the SEI layer.  $^{192} \,$ 

Despite the extensive use of Cryo-FIB for studying alkali metal anode morphology, the Ga<sup>+</sup> ion milling is relatively slow, and the milling depth/area is limited, making it difficult to image the entire electrode stacks or wider region of interest. With higher maximum volume and current, laser ablation is 15000 times faster than that for Ga<sup>+</sup> FIB or 500 times faster than that for Xe<sup>+</sup> PFIB if using Si standard sample, which makes it more suitable for the samples with thick layers of packaging to maintain their chemical integrity.<sup>51,67,92</sup> Recently, Cryo-laser PFIB shortened the milling rate and enabled cross-sectioning of the entire coin cell including the steel casing with width up to mm scale. A series of works using Cryo-laser PFIB to characterize the lithium morphology were reported, exhibiting lithium metal volume expansion and penetration into and through separators to cause short circuits in the extended cycles (Figure 31g and 31h).<sup>64–66</sup> With the utilization of (laser) PFIB, the milling time can be significantly reduced, which will benefit the auto slice and view function when conducting serial sectioning for 3D reconstruction while covering more than 40 times the larger volume of interest.<sup>18</sup> In addition, the surface quality for various battery materials can be greatly improved with less artifacts when fs-laser ablation is applied during milling and cleaning.<sup>1</sup>

Furthermore, integrating FIB-SEM with EDS mapping enables detailed spatial elemental analysis along the anode cross-section, including element composition, spatial distribution, layer thickness, and phase heterogeneity. However, twodimensional images alone may not accurately represent the true structure of materials, as they only offer morphological information on a specific plane, lacking spatial context in the perpendicular direction.

3D FIB-SEM image reconstruction, achieved through serial FIB sectioning with depth visualization, provides a more realistic and detailed view of the microstructure. As discussed in section 2.4.2, with proper image segmentation, 3D FIB-SEM tomography allows for quantitative analysis of the reconstructed model, including volume fraction, particle size distribution, effective surface area, porosity, and tortuosity. For alkali metal anodes, 3D tomography provides a quantitative analysis to decipher the porosity and visualization of the detailed microstructure of metal deposits, dendrites, and inactive metal. In 2018, Cryo-FIB was first employed to reconstruct the 3D structure of two types of lithium dendrite, one showing larger size and low curvature and another showing tortuous and branch-like morphology.<sup>144</sup> Later, another work used Cryo-FIB 3D reconstruction to individually visualize the deposited lithium

metal and voids through segmentation, enabling the quantitative analysis of lithium deposit porosity in different electrolytes<sup>188</sup> (Figure 32a-32c) and under different stack pressures.<sup>190</sup> The 3D porosity and volume analysis provided a precise and quantitative comparison between the deposited lithium morphology under different experimental parameters.

3.2.1.3. Interphase Characteristics of Alkali Metal Anode. The interaction between the alkali metal anode and liquid electrolyte interface has always been critical to elucidate the reaction mechanism upon cycling and provide guidance for performance improvement. In particular, the SEI formation and its properties significantly impact the electrochemical performance of alkali metal anodes. Electrolyte formulation and additives intimately dominate the composition and properties of SEI. Generally, the SEI consists of organic and inorganic phases, with common phases including LiF, Li<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub>, Li<sub>3</sub>N, lithium semicarbonates, and other polymeric compo-nents.<sup>187,193,194</sup> It is widely rationalized that LiF is the desirable SEI phase that is beneficial to lithium deposition/stripping due to its chemical inertness and high mechanical strength.<sup>195</sup> Yet, recent studies have shown that Li<sub>2</sub>O has better SEI transport properties and the strongest positive correlation with lithium plating/stripping CE over other SEI phases, even LiF.<sup>193,196</sup> The findings open up a new perspective on SEI oxygenation as an alternative approach to fluorination for future electrolyte development.

Many qualitative techniques have been applied to study and characterize the bulk properties of SEI. XPS, for instance, has been widely used to study the interphase compositions for battery research and served as the major tool to identify the SEI phases on alkali metal anodes.<sup>197</sup> Yet, XPS provides limited information on the 3D distribution of the SEI phases. Meanwhile, TOF-SIMS can characterize the spatially resolved 3D chemical properties of SEI under micron-meter scales.<sup>15</sup> The distribution of the bilayer SEI with  $LiN_{y}O_{y}$  in the top layer and LiF in the bottom layer was observed using TOF-SIMS, which is found to improve the uniformity of the deposited lithium in the LHCE.<sup>199</sup> Similar work also adopted TOF-SIMS to probe each SEI phase on the lithium metal anode. It was found that the organic phase layer can accommodate electrolytes that enhance ionic conductivity, and most inorganic phases are buried beneath the organic phases.<sup>200</sup>

Quantifying the fraction of SEI and the amount of each phase in SEI is always difficult; titration gas chromatography (TGC) was developed to quantify the fraction of inactive Li<sup>0</sup> and SEI-Li<sup>+</sup> in the lithium inventory loss of lithium metal anode. Different electrolyte formulations were studied using the TGC method and compared with the CE of lithium plating/stripping. The work identified the unreacted metallic Li<sup>0</sup>, not the (electro) chemically formed SEI-Li<sup>+</sup>, as the dominant source of inactive lithium and capacity loss.<sup>187</sup> More recently, researchers at MIT reported a chemical titration suite followed by Karl Fischer analysis to selectively quantify a variety of SEI phases, including Li<sub>2</sub>O; LiF; Li<sub>3</sub>N; S-, P-, B-containing phases; Li<sub>2</sub>CO<sub>3</sub>/semicarbonates (collectively, ROCO<sub>2</sub>Li); Li<sub>2</sub>C<sub>2</sub>; RLi, and inactive Li<sup>0</sup>. The work demonstrates the still-growing methodology of probing/quantifying SEI phases and discloses the counterintuitive findings on Li<sub>2</sub>O being the abundant phase at high CE and the strongest CE descriptor across 10 diverse electrolytes.<sup>193</sup>

It should be noted that each technique possesses its own strengths and weaknesses; thus, characterizing the SEI of the alkali metal anode requires different complementary techniques to better understand both the chemical composition and interfacial properties at the alkali metal anode interface.<sup>201</sup> In this subsection, we focus on the discussion of characterizing the interface/interphase of alkali metal anodes at atomic scale using FIB-SEM application and TEM techniques.

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Cryogenic transmission electron microscopes (Cryo-TEM) are often adopted to study the interfacial reactions and characterize the complex interphases on the alkali metal anode.<sup>162</sup> Due to the sample size constraints and electron penetration limitations of Cryo-TEM, lift-out has come to rise as an effective sample preparation method, which can selectively extract the sample from the region of interest and thin the sample to the ideal electron-transparent thickness of less than 200 nm. This provides the possibility of revealing the nanostructure at the interface from bulk materials and probing the chemical bonding environment at atomic resolution for low Z materials, especially for H, Li, and B.<sup>202-204</sup> Coupled with cryogenic transmission electron microscopy, researchers identified the two types of dendrites in lithium-metal batteries. Type I dendrite exhibits lower curvature with a size of around 5  $\mu$ m, while type II dendrite shows several hundred nanometers and is tortuous. This work observed the existence of LiH in the type II dendrite upon lithium metal batteries cycling, and the authors suggested the formation of LiH could be a possible reason for the capacity loss (Figure 33).<sup>144</sup> It is noteworthy to



**Figure 33.** Lamella and mapping of solid—electrolyte interphases and dendrites in lithium—metal batteries. Electron-transparent Cryo-FIB lift-out lamellae of type I (low curvature) (a) and type II (tortuous) (b) dendrites. HAADF Cryo-STEM imaging reveals an extended SEI layer on the type I dendrite (c) but not on the type II dendrite (d). EELS elemental mapping shows that both SEIs are oxygen-rich but that the type II SEI contains no carbon. The type I dendrite has an appreciable oxygen content (e), whereas the type II dendrite does not (f). Fluorine-rich structures were often observed near both dendrite types. Scale bars, 1  $\mu$ m (a, b), 300 nm (c–f). Reproduced with permission from ref 144. Copyright 2018 Springer Nature.

mention that in this workflow, the sample was plunged into the slush nitrogen and transferred into the Cryo-FIB chamber for the best protection of electrolyte. Unlike other Cryo-TEM work with liquid removed, this provides the possibilities of examining the morphology of the interface at the intact state.

In addition, dissimilar to the conventional lift-out method in the semiconductor industry where samples are welded using Pt deposition, in Cryo-FIB lift-out, redeposition of materials is processed to fill the gaps. Meanwhile, as a consequence of unavoidable thermal exchange with the environment and reduced electronic conductivity of materials at cryogenic temperature, sample drifting and charging are well expected, while the image resolution is compromised, which requires a higher standard for sample handling in the milling and cleaning process.



**Figure 34.** FIB-SEM characterization on carbon-based anode materials. Cross-sectional FIB-SEM images of (a) HOPG, (b) MCMB graphite, and (c) HC samples with SEI. Adapted with permission from ref 215. Copyright 2020 Springer Nature. (d) FIB tomograms of natural graphite obtained from spheroidization with 15,000 rpm for 480 s. Open pores are shown in green and closed pores in red. Adapted with permission from ref 214. Copyright 2017 Elsevier. The cross-sectional FIB-SEM image of (e) the naturally folded graphite anode and (f) the magnification of the graphite seen in (e). The thicknesses of the current collector and the electrode are indicated. Adapted with permission from ref 217. Copyright 2017 IOP Science. The FIB cross-sectional images of Si–C composites: (g) surface-coated; (h) inner-particle embedded. Adapted with permission from ref 48. Copyright 2010 Elsevier.

It is noteworthy that other methods have also been used to investigate SEI on alkali metal anodes by either electrochemi-cally depositing alkali metal on a grid<sup>205–207</sup> or dropping metal dendrites from the disassembled cells on the TEM grid,<sup>208-210</sup> and then characterizing them using Cryo-TEM without integrating with FIB-SEM lift-out. For instance, using a fluorinated electrolyte with tris(2,2,2-trifluoroethyl)orthoformate (TFEO), the SEI layer was characterized using Cryo-TEM on lithium metal in the TFEO-based electrolyte (1 M LiFSI in DME-TFEO). The SEI was found to be a uniform, single-layered, 10 nm thick amorphous phase mainly consisting of inorganic species. The homogeneous, amorphous, and inorganic-rich SEI led to a high CE of lithium metal anode without dendrite formation.<sup>211</sup> Coupling Cryo-FIB, TGC method, and Cryo-TEM, researchers studied the two types of inactive lithium formation mechanisms, namely sheet-like and whisker-like inactive lithium in the high-concentration electrolyte (HCE) and commercial carbonate electrolyte (CCE), respectively.<sup>187</sup> Similar work, by integrating the chemical titration method and Cryo-HRTEM, selectively quantified the amount of Li2O in the SEI and studied the distribution and function of Li2O in improving the CE of lithium plating/ stripping. It is also observed that the amorphous SEI matrix dominated in the high-CE electrolyte while primarily mosaiclike SEI nanostructure dominated in the low-CE electrolyte. The initial SEI formation and lithium deposit morphology are mainly governed by the formed Li<sub>2</sub>O and organofluorine.

To conclude, contemporary methods for studying anode interfaces, such as in situ deposition onto TEM grids within custom coin cells<sup>212</sup> and the scraping of materials onto traditional TEM grids, are limited in their ability to control the orientation and thickness of the interfaces available for study. In contrast, coupling FIB-SEM lift-out lamella preparation with Cryo-STEM provides precise control over both orientation and thickness, as well as site selectivity. These capabilities are crucial for accurate spectroscopic quantification in EDS and EELS experiments, where proper background subtraction is essential. Despite these advantages, the application of FIB-SEM lift-out combined with Cryo-STEM characterization for alkali metal anodes remains underexplored.

**3.2.2. FIB-SEM for Other Types of Anodes.** 3.2.2.1. FIB-SEM for Carbon-Based Anodes. Carbon-based anode materials

have been and still are the dominating anode materials in stateof-the-art LIBs ever since the commercialization of LIBs. This is due to their intrinsic earth abundance, low cost, and long cycle life compared to other anode materials. Yet, their theoretical capacity of 372 mAh g<sup>-1</sup> limits the practical energy density of current LIBs. Moreover, the repeated volume expansion/ shrinkage upon long-term charge/discharge cycles leads to structural degradation. SEI formation on caron-based materials, just like alkali metal anodes, also plays a critical role in the electrochemical performance in the long term. Lastly, the slow Li<sup>+</sup> intercalation and deintercalation kinetics hinder the fastcharging capability, which could lead to localized dendrite formation and safety concerns.<sup>213</sup> To further improve the electrochemical performance of carbon-based anode materials, researchers have put effort into studying the SEI properties and morphological and structural evolution during cycling. Below, we discuss the use of the FIB-SEM technique to characterize and gain more in-depth understanding of carbon-based anode materials.

Integrating in situ Atomic Force Microscopy (AFM) and PFIB-SEM, the SEI formation on cross-sectioned carbon-based anode materials was studied. The cross-section PFIB-SEM images of the cycled carbon-based anode electrodes, including highly oriented pyrolytic graphite (HOPG), Meso Carbon Micro Bead (MCMB) graphite, and hard carbon (HC), disclosed the thickness and microstructure of SEI formed in different anodes (Figure 34a-c). As mentioned earlier, the internal microstructure of the anode materials buried under the surface is hard to probe. However, 3D FIB-SEM tomography enabled detailed and quantitative analysis of the internal morphology and texture of spheroidized natural graphite milled under different experimental conditions. The internal porosity was especially quantified to gain insights into the spheroidization process and its correlation with electrochemical performance (Figure 34d).<sup>214</sup> The findings from PFIB-SEM images suggested that the adhesion of SEI correlates with the surface roughness of the carbonaceous materials.<sup>215</sup> FIB-SEM was used to visualize the difference in microstructures of graphite anode and SEI morphologies at high and low scan rates of linear sweep voltammetry. The authors were able to observe the internal pores of graphite and cracks at the SEI/graphite interface and quantified the thickness of SEI deposits. The results suggested



**Figure 35.** FIB-SEM characterization on Si-based anodes. Cryo-FIB for cross-sectional and top-view surfaces of the Si thin-film electrode. (a) Pristine. (b) After 1 cycle. (c) After 10 cycles. (d) After 30 cycles. Adapted with permission from ref 219. Copyright 2021 Elsevier. (e) 3D image representation of Si anodes in the 10% FEC-containing electrolyte after different cycles. (f) 3D image representation of Si anodes in the FEC-free electrolyte after different cycles. Adapted with permission from ref 221. Copyright 2023 Elsevier.

that the low scan rate facilitated the uniform and tubular SEI formation covering the surface of graphite that mitigated the further electrolyte decomposition and degradation.<sup>216</sup> The internal structure and thickness of graphite anodes in the aged Tesla's 18650 cells were imaged using FIB-SEM (Figure 34e and 34f). The FIB-SEM results showed a 10% thickness increase, and the fluorine EDS mapping indicated an increase in fluorine concentration originating from LiF SEI at the graphite surface/ interface after 500 cycles.<sup>217</sup> Similarly, using FIB-SEM and EDS mapping, the synthesis of two types of Si-graphite (Si–C) composite anodes was evaluated by visualizing the ~1  $\mu$ m Si coating layer on graphite in the surface-coated Si–C composites (Figure 34g) and Si agglomerate particles embedded between the empty volume of graphite in the inner-particle embedded Si–C composites (Figure 34h), respectively.<sup>48</sup>

3.2.2.2. FIB-SEM for Si-Based Anodes. Silicon has been recognized as one of the most promising anode materials for the next-generation LIBs due to its ultrahigh theoretical specific capacity (4200 mAh g<sup>-1</sup> at Li<sub>22</sub>Si<sub>5</sub> alloy state), low working potential (<0.4 V vs Li/Li<sup>+</sup>), and earth abundance.<sup>5</sup> However, the practical application of Si anodes has been hindered by several obstacles. The main challenge arises from the severe volume change (300-400%) during the lithiation/delithiation processes. This leads to the pulverization of Si particles, resulting in uncontrollable SEI formation, loss of contact between Si and the current collector, and low initial Coulombic efficiency (ICE). Different approaches have been developed to tackle this intrinsic scientific issue, including novel electrolyte/binder design, Si-graphite composite anode, and electrode/interface engineering. This subsection provides an overview of the FIB-SEM application to characterize Si-based anodes in LIBs.

The failure mechanism of the single crystal Si (100) anode was studied by visualizing the evolution of Si fracture over extended lithiation/delithiation cycles using cross-sectional FIB-SEM images and demonstrated the fracture mitigating effect of the electrolyte additive.<sup>218</sup> Later, the SEI formation and evolution of trapped Li–Si alloy as the source of lithium inventory loss in the amorphous Si thin-film anode were characterized. They utilized cross-sectional Cryo-FIB images to visualize the microstructure and morphology of the Si thin-film anode after different cycles and characterized the nanostructure

of trapped Li–Si alloy using Cryo-TEM (Figure 35a–d). The work identified the dominant factor of lithium inventory loss in the Si thin-film anode originated from the trapped Li–Si alloy, providing quantitative insights and pointing out the bottleneck of Si anodes.<sup>219</sup>

Using 3D FIB-SEM, the microstructural evolution of the Sibased anode upon cycling was investigated. The 3D model of the Si-based anode was reconstructed with phases of Si particles and pores identified. The morphological characteristics (volume fraction, spatial distribution, size, specific surface area, connectivity, and tortuosity) were dissected in the three spatial directions and their evolution upon cycling was also evaluated.<sup>220</sup> Applying the multiscale 3D FIB-SEM technique, the effect of fluoroethylene carbonate (FEC) additive on the structural evolution of Si anode was visualized and systematically compared. At the macroscale, they quantitatively analyzed the volume fraction of Si particles, inactive components, and voids after the first, 30th, and 100th cycles (Figure 35e). At the microscale, single Si particles were reconstructed to gain statistical average particle sizes and their evolution at extended cycling. It was revealed that the stable SEI formed in the early cycling stage with FEC additive effectively suppressed the pulverization of Si and thus improved the cycle life.<sup>221</sup> In 2022, another work also leveraged 3D FIB-SEM tomography to reveal the morphological evolution of SEI on the  $SiO_x$  anode. The dynamic aging of  $SiO_x$  and propagation of the SEI layer into the SiO<sub>x</sub> particle was deciphered from the 3D reconstructed SiO<sub>x</sub> covered by different thicknesses of the SEI layer.<sup>222</sup>

**3.2.3.** Outlook on FIB-SEM Application for Anode Materials. Given the sensitivity of most metallic and lithiated anodes to air and moisture, the redesign of sample preparation, transfer, and measurement workflows is crucial. Even brief exposure to air, lasting mere seconds, can lead to contamination and structural degradation of alkali metal anodes. Therefore, airfree transfer methods must be developed to maintain the integrity of these samples. Recent advancements in (laser) plasma FIB technology have significantly increased milling speed and expanded the scope of imaging areas. This progress allows for 3D reconstructions at scales up to hundreds of cubic micrometers, with voxel sizes around ~15 nm<sup>3</sup>. Analyzing these large data sets, often consisting of tens to hundreds of billions of

voxels, demands advancements in software and algorithms, particularly in AI-assisted or deep-learning-based segmentation and denoising techniques. The emergence of TOF-FIB-SEM offers enhanced surface sensitivity, facilitating the detection of lighter elements such as Li, C, O, and F. This opens up new possibilities for probing the surface elemental composition of anode materials, including their SEI layers. Additionally, it provides improved depth and spatial resolution, which is crucial for analyzing various interfacial properties. EBSD further enhances our ability to study grain boundaries and crystal orientations, which can provide valuable insights into metallic anodes like Li and Na, as well as crystalline materials such as Si. However, precise sample handling and surface preparation are essential to prevent the formation of decomposition layers, ensuring accurate EBSD measurements and analyses.

As the energy storage field shifts toward post-Li-ion technologies, alkali metal anodes will play a pivotal role in realizing next-generation lithium/sodium metal batteries. While ongoing research is developing strategies to improve cycling performance and plating/stripping efficiency, key aspects of SEI/inactive metal formation and growth mechanisms remain poorly understood. The application of dual-beam FIB-SEM in anode research will be instrumental in overcoming these challenges and advancing the implementation of alkali metal anodes in rechargeable batteries.

## 3.3. FIB-SEM Characterizations for Solid State Battery

As some of the most promising next-generation energy storage technologies, all solid-state batteries (ASSBs) hold promise to combine large energy density with intrinsic safety and stability. Critically, replacing liquid electrolytes with superionic solidstate electrolytes (SSEs) helps to overcome central challenges associated with conventional LIBs, such as flammability, electrochemical compatibility, and active-material crossover.<sup>2</sup> Realizing ASSBs with large energy density in practical configurations relies on efficient use of both anodes with large capacity (e.g., alkali metals, alloys) and state-of-the-art cathodes (e.g., oxide insertion hosts, conversion chemistry) in composite microstructures with large areal capacity.<sup>224</sup> This full cell chemistry must be integrated together with thin and dense SSE separators (<50  $\mu$ m, <10% relative porosity) with efficient manufacturing methods.<sup>225</sup> With this approach, ASSBs based on lithium chemistries approach gravimetric energy densities of 400 Wh kg<sup>-1</sup>, a milestone for battery technology. Further, advancements of sustainable Na ASSBs are projected to enable volumetric energy density competitive for stationary storage applications ( $\sim$ 700 Wh L<sup>-1</sup>) with low cost (<\$50 kWh<sup>-1</sup>).<sup>226</sup> However, various challenges, such as electro-chemo-mechanical degradation at SSE/cathode/anode interfaces, have restricted implementation of ASSBs to date.<sup>7</sup> Despite these challenges, innovations in fundamental materials chemistry, full-cell fabrication approaches, and scalable manufacturing routes continue to advance the achievable performance of ASSBs.

The successful application of ASSBs relies on intimate coupling between (electro)chemical compatibility of material components and mechanical phenomena upon battery cycling.<sup>227,228</sup> Electrochemical stability between SSEs and battery active materials must be ensured to avoid production of parasitic interphases that irreversibly consume active material inventory and decrease cycling efficiency. In addition, unlike traditional LIBs with liquid electrolytes, mismatch in the volume change of ASSB components upon (dis)charge can result in generation of internal stress within the battery stack.<sup>229</sup> Further,

the application of external pressure is crucial to enable active material contact for successful operation of ASSBs. However, generation of excessive and nonuniform stress fields can lead to mechanical degradation, such as fracture and irreversible deformation, which can lead to cell failure of ASSBs. For this reason, buried solid-solid interfaces play a dominant role in the achievable performance and stability of all-solid-state batteries (ASSBs).<sup>7,8</sup> As such, FIB-SEM represents an invaluable diagnostic tool for investigating and understanding ASSBs. As previously discussed, both slice-and-view imaging and tomographic 3D reconstruction give critical insight into morphology and interfacial contact at the nanometer scale. In addition, coupling FIB with other techniques with combined chemical or structural sensitivity, such as EDS, EBSD, and TOF-SIMS, enables spatially resolved observations of chemical (in)compatibility to yield mechanistic information, especially at solid-solid interfaces. As a result, application of Cryo-FIB (and coupled techniques) can yield rich insight into the performance and operating mechanisms of each component of ASSBs, including SSE separators, composite cathodes, and anode interfaces, as summarized in Figure 36. In addition, FIB-SEM



Figure 36. Summary schematic of various key areas where FIB-SEM can yield important insights for ASSBs, including anode, separator, cathode, and sample preparation.

techniques are routinely employed for preparation of ASSB samples for other high-resolution analyses, such as lamella for study by transmission electronic microscopy and other advanced techniques, such as electron diffraction and spectroscopy.<sup>230</sup>

3.3.1. FIB-SEM for Solid Electrolyte Separators. The effective ionic conductivity of solid-state electrolyte (SSE) separators strongly influences the performance of ASSBs. Ideal SSE separators allow facile ion transfer via superionic conduction without electronic leakage between the electrodes of an ASSB. Even outside of the fundamental mechanisms of solid-state ion conduction at the angstrom-scale, the impact of processing and/or operating conditions on the resulting morphology and microstructure of SSE separators can play dominating roles in active material utilization, rate capability, and cycling fatigue. For example, as shown in Figure 37a,<sup>231</sup> 3D reconstructions of SSE separators enabled accurate quantification of the voids and porosity as a function of fabrication pressure. For this solid electrolyte (i.e., the argyrodite Li<sub>6</sub>PS<sub>5</sub>Cl, LPSCl), increasing the fabrication pressure from 50 to 370 MPa resulted in an increase in the relative density of the SSE separator from 68 to 77%.<sup>231</sup> This increase in relative density more than

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Figure 37. Analysis of the microstructure of SSE separators by FIB-SEM. (a) Impact of pressure on relative density and effective ionic conductivity of LPSCl separators. Adapted with permission from ref 231. Copyright 2020 Royal Society of Chemistry, and (b) reconstruction and labeling of connected pore networks and resulting impact on lithium intrusion for LPS separators. Adapted with permission from ref 232. Copyright 2024 Springer Nature.



Figure 38. Application of FIB-SEM techniques to cathode/electrolyte composites in ASSBs. (a) Segmentation of PFIB-SEM cross sections with

porosity quantification; Adapted with permission from ref 239, Copyright 2024 Wiley-VCH GmbH, and (b) 3D reconstruction with quantification of two-phase boundaries; Adapted with permission from ref 240, Copyright 2018 American Chemical Society, and by SIMS imaging of (c) oxidative degradation after cycling a cathode composite; Adapted with permission from ref 247, Copyright 2020 American Chemical Society, and (d) chemical compatibility of sulfide/halide bilayers; Adapted with permission from ref 246, Copyright 2023 Wiley-VCH GmbH.

doubled the effective ionic conductivity of the SSE separators from 0.99 mS cm<sup>-1</sup> to 2.28 mS cm<sup>-1</sup> at room temperature, which translated to increased rate capability due to a decreased ohmic polarization during cycling. The results of this study, enabled by 3D reconstruction via FIB-SEM, reconciled discrepancies in the reported conductivity of this LPSCl SSE by identifying the critical importance of controlling the porosity of SSE separators via application of uniaxial pressure during fabrication. In another study, the relative density of thiophosphate SSE separators was also shown to impact the performance of lithium metal anodes.<sup>232</sup> Increasing the fabrication pressure enabled the production of SSE separators with relative densities more than 95%. Surpassing this threshold relative density mitigated the growth and penetration of parasitic lithium filaments that cause cell failure. Here, tomographic reconstruction via FIB-SEM revealed that separators fabricated with lower pressures exhibited smaller relative density, which both increased the bulk resistance to ion transfer and encouraged propagation of

Alongside relative density, the bulk grain structure of SSE separators impacts the resulting performance for ASSBs, especially when employing soft alkali metal anodes prone to growth of protrusions and filaments that can fracture the separator and cause short-circuits. For instance, the grain size of LPSCl SSE impacts the mechanism of filament growth and protrusion through SSE separators and influences rate capability.<sup>236</sup> The application of FIB-SEM enabled imaging of the separators after cycling to reveal that SSE separators with larger grains exhibited less porosity but enhanced surface roughness, resulting in cell failure at lower current densities as compared to SSE separators with smaller grain size. Further work found that mechanical milling of LPSCI SSEs before fabrication of separators led to a reduction in the grain size and a more uniform pellet with reduced surface roughness and smaller standard deviation in hardness.<sup>237</sup> In line with the previous results, smaller grain sizes were associated with increased rate capability. Further, FIB-SEM imaging revealed the origin of cell failure at increased current density to be the growth and penetration of lithium filaments across the SSE separator intergranularly, causing excessive SSE decomposition upon continuous SEI formation and short-circuiting. In addition to bulk properties, the presence of surface defects in SSE separators can lead to failure of ASSBs. For example, an in-operando study of lithium intrusion into an oxide SSE (Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>, LLZO) employed a cantilever and a microprobe inside a dual-beam FIB-SEM to study the impact of surface defects on intrusion of lithium filaments.<sup>238</sup> After application of plating currents, FIB-SEM was employed to investigate how the cracks visible on the surface of the LLZO pellet related to the morphology of subsurface growth and propagation of lithium filaments. The results of the analysis suggested that current focusing and nanoscale cracks from mechanical stress, rather than electronic leakage or electrochemical reduction, initiate the intrusion of lithium filaments. These FIB-SEM results demonstrate some of the key challenges to scaling up the production of dense separators, especially for brittle SSEs, as even the presence of a small number of nanoscale microstructural defects can lead to eventual cell failure.

3.3.2. FIB-SEM for Cathode/Electrolyte Composites. In addition to the central importance of SSE separators for enabling ASSBs, the microstructure of composite cathodes also greatly impacts the performance of ASSBs. Composite cathodes, which are comprised of cathode active materials (CAMs), SSEs, and conductive additives, are effectively mixed conductors wherein electrons and ions must both be transported to cathode active materials for reversible energy storage upon (dis)charge. Both intimate contact between the CAMs and SSE materials as well as percolating networks for ion and electron transport are required for efficient utilization of active materials. As a result, and in contrast to batteries with traditional liquid electrolytes, contact loss between the CAMs and the electron- or ion-conducting phase upon the volume change of cycling can lead to significant capacity decay, particularly at low fabrication or cycling pressures. For example, segmented PFIB-SEM images of cathode composites of LPSCl and NMC811 revealed a decrease in porosity from 16.3% to 8.95% when the fabrication pressure

was increased from 150 to 500 MPa (Figure 38a).<sup>239</sup> Increasing the fabrication pressure enhanced the contact between cathode active materials and the SSE, resulting in reduced impedance and increased active material utilization and capacity retention. Further, beneficial microstructures that achieve low ionic tortuosity and well-dispersed triple-phase boundaries are crucial for the cycling kinetics of thick cathodes with large areal capacity. Here, quantitative analysis by 3D reconstruction via (P) FIB-SEM can reveal the bottlenecks to charge transport in composite cathodes of ASSBs. Proof-of-concept of this approach was reported in 2018 for a cathode composite comprised of a sulfide SSE (i.e., (Li<sub>2</sub>S)<sub>8</sub>(P<sub>2</sub>S<sub>5</sub>)<sub>2</sub>(Ni<sub>3</sub>S<sub>2</sub>)) and LiNbO<sub>3</sub>-coated NMC 811, as adapted in Figure 38b.<sup>240</sup> After tomographic reconstruction and segmentation of voxels by phase (i.e., CAM, SSE, conductive additive, and pores), two-phase boundaries representing the electrochemically active surface area could be identified. In this study, the effective reaction area was suggested to be limited to only 23% of the total available volume due to agglomeration of conductive additives and the presence of pores from contact loss. Here, FIB-SEM revealed that the heterogeneous microstructure of the cathode composite severely limited the (dis)charging kinetics and CAM utilization. Similar work in 2024 employed PFIB-SEM tomography on composites of LiNi<sub>0.83</sub>Mn<sub>0.06</sub>Co<sub>0.11</sub>O<sub>2</sub> (NMC) and a thiophosphate SSE (i.e., Li<sub>3</sub>PS<sub>4</sub>-0.5LiI).<sup>241</sup> By varying processing conditions, the impact of the particle size of SSEs on the tortuosity and active material utilization were studied by microstructural modeling and electrochemical measurements. Here, imaging in both SE and BSE modes facilitated quantitative segmentation and reconstruction of the various composite components. The results suggested that smaller particle sizes facilitated enhanced active material utilization due to increased contact area within a more homogeneous composite microstructure. However, slight disagreement between quantities predicted from image analysis and those measured with electrochemistry suggested some limitations for the PFIB reconstruction method. For example, ionic tortuosity was underpredicted, perhaps due to the lack of resolution of fine porosity (i.e., smaller than 100 nm voxel size).

In addition to microstructure, the chemical (in)compatibility of SSEs with other cell components regulates achievable ASSB performance. The applied (electro)chemical potential at a solid-solid interface can cause oxidative or reductive composition of SSEs to form CEI or SEI, respectively.<sup>242</sup> Decomposition products of SSEs can exhibit undesired properties, such as hindered ion transport or electronic leakage that encourages sustained decomposition due to a lack of kinetic passivation. As a result, when employed in cathode composites, the oxidative stability of SSEs has a strong impact on the cycling performance. For example, one study focused on cathode composites employing carbon-coated LFP found that substituting a sulfide SSE (LPSCI) with more mechanically compliant and oxidatively stable lithium zirconium halide (LZC) SSE resulted in reduced porosity and enhanced contact with the nanosized LFP.<sup>233</sup> Whereas a cathode-electrolyte interphase that caused voiding and contact loss for the LPSCl/LFP composite was observed via FIB-SEM, the more oxidatively stable LZC enabled sustained interfacial contact without degradation against the carbon-coated LFP for prolonged cycle life. Another study revealed that employing another halide SSE (lithium yttrium chloride, LYC), in addition to an oxide coating layer on the spinel CAM (lithium nickel manganese oxide, LNMO), enabled the reversible energy storage even when cycling at potentials as high as 4.8 V vs Li/Li<sup>+.243</sup> In this work,

FIB-SEM revealed that LNMO chemically degraded the sulfide SSE LPSCl, even before cycling, and resulted in contact loss at the CAM/SSE interface. In contrast, cross-sectional images of cathode composites with the more oxidatively stable LYC revealed good interfacial contact by avoiding SSE degradation.

Further insight into degradation at solid-solid interfaces in ASSBs is provided by coupling FIB to other methods with chemical specificity. For example, one of the earliest applications of FIB-coupled TOF-SIMS to visualize the degradation of sulfide SSE against NMC active materials in ASSBs was reported in 2019.<sup>244</sup> Tracking the spatial occurrence of  $PO_x^{-1}$  secondary ion fragments - corresponding to oxidation of LPSCl from oxygen release at the NMC/SSE interface - revealed the mechanism of degradation with prolonged cycling, unequivocally demonstrating the formation of a CEI on the surface of NMC CAMs. Follow-up work examined how the mechanism of SSE oxidation was impacted by the presence of a carbon conductive additive (vapor-grown carbon fibers, VGCF) (Figure 38c). Although the initial CAM utilization and rate capability were increased in the presence of VGCF, capacity retention and cycling stability were significantly decreased due to electrochemical oxidation of LPSCl at the carbon/SSE interface. These studies demonstrated the ability for ToF-SIMS coupled with FIB-SEM to investigate oxidative degradation of SSEs in ASSB cathode composites. Analogous work on sodium ASSBs<sup>245</sup> found similar results, wherein oxidation of a sulfide solid electrolyte (i.e.,  $Na_3SbS_4$ ) was observed via the presence of sulfoxide fragments near interfaces with oxide CAM. Further work demonstrated degradation of SSEs, even in the absence of applied potential.<sup>246</sup> As shown in Figure 38d, a clear decomposition layer comprised of InS<sup>-</sup> secondary ion fragments is observed at the interface of the sulfide LPSCl and halide LiInCl<sub>6</sub>. While this decomposition layer points toward chemical incompatibility of the two electrolytes, the prevalence of the InS<sup>-</sup> fragments tended to increase near the triple phase boundary of the CAM composite. Together, these results suggest (electro)chemical crosstalk between the CAM and the chemical incompatibility of the interface of bilayer solid electrolyte separators. Such insight was only possible through the combined spatial and chemical resolution achieved when employing FIB-SEM and TOF-SIMS.

3.3.3. FIB-SEM for Interfaces and Interphases of ASSBs with Metal Anodes. Alongside SSE separators and CAM composites, the microstructure, compatibility, and chemomechanical stability of negative electrodes are critical for the performance and cycle life of ASSBs. Since energy density is maximized when anodes are operated at extremely reducing conditions (i.e., low working potentials), the reduction of SSE separators at the anode-SSE interface commonly results in the formation of a SEI. As in traditional LIBs, the properties of the SEI strongly impact the operation of ASSBs by irreversibly consuming an inventory of active materials (e.g., Li<sup>+</sup>, Na<sup>+</sup>, etc.) and impacting the kinetics of ion transport and charge transfer. For example, FIB-SEM coupled with EDS revealed the stability of the SSE-anode interface for various Na SSEs.<sup>248</sup> As shown in Figure 39a, a thick decomposition layer (i.e., SEI) was observed for a sulfide SSE (i.e., Na<sub>3</sub>PS<sub>4</sub>) after cycling a Sn anode in a halfcell configuration. While even more severe degradation was observed for a Na halide SSE (i.e., Na<sub>2.25</sub>Y<sub>0.25</sub>Zr<sub>0.75</sub>Cl<sub>6</sub>, NYZC), an appreciable SEI was not detected for the more reductively stable Na hydroborate SSE (i.e., Na<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)<sub>0.5</sub>(B<sub>12</sub>H<sub>12</sub>)<sub>0.5</sub>, NBH). These results demonstrate how FIB-SEM can explain



**Figure 39.** Application of FIB-SEM for understanding the compatibility of electrolytes at anodes of SSB. (a) EDS of FIB cross sections to visualize the SEI between an  $Na_3PS_4$  solid electrolyte a Sn anode. Adapted with permission from ref 248. Copyright 2022 American Chemical Society. (b) FIB-SEM to investigate protrusion of lithium metal in intergranular cracks of oxide SSEs. Adapted with permission from ref 250. Copyright 2017. (c) Cryo-FIB imaging of the contact area between lithium and sulfide SSE. Adapted with permission from ref 252. Copyright 2023 Elsevier. (d) Cryo-FIB of Na metal plated onto a bare Al powder current collector (i.e., anode-free configuration) from NBH electrolyte. Adapted with permission from ref 235. Copyright 2024 Springer Nature.

electrochemical performance in the context of visualizing degradation at buried interfaces of ASSBs.

For negative electrodes of ASSBs, Cryo-FIB has further provided a useful approach to study the impact of chemomechanics and microstructure on the performance of alloy active materials, alkali metal anodes, and so-called "anode-" or "reservoir-free" current collectors.<sup>249</sup> In 2017 FIB-SEM showed the propagation of lithium filaments along the grain boundaries of an oxide SSE (LLZO) (Figure 39b).<sup>250</sup> Cross sectional imaging via FIB-SEM concretely demonstrated the formation of subsurface cracks from the filament propagation in contrast with other previous speculations of transgranular (rather than intergranular) filament growth and helped to establish the critical importance of grain boundary resistance. In another study, the mechanism of intrusion of lithium filaments into an oxide SSE (LLZO) was investigated in further detail.<sup>251</sup> FIB-SEM of buried interfaces was combined with operando optical microscopy to visualize the dynamics and evolution of lithium filaments while controlling the cell electrochemistry. The resulting FIB cross sections revealed the growth of lithium both along grain boundaries and through a crack-opening mechanism, and 3D reconstruction showed the morphology of a lithium filament that shorted the cell after traversing a crack through the SSE separator. In addition, after deep discharge tests at variable current density, FIB-SEM cross sections unveiled contact loss at the Li-SSE interface. The contact area decreased due to void formation upon pitting of the lithium electrode during electrodissolution at accelerated rates. Further FIB-SEM tomographic reconstruction and segmentation of the Li/SSE interface enabled quantification of voids and resulting contact loss after fast stripping. This work, made possible by the combination of optical microscopy with FIB-SEM, demonstrated crucial mechanistic insight into the complexity of lithium intrusion, propagation, and voiding in ASSBs.

Other studies have also employed FIB-SEM to study the impacts of contact area and cycling kinetics. For example, altering the protocols during fabrication of ASSBs with lithium metal anodes impacts the critical current density by modifying the morphology of the Li/SSE interface.<sup>252</sup> Here, the critical



**Figure 40.** Application of FIB-SEM and coupled techniques for cross-sectional imaging of interfacial layers and alloy anodes for ASSBs. (a) FIB-SEM of the impact of Ag/C interlayer on dense lithium deposition. Adapted with permission from ref 254. Copyright 2020 Springer Nature. (b) PFIB-SEM of Ag and Au layers that facilitated plating and stripping of lithium. Adapted with permission from ref 56. Copyright 2023 Elsevier. (c) FIB-SEM and EDS imaging of pure micron Si anodes in ASSB. Adapted with permission from ref 256. Copyright 2021 The American Association for the Advancement of Science. (d) FIB-SEM and ToF-SIMS imaging of chemomechanical degradation of Si/LPSCl composite anodes, including SEI growth. Adapted with permission from ref 258. Copyright 2021 Springer Nature.

current density reflects the maximum current that can reproducibly be applied in a symmetric solid-state cell while avoiding the growth and penetration of lithium filaments across the SSE separator. As shown in Figure 39c, Cryo-FIB revealed that insufficient hold time during cell fabrication at 25 MPa resulted in voids at the Li/SSE interface. Increasing the contact time to 30 min prompted much more uniform contact of lithium metal with the SSE surface via lithium creep deformation. As a result, the critical current density was increased and the growth of lithium filaments was avoided due to the more uniform current distribution over the larger effective contact area. In another study, focused on anode-free lithium ASSBs with sulfide SSE (LPSCl), Cryo-FIB and synchrotron tomography were used to understand the morphology of lithium deposits onto a Cu current collector.<sup>253</sup> The authors found that the morphology and thickness of lithium deposits was dependent on the applied current density, with larger current densities resulting in more nonuniformity in electrodeposition and accelerated shortcircuiting. The results suggested that anode-free ASSBs could be fundamentally limited by the current constrictions that form when the local current density exceeds the critical current density for void formation. Compared to ASSBs with lithium metal anodes, the anode-free configuration induced more extreme loss of active surface area and accelerated cell failure due to pitting and void formation. Another study of anode-free ASSBs demonstrated the importance of intimate contact between the negative current collector and the SSE separator to maintain stable and efficient cycling of Na ASSBs.<sup>235</sup> Employing an Al powder as current collector to replace a traditional aluminum foil enhanced the surface roughness at the interface with NBH SSE, as visualized in the Cryo-FIB cross section shown in Figure 39d. The pelletized current collector enabled plating of 7 mAh cm<sup>-2</sup> of Na in an anode-free half-cell for more than 30 cycles with average Coulombic efficiency surpassing 99.5%. In addition, an anode-free full-cell with an Al pellet current collector achieved a capacity retention of 70% after 400 cycles, as compared to an analogous ASSB with an Al foil current collector which failed after only 25 cycles. Here, the application of Cryo-FIB emphasized the importance of interfacial contact for anode-free ASSBs.

3.3.4. FIB-SEM for Interfaces and Interphases of ASSBs with Alloy Anodes. Some of the challenges associated with alkali metal anodes such as chemical incompatibility, filament intrusion, pitting, and low Coulombic efficiency motivate the use of alloy anodes and interfacial layers to host and regulate alkali insertion/plating, respectively. Despite reducing the specific and volumetric energy density, alloy anodes or interfacial layers could incur practical benefits with respect to safety and power density. For example, in a seminal 2019 report, the application of silver-carbon (Ag/C) nanocomposites as interfacial layers facilitated reversible and efficient lithium plating/stripping from a sulfide SSE (LPSCl).<sup>254</sup> In this study, FIB-SEM investigations revealed an unfavorable dendritic morphology when plating lithium directly in an anode-free configuration on a stainless steel current collector, resulting in loss of lithium inventory from the formation of dead lithium and eventual cell failure. In contrast, cross-sectional FIB-SEM images revealed dense lithium deposition when employing the pseudoanode free configuration enabled by the Ag/C interfacial layer (Figure 40a). This important work demonstrated the capability for ASSBs to achieve performance that competes with industrial LIBs, achieving uniform and filament-free plating of lithium metal in a pouch cell with energy density >900 Wh  $L^{-1}$ and cycle life surpassing 1000. Another study focused on interfacial alloy layers was reported in 2023.<sup>56</sup> In this work, the combination of FIB-SEM and synchrotron tomography

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demonstrated that alloy interfacial layers of Ag or Au with thickness of only 100 nm facilitated uniform, dense, and reversible plating of lithium in an anode-free configuration. PFIB-SEM imaging coupled with EDS demonstrated the dense and uniform lithium deposition over a large field of view (>50  $\mu$ m) and enabled tracking of the Ag and Au particles at various stages of cycling (Figure 40b). Further Cryo-FIB enabled accurate investigation of lithium morphology with enhanced resolution by avoiding implantation artifacts. Pairing the FIB-SEM results with synchrotron tomography, which achieved a much larger field of view but at lower resolution, demonstrated that the interfacial Ag and Au layers increased the nucleation density and, importantly, avoided the contact loss upon stripping typically seen in anode-free ASSBs by preventing isolated lithium islands. Other work employed Cryo-FIB and EDS to demonstrate similar results with Te interfacial layers.<sup>255</sup> The Li2Te alloy enabled more stable cycling of ASSBs with NMC CAMs as compared to a pure lithium metal anode. The Cryo-FIB/EDS results demonstrated that the alloy layer both mitigated the voiding at the Li/SSE interface and lessened the degradation of the LPSCl SSE, resulting in a more passivated and uniform SEI that enabled continuous plating of lithium of more than 12 mAh cm<sup>-2</sup> in a (pseudo-) anode-free half-cell configuration and stable full-cell cycling up to 400 cycles.

Besides the use of interfacial layers, alloys as anode active materials have also enabled excellent ASSB performance. In particular, Si anodes have achieved some of the most stable cycling for Li-ion ASSBs to date. For example, in 2021 carbonfree alloy anodes comprised of micron-sized Si particles with sulfide (LPSCl) SSE achieved groundbreaking performance of 80% capacity retention after 500 cycles for an ASSB with NMC CAM at room temperature.<sup>256</sup> Effective passivation of a thin SEI at the Si/SSE interface enabled outstanding average Coulombic efficiency of 99.95%. The use of FIB-SEM coupled with EDS revealed a chemomechanical phenomenon by which the micronsized Si particles transformed to a more densified morphology upon lithiation and a porous columnar structure upon delithiation (Figure 40c). The chemical compatibility of the LPSCl SSE with the micron-Si anode, coupled with the unique chemomechanical morphology response, enabled the outstanding performance by facilitating effective ion and electron transport throughout the carbon-free anode. Further work in 2024 demonstrated a facile prelithiation strategy to enhance the initial Coulombic efficiency of the micron-Si anodes and increase the accessible cell-level energy density and cycling performance.<sup>257</sup> In this study, the application of FIB-SEM crosssectional imaging and EDS analysis revealed how the uniaxial pressurization of a mixture of stabilized lithium metal powder and micron-Si enabled prelithiation in a single step to enhance both the electronic and ionic conductivity of the Si anode. Compared to the pure Si anode, the prelithiated Si achieved enhanced initial Coulombic efficiency (95.7 vs 78.3%), discharge capacity ( $\sim 2$  vs  $\sim 1.3$  mAh cm<sup>-2</sup>), and capacity retention (73.8 vs 58.7%) after 1000 cycles in full ASSB cells with LCO CAMs. The FIB-SEM and EDS line scans further revealed that the Si anode was only partially utilized due to the large N/P ratio, wherein only the Si active materials closest to the SSE were lithiated. Other work employed FIB-SEM and ToF-SIMS to visualize chemical maps of the SEI produced at Si/ LPSCl interfaces, demonstrating evidence for an SEI rich in Li<sub>2</sub>S after extensive cycling (Figure 40d).<sup>258</sup> Additionally, a composite anode approach was employed in an attempt to reduce the contact loss upon cycling at lower stack pressures, but

extensive SEI formation and volume expansion of Si particles resulted in degradation and cracking of the LPSCl SSE and poor capacity retention.

Besides Si, other alloys hold promise to enable ASSBs with large energy density. For example, Al foils with unique microstructure were reported as negative electrodes for Li-ion ASSBs.<sup>259</sup> In contrast to LIBs with traditional liquid electrolytes, the parasitic porosity formation, electrolyte degradation, and lithium trapping that occurs for Al anodes was avoided in the SSBs due to the application of uniaxial pressure and confinement in a fixed-gap stack configuration. In this study, cross-sectional Cryo-FIB and EDS revealed a layered multiphase microstructure of the rolled Al<sub>94</sub> In<sub>55</sub> electrodes. Further Cryo-FIB measurements of the foil electrodes at different stages of cycling revealed that, although the volume expanded during lithiation, delithiation proceeded with reversible extraction of lithium and contraction toward the pristine morphology. This multiphase alloy foil strategy enabled a reversible areal capacity of more than 6 mAh  $\text{cm}^{-2}$  at a moderate current density of 0.8 mA  $\rm cm^{-2}$  and 2 mAh cm<sup>-2</sup> at a large current density of 6.5 mA cm<sup>-2</sup>, respectively. The use of Cryo-FIB revealed the reversible morphology change of the multiphase foil electrode that enabled the ASSB performance without any artifacts from Ga<sup>+</sup> implantation. In 2024, the electrochemical behavior of a wide range of alloy foil anodes for Li-ion ASSBs was studied in depth.<sup>260</sup> Cross-sectional Cryo-FIB imaging revealed that the primary mode of capacity decay and ASSB degradation stemmed from lithium trapping within the foil microstructures. After lithiation, the alloy delithiated inhomogeneously, wherein lithium was preferentially removed from the alloy/SSE interface when the stripping rate exceeded the rate of solid-state diffusion. These results motivate further investigation of alloy foils as negative electrodes for ASSBs and emphasize how the use of FIB-SEM can unveil mechanistic understanding for improvement in ASSB performance.

3.3.5. Outlook on FIB-SEM for Solid State Batteries. The application of FIB-SEM is an invaluable diagnostic tool to understand the performance limits and mechanisms of ASSBs which rely on efficient transfer of ions at buried solid-solid interfaces. Tomographic 3D reconstruction is a worthwhile approach to understanding microstructure with a good combination of spatial resolution and statistically relevant field-of-view. After segmentation, quantitative phase maps can enable the production of structure-property relationships for important problems, such as the impact of porosity on the conductivity of SSE separators; the role of triple-phase boundaries on the cycling kinetics of CAM composites; and the mechanisms of filament intrusion and propagation before eventual cell failure via internal short. Employing Cryo-FIB helps to minimize artifacts related to reaction or implantation of Ga<sup>+</sup>, especially for Li or Na anodes. Further, coupling FIB-SEM with other techniques with chemical sensitivity (e.g., EDS, SIMS) can unveil how chemical (in)compatibility relates to resistance to charge transfer or ion conduction. State-of-the-art ASSBs benefit from this enhanced understanding, and further improvements in performance can be achieved from more widespread application and improvement of FIB-SEM methodologies. For example, the application of EBSD with tomographic reconstruction could reveal how the grain structure of SSE separators or active materials impacts ASSB performance. Further, increasing the field of view through application of laser cross sections will be important when considering the relationship between manufacturing scale-up, defect formation,

		Sample Handling		Characterization
	Sample preparation	Transfer to FIB-SEM	Transfer to TEM	Within FIB-SEM
Goal	Preserve samp	ole integrity from enviror	nmental probe	Preserve sample integrity from focused beam probes
Methods	Ambient/RT	Ambient/RT	Ambient/RT	RT and Cryogenic temperature: imaging, 2D milling, 3D ASV, lift out, EDS,
	Air Free/Inert Gas	Air Free/Inert Gas	Air Free/Inert Gas	EBSD, SIMS
	Cryogenic	Cryogenic	Cryogenic	
		Air Free and Cryogenic		

Table 5. Sample Handling and Characterization Approaches for Multiscale and Multimodal Characterization

and cell-level performance of pouch cell ASSBs. In addition, automated data acquisition and workflows and the application of machine learning methods for image processing could enable much higher throughput for quality inspection or more accurate segmentation for quantitative analysis. Finally, with only a few exceptions, the use of FIB-SEM for in situ or in-operando analysis has been extremely limited to date, so advancements in instrumentation, sample holders, and air-free transfer protocols will enable a deeper and richer understanding of the interplay of chemomechanics and electrochemistry for ASSBs. Although ASSBs hold great promise to enable stable, low-cost, and energydense energy storage solutions, the manufacturing and scale-up of ASSBs is in its infancy. There is much room for scientific and engineering breakthroughs enabled by dual-beam FIB-SEM technology to contribute to this important technical challenge.

### 4. EMERGING FIB-SEM TECHNIQUES AND WORKFLOWS FOR FUTURE PERSPECTIVE

As a powerful technique that allows for detailed imaging, chemical and crystallographic analysis, as well as sample modification and preparation, FIB-SEM has demonstrated itself as an invaluable diagnostic tool to enable in-depth understanding of battery structure-performance correlations for advancing a variety of battery materials systems, including cathode, anode, and ASSBs. Looking forward, as the continuously increasing demand for further improvement in battery performance required more in-depth understanding of the battery structure from research and development to manufacturing scale-up, more advanced techniques and workflows related to FIB-SEM methodologies are essential. In the following section, perspectives including properly enabled sample handling to minimize beam damage to enable observation of sample at a material's native state, in situ and in-operando workflows to capture real time chemomechanics and electrochemistry phenomena, correlative imaging to analyze a sample across a statistically relevant field, and leveraging artificial intelligence (AI) and machine learning (ML) to enable efficient data collection and analysis are discussed.

#### 4.1. Strategy to Preserve Battery Sample Integrity: Challenges and Opportunities

In previous sections, it has been discussed that various battery materials systems, including SEI/CEI, alkali metal anodes, SSEs are all facing challenges to preserve their sample integrity due to their sensitivity to multiple external probes, from environmental probes such as air contamination or temperature to focused ion or electron probes. To enable preservation of the sample integrity of different materials systems for accurate imaging characterization at multiple length scales, different strategies are needed.

To characterize a battery sample at multiple length scales with multimodal information involves multiple steps that can be

classified either as sample handling steps or characterization steps within FIB-SEM. Table 5 summarizes various approaches for each sample handling step and the available characterization methods within FIB-SEM. Depending on the sensitivity of the battery sample type to external probes, a strategy that combines different approaches at each step is needed to preserve sample integrity to enable accurate characterization. For example, for cathode materials, such as pristine NMC, the sample is neither beam nor air sensitive, and sample handling at room temperature with air exposure is commonly used, coupled with room temperature FIB-SEM characterization.<sup>18</sup> For alkali metals, such as Li or Na, due to air sensitivity and beam sensitivity, air free transfer or inert gas sample transfer is essential to protect sample from contamination while, within the FIB-SEM, Cryo-FIB is needed to protect sample from beam damage from both the ion beam Joule heat effect and Ga<sup>+</sup> reactivity.<sup>47,235</sup> If SEI is of interest in a liquid electrolyte system, then the sample handling process from preparation to transfer requires a full Cryo-transfer process to maintain the sample integrity.<sup>144</sup>

Among all the strategies, the full Cryo-transfer process is the most challenging due to the complexity of handling samples across different stages, from preparation to instrumentation, while simultaneously preventing contamination, such as ice formation or the risk of melting. These challenges are particularly pronounced during the transfer and storage of cryogenic samples, where contamination can severely impact experimental results.

Three major types of contamination in the Cryo-workflow can negatively affect outcomes:

- I. Large ice particles, which form nonhomogeneously on the sample surface when prepared in liquid nitrogen, typically caused by improperly dried tools, dewars, or LN2 filling hoses, as well as room humidity or human breath. These crystals can obstruct regions of interest during imaging.
- II. Speckle-like particles, uniformly distributed small ice particles, are particularly noticeable in high-magnification SEM images and result from sample exposure to humidity during transfer. It is important to note that both (i) and (ii) occur before the sample enters the microscope chamber, where the crystals become embedded in the GIS layer, potentially evaporating during ion milling and creating empty holes in the GIS layer, forming curtains on the sample's milling surface.
- III. Homogeneous ice layer growth occurs inside the FIB-SEM microscope chamber when gaseous water molecules condense on the cold sample surface, forming a uniform ice layer. Although this ice layer can affect TEM data, especially on polished lamellae, its growth is relatively slow in modern FIB-SEM systems, usually less than a few nanometers per hour.

Given these contamination risks, maintaining low moisture levels and employing rapid, Cryo-transfer methods are essential for minimizing contamination and preserving sample integrity throughout the Cryo-workflow.

Within the FIB-SEM characterization, the challenges are mainly related to the complexity added when switching from room temperature FIB to Cryo-FIB for reducing sample damage. One of the major challenges relates to the different deposition process at cryogenic temperature within the FIB-SEM compared to the room temperature operation. The deposition process enables depositing of a protective layer such as platinum, tungsten, or carbon to safeguard the underlying materials from ion beam damage as well as reduce milling artifacts. A high quality protective cap layer is therefore the foundation for assuring a high quality 2D cross-section, TEM sample preparation, and 3D tomography.

At room temperature, the GIS system consists of a reservoir of precursor material attached to a needle, which can be precisely positioned approximately  $100-150 \ \mu m$  above the sample surface, as shown in Figure 41a. As the precursor gases are



**Figure 41.** A comparison of protective layer deposition at room temperature versus cryogenic temperature. (a) Deposition position at room temperature. (b) A 20  $\mu$ m × 2  $\mu$ m × 2  $\mu$ m Pt protective layer deposited on a Si substrate. (c) Cross-sectional view showing the Pt protective layer and Si substrate. (d) Deposition position at cryogenic temperature. (e) The Pt organic precursor condensed over a surface area spanning several mm<sup>2</sup>. (f) Cross-sectional view showing the Pt protective layer after curing (indicated by the white arrows) and the Si substrate. The scale bar is 250  $\mu$ m for a and d, 20  $\mu$ m for b and e, and 10  $\mu$ m for c and f.

released, they adsorb onto the sample surface. When a charged beam (ion or electron) is applied, it breaks down the adsorbed molecules, leaving behind a conductive (metallic/carbon) layer, while the remaining volatile components are pumped away. By using specialized FIB or SEM scanning patterns (adjusting size, position, shape, and predefined application files), users can finetune the deposition characteristics of specific beam chemistry, enabling the creation of a highly localized protective layer, as illustrated in Figure 41b and 41c.

At cryogenic temperatures, the process is different. The cold sample causes the organic precursor to condense when the GIS valve is opened. The rate of condensation is largely determined by the vapor pressure inside the precursor crucible and the distance between the GIS needle and the sample surface. The vapor pressure depends on the type of precursor and its temperature. Since rapid condensation can lead to the formation of a low-quality, porous layer, the crucible is typically kept at room temperature, and the GIS needle is positioned several millimeters away from the sample for the cryogenic applications shown in Figure 41d to better control the deposition process. Compared to room-temperature deposition, the gas condensation mechanism makes it easier to coat a large area uniformly as shown in Figure 41e.

However, several challenges arise: (i) Coating a large area may obscure sample features, particularly if the sample is not homogeneous or requires site-specific preparation; (ii) Once the precursor and GIS needle are set, users have limited control over the deposition outcome; (iii) The organic precursor does not decompose under the charged beam during deposition, leading to a nonconductive layer, which is suboptimal for imaging and milling. To address these challenges, an in situ sputter coater can be used to apply a thin metallic layer to enhance conductivity. Additionally, electron or ion beam assistance can improve the deposition process, similar to room-temperature deposition, but it requires careful parameter optimization to avoid excessive accumulation in areas not exposed to the beam. An ion beam curing process is applied after the condensation to enhance its conductivity and resistance to the beam, which is shown in Figure 41f.

Just as there is complexity added during the deposition process at cryogenic temperature, many traditional room temperature techniques become more time-consuming or challenging as well, for example in the TEM sample preparation process. At room temperature, the GIS deposition method is well established for the TEM sample attached first to the nanomanipulator and subsequently onto the TEM grid (Section 2.4.3). While at cryogenic conditions, because of limited control of the condensation process, the GIS deposition method could lead to uncontrolled uniformity and thickness, for example, a thicker Pt layer requiring extra cleaning steps after attachment.<sup>121,261</sup> Alternatively, several studies have highlighted the



**Figure 42.** GIS-free Cryo-lift-out using redeposition from a copper block. (a) The micromanipulator with the copper block is brought close to the sample surface. (b) The micromanipulator is attached to the extraction volume by redeposition from the copper block. (c) The sample is lifted out from the trench. (d) A zoomed-in image showing the tungsten needle with the copper block attached to the specimen via the redeposition method.



**Figure 43.** A workflow for double-sided attachment serial lift-out. Adapted with permission from ref 267. Copyright 2023 Springer Nature. (a) FIB image of the prepared extraction site with overlaid correlated fluorescence data (green), highlighting the targeted larva. The micromanipulator is attached to the extraction volume using redeposition from the copper block. (b) The extracted volume (outlined by the orange dashed line) is lowered into position between two grid bars in a lamella-milling orientation. The lower front edge of the volume (indicated by yellow arrows) is aligned with the premilled line mark (indicated by black arrows). (c) Double-sided attachment is achieved through redeposition from the grid bars (yellow arrows indicate the direction of milling), followed by line pattern milling to release the section of the desired thickness (marked by the dashed yellow line). The orange dashed line shows the outline of the extracted volume. (d) SEM image of a typical section after being released from the extracted volume, with the black dashed line indicating the outline of the worm cross-section. SEM (e) and TEM (f) overview images of the 40 double-sided attached sections and the resulting lamellae.



**Figure 44.** Battery preparation within FIB: (a) scheme of the setup with isolated manipulator (EasyLift) needle and lithium electrode & EMIMBF electrolyte placed on an SEM stage. Both the needle and the SEM stage were connected to a potentiostat. (b) Lithium titanate electrode was prepared by FIB and glued to the needle by FIB induced carbon deposition. (c) The needle was moved away from the  $Li_4Ti_5O_{12}$  bulk and connected with the rest of the battery on the SEM stage. (d) SEM imaging can reveal changes in the electrode during cycling of the battery. (e) The formation of dendrites can be controlled during the SEM experiment in a disconnected state when the electrode placed on the needle is pulled out from the electrolyte. (f) FIB cut can be prepared to reveal changes inside the electrode. FIB can optionally be used for TEM lamella preparation from the electrode on the needle. Adapted with permission from ref 270. Copyright LYRASIS, Ústřední knihovna VUT.

advantages of using water-based GIS.<sup>127,145,262</sup> Owing to the lower atomic numbers of its constituent elements, water GIS minimizes residual material effects in Cryo-STEM, prevents artificial carbon contamination in carbon-sensitive samples, and provides precise, real-time control of deposition while reducing thermal drift during attachment. For systems where water or Pt GIS is unavailable or when minimal GIS coverage is preferred in

the regions surrounding the sample, a GIS-free method<sup>126,263,264</sup> can be employed, which relies on the redeposition of sputtering materials at the interface to facilitate attachment. As Cu is proved to effectively enable sample attachment, recently, researchers have developed a method that lifts out a chunk of Cu metal;<sup>265</sup> attaching it to the nanomanipulator makes the attachment and transfer process significantly easier and more

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**Figure 45.** FIB preparation of model battery on SEM biasing holder: (a) CleanConnect capsule used for the airless transfer between the glovebox and SEM.<sup>276</sup> (b) Lithium sample and biasing holder were placed in the transfer shuttle moved into the SEM stage (b). (c-e) Lithium chunk was extracted by FIB, fastened to the manipulator needle, and moved onto the biasing holder. (f) FIB-induced carbon deposition was used to glue the lithium chunk on the biasing contact. (g) The biasing holder already contained a FIB-prepared Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrode and ionic liquid (EMIMBF with 0.5 M LiBF<sub>6</sub> salt) electrolyte. (h) FIB scanning was used to move the ionic liquid between the electrodes and complete the battery.

reliable. Figure 42 shows the GIS-free Cryo-lift-out process using a copper block. Compared to traditional redeposition methods, the Cu chunk method conserves more needle material, allowing multiple attachments before the Cu chunk is depleted, and enables the lifting out of larger sample volumes due to the strong redeposition facilitated by the ion beam. Excessive Cu deposition on the lamella is significantly reduced when the lamella is further thinned to electron transparency after the welding. In addition to Cu, other metals, such as Cr, have also been utilized for Cryo-APT sample preparation.<sup>266</sup> Cr was selected due to its excellent adhesion to both flat and curved surfaces, making it a reliable material for securing lamella during lift-out processes. Comprehensive reviews by various groups<sup>22,261</sup> provide in-depth discussion on the challenges and practical tips for individual steps involved in Cryo lift-out procedures.

Given the complexity of Cryo-FIB as outlined above, a high level of expertise as well as significant operator and microscope time is still required to accomplish the work. Therefore, there is demand and opportunity for workflow development with higher throughput and automation. The workflow may leverage learning from the field of life science, where automation, e.g. on-the-grid lamella preparation, and the high throughput method have already been developed in life science samples.<sup>124,267</sup> Figure 43 shows an example of a new technique that enables high efficiency and throughput in Cryo-FIB called 'serial lift-out'. Instead of extracting a volume approximately the size of the final lamella, this technique extracts a much larger volume (around 110  $\mu$ m × 30  $\mu$ m × 25  $\mu$ m), combined with the copper chunk method to enable multiple lamellae prepared at the same time on a customized grid. This method, for example, could be particularly beneficial for studying the inhomogeneous electrochemical mechanism across a thick electrode sample at nanoscale.

#### 4.2. In-Operando Characterization of Battery in FIB-SEM

As instrumentation techniques advance, there is a growing demand for enabling in-operando measurements for battery research. Compared to ex-situ measurement, in-operando measurements provide direct correlations between electrochemical and physicochemical properties in battery systems, enhancing the fundamental understanding of these systems. Implementing in-operando characterization in FIB-SEM is valuable, as it provides a combination of high-resolution micro-/nanostructural data with chemical and crystallographic information at both the surface and interfaces, potentially in both 2D and 3D, to probe how microstructures evolve during battery operation.<sup>268,269</sup>

To study microstructural evolution during electrochemical charge and discharge processes in FIB-SEM, there are three major approaches in cell design. The first design concept is directly attaching the target sample, either electrode or active particles, to the nanomanipulator to build a battery with electrolyte and counter electrode sitting on the stage, as shown in Figure 44.<sup>270,271</sup> The testing circuit is connected to a potentiostat placed outside of the FIB-SEM chamber through the isolated needle of the EasyLift manipulator and the SEM stage.<sup>272</sup> In general, the sample electrode can be prepared by FIB to the size of microns to tens of microns. FIB milling can further be used to inspect changes inside the electrode placed on the manipulator needle. In terms of electrolyte selection, ionic liquid or low vapor pressure electrolyte can be used in this approach that enables observation of various shapes of samples including nanowires or single particles attached to the manipulator.<sup>273,27</sup> This approach is advantageous, as it provides an easy way of disconnecting the battery and imaging the interfaces in SEM. It also allows for multiple nanomanipulator needles set up as well as air-free or inert gas sample transfer to study air sensitive battery systems.<sup>275</sup>

The second approach is using FIB to directly prepare a battery on a biasing holder inside of the FIB-SEM system. Air sensitive bulk materials of the electrodes can be loaded to FIB-SEM, for example, via an air free transfer device.<sup>276</sup> The entire biasing holder can be transferred into an SEM stage in an argon-filled capsule (Figure 45a) and loaded into the SEM stage adapter (Figure 45b). A (microelectro-mechanical systems) MEMS heating and biasing chip<sup>277</sup> is used for battery biasing in this case (Figure 45e). Figure 45f shows the chip that has a FIB-prepared Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) electrode connected to a biasing contact by FIB-assisted carbon deposition from a gas injection system of the FIB-SEM. A droplet of vacuum-compatible ionic liquid can be placed on the chip manually by a pipet close to the biasing contacts. A Plasma FIB with Xe<sup>+</sup> or Ar<sup>+</sup> is recommended during all the sample preparation steps. Commonly used Ga<sup>+</sup> FIB can introduce gallium contamination into the model battery, especially when a lithium electrode is used. In the last preparation step, the ionic liquid can be moved in between the electrodes using FIB scanning, which changes the viscosity of the ionic liquid (Figure 45g and 45h) and makes it flow on the surface of the testing holder. This advantageous step allows for the omission of a dedicated liquid injection system on the FIB-SEM. The model battery approach has advantages and flexibility to build and customize the battery within the FIB-SEM, allowing for the study of the mechanism of the new battery materials system.

The third approach is cycling the full bulk battery within the FIB-SEM. In this approach, the entire battery can be moved into the FIB-SEM in an airless transfer device shuttle and loaded into the stage of a FIB-SEM system<sup>278–281</sup> as shown in Figure 46a



**Figure 46.** (a) Examples of bulk battery testing holders transferable under argon by the CleanConnect. (b) Cross-sectional battery holder with contact plates (yellow arrows) compressing the battery during cycling and imaging in SEM. (c) SEM holder for coin cell batteries. Grid in the coin cell cover enables SEM imaging of the electrode–electrolyte interface.

and 46b. The electrical contacts between the battery and a testing device are established once the transfer shuttle with the battery is attached to the stage counterpart, 282,283 and manipulator needles or movable probes can also be used to build additional contact to the battery inside the SEM.<sup>281,284</sup> With different sample holders, different battery cells, such as a pouch cell or coin cell (Figure 46c), can be transferred and coupled with different dedicated SEM adaptors. The full bulk battery approach provides more flexibility in electrolyte system selection, which supports both nonevaporating electrolyte (e.g., ionic liquid, solid state electrolyte) or evaporating electrolyte in an in-operando cell.<sup>285</sup> It can be noted that the SEM image resolution will be influenced when conducting an experiment with an in-operando cell due to electron scattering in a membrane to encapsulate the liquid electrolyte. In addition, it also provides capability for multiple testing environments, such as heating<sup>286,287</sup> and compression.<sup>2</sup>

The bulk battery sample approach allows for imaging two types of sample geometry in SEM, namely the cross-sectional

view and surface view. The cross-sectional view allows interfaces between battery parts to be imaged when a cross-section is made and oriented toward the electron beam.<sup>289,290</sup> In this setup, proper sample preparation to generate a smooth cross-section is recommended to ensure high-quality SEM imaging results.<sup>287,291</sup> For the surface view geometry, the electron beam is perpendicular to the surface of the electrodes, where only one electrode-electrolyte interface can be imaged. This geometry allows for observing the phenomena that happen on the top surface of the electrode, such as dendrite formation.<sup>280,292,1</sup> Although the focus of this set up is to image the electrode top surface, it is still possible to image within the bulk by leveraging the FIB milling process in FIB-SEM. The summary of the above solutions for the in-operando electrochemical testing battery in FIB-SEM is shown in Table 6; the specific in-operando testing approach varies depending on the battery system under study, as different methods are needed to meet research goals.

In addition to in-operando electrochemical testing, inoperando high-temperature synthesis of battery materials can also be studied in SEM and FIB-SEM, particularly with the  $\mu$ Reactor attachment.<sup>294</sup> It facilitates the airless transfer of a sample on a MEMS heating chip (Figure 45e) into the SEM, enabling controlled heating within a preselected gas environment. Compared to the more commonly used environmental scanning electron microscopy,<sup>295</sup> this method offers a cleaner and controllable environment,<sup>296</sup> along with a broader range of usable gases. These advantages make it a powerful approach for investigating the fundamental processes involved in cathode formation and recycling.<sup>297</sup>

In-operando electrochemical testing within FIB-SEM offers more opportunities for a fundamental understanding of the battery reaction process. Future opportunities in this field including workflow development for ease of sample handling and transfer, accurate electrochemical measurement, combination of different testing environments including mechanical force, heating, cooling, and gas environment,<sup>298</sup> and setup accommodation of multimodal information (e.g., EDS, EBSD, SIMS, AFM) within the FIB-SEM.

#### 4.3. Correlative Microscopy for Battery Application

Although FIB-SEM can already cover multiple length scales from mm to sub-nanometer, to bridge the knowledge from cell level performance to atomic scale structures, imaging characterization techniques that cover multiple length scales while pinpointing the same region of interest is essential to enable that knowledge. CM integrates multiple imaging modalities, often having different resolutions, to study the same ROI in a specimen that can fit these needs in battery research.<sup>299</sup> This methodology combines the strengths of different imaging methods, such as light microscopy, X-ray imaging, electron

Table 6. Comparison of In-Operando Testing Set up for Battery Research in FIB-SEM

Approaches	EasyLift needle & SEM stage (Figure 44)	SEM biasing stage (Figure 45)	Cross-sectional battery SEM testing tool (Figure 46a and 46b)	Coin cell SEM testing tool (Figure 46c)
Electrolyte Type	Ionic liquid electrolyte, polymer electrolyte, ASSBs	Ionic liquid electrolyte	Ionic liquid electrolyte, polymer electrolyte, solid-state electrolyte	Coin cells: Ionic liquid electrolyte, polymer electrolyte, ASSBs
Sample size	Few tens of microns for the electrode on the needle	Tens of microns	Typically $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$	Coin cells up to 30 mm in diameter
Sample preparation	Electrode on needle prepared by FIB	Both electrodes prepared by FIB. FIB used to move the electrolyte.	Cross-section prepared mechanically and polished by BIB or FIB.	Modified coin cell allowing SEM acces. Optional FIB polishing
Airless transfer	Possibly on the way to FIB-SEM. One electrode remains on the needle.	Possibly from glovebox to SEM and back.	Possibly from glovebox to SEM and back.	Possible from glovebox to SEM and back.

microscopy, and various spectroscopy techniques, to provide a more comprehensive understanding of the sample. Figure 47



**Figure 47.** Graphics illustrating the various experimental techniques, and the corresponding length scales they can explore.

illustrates the various experimental techniques and the corresponding length scales they can explore.<sup>50</sup> 2D correlative analysis is relatively simple to apply since it requires coregistration of only planar data. It is most often used in materials science to study nanoparticles, surfaces and near-surface ROIs,<sup>300,301</sup> and life science to study cells mainly by correlative light and electron microscopy.<sup>302,303</sup> 3D correlative analysis requires coregistration of volumetric data, e.g. X-ray computed tomography (CT), FIB serial SST, electron tomography, APT, etc., making the task much more complex to archive.

For battery imaging characterization, X-ray computed tomography (CT) is the most employed nondestructive technique to screen the entire battery cell for internal component defects and failure mechanism understanding.<sup>304</sup> This screening typically provides insights at the macro- to mesoscale levels, enabling the detection of significant defects and imperfections in battery components. If more detailed examination using higher resolution and other imaging modalities at the micro- to nanoscale levels is needed to further understand the defects and failure, correlative analysis can be subsequently performed on selected regions of interest (ROIs) identified from the CT data.<sup>305</sup> Figure 48 illustrates the potential steps involved in a correlative multiscale and multimodal analysis of an 18650-battery cell. In most use-cases, a comprehensive correlative study is achieved by utilizing three types of microscopes: X-ray CT, PFIB-SEM or FIB-SEM, and TEM, all equipped with analytical detectors. Defects detected by X-ray CT are further investigated using Plasma FIB-SEM to capture cross-sectional images of the ROIs, collect serial sections for 3D reconstruction, or prepare TEM lamella for detailed nanoscale analysis (Figure 48d-48f). A similar concept can also be used for next-generation battery development, such as SSE to enhance the understanding of the local nanoscopic interfacial chemistry and structure's relationship with overall solid state battery cell performance.<sup>306</sup> CM is anticipated to play a crucial role in advancing battery research and development, as well as accelerating the failure analysis process in battery manufacturing.

# 4.4. The Role of Artificial Intelligence for FIB-SEM Data Analysis and Modeling

FIB-SEM data analysis is computationally demanding and typically requires significant expertise in image processing to achieve accurate image segmentation and quantification. In the realm of AI, machine learning (ML) and deep learning (DL) utilize neural network layers that replicate human decisionmaking processes, improving the analysis of the extensive data sets produced by FIB-SEM and other analytical and imaging methods used in battery research. AI methods, including Convolutional Neural Networks (CNNs), Generative Adversarial Networks (GANs), and Random Forests (RFs), are particularly adept at object detection, classification, and predictive modeling—critical processes for detailed material characterization and data analysis at the nanoscale.<sup>308</sup>

One could split AI for FIB-SEM into two categories, namely enhanced data analysis and predictive modeling. For data analysis, AI methods improve the accuracy and efficiency of data segmentation and consecutive data analysis. Figure 49a shows an example of applying RF classifiers for data classification in threedimensional image data from FIB-SEM tomography using two different image signals.<sup>309</sup> This method improves the accuracy in multiphase material classification and effectively manages common image artifacts, significantly enhancing the analysis accuracy of NMC battery electrode materials. The AI method



(2D & 3D information) Scanning/Transmission Electron Microscopy

**Figure 48.** Typical correlative multiscale and multimodal analysis steps of an 18650-battery cell. (a) X-ray CT of the whole battery cell; (b) Large crosssection of the cathode prepared and imaged by plasma FIB-SEM; inspection at particle level by SEM (c) and (d); (e) Particle cross-section; detailed TEM study of doping, (f) interfaces and lattices. Adapted with the permission from ref.<sup>307</sup> Copyright 2023 American Chemical Society.

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**Figure 49.** Application of AI methods for FIB-SEM data analysis and modeling. (a) Segmentation of cathode particles using a random forest algorithm that utilizes tailored features from multiple detectors for accurate analysis. Adapted with the permission from ref 309. Copyright 2023 Elsevier. (b) Grain segmentation achieved by cleaning up image quality (IQ) maps using deep learning, followed by classical watershed segmentation to identify individual grains. Adapted with the permission from ref 310. Copyright 2021 Elsevier. (c) Deep learning-based segmentation applied to multicomponent negative electrodes, enhancing microstructural analysis. Adapted with the permission from ref 311. Copyright 2022 Elsevier. (d) Prediction of composition and state of lithium-ion cathodes using a convolutional neural network (CNN) trained on SEM images, with the associated gradient class activation map highlighting influential regions in the prediction. Adapted with the permission from ref 315. Copyright 2024 Springer Nature.

can also facilitate the grain boundary visualization Figure 49b. By using CNN methods to analyze EBSD IQ images, the intraparticle grains can be distinctly labeled for further correlative analysis between grain features and electrode properties.<sup>310</sup> Furthermore, at electrode level data analysis, a U-Net was employed to segment and analyze the microstructure of lithium-ion battery electrodes across different states of charge to gain insights of the electrode microstructure evolution during cycling status (Figure 49c).<sup>311</sup> For predictive modeling and classification, AI methods provide essential capabilities for anticipating material behaviors and improving battery manufacturing based on electron microscopic data. As shown in Figure 49d, a model that classifies major composition and different electrochemical cycling states of various NMC cathodes was developed based on SEM images, which can accelerate the process of NMC cathode screening in identifying battery material states for performance optimization. Furthermore, the AI method can also be used for predicting electrode properties based on building machine learning models at mesoscale image data sets. In this approach, electrode microstructure data consists of various shapes, sizes, orientations, and chemical compositions that can be generated for electrode property estimation with high accuracy and that improves the efficiency in the electrode structure optimization process.

By integrating experimental data, such as that from FIB-SEM, along with physics-based models and machine learning, digital twins can be built as virtual replicas of the LIB manufacturing process. This enables real-time simulation and optimization of electrode design, fabrication, and failure prediction.<sup>312–314</sup> For instance, high-fidelity 3D FIB-SEM data of electrode structures capture essential microstructural characteristics, such as pore network structure, interfacial areas, tortuosity and connectivity, and phase and size distribution. These data facilitate the creation of a digital twin integrated with multiphysics simulations that can accurately simulate battery behavior under various operating and manufacturing conditions. Insights from these simulations can guide manufacturing steps like calendaring, pressing, and coating, allowing for in-silico process optimization to reduce costs and improve efficiency. Additionally, parameters captured from FIB-SEM, such as cracks, delamination, or porosity nonuniformity, enable the development of digital twins for failure analysis diagnostics. For example, a digital twin using electro-chemomechanical models can predict stress-induced

failure processes, aiding in material selection and structural design optimization. It is expected that these digital twins will provide recommendations for process improvements, thereby enhancing both efficiency and reliability in battery manufacturing.

Integrating AI with FIB-SEM workflows is transforming battery research by accelerating material discovery and providing deeper insights into battery behaviors. AI techniques-such as image segmentation, data analysis, and predictive modeling-enhance battery characterization by automating feature identification and quantification, reducing manual effort and speeding up data processing. By correlating microstructural features with battery performance, AI helps optimize materials for improved efficiency and longer lifespan. We anticipate that AI will continue to revolutionize battery research, particularly through advanced predictive modeling and automated image analysis. The adoption of generative AI models and open-source data-sharing initiatives will promote data standardization, foster interdisciplinary collaboration, and accelerate material screening. By refining these AI-enhanced methods, the research community can optimize performance predictions and drive innovation toward more sustainable and efficient battery technologies.

## 5. CONCLUSION

As a powerful characterization technique that combines a focused ion beam with a scanning electron microscope to provide high-resolution imaging and precise material manipulation, FIB-SEM has provided great influence in not only accelerating material discovery and optimization but also providing deeper insights into the intricate behaviors of battery systems, paving the way for the development of more efficient, durable, and high-performing batteries. Its characterization capability including 2D cross-sectioning and imaging, 3D tomography analysis, and sample modification for sample preparation (e.g., TEM lamella) enables it to analyze the battery structure across multiple length scales in multidimensions to probe the battery structure from cell level to nanoscale. Combining multiscale information with various analytical capabilities within the FIB-SEM including EDS, EBSD, and SIMS further enhanced its capability to gain more comprehensive understanding between macroscopic performance and microscopic phenomena.

Looking forward, the next frontier in FIB-SEM characterization of batteries shall center on developing workflows that enable real time, multiscale, and multimodal analysis with AIdriven automation, while preserving sample integrity, to address the increasing complexity of battery materials and structure design required to meet the growing performance demands. Developing in-operando workflows, such as biasing and heating, are critical, as they provide in-depth understanding of the interplay between electrochemistry and structure evolution tied to the framework of battery materials synthesis and battery operation. For example, in ASSBs studies, in-operando analysis is effective for understanding the electro-chemomechanical behavior and degradation process. The CM workflow provides a holistic insight across different length scales, from cell level to nanoscale, using various imaging modalities. It is important to note that the enhancement of spatially resolved chemical mapping with light element detection capability (e.g., lithium) is crucial for the development of next-gen batteries. AI-driven automation and analysis for FIB-SEM are becoming increasingly important, potentially revolutionizing high-throughput data collection and enabling efficient and accurate analysis. Digital twins built on high-fidelity 3D FIB-SEM data can then contribute to optimizing electrode design and manufacturing processes. Finally, due to the intrinsic reactivity of many battery materials, such as lithium metal and SEI, preserving sample integrity is always necessary. Strategies such as cryogenic temperature operation, low-dose imaging, inert gas sample transfer, or cryo-transfer are needed to enable characterization of battery samples in their native state. Overall, with ongoing efforts to improve these methodologies in FIB-SEM, it is expected to remain an indispensable technique for supporting battery innovation in both battery R&D and manufacturing.

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Z.L. and M.Z. led the project. All coauthors equally contributed to the planning, discussion, and writing of the review. CRediT: Zhao Liu conceptualization, investigation, supervision, writing original draft, writing - review & editing; Shuang Bai writing original draft; Sven Burke writing - original draft; James N. Burrow writing - original draft; Remco Geurts writing - original draft; Chen-Jui Huang writing - original draft; Chengge Jiao writing - original draft; Hee-beom Lee writing - original draft; Libor Novák writing - original draft; Bartłomiej Winiarski writing - original draft; Jing Wang writing - original draft; Ken Wu writing - original draft; Minghao Zhang conceptualization, investigation, supervision, writing - original draft, writing review & editing.

#### Notes

The authors declare the following competing financial interest(s): Prof. Y. Shirley Meng is the founding directors of Energy Transition Network at the University of Chicago, where Thermo Fisher Scientific is one of the founding members.

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## GLOSSARY

APT = Atomic Probe Tomography At.% = Atomic Percent AFM = Atomic Force Microscopy ASSBs = All-Solid-State Batteries BIB = Broad ion Beam BSE = Backscattered Electrons CL = Cathodoluminescence CM = Correlative Microscopy CBS = Concentric Backscattered Cryo-EM = Cryogenic Electron Microscopy Cryo-TEM = Cryogenic Transmission Electron Microscopes Cryo-FIB = Cryogenic-FIB CEI = Cathode Electrolyte Interphase CE = Coulombic Efficiency CAMs = Cathode Active Materials CNNs = Convolutional Neural Networks DL = Deep Learning EELS = Electron Energy Loss Spectroscopy ECR = Electron Cyclotron Resonance EBSD = Electron Backscattered Diffraction EDS = Energy Dispersive X-ray Spectroscopy ETD = Everhart-Thornley Detector ICE = Initial Coulombic efficiency FEG = Field Emission Guns FOV = Field of View FEC = Fluoroethylene Carbonate FIB-SEM = Focused Ion Beam–Scanning Electron Microscope FIB-SEM = Focused Ion Beam-Scanning Electron Microscopy GFIS = Gas Field Ion Sources GIS = Gas Injection Systems GANs = Generative Adversarial Networks HOPG = Highly oriented pyrolytic graphite HC = Hard Carbon ICP = Inductively Coupled Plasma LMAIS = Liquid Metal Alloy Ion Sources LOTIS = Low-Temperature Ion Sources LFP = Lithium Ferrophosphate LHCE = Localized High Concentration Electrolyte  $LPSCl = Li_6PS_5Cl$  $LLZO = Li_7La_3Zr_2O_{12}$ LZC = Lithium Zirconium Halide LNMO = Lithium Nickel Manganese Oxide LYC = Lithium Yttrium Chloride LIBS = Laser-Induced Breakdown Spectroscopy LMIS = Liquid Metal Ion Source NMC811 = Li Ni<sub>0.8</sub>  $Mn_{0.1}Co_{0.1}O_2$ LIB = Lithium-ion battery MCMB = Meso Carbon Micro Beads ML = Machine Learning MOTIS = Magneto-Optical Trap Ion Sources ML = Machine Learning MEMS = Micro-Electro-Mechanical Systems  $NBH = Na_2(B_{10}H_{10})_{0.5}(B_{12}H_{12})_{0.5}$ PFIB = Plasma FIB PFIB-SM = Plasma focused ion beam spin milling ROI = Region of interest RFs = Random Forests

- SE = Secondary Electrons
- SEM = Scanning Electron Microscopes
- SEI = Solid-electrolyte interfaces
- SIMS = Secondary Ion Mass Spectroscopy
- SIM = Scanning Ion Microscopes
- SHIM = Scanning Helium Ion Microscopes
- SST = Serial Sectioning Tomography
- SSE = Solid-State Electrolyte
- 2D = Two-Dimensional
- 3D = Three-Dimensional
- TEM = Transmission Electron Microscopes
- TLD = Through Lens Detector
- TOF-SIMS = Time-Of-Flight Secondary Ion Mass Spectroscopy
- TGC = Titration Gas Chromatography
- UHV = Ultra-High Vacuum
- USPL = Ultra-Short Pulsed Lasers
- VGCF = Vapor-Grown Carbon Fibers
- Wt.% = Weight Percent
- WDS = Wavelength Dispersive X-ray Spectroscopy
- SXES = X-ray Emission Spectrometry
- XPS = X-ray Photoelectron Spectroscopy
- CT = X-ray Computed Tomography

## REFERENCES

(1) Naguara, T.; Tozawa, K. Lithium Ion Rechargeable Battery. Progress in Batteries and Solar Cells; JEC Press Inc., Cleveland, OH (United States), 1990.

(2) Whittingham, M. S.; Xiao, J. Fifty Years of Lithium-Ion Batteries and What Is Next? *MRS Bull.* **2023**, *48* (11), 1118–1124.

(3) Wu, Z.; Zhang, C.; Yuan, F.; Lyu, M.; Yang, P.; Zhang, L.; Zhou, M.; Wang, L.; Zhang, S.; Wang, L. Ni-Rich Cathode Materials for Stable High-Energy Lithium-Ion Batteries. *Nano Energy* **2024**, *126*, 109620.

(4) Radin, M. D.; Hy, S.; Sina, M.; Fang, C.; Liu, H.; Vinckeviciute, J.; Zhang, M.; Whittingham, M. S.; Meng, Y. S.; Van der Ven, A. Narrowing the Gap between Theoretical and Practical Capacities in Li-Ion Layered Oxide Cathode Materials. *Adv. Energy Mater.* **2017**, *7* (20), 1602888.

(5) Sun, L.; Liu, Y.; Shao, R.; Wu, J.; Jiang, R.; Jin, Z. Recent Progress and Future Perspective on Practical Silicon Anode-Based Lithium Ion Batteries. *Energy Storage Mater.* **2022**, *46*, 482–502.

(6) Szczech, J. R.; Jin, S. Nanostructured Silicon for High Capacity Lithium Battery Anodes. *Energy Environ. Sci.* **2011**, *4* (1), 56–72.

(7) Janek, J.; Zeier, W. G. Challenges in Speeding up Solid-State Battery Development. *Nat. Energy* **2023**, *8* (3), 230–240.

(8) Banerjee, A.; Wang, X.; Fang, C.; Wu, E. A.; Meng, Y. S. Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes. *Chem. Rev.* **2020**, *120* (14), 6878–6933.

(9) Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Zhang, Q. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117* (15), 10403–10473.

(10) Ding, J. F.; Zhang, Y. T.; Xu, R.; Zhang, R.; Xiao, Y.; Zhang, S.; Bi, C. X.; Tang, C.; Xiang, R.; Park, H. S.; Zhang, Q.; Huang, J. Q. Review on Lithium Metal Anodes towards High Energy Density Batteries. *Green Energy Environ.* **2023**, *8* (6), 1509–1530.

(11) Franco, A. A.; Rucci, A.; Brandell, D.; Frayret, C.; Gaberscek, M.; Jankowski, P.; Johansson, P. Boosting Rechargeable Batteries R&D by Multiscale Modeling: Myth or Reality? *Chem. Rev.* **2019**, *119* (7), 4569–4627.

(12) Höflich, K.; Hobler, G.; Allen, F. I.; Wirtz, T.; Rius, G.; McElwee-White, L.; Krasheninnikov, A. V.; Schmidt, M.; Utke, I.; Klingner, N.; Osenberg, M.; Córdoba, R.; Djurabekova, F.; Manke, I.; Moll, P.; Manoccio, M.; De Teresa, J. M.; Bischoff, L.; Michler, J.; De Castro, O.; Delobbe, A.; Dunne, P.; Dobrovolskiy, O. V.; Frese, N.; Gölzhäuser, A.; Mazarov, P.; Koelle, D.; Möller, W.; Pérez-Murano, F.; Philipp, P.; Vollnhals, F.; Hlawacek, G. Roadmap for Focused Ion Beam Technologies. *Appl. Phys. Rev.* **2023**, *10* (4), DOI: 10.1063/5.0162597. (13) Wilson, J. R.; Cronin, J. S.; Barnett, S. A.; Harris, S. J. Measurement of Three-Dimensional Microstructure in a LiCoO2 Positive Electrode. *J. Power Sources* **2011**, *196* (7), 3443–3447.

(14) Liu, Z.; Scott Cronin, J.; Chen-Wiegart, Y. C. K.; Wilson, J. R.; Yakal-Kremski, K. J.; Wang, J.; Faber, K. T.; Barnett, S. A. Three-Dimensional Morphological Measurements of LiCoO2 and LiCoO2/ Li(Ni1/3Mn1/3Co1/3)O2 Lithium-Ion Battery Cathodes. *J. Power Sources* 2013, 227, 267–274.

(15) Golozar, M.; Paolella, A.; Demers, H.; Bessette, S.; Lagacé, M.; Bouchard, P.; Guerfi, A.; Gauvin, R.; Zaghib, K. In Situ Observation of Solid Electrolyte Interphase Evolution in a Lithium Metal Battery. *Commun. Chem.* **2019**, 2 (1), 1–9.

(16) Zhang, R.; Strauss, F.; Jiang, L.; Casalena, L.; Li, L.; Janek, J.; Kondrakov, A.; Brezesinski, T. Transition-Metal Interdiffusion and Solid Electrolyte Poisoning in All-Solid-State Batteries Revealed by Cryo-TEM. *Chem. Commun.* **2023**, *59* (31), 4600–4603.

(17) Gholinia, A.; Donoghue, J.; Garner, A.; Curd, M.; Lawson, M. J.; Winiarski, B.; Geurts, R.; Withers, P. J.; Burnett, T. L. Exploration of Fs-Laser Ablation Parameter Space for 2D/3D Imaging of Soft and Hard Materials by Tri-Beam Microscopy. *Ultramicroscopy* **2024**, 257, 113903.

(18) Zhang, M.; Chouchane, M.; Shojaee, S. A.; Winiarski, B.; Liu, Z.; Li, L.; Pelapur, R.; Shodiev, A.; Yao, W.; Doux, J. M.; Wang, S.; Li, Y.; Liu, C.; Lemmens, H.; Franco, A. A.; Meng, Y. S. Coupling of Multiscale Imaging Analysis and Computational Modeling for Understanding Thick Cathode Degradation Mechanisms. *Joule* **2023**, *7* (1), 201–220.

(19) Cheng, D.; Wynn, T.; Lu, B.; Marple, M.; Han, B.; Shimizu, R.; Sreenarayanan, B.; Bickel, J.; Hosemann, P.; Yang, Y.; Nguyen, H.; Li, W.; Zhu, G.; Zhang, M.; Meng, Y. S. A Free-Standing Lithium Phosphorus Oxynitride Thin Film Electrolyte Promotes Uniformly Dense Lithium Metal Deposition with No External Pressure. *Nat. Nanotechnol.* **2023**, *18* (12), 1448–1455.

(20) Matthews, K. C.; Rush, B.; Gearba, R.; Guo, X.; Yu, G.; Warner, J. H. Cryo-Electron Microscopy Reveals Na Infiltration into Separator Pore Free-Volume as a Degradation Mechanism in Na Anode:Liquid Electrolyte Electrochemical Cells. *Adv. Mater.* **2024**, *36* (23), 2308711.

(21) Cheng, D.; Lu, B.; Raghavendran, G.; Zhang, M.; Meng, Y. S. Leveraging Cryogenic Electron Microscopy for Advancing Battery Design. *Matter* **2022**, *5* (1), 26–42.

(22) Long, D. M.; Singh, M. K.; Small, K. A.; Watt, J. Cryo-FIB for TEM Investigation of Soft Matter and Beam Sensitive Energy Materials. *Nanotechnology* **2022**, *33* (50), 503001.

(23) Choudhury, S.; Wei, S.; Ozhabes, Y.; Gunceler, D.; Zachman, M. J.; Tu, Z.; Shin, J. H.; Nath, P.; Agrawal, A.; Kourkoutis, L. F.; Arias, T. A.; Archer, L. A. Designing Solid-Liquid Interphases for Sodium Batteries. *Nat. Commun.* **2017**, *8* (1), 1–10.

(24) Tu, Z.; Choudhury, S.; Zachman, M. J.; Wei, S.; Zhang, K.; Kourkoutis, L. F.; Archer, L. A. Designing Artificial Solid-Electrolyte Interphases for Single-Ion and High-Efficiency Transport in Batteries. *Joule* **2017**, *1* (2), 394–406.

(25) Choudhury, S.; Tu, Z.; Nijamudheen, A.; Zachman, M. J.; Stalin, S.; Deng, Y.; Zhao, Q.; Vu, D.; Kourkoutis, L. F.; Mendoza-Cortes, J. L.; Archer, L. A. Stabilizing Polymer Electrolytes in High-Voltage Lithium Batteries. *Nat. Commun.* **2019**, *10* (1), 1–11.

(26) Jungjohann, K.; Merrill, L.; Gannon, R.; Randolph, S.; Long, D.; Harrison, K. Electrolyte Comparison for Li-Metal Anodes with Cryo-Laser PFIB. *Microsc. Microanal.* **2021**, *27* (S1), 1504–1505.

(27) Koh, H.; Detsi, E.; Stach, E. A. Understanding Ion-Beam Damage to Air-Sensitive Lithium Metal With Cryogenic Electron and Ion Microscopy. *Microsc. Microanal.* **2023**, *29* (4), 1350–1356.

(28) Koh, H.; Hassan, M. H.; Lin, S.; Wang, L.; Stach, E. A.; Detsi, E. Liquid Na-K Alloy Is Not Viable Anode Material for High-Performance Na-Ion Batteries. *Chem. Eng. J.* **2024**, *490*, 151578.

(29) Kanaya, K.; Okayama, S. Penetration and Energy-Loss Theory of Electrons in Solid Targets. J. Phys. D. Appl. Phys. **1972**, 5 (1), 43.

(30) Twedt, K. A.; Chen, L.; McClelland, J. J. Scanning Ion Microscopy with Low Energy Lithium Ions. *Ultramicroscopy* **2014**, *142*, 24–31.

(31) Ziegler, J. F.; Manoyan, J. M. The Stopping of Ions in Compounds. Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms **1988**, 35 (3-4), 215–228.

(32) Sundaram, S. K.; Mazur, E. Inducing and Probing Non-Thermal Transitions in Semiconductors Using Femtosecond Laser Pulses. *Nat. Mater.* **2002**, *1* (4), 217–224.

(33) Chichkov, B. N.; Momma, C.; Nolte, S.; Von Alvensleben, F.; Tünnermann, A. Femtosecond, Picosecond and Nanosecond Laser Ablation of Solids. *Appl. Phys. A Mater. Sci. Process.* **1996**, 63 (2), 109– 115.

(34) Labutin, T. A.; Lednev, V. N.; Ilyin, A. A.; Popov, A. M. Femtosecond Laser-Induced Breakdown Spectroscopy. J. Anal. At. Spectrom. 2016, 31 (1), 90–118.

(35) Williams, D. B.; Carter, C. B. *Transmission Electron Microscopy*; Springer US: Boston, MA, 1996. DOI: 10.1007/978-1-4757-2519-3.

(36) Van Kouwen, L. Introduction to Focused Ion Beams, Ion Sources, and the Nano-Aperture Ion Source. *Adv. Imaging Electron Phys.* **2019**, *212*, 181–216.

(37) Nabhiraj, P. Y.; Menon, R.; Mohan Rao, G.; Mohan, S.; Bhandari, R. K. Characterization of Compact ICP Ion Source for Focused Ion Beam Applications. *Nucl. Instruments Methods Phys. Res. Sect. A Accel.* Spectrometers, Detect. Assoc. Equip. **2010**, 621 (1–3), 57–61.

(38) Boukari, F.; Wartski, L.; Coste, P.; Farchi, A.; Roy, V.; Aubert, J. A Very Compact Electron Cyclotron Resonance Ion Source. *Rev. Sci. Instrum.* **1994**, *65* (4), 1097–1099.

(39) Fermann, M. E.; Hartl, I. Ultrafast Fibre Lasers. *Nat. Photonics* **2013**, 7 (11), 868-874.

(40) Wan, Y.; Jiang, C.; Wen, J.; Yusufu, T.; Zhang, Z.; Liu, B. Femtosecond Harmonic Mode-Locked Fiber Laser Based on Centimeter-Level Er: YAG Crystal-Derived Silica Fiber. *Opt. Laser Technol.* **2024**, *177*, 111177.

(41) How the gun works - SEM. https://myscope.training/SEM\_ How the gun works.

(42) Van Der Heide, P. Secondary Ion Mass Spectrometry: An Introduction to Principles and Practices; Wiley Blackwell, 2014. DOI: 10.1002/9781118916780.

(43) Krohn, V. E.; Ringo, G. R. Ion Source of High Brightness Using Liquid Metal. *Appl. Phys. Lett.* **1975**, *27* (9), 479–481.

(44) Giannuzzi, L. A.; Utlaut, M. A Review of Ga+ FIB/SIMS. Surf. Interface Anal. 2011, 43 (1-2), 475-478.

(45) Ding, Z.; Tang, Y.; Chakravadhanula, V. S. K.; Ma, Q.; Tietz, F.; Dai, Y.; Scherer, T.; Kübel, C. Exploring the Influence of Focused Ion Beam Processing and Scanning Electron Microscopy Imaging on Solid-State Electrolytes. *Microscopy* **2023**, *72* (4), 326–335.

(46) Devaraj, A.; Gu, M.; Colby, R.; Yan, P.; Wang, C. M.; Zheng, J. M.; Xiao, J.; Genc, A.; Zhang, J. G.; Belharouak, I.; Wang, D.; Amine, K.; Thevuthasan, S. Visualizing Nanoscale 3D Compositional Fluctuation of Lithium in Advanced Lithium-Ion Battery Cathodes. *Nat. Commun.* **2015**, *6* (1), 1–8.

(47) Lee, J. Z.; Wynn, T. A.; Schroeder, M. A.; Alvarado, J.; Wang, X.; Xu, K.; Meng, Y. S. Cryogenic Focused Ion Beam Characterization of Lithium Metal Anodes. *ACS Energy Lett.* **2019**, *4* (2), 489–493.

(48) Jo, Y. N.; Kim, Y.; Kim, J. S.; Song, J. H.; Kim, K. J.; Kwag, C. Y.; Lee, D. J.; Park, C. W.; Kim, Y. J. Si-Graphite Composites as Anode Materials for Lithium Secondary Batteries. *J. Power Sources* **2010**, *195* (18), 6031–6036.

(49) Abmosberg. Schematic of Liquid Metal Ion Source (LMIS) common in Focused Ion Beam (FIB) systems. https://commons.wikimedia.org/ wiki/File:LMIS\_schematic.png (accessed 2025-04-03).

(50) Burnett, T. L.; Kelley, R.; Winiarski, B.; Contreras, L.; Daly, M.; Gholinia, A.; Burke, M. G.; Withers, P. J. Large Volume Serial Section Tomography by Xe Plasma FIB Dual Beam Microscopy. *Ultramicroscopy* **2016**, *161*, 119–129.

(51) Winiarski, B.; Geurts, R. Laser Xe+ Plasma FIB-SEM: Correlative Microscopy of 3D Microstructures from Nanometers to Millimeters. *Microsc. Microanal.* **2020**, *26*, S4–S8.

(52) Harris, W. M.; Chiu, W. K. S. Determining the Representative Volume Element Size for Three-Dimensional Microstructural Material Characterization. Part 2: Application to Experimental Data. *J. Power Sources* **2015**, *282*, 622–629.

(53) Jiao, C. Using Focused Ion Beam Without Gallium For "Damage-Free" TEM Specimen Preparation. *AZO Mater.* **2022**.

(54) Lejček, P.; Šob, M.; Paidar, V. Interfacial Segregation and Grain Boundary Embrittlement: An Overview and Critical Assessment of Experimental Data and Calculated Results. *Prog. Mater. Sci.* **2017**, *87*, 83–139.

(55) Jiruše, J.; Hrnčir, T.; Lopour, F.; Zadražil, M.; Delobe, A.; Salord, O. Combined Plasma FIB-SEM. *Microsc. Microanal.* **2012**, *18* (S2), 652–653.

(56) Sandoval, S. E.; Lewis, J. A.; Vishnugopi, B. S.; Nelson, D. L.; Schneider, M. M.; Cortes, F. J. Q.; Matthews, C. M.; Watt, J.; Tian, M.; Shevchenko, P.; Mukherjee, P. P.; McDowell, M. T. Structural and Electrochemical Evolution of Alloy Interfacial Layers in Anode-Free Solid-State Batteries. *Joule* **2023**, 7 (9), 2054–2073.

(57) Smith, N. S.; Notte, J. A.; Steele, A. V. Advances in Source Technology for Focused Ion Beam Instruments. *MRS Bull.* **2014**, *39* (4), 329–335.

(58) Jaiser, S.; Kumberg, J.; Klaver, J.; Urai, J. L.; Schabel, W.; Schmatz, J.; Scharfer, P. Microstructure Formation of Lithium-Ion Battery Electrodes during Drying - An Ex-Situ Study Using Cryogenic Broad Ion Beam Slope-Cutting and Scanning Electron Microscopy (Cryo-BIB-SEM). J. Power Sources 2017, 345, 97–107.

(59) Liu, Z.; Chen-Wiegart, Y. C. K.; Wang, J.; Barnett, S. A.; Faber, K. T. Three-Phase 3D Reconstruction of a LiCoO2 Cathode via FIB-SEM Tomography. *Microsc. Microanal.* **2016**, *22* (1), 140–148.

(60) Stopping and Range of Ions in Matter. http://www.srim.org/ SRIM/SRIMPICS/STOPPLOTS.htm.

(61) Demers, H.; Horny, P.; Gauvin, R.; Lifshin, E. *Win X-Ray - What is Win X-Ray*? https://montecarlomodeling.mcgill.ca/software/winxray/winxray.html.

(62) Strickland, D.; Mourou, G. Compression of Amplified Chirped Optical Pulses. *Opt. Commun.* **1985**, *56* (3), 219–221.

(63) Section 2.5: Ultra-short Pulsed Lasers (3). http://www.aml. engineering.columbia.edu/ntm/level3/ch02/html/l3c02s05.html.

(64) Harrison, K. L.; Merrill, L. C.; Long, D. M.; Randolph, S. J.; Goriparti, S.; Christian, J.; Warren, B.; Roberts, S. A.; Harris, S. J.; Perry, D. L.; Jungjohann, K. L. Cryogenic Electron Microscopy Reveals That Applied Pressure Promotes Short Circuits in Li Batteries. *iScience* **2021**, *24* (12), 103394.

(65) Jungjohann, K. L.; Gannon, R. N.; Goriparti, S.; Randolph, S. J.; Merrill, L. C.; Johnson, D. C.; Zavadil, K. R.; Harris, S. J.; Harrison, K. L. Cryogenic Laser Ablation Reveals Short-Circuit Mechanism in Lithium Metal Batteries. *ACS Energy Lett.* **2021**, *6* (6), 2138–2144.

(66) Merrill, L. C.; Gannon, R. N.; Jungjohann, K. L.; Randolph, S. J.; Goriparti, S.; Zavadil, K. R.; Johnson, D. C.; Harrison, K. L. Evaluation of Lithium Metal Anode Volumetric Expansion through Laser Plasma Focused Ion Beam Cross-Sectional Imaging. *J. Electrochem. Soc.* **2023**, *170* (8), 080527.

(67) Echlin, M. P.; Straw, M.; Randolph, S.; Filevich, J.; Pollock, T. M. The TriBeam System: Femtosecond Laser Ablation in Situ SEM. *Mater. Charact.* **2015**, *100*, 1–12.

(68) Ruska, E. The Early Development of Electron Lenses and Electron Microscopy. *ApOpt* **1986**, *25* (6), 820.

(69) Hawkes, P. W. The Beginnings of Electron Microscopy; Academic Press, 1985.

(70) Von Ardenne, M.; Hawkes, P.; Mulvey, T. On the History of Scanning Electron Microscopy, of the Electron Microprobe, and of Early Contributions to Transmission Electron Microscopy. *Adv. Imaging Electron Phys.* **2021**, 220, 25–50.

(71) McMullan, D. Scanning Electron Microscopy 1928–1965. *Scanning* **1995**, *17* (3), 175–185.

(72) Orloff, J.; Swanson, L. W.; Utlaut, M. Fundamental Limits to Imaging Resolution for Focused Ion Beams. *J. Vac. Sci. Technol. B* **1996**, *14* (6), 3759–3763. (73) Nishizawa, J. i. Extension of Frequencies from Maser to Laser: How the Laser Evolved and Was Extended to Terahertz during My Research Life A Personal Review. *Proc. Jpn. Acad. Ser. B. Phys. Biol. Sci.* **2009**, *85* (10), 454.

(74) Schawlow, A. L.; Townes, C. H. Infrared and Optical Masers. *Phys. Rev.* **1958**, *112* (6), 1940.

(75) Sooy, W. R. THE NATURAL SELECTION OF MODES IN A PASSIVE Q-SWITCHED LASER. *Appl. Phys. Lett.* **1965**, 7 (2), 36–37.

(76) Goldstein, J. I.; Newbury, D. E.; Michael, J. R.; Ritchie, N. W. M.; Scott, J. H. J.; Joy, D. C. Scanning Electron Microscopy and X-Ray Microanalysis; Springer New York, 2017. DOI: 10.1007/978-1-4939-6676-9/COVER.

(77) Springer Handbook of Microscopy; Hawkes, P. W.; Spence, J. C. H., Eds.; Springer Handbooks; Springer International Publishing: Cham, 2019. DOI: 10.1007/978-3-030-00069-1.

(78) Carl Zeiss ships first helium ion microscope. https://www. outsourcing-pharma.com/Article/2007/07/19/carl-zeiss-ships-firsthelium-ion-microscope.

(79) FEI Announces New Vion PFIB System for Advanced IC Packaging. https://www.nbcnews.com/id/wbna43377590.

(80) Knuffman, B.; Steele, A. V.; McClelland, J. J. Cold Atomic Beam Ion Source for Focused Ion Beam Applications. *J. Appl. Phys.* **2013**, *114* (4), 44303.

(81) Pilz, W.; Klingner, N.; Bischoff, L.; Mazarov, P.; Bauerdick, S. Lithium Ion Beams from Liquid Metal Alloy Ion Sources. J. Vac. Sci. Technol. B 2019, 37 (2), DOI: 10.1116/1.5086271.

(82) Bassim, N.; Scott, K.; Giannuzzi, L. A. Recent Advances in Focused Ion Beam Technology and Applications. *MRS Bull.* **2014**, 39 (4), 317–325.

(83) Feng, Q.; Picard, Y. N.; Liu, H.; Yalisove, S. M.; Mourou, G.; Pollock, T. M. Femtosecond Laser Micromachining of a Single-Crystal Superalloy. *Scr. Mater.* **2005**, *53* (5), 511–516.

(84) SEM vs TEM | Technology Networks. https://www.technologynetworks.com/analysis/articles/sem-vs-tem-331262.

(85) Williams, J. The Dual-Beam—Its Birth, Progress, and Future. *Microsc. Today* **2014**, *22* (4), 32–37.

(86) Nan, Y. Focused Ion Beam Systems: Basics and Applications; Cambridge University Press, 2007; Vol. 9780521831. DOI: 10.1017/ CBO9780511600302.

(87) Winiarski, B.; Geurts, R.; Randolph, S. J.; Gannon, R.; Pyka, G.; Varslot, T.; Withers, P. J. Advances in Multi-Beam and Multi-Ion FIB-SEM for 3D Correlative Microscopy. *Microsc. Microanal.* **2019**, *25* (S2), 870–871.

(88) Cressa, L.; Fell, J.; Pauly, C.; Hoang, Q. H.; Mücklich, F.; Herrmann, H. G.; Wirtz, T.; Eswara, S. A FIB-SEM Based Correlative Methodology for X-Ray Nanotomography and Secondary Ion Mass Spectrometry: An Application Example in Lithium Batteries Research. *Microsc. Microanal.* **2022**, *28* (6), 1890–1895.

(89) Winiarski, B.; Rue, C.; Withers, P. J. Plasma FIB Spin Milling for Large Volume Serial Sectioning Tomography. *Microsc. Microanal.* **2019**, 25 (S2), 350–351.

(90) Eder, K.; Bhatia, V.; Qu, J.; Van Leer, B.; Dutka, M.; Cairney, J. M. A Multi-Ion Plasma FIB Study: Determining Ion Implantation Depths of Xe, N, O and Ar in Tungsten via Atom Probe Tomography. *Ultramicroscopy* **2021**, *228*, 113334.

(91) Wang, J.; Randolph, S.; Wu, Q.; Botman, A.; Schardt, J.; Bouchet-Marquis, C.; Nan, X.; Rue, C.; Straw, M. Reactive Oxygen FIB Spin Milling Enables Correlative Workflow for 3D Super-Resolution Light Microscopy and Serial FIB/SEM of Cultured Cells. *Sci. Rep.* **2021**, *11* (1), 1–15.

(92) Pfeifenberger, M. J.; Mangang, M.; Wurster, S.; Reiser, J.; Hohenwarter, A.; Pfleging, W.; Kiener, D.; Pippan, R. The Use of Femtosecond Laser Ablation as a Novel Tool for Rapid Micro-Mechanical Sample Preparation. *Mater. Des.* **2017**, *121*, 109–118.

(93) Hu, J.; Zhang, J.; Li, H.; Chen, Y.; Wang, C. A Promising Approach for the Recovery of High Value-Added Metals from Spent Lithium-Ion Batteries. *J. Power Sources* **2017**, *351*, 192–199.

(94) Wang, G. X.; Bradhurst, D. H.; Liu, H. K.; Dou, S. X. Improvement of Electrochemical Properties of the Spinel LiMn2O4 Using a Cr Dopant Effect. *Solid State Ionics* 1999, 120 (1-4), 95-101.
(95) Zheng, J.; Myeong, S.; Cho, W.; Yan, P.; Xiao, J.; Wang, C.; Cho,

J.; Zhang, J. G. Li- and Mn-Rich Cathode Materials: Challenges to Commercialization. *Adv. Energy Mater.* **2017**, *7* (6), 1601284.

(96) Li, G.; Huang, Z.; Zuo, Z.; Zhang, Z.; Zhou, H. Understanding the Trace Ti Surface Doping on Promoting the Low Temperature Performance of LiNi1/3Co1/3Mn1/3O2 Cathode. *J. Power Sources* **2015**, 281, 69–76.

(97) Hong, J.; Wang, F.; Wang, X.; Graetz, J. LiFexMn1-xPO4: A Cathode for Lithium-Ion Batteries. J. Power Sources 2011, 196 (7), 3659–3663.

(98) Qi, W.; Ben, L.; Yu, H.; Zhao, W.; Zhao, G.; Huang, X. Improving the Rate Capability of a SiOx/Graphite Anode by Adding LiNO3. *Prog. Nat. Sci. Mater. Int.* **2020**, *30* (3), 321–327.

(99) Hang, B. T.; Eashira, M.; Watanabe, I.; Okada, S.; Yamaki, J. I.; Yoon, S. H.; Mochida, I. The Effect of Carbon Species on the Properties of Fe/C Composite for Metal-Air Battery Anode. *J. Power Sources* **2005**, *143* (1–2), 256–264.

(100) Hassan, M. F.; Guo, Z. P.; Chen, Z.; Liu, H. K. Carbon-Coated MoO3 Nanobelts as Anode Materials for Lithium-Ion Batteries. *J. Power Sources* **2010**, *195* (8), 2372–2376.

(101) Chen, L. B.; Xie, J. Y.; Yu, H. C.; Wang, T. H. Si-Al Thin Film Anode Material with Superior Cycle Performance and Rate Capability for Lithium Ion Batteries. *Electrochim. Acta* **2008**, *53* (28), 8149–8153.

(102) Arie, A. A.; Song, J. O.; Lee, J. K. Structural and Electrochemical Properties of Fullerene-Coated Silicon Thin Film as Anode Materials for Lithium Secondary Batteries. *Mater. Chem. Phys.* **2009**, *113* (1), 249–254.

(103) Sun, Y.; Yuan, Y.; Lu, L.; Han, X.; Kong, X.; Wang, H.; Ouyang, M.; Gao, P.; Zheng, H.; Wang, K. A Comprehensive Research on Internal Short Circuits Caused by Copper Particle Contaminants on Cathode in Lithium-Ion Batteries. *eTransportation* **2022**, *13*, 100183.

(104) Hovington, P.; Timoshevskii, V.; Burgess, S.; Demers, H.; Statham, P.; Gauvin, R.; Zaghib, K. Can We Detect Li K X-Ray in Lithium Compounds Using Energy Dispersive Spectroscopy? *Scanning* **2016**, 38 (6), 571–578.

(105) Domi, Y.; Usui, H.; Ando, A.; Nishikawa, K.; Sakaguchi, H. Analysis of the Li Distribution in Si-Based Negative Electrodes for Lithium-Ion Batteries by Soft X-Ray Emission Spectroscopy. *ACS Appl. Energy Mater.* **2020**, *3* (9), 8619–8626.

(106) Fuchs, T.; Ortmann, T.; Becker, J.; Haslam, C. G.; Ziegler, M.; Singh, V. K.; Rohnke, M.; Mogwitz, B.; Peppler, K.; Nazar, L. F.; Sakamoto, J.; Janek, J. Imaging the Microstructure of Lithium and Sodium Metal in Anode-Free Solid-State Batteries Using Electron Backscatter Diffraction. *Nat. Mater.* **2024**, *23*, 1678.

(107) Quinn, A.; Moutinho, H.; Usseglio-Viretta, F.; Verma, A.; Smith, K.; Keyser, M.; Finegan, D. P. Electron Backscatter Diffraction for Investigating Lithium-Ion Electrode Particle Architectures. *Cell Reports Phys. Sci.* **2020**, *1* (8), DOI: 10.1016/J.XCRP.2020.100137.

(108) Zhang, M.; Tantratian, K.; Ham, S.-Y.; Wang, Z.; Chouchane, M.; Shimizu, R.; Bai, S.; Yang, H.; Liu, Z.; Li, L.; Avishai, A.; Chen, L.; Meng, Y. S. Grain Selection Growth of Soft Metal in Electrochemical Processes. *Joule* **2025**, *9*, 101847.

(109) Aspinall, J.; Armstrong, D. E. J.; Pasta, M. EBSD-Coupled Indentation: Nanoscale Mechanics of Lithium Metal. *Mater. Today Energy* **2022**, *30*, 101183.

(110) Hovington, P.; Drouin, D.; Gauvin, R. CASINO: A New Monte Carlo Code in C Language for Electron Beam Interaction —Part I: Description of the Program. *Scanning* **1997**, *19* (1), 1–14.

(111) Priebe, A.; Sastre, J.; Futscher, M. H.; Jurczyk, J.; Puydinger Dos Santos, M. V.; Romanyuk, Y. E.; Michler, J. Detection of Au+Ions during Fluorine Gas-Assisted Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) for the Complete Elemental Characterization of Microbatteries. *ACS Appl. Mater. Interfaces* **2021**, *13* (34), 41262–41274.

(112) Pillatsch, L.; Östlund, F.; Michler, J. FIBSIMS: A Review of Secondary Ion Mass Spectrometry for Analytical Dual Beam Focussed Ion Beam Instruments. Prog. Cryst. Growth Charact. Mater. 2019, 65 (1), 1–19.

(113) Lombardo, T.; Walther, F.; Kern, C.; Moryson, Y.; Weintraut, T.; Henss, A.; Rohnke, M. ToF-SIMS in Battery Research: Advantages, Limitations, and Best Practices. *J. Vac. Sci. Technol. A* **2023**, *41* (5), 53207.

(114) Bessette, S.; Paolella, A.; Kim, C.; Zhu, W.; Hovington, P.; Gauvin, R.; Zaghib, K. Nanoscale Lithium Quantification in LiXNiyCowMnZO2 as Cathode for Rechargeable Batteries. *Sci. Rep.* **2018**, *8* (1), 1–9.

(115) Jiao, C.; Pillatsch, L.; Mulders, J.; Wall, D. Three-Dimensional Time-of-Flight Secondary Ion Mass Spectrometry and DualBeam FIB/ SEM Imaging of Lithium-Ion Battery Cathode. *Microsc. Microanal.* **2019**, *25* (S2), 876–877.

(116) Cooper, S. J.; Roberts, S. A.; Liu, Z.; Winiarski, B. Methods— Kintsugi Imaging of Battery Electrodes: Distinguishing Pores from the Carbon Binder Domain Using Pt Deposition. *J. Electrochem. Soc.* **2022**, *169* (7), 070512.

(117) Miller, D. J.; Proff, C.; Wen, J. G.; Abraham, D. P.; Bareño, J. Observation of Microstructural Evolution in Li Battery Cathode Oxide Particles by In Situ Electron Microscopy. *Adv. Energy Mater.* **2013**, *3* (8), 1098–1103.

(118) Zhou, X.; Li, T.; Cui, Y.; Fu, Y.; Liu, Y.; Zhu, L. In Situ Focused Ion Beam Scanning Electron Microscope Study of Microstructural Evolution of Single Tin Particle Anode for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11* (2), 1733–1738.

(119) Demuth, T.; Fuchs, T.; Beyer, A.; Janek, J.; Volz, K. "Depo-Allaround": A Novel FIB-Based TEM Specimen Preparation Technique for Solid State Battery Composites and Other Loosely Bound Samples. *Ultramicroscopy* **2024**, 257, 113904.

(120) Medalia, O.; Weber, I.; Frangakis, A. S.; Nicastro, D.; Gerisch, G.; Baumeister, W. Macromolecular Architecture in Eukaryotic Cells Visualized by Cryoelectron Tomography. *Science* (80-.). **2002**, 298 (5596), 1209–1213.

(121) Rubino, S.; Akhtar, S.; Melin, P.; Searle, A.; Spellward, P.; Leifer, K. A Site-Specific Focused-Ion-Beam Lift-out Method for Cryo Transmission Electron Microscopy. *J. Struct. Biol.* **2012**, *180* (3), 572–576.

(122) Mahamid, J.; Schampers, R.; Persoon, H.; Hyman, A. A.; Baumeister, W.; Plitzko, J. M. A Focused Ion Beam Milling and Lift-out Approach for Site-Specific Preparation of Frozen-Hydrated Lamellas from Multicellular Organisms. *J. Struct. Biol.* **2015**, *192* (2), 262–269. (123) Rigort, A.; Bäuerlein, F. J. B.; Villa, E.; Eibauer, M.; Laugks, T.;

Baumeister, W.; Plitzko, J. M. Focused Ion Beam Micromachining of Eukaryotic Cells for Cryoelectron Tomography. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (12), 4449–4454.

(124) Klumpe, S.; Fung, H. K. H.; Goetz, S. K.; Zagoriy, I.; Hampoelz, B.; Zhang, X.; Erdmann, P. S.; Baumbach, J.; Müller, C. W.; Beck, M.; Plitzko, J. M.; Mahamid, J. A Modular Platform for Automated Cryo-FIB Workflows. *Elife* **2021**, *10*, DOI: 10.7554/eLife.70506.

(125) Rigort, A.; Plitzko, J. M. Cryo-Focused-Ion-Beam Applications in Structural Biology. *Arch. Biochem. Biophys.* **2015**, *581*, 122–130.

(126) Klumpe, S.; Kuba, J.; Schioetz, O. H.; Erdmann, P. S.; Rigort, A.; Plitzko, J. M. Recent Advances in Gas Injection System-Free Cryo-FIB Lift-Out Transfer for Cryo-Electron Tomography of Multicellular Organisms and Tissues. *Microsc. Today* **2022**, *30* (1), 42–47.

(127) Antoniou, N.; Graham, A.; Hartfield, C.; Amador, G. Failure Analysis of Electronic Material Using Cryogenic FIB-SEM. *EDFA Technol. Artic.* **2013**, *15* (3), 12–19.

(128) Kuroda, C. S.; Yamazaki, Y. Novel Technique of MEA Sample Preparation Using a Focused Ion Beam for Scanning Electron Microscope Investigation. *ECS Trans.* **2007**, *11* (1), 509–516.

(129) Sardashti, K.; Haight, R.; Anderson, R.; Contreras, M.; Fruhberger, B.; Kummel, A. C. Grazing Incidence Cross-Sectioning of Thin-Film Solar Cells via Cryogenic Focused Ion Beam: A Case Study on CIGSe. ACS Appl. Mater. Interfaces **2016**, 8 (24), 14994– 14999.

(130) Zhou, J.; Wei, N.; Zhang, D.; Wang, Y.; Li, J.; Zheng, X.; Wang, J.; Alsalloum, A. Y.; Liu, L.; Bakr, O. M.; Han, Y. Cryogenic Focused Ion

Beam Enables Atomic-Resolution Imaging of Local Structures in Highly Sensitive Bulk Crystals and Devices. *J. Am. Chem. Soc.* **2022**, 144 (7), 3182–3191.

(131) Michael, J. R.; Perry, D. L.; Cummings, D. P.; Walraven, J. A.; Jordan, M. B. Focused Ion Beam Preparation of Low Melting Point Metals: Lessons Learned From Indium. *Microsc. Microanal.* **2022**, 28 (3), 603-610.

(132) Chang, Y.; Lu, W.; Guénolé, J.; Stephenson, L. T.; Szczpaniak, A.; Kontis, P.; Ackerman, A. K.; Dear, F. F.; Mouton, I.; Zhong, X.; Zhang, S.; Dye, D.; Liebscher, C. H.; Ponge, D.; Korte-Kerzel, S.; Raabe, D.; Gault, B. Ti and Its Alloys as Examples of Cryogenic Focused Ion Beam Milling of Environmentally-Sensitive Materials. *Nat. Commun.* **2019**, *10* (1), 1–10.

(133) Xia, D.; Jiang, Y. B.; Notte, J.; Runt, D. GaAs Milling with Neon Focused Ion Beam: Comparison with Gallium Focused Ion Beam Milling and Subsurface Damage Analysis. *Appl. Surf. Sci.* **2021**, *538*, 147922.

(134) Sun, J.; Zhang, Y.; Xiao, Q.; Han, Y.; Zhang, L. Cryo-FIB Machining of Group III-V Semiconductors Suppresses Surface Nanodroplets. *CIRP Ann.* **2024**, 73 (1), 169–172.

(135) Schreiber, D. K.; Perea, D. E.; Ryan, J. V.; Evans, J. E.; Vienna, J. D. A Method for Site-Specific and Cryogenic Specimen Fabrication of Liquid/Solid Interfaces for Atom Probe Tomography. *Ultramicroscopy* **2018**, *194*, 89–99.

(136) Zachman, M. J.; De Jonge, N.; Fischer, R.; Jungjohann, K. L.; Perea, D. E. Cryogenic Specimens for Nanoscale Characterization of Solid-Liquid Interfaces. *MRS Bull.* **2019**, *44* (12), 949–955.

(137) Zachman, M. J.; Tu, Z.; Archer, L. A.; Kourkoutis, L. F. Nanoscale Elemental Mapping of Intact Solid-Liquid Interfaces and Reactive Materials in Energy Devices Enabled by Cryo-FIB/SEM. ACS Energy Lett. **2020**, 5 (4), 1224–1232.

(138) Prasad, B.; Pfanzelt, G.; Fillis-Tsirakis, E.; Zachman, M. J.; Kourkoutis, L. F.; Mannhart, J. Integrated Circuits Comprising Patterned Functional Liquids. *Adv. Mater.* **2018**, *30* (35), 1802598.

(139) Ju, Z.; Yuan, H.; Sheng, O.; Liu, T.; Nai, J.; Wang, Y.; Liu, Y.; Tao, X. Cryo-Electron Microscopy for Unveiling the Sensitive Battery Materials. *Small Sci.* **2021**, *1* (11), 2100055.

(140) Ren, X. C.; Zhang, X. Q.; Xu, R.; Huang, J. Q.; Zhang, Q. Analyzing Energy Materials by Cryogenic Electron Microscopy. *Adv. Mater.* **2020**, 32 (24), 1908293.

(141) Tu, Z.; Choudhury, S.; Zachman, M. J.; Wei, S.; Zhang, K.; Kourkoutis, L. F.; Archer, L. A. Fast Ion Transport at Solid-Solid Interfaces in Hybrid Battery Anodes. *Nat. Energy* **2018**, *3* (4), 310–316. (142) Tu, Z.; Zachman, M. J.; Choudhury, S.; Khan, K. A.; Zhao, Q.;

Kourkoutis, L. F.; Archer, L. A. Stabilizing Protic and Aprotic Liquid Electrolytes at High-Bandgap Oxide Interphases. *Chem. Mater.* **2018**, 30 (16), 5655–5662.

(143) Quinn, J.; Kim, J. M.; Yi, R.; Zhang, J. G.; Xiao, J.; Wang, C. Fluoro-Ethylene-Carbonate Plays a Double-Edged Role on the Stability of Si Anode-Based Rechargeable Batteries During Cycling and Calendar Aging. *Adv. Mater.* **2024**, *36* (30), 2402625.

(144) Zachman, M. J.; Tu, Z.; Choudhury, S.; Archer, L. A.; Kourkoutis, L. F. Cryo-STEM Mapping of Solid-Liquid Interfaces and Dendrites in Lithium-Metal Batteries. *Nature* **2018**, *560* (7718), 345– 349.

(145) Zachman, M. J.; Asenath-Smith, E.; Estroff, L. A.; Kourkoutis, L. F. Site-Specific Preparation of Intact Solid-Liquid Interfaces by Label-Free In Situ Localization and Cryo-Focused Ion Beam Lift-Out. *Microsc. Microanal.* **2016**, *22* (6), 1338–1349.

(146) Tu, Z.; Zachman, M. J.; Choudhury, S.; Wei, S.; Ma, L.; Yang, Y.; Kourkoutis, L. F.; Archer, L. A. Nanoporous Hybrid Electrolytes for High-Energy Batteries Based on Reactive Metal Anodes. *Adv. Energy Mater.* **2017**, *7* (8), 1602367.

(147) Uchic, M. D.; Holzer, L.; Inkson, B. J.; Principe, E. L.; Munroe, P. Three-Dimensional Microstructural Characterization Using Focused Ion Beam Tomography. *MRS Bull.* **2007**, 32 (5), 408–416.

(148) Zaefferer, S.; Wright, S. I.; Raabe, D. Three-Dimensional Orientation Microscopy in a Focused Ion Beam-Scanning Electron Microscope: A New Dimension of Microstructure Characterization. *Metall. Mater. Trans. A* **2008**, 39 (2), 374–389.

(149) Analytical Answers: Focused Ion Beam. https://analyticalanswersinc.com/focused-ion-beam-2/.

(150) Winiarski, B.; Barthelemy, P.; Jiao, C.; Laeveren, D.; Cox, D.; Barnett, S. A. Solid Oxide Cells: From 3D Microstructure to Comprehensive Quantification. *Microsc. Microanal.* **2024**, 30 (Supplement 1), DOI: 10.1093/mam/ozae044.139.

(151) Winiarski, B. Plasma FIB Spin Milling Accelerates Battery Research. *Microsc. Microanal.* **2020**, *26* (S2), 2226–2227.

(152) Scipioni, R.; Jørgensen, P. S.; Ngo, D. T.; Simonsen, S. B.; Liu, Z.; Yakal-Kremski, K. J.; Wang, H.; Hjelm, J.; Norby, P.; Barnett, S. A.; Jensen, S. H. Electron Microscopy Investigations of Changes in Morphology and Conductivity of LiFePO4/C Electrodes. *J. Power Sources* **2016**, *307*, 259–269.

(153) Lee, H. B.; Jung, M. H.; Kim, Y. H.; Park, E. B.; Jang, W. S.; Kim, S. J.; Choi, K. ju; Park, J. young; Hwang, K. bum; Shim, J. H.; Yoon, S.; Kim, Y. M. Deep Learning Image Segmentation for the Reliable Porosity Measurement of High-Capacity Ni-Based Oxide Cathode Secondary Particles. J. Anal. Sci. Technol. **2023**, 14 (1), 1–11.

(154) Young, I. T.; van Vliet, L. J. Recursive Implementation of the Gaussian Filter. *Signal Processing* **1995**, *44* (2), 139–151.

(155) Liu, Z.; Verhallen, T. W.; Singh, D. P.; Wang, H.; Wagemaker, M.; Barnett, S. Relating the 3D Electrode Morphology to Li-Ion Battery Performance; a Case for LiFePO4. *J. Power Sources* **2016**, *324*, 358–367.

(156) Wiedemann, A. H.; Goldin, G. M.; Barnett, S. A.; Zhu, H.; Kee, R. J. Effects of Three-Dimensional Cathode Microstructure on the Performance of Lithium-Ion Battery Cathodes. *Electrochim. Acta* **2013**, *88*, 580–588.

(157) Carter, C. B.; Williams, D. B. *Transmission Electron Microscopy: Diffraction, Imaging, and Spectrometry*; Springer International Publishing, 2016. DOI: 10.1007/978-3-319-26651-0/COVER.

(158) McPhail, D. S. Applications of Secondary Ion Mass Spectrometry (SIMS) in Materials Science. J. Mater. Sci. 2006, 41 (3), 873–903.

(159) Jublot, M.; Texier, M. Sample Preparation by Focused Ion Beam Micromachining for Transmission Electron Microscopy Imaging in Front-View. *Micron* **2014**, *56*, 63–67.

(160) Lee, H. B.; Kim, S. J.; Jung, M. H.; Kim, Y. H.; Kim, S. J.; Gao, H. F.; Van Leer, B.; Jeong, S. Y.; Jeong, H. Y.; Kim, Y. M. Artifact-Free Sample Preparation of Metal Thin Films Using Xe Plasma-Focused Ion Beam Milling for Atomic Resolution and in Situ Biasing Analyses. *Mater. Charact.* **2024**, *216*, 114260.

(161) Zhong, X.; Wade, C. A.; Withers, P. J.; Zhou, X.; Cai, C.; Haigh, S. J.; Burke, M. G. Comparing Xe+pFIB and Ga+FIB for TEM Sample Preparation of Al Alloys: Minimising FIB-Induced Artefacts. *J. Microsc.* **2021**, *282* (2), 101–112.

(162) Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C. L.; Joubert, L. M.; Chin, R.; Koh, A. L.; Yu, Y.; Perrino, J.; Butz, B.; Chu, S.; Cui, Y. Atomic Structure of Sensitive Battery Materials and Interfaces Revealed by Cryo-Electron Microscopy. *Science* (80-.). **2017**, 358 (6362), 506–510. (163) Wagner, F. R.; Watanabe, R.; Schampers, R.; Singh, D.; Persoon, H.; Schaffer, M.; Fruhstorfer, P.; Plitzko, J.; Villa, E. Preparing Samples from Whole Cells Using Focused-Ion-Beam Milling for Cryo-Electron Tomography. *Nat. Protoc.* **2020**, 15 (6), 2041–2070.

(164) Bassim, N. D.; De Gregorio, B. T.; Kilcoyne, A. L. D.; Scott, K.; Chou, T.; Wirick, S.; Cody, G.; Stroud, R. M. Minimizing Damage during FIB Sample Preparation of Soft Materials. *J. Microsc.* **2012**, 245 (3), 288–301.

(165) Dai, J. Y.; Tee, S. F.; Tay, C. L.; Song, Z. G.; Ansari, S.; Er, E.; Redkar, S. Development of a Rapid and Automated TEM Sample Preparation Method in Semiconductor Failure Analysis and the Study of the Relevant TEM Artifact. *Microelectronics J.* **2001**, *32* (3), 221–226. (166) Giannuzzi, L. A.; Stevie, F. A. A Review of Focused Ion Beam Milling Techniques for TEM Specimen Preparation. *Micron* **1999**, *30* (3), 197–204. (167) Uusimaeki, T.; Wagner, T.; Lipinski, H. G.; Kaegi, R. AutoEM: A Software for Automated Acquisition and Analysis of Nanoparticles. *J. Nanoparticle Res.* **2019**, *21* (6), 1–11.

(168) Qiu, B.; Zhang, M.; Xia, Y.; Liu, Z.; Meng, Y. S. Understanding and Controlling Anionic Electrochemical Activity in High-Capacity Oxides for Next Generation Li-Ion Batteries. *Chem. Mater.* **2017**, 29 (3), 908–915.

(169) Zhang, M.; Kitchaev, D. A.; Lebens-Higgins, Z.; Vinckeviciute, J.; Zuba, M.; Reeves, P. J.; Grey, C. P.; Whittingham, M. S.; Piper, L. F. J.; Van der Ven, A.; Meng, Y. S. Pushing the Limit of 3d Transition Metal-Based Layered Oxides That Use Both Cation and Anion Redox for Energy Storage. *Nat. Rev. Mater.* **2022**, *7* (7), 522–540.

(170) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. LixCoO2 (0 < x < -1): A New Cathode Material for Batteries of High Energy Density. *Mater. Res. Bull.* **1980**, *15* (6), 783–789.

(171) Radin, M. D.; Hy, S.; Sina, M.; Fang, C.; Liu, H.; Vinckeviciute, J.; Zhang, M.; Whittingham, M. S.; Meng, Y. S.; Van der Ven, A. Narrowing the Gap between Theoretical and Practical Capacities in Li-Ion Layered Oxide Cathode Materials. *Adv. Energy Mater.* **2017**, *7* (20), 1602888.

(172) Sun, H. H.; Dolocan, A.; Weeks, J. A.; Heller, A.; Mullins, C. B. Stabilization of a Highly Ni-Rich Layered Oxide Cathode through Flower-Petal Grain Arrays. *ACS Nano* **2020**, *14* (12), 17142–17150.

(173) Alvarado, J.; Schroeder, M. A.; Zhang, M.; Borodin, O.; Gobrogge, E.; Olguin, M.; Ding, M. S.; Gobet, M.; Greenbaum, S.; Meng, Y. S.; Xu, K. A Carbonate-Free, Sulfone-Based Electrolyte for High-Voltage Li-Ion Batteries. *Mater. Today* **2018**, *21* (4), 341–353.

(174) Liu, H.; Wolfman, M.; Karki, K.; Yu, Y.-S.; Stach, E. A.; Cabana, J.; Chapman, K. W.; Chupas, P. J. Intergranular Cracking as a Major Cause of Long-Term Capacity Fading of Layered Cathodes. *Nano Lett.* **2017**, *17* (6), 3452–3457.

(175) Bi, Y.; Tao, J.; Wu, Y.; Li, L.; Xu, Y.; Hu, E.; Wu, B.; Hu, J.; Wang, C.; Zhang, J. G.; Qi, Y.; Xiao, J. Reversible Planar Gliding and Microcracking in a Single-Crystalline Ni-Rich Cathode. *Science* (80-.). **2020**, 370 (6522), 1313–1318.

(176) Lee, E. J.; Chen, Z.; Noh, H. J.; Nam, S. C.; Kang, S.; Kim, D. H.; Amine, K.; Sun, Y. K. Development of Microstrain in Aged Lithium Transition Metal Oxides. *Nano Lett.* **2014**, *14* (8), 4873–4880.

(177) Landesfeind, J.; Hattendorff, J.; Ehrl, A.; Wall, W. A.; Gasteiger, H. A. Tortuosity Determination of Battery Electrodes and Separators by Impedance Spectroscopy. *J. Electrochem. Soc.* **2016**, *163* (7), A1373–A1387.

(178) Nguyen, T. T.; Demortière, A.; Fleutot, B.; Delobel, B.; Delacourt, C.; Cooper, S. J. The Electrode Tortuosity Factor: Why the Conventional Tortuosity Factor Is Not Well Suited for Quantifying Transport in Porous Li-Ion Battery Electrodes and What to Use Instead. *npj Comput. Mater.* **2020**, *6* (1), 1–12.

(179) Liu, C.; Neale, Z. G.; Cao, G. Understanding Electrochemical Potentials of Cathode Materials in Rechargeable Batteries. *Mater. Today* **2016**, *19* (2), 109–123.

(180) Yin, C.; Wei, Z.; Zhang, M.; Qiu, B.; Zhou, Y.; Xiao, Y.; Zhou, D.; Yun, L.; Li, C.; Gu, Q.; Wen, W.; Li, X.; Wen, X.; Shi, Z.; He, L.; Shirley Meng, Y.; Liu, Z. Structural Insights into Composition Design of Li-Rich Layered Cathode Materials for High-Energy Rechargeable Battery. *Mater. Today* **2021**, *51*, 15–26.

(181) Zhang, M.; Liu, H.; Liu, Z.; Fang, C.; Meng, Y. S. Modified Coprecipitation Synthesis of Mesostructure-Controlled Li-Rich Layered Oxides for Minimizing Voltage Degradation. *ACS Appl. Energy Mater.* **2018**, *1* (7), 3369–3376.

(182) Zheng, J.; Gu, M.; Genc, A.; Xiao, J.; Xu, P.; Chen, X.; Zhu, Z.; Zhao, W.; Pullan, L.; Wang, C.; Zhang, J. G. Mitigating Voltage Fade in Cathode Materials by Improving the Atomic Level Uniformity of Elemental Distribution. *Nano Lett.* **2014**, *14* (5), 2628–2635.

(183) Zhang, M.; Qiu, B.; Gallardo-Amores, J. M.; Olguin, M.; Liu, H.; Li, Y.; Yin, C.; Jiang, S.; Yao, W.; Arroyo-de Dompablo, M. E.; Liu, Z.; Meng, Y. S. High Pressure Effect on Structural and Electrochemical Properties of Anionic Redox-Based Lithium Transition Metal Oxides. *Matter* **2021**, *4* (1), 164–181. (184) Hy, S.; Liu, H.; Zhang, M.; Qian, D.; Hwang, B.-J.; Meng, Y. S. Performance and Design Considerations for Lithium Excess Layered Oxide Positive Electrode Materials for Lithium Ion Batteries. *Energy Environ. Sci.* **2016**, *9* (6), 1931–1954.

(185) Hobold, G. M.; Lopez, J.; Guo, R.; Minafra, N.; Banerjee, A.; Shirley Meng, Y.; Shao-Horn, Y.; Gallant, B. M. Moving beyond 99.9% Coulombic Efficiency for Lithium Anodes in Liquid Electrolytes. *Nat. Energy* **2021**, *6* (10), 951–960.

(186) Guillaume, C. L.; Gregoryanz, E.; Degtyareva, O.; McMahon, M. I.; Hanfland, M.; Evans, S.; Guthrie, M.; Sinogeikin, S. V.; Mao, H. K. Cold Melting and Solid Structures of Dense Lithium. *Nat. Phys.* **2011**, 7 (3), 211–214.

(187) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M. H.; Alvarado, J.; Schroeder, M. A.; Yang, Y.; Lu, B.; Williams, N.; Ceja, M.; Yang, L.; Cai, M.; Gu, J.; Xu, K.; Wang, X.; Meng, Y. S. Quantifying Inactive Lithium in Lithium Metal Batteries. *Nature* **2019**, *572* (7770), 511–515.

(188) Yang, Y.; Davies, D. M.; Yin, Y.; Borodin, O.; Lee, J. Z.; Fang, C.; Olguin, M.; Zhang, Y.; Sablina, E. S.; Wang, X.; Rustomji, C. S.; Meng, Y. S. High-Efficiency Lithium-Metal Anode Enabled by Liquefied Gas Electrolytes. *Joule* **2019**, *3* (8), 1986–2000.

(189) Yang, Y.; Yin, Y.; Davies, D. M.; Zhang, M.; Mayer, M.; Zhang, Y.; Sablina, E. S.; Wang, S.; Lee, J. Z.; Borodin, O.; Rustomji, C. S.; Meng, Y. S. Liquefied Gas Electrolytes for Wide-Temperature Lithium Metal Batteries. *Energy Environ. Sci.* **2020**, *13* (7), 2209–2219.

(190) Fang, C.; Lu, B.; Pawar, G.; Zhang, M.; Cheng, D.; Chen, S.; Ceja, M.; Doux, J. M.; Musrock, H.; Cai, M.; Liaw, B.; Meng, Y. S. Pressure-Tailored Lithium Deposition and Dissolution in Lithium Metal Batteries. *Nat. Energy* **2021**, *6* (10), 987–994.

(191) Lu, B.; Li, W.; Cheng, D.; Bhamwala, B.; Ceja, M.; Bao, W.; Fang, C.; Meng, Y. S. Suppressing Chemical Corrosions of Lithium Metal Anodes. *Adv. Energy Mater.* **2022**, *12* (48), 2202012.

(192) Sayahpour, B.; Li, W.; Bai, S.; Lu, B.; Han, B.; Chen, Y. T.; Deysher, G.; Parab, S.; Ridley, P.; Raghavendran, G.; Nguyen, L. H. B.; Zhang, M.; Meng, Y. S. Quantitative Analysis of Sodium Metal Deposition and Interphase in Na Metal Batteries. *Energy Environ. Sci.* **2024**, 17 (3), 1216–1228.

(193) Hobold, G. M.; Wang, C.; Steinberg, K.; Li, Y.; Gallant, B. M. High Lithium Oxide Prevalence in the Lithium Solid-Electrolyte Interphase for High Coulombic Efficiency. *Nat. Energy* **2024**, *9* (5), 580–591.

(194) Li, Y.; Huang, W.; Li, Y.; Pei, A.; Boyle, D. T.; Cui, Y. Correlating Structure and Function of Battery Interphases at Atomic Resolution Using Cryoelectron Microscopy. *Joule* **2018**, *2* (10), 2167–2177.

(195) Li, T.; Zhang, X. Q.; Shi, P.; Zhang, Q. Fluorinated Solid-Electrolyte Interphase in High-Voltage Lithium Metal Batteries. *Joule* **2019**, 3 (11), 2647–2661.

(196) Guo, R.; Gallant, B. M. Li2O Solid Electrolyte Interphase: Probing Transport Properties at the Chemical Potential of Lithium. *Chem. Mater.* **2020**, *32* (13), 5525–5533.

(197) Wu, H.; Jia, H.; Wang, C.; Zhang, J. G.; Xu, W. Recent Progress in Understanding Solid Electrolyte Interphase on Lithium Metal Anodes. *Adv. Energy Mater.* **2021**, *11* (5), 2003092.

(198) Sim, R.; Su, L.; Dolocan, A.; Manthiram, A. Delineating the Impact of Transition-Metal Crossover on Solid-Electrolyte Interphase Formation with Ion Mass Spectrometry. *Adv. Mater.* **2024**, *36* (14), 2311573.

(199) Zhang, Q. K.; Sun, S. Y.; Zhou, M. Y.; Hou, L. P.; Liang, J. L.; Yang, S. J.; Li, B. Q.; Zhang, X. Q.; Huang, J. Q. Reforming the Uniformity of Solid Electrolyte Interphase by Nanoscale Structure Regulation for Stable Lithium Metal Batteries. *Angew. Chemie Int. Ed.* **2023**, *62* (42), No. e202306889.

(200) Ma, C.; Xu, F.; Song, T. Dual-Layered Interfacial Evolution of Lithium Metal Anode: SEI Analysis via TOF-SIMS Technology. ACS Appl. Mater. Interfaces **2022**, *14* (17), 20197–20207.

(201) Otto, S. K.; Moryson, Y.; Krauskopf, T.; Peppler, K.; Sann, J.; Janek, J.; Henss, A. In-Depth Characterization of Lithium-Metal Surfaces with XPS and ToF-SIMS: Toward Better Understanding of the Passivation Layer. *Chem. Mater.* **2021**, 33 (3), 859–867.

(202) Park, N. R.; Li, Y.; Yao, W.; Zhang, M.; Han, B.; Mejia, C.; Sayahpour, B.; Shimizu, R.; Bhamwala, B.; Dang, B.; Kumakura, S.; Li, W.; Meng, Y. S. Understanding the Role of Lithium Borate as the Surface Coating on High Voltage Single Crystal LiNi0.5Mn1.5O4. *Adv. Funct. Mater.* **2024**, *34* (13), 2312091.

(203) Cheng, D.; Wynn, T. A.; Wang, X.; Wang, S.; Zhang, M.; Shimizu, R.; Bai, S.; Nguyen, H.; Fang, C.; Kim, M. cheol; Li, W.; Lu, B.; Kim, S. J.; Meng, Y. S. Unveiling the Stable Nature of the Solid Electrolyte Interphase between Lithium Metal and LiPON via Cryogenic Electron Microscopy. *Joule* **2020**, *4* (11), 2484–2500.

(204) Vilá, R. A.; Boyle, D. T.; Dai, A.; Zhang, W.; Sayavong, P.; Ye, Y.; Yang, Y.; Dionne, J. A.; Cui, Y. LiH Formation and Its Impact on Li Batteries Revealed by Cryogenic Electron Microscopy. *Sci. Adv.* **2023**, *9* (12), DOI: 10.1126/sciadv.adf3609.

(205) Dong, K.; Xu, Y.; Tan, J.; Osenberg, M.; Sun, F.; Kochovski, Z.; Pham, D. T.; Mei, S.; Hilger, A.; Ryan, E.; Lu, Y.; Banhart, J.; Manke, I. Unravelling the Mechanism of Lithium Nucleation and Growth and the Interaction with the Solid Electrolyte Interface. *ACS Energy Lett.* **2021**, *6* (5), 1719–1728.

(206) Wang, X.; Pawar, G.; Li, Y.; Ren, X.; Zhang, M.; Lu, B.; Banerjee, A.; Liu, P.; Dufek, E. J.; Zhang, J. G.; Xiao, J.; Liu, J.; Meng, Y. S.; Liaw, B. Glassy Li Metal Anode for High-Performance Rechargeable Li Batteries. *Nat. Mater.* **2020**, *19* (12), 1339–1345.

(207) Han, B.; Li, X.; Bai, S.; Zou, Y.; Lu, B.; Zhang, M.; Ma, X.; Chang, Z.; Meng, Y. S.; Gu, M. Conformal Three-Dimensional Interphase of Li Metal Anode Revealed by Low-Dose Cryoelectron Microscopy. *Matter* **2021**, *4* (11), 3741–3752.

(208) Han, B.; Zou, Y.; Zhang, Z.; Yang, X.; Shi, X.; Meng, H.; Wang, H.; Xu, K.; Deng, Y.; Gu, M. Probing the Na Metal Solid Electrolyte Interphase via Cryo-Transmission Electron Microscopy. *Nat. Commun.* **2021**, *12* (1), 1–8.

(209) Boyle, D. T.; Huang, W.; Wang, H.; Li, Y.; Chen, H.; Yu, Z.; Zhang, W.; Bao, Z.; Cui, Y. Corrosion of Lithium Metal Anodes during Calendar Ageing and Its Microscopic Origins. *Nat. Energy* **2021**, *6* (5), 487–494.

(210) Wi, T. U.; Park, S. O.; Yeom, S. J.; Kim, M. H.; Kristanto, I.; Wang, H.; Kwak, S. K.; Lee, H. W. Revealing the Dual-Layered Solid Electrolyte Interphase on Lithium Metal Anodes via Cryogenic Electron Microscopy. *ACS Energy Lett.* **2023**, *8* (5), 2193–2200.

(211) Cao, X.; Ren, X.; Zou, L.; Engelhard, M. H.; Huang, W.; Wang, H.; Matthews, B. E.; Lee, H.; Niu, C.; Arey, B. W.; Cui, Y.; Wang, C.; Xiao, J.; Liu, J.; Xu, W.; Zhang, J. G. Monolithic Solid-Electrolyte Interphases Formed in Fluorinated Orthoformate-Based Electrolytes Minimize Li Depletion and Pulverization. *Nat. Energy* **2019**, *4* (9), 796–805.

(212) Zhang, Z.; Li, Y.; Xu, R.; Zhou, W.; Li, Y.; Oyakhire, S. T.; Wu, Y.; Xu, J.; Wang, H.; Yu, Z.; Boyle, D. T.; Huang, W.; Ye, Y.; Chen, H.; Wan, J.; Bao, Z.; Chiu, W.; Cui, Y. Capturing the Swelling of Solid-Electrolyte Interphase in Lithium Metal Batteries. *Science* (80-.). **2022**, 375 (6576), 66–70.

(213) Nzereogu, P. U.; Omah, A. D.; Ezema, F. I.; Iwuoha, E. I.; Nwanya, A. C. Anode Materials for Lithium-Ion Batteries: A Review. *Appl. Surf. Sci. Adv.* **2022**, *9*, 100233.

(214) Mundszinger, M.; Farsi, S.; Rapp, M.; Golla-Schindler, U.; Kaiser, U.; Wachtler, M. Morphology and Texture of Spheroidized Natural and Synthetic Graphites. *Carbon N. Y.* **2017**, *111*, 764–773.

(215) Luchkin, S. Y.; Lipovskikh, S. A.; Katorova, N. S.; Savina, A. A.; Abakumov, A. M.; Stevenson, K. J. Solid-Electrolyte Interphase Nucleation and Growth on Carbonaceous Negative Electrodes for Li-Ion Batteries Visualized with in Situ Atomic Force Microscopy. *Sci. Rep.* **2020**, *10* (1), 1–10.

(216) Bhattacharya, S.; Alpas, A. T. Micromechanisms of Solid Electrolyte Interphase Formation on Electrochemically Cycled Graphite Electrodes in Lithium-Ion Cells. *Carbon N. Y.* **2012**, *50* (15), 5359–5371.

(217) Uitz, M.; Sternad, M.; Breuer, S.; Täubert, C.; Traußnig, T.; Hennige, V.; Hanzu, I.; Wilkening, M. Aging of Tesla's 18650 LithiumIon Cells: Correlating Solid-Electrolyte-Interphase Evolution with Fading in Capacity and Power. J. Electrochem. Soc. 2017, 164 (14), A3503–A3510.

(218) Shi, F.; Song, Z.; Ross, P. N.; Somorjai, G. A.; Ritchie, R. O.; Komvopoulos, K. Failure Mechanisms of Single-Crystal Silicon Electrodes in Lithium-Ion Batteries. *Nat. Commun.* **2016**, 7 (1), 1–8.

(219) Bao, W.; Fang, C.; Cheng, D.; Zhang, Y.; Lu, B.; Tan, D. H. S.; Shimizu, R.; Sreenarayanan, B.; Bai, S.; Li, W.; Zhang, M.; Meng, Y. S. Quantifying Lithium Loss in Amorphous Silicon Thin-Film Anodes via Titration-Gas Chromatography. *Cell Reports Phys. Sci.* **2021**, *2* (10), 100597.

(220) Etiemble, A.; Tranchot, A.; Douillard, T.; Idrissi, H.; Maire, E.; Roué, L. Evolution of the 3D Microstructure of a Si-Based Electrode for Li-Ion Batteries Investigated by FIB/SEM Tomography. *J. Electrochem. Soc.* **2016**, *163* (8), A1550–A1559.

(221) Zhu, C.; Chen, S.; Li, K.; Yin, Z. W.; Xiao, Y.; Lin, H.; Pan, F.; Yang, L. Quantitative Analysis of the Structural Evolution in Si Anode via Multi-Scale Image Reconstruction. *Sci. Bull.* **2023**, *68* (4), 408–416.

(222) Qian, G.; Li, Y.; Chen, H.; Xie, L.; Liu, T.; Yang, N.; Song, Y.; Lin, C.; Cheng, J.; Nakashima, N.; Zhang, M.; Li, Z.; Zhao, W.; Yang, X.; Lin, H.; Lu, X.; Yang, L.; Li, H.; Amine, K.; Chen, L.; Pan, F. Revealing the Aging Process of Solid Electrolyte Interphase on SiOx Anode. *Nat. Commun.* **2023**, *14* (1), 1–9.

(223) Kim, J. T.; Su, H.; Zhong, Y.; Wang, C.; Wu, H.; Zhao, D.; Wang, C.; Sun, X.; Li, Y. All-Solid-State Lithium-Sulfur Batteries through a Reaction Engineering Lens. *Nat. Chem. Eng.* **2024**, *1* (6), 400–410.

(224) Tan, D. H. S.; Meng, Y. S.; Jang, J. Scaling up High-Energy-Density Sulfidic Solid-State Batteries: A Lab-to-Pilot Perspective. *Joule* **2022**, *6* (8), 1755–1769.

(225) Randau, S.; Weber, D. A.; Kötz, O.; Koerver, R.; Braun, P.; Weber, A.; Ivers-Tiffée, E.; Adermann, T.; Kulisch, J.; Zeier, W. G.; Richter, F. H.; Janek, J. Benchmarking the Performance of All-Solid-State Lithium Batteries. *Nat. Energy* **2020**, *5* (3), 259–270.

(226) Hirsh, H. S.; Li, Y.; Tan, D. H. S.; Zhang, M.; Zhao, E.; Meng, Y. S. Sodium-Ion Batteries Paving the Way for Grid Energy Storage. *Adv. Energy Mater.* **2020**, *10* (32), 2001274.

(227) Sandoval, S. E.; Haslam, C. G.; Vishnugopi, B. S.; Liao, D. W.; Yoon, J. S.; Park, S. H.; Wang, Y.; Mitlin, D.; Hatzell, K. B.; Siegel, D. J.; Mukherjee, P. P.; Dasgupta, N. P.; Sakamoto, J.; McDowell, M. T. Electro-Chemo-Mechanics of Anode-Free Solid-State Batteries. *Nat. Mater.* 2025, 1–9.

(228) Deysher, G.; Ridley, P.; Ham, S. Y.; Doux, J. M.; Chen, Y. T.; Wu, E. A.; Tan, D. H. S.; Cronk, A.; Jang, J.; Meng, Y. S. Transport and Mechanical Aspects of All-Solid-State Lithium Batteries. *Mater. Today Phys.* **2022**, *24*, 100679.

(229) De Gol, A.; Dermenci, K. B.; Farkas, L.; Berecibar, M. Electro-Chemo-Mechanical Degradation in Solid-State Batteries: A Review of Microscale and Multiphysics Modeling. *Adv. Energy Mater.* **2024**, *14* (47), 2403255.

(230) Wynn, T. A.; Lee, J. Z.; Banerjee, A.; Meng, Y. S. In Situ and Operando Probing of Solid-Solid Interfaces in Electrochemical Devices. *MRS Bull.* **2018**, *43* (10), 768–774.

(231) Doux, J. M.; Yang, Y.; Tan, D. H. S.; Nguyen, H.; Wu, E. A.; Wang, X.; Banerjee, A.; Meng, Y. S. Pressure Effects on Sulfide Electrolytes for All Solid-State Batteries. *J. Mater. Chem. A* **2020**, *8* (10), 5049–5055.

(232) Diallo, M. S.; Shi, T.; Zhang, Y.; Peng, X.; Shozib, I.; Wang, Y.; Miara, L. J.; Scott, M. C.; Tu, Q. H.; Ceder, G. Effect of Solid-Electrolyte Pellet Density on Failure of Solid-State Batteries. *Nat. Commun.* **2024**, *15* (1), 1–9.

(233) Cronk, A.; Chen, Y. T.; Deysher, G.; Ham, S. Y.; Yang, H.; Ridley, P.; Sayahpour, B.; Nguyen, L. H. B.; Oh, J. A. S.; Jang, J.; Tan, D. H. S.; Meng, Y. S. Overcoming the Interfacial Challenges of LiFePO4 in Inorganic All-Solid-State Batteries. *ACS Energy Lett.* **2023**, *8* (1), 827– 835.

(234) Ridley, P.; Nguyen, L. H. B.; Sebti, E.; Han, B.; Duong, G.; Chen, Y. T.; Sayahpour, B.; Cronk, A.; Deysher, G.; Ham, S. Y.; Oh, J. A. S.; Wu, E. A.; Tan, D. H. S.; Doux, J. M.; Clément, R.; Jang, J.; Meng, Y. S. Amorphous and Nanocrystalline Halide Solid Electrolytes with Enhanced Sodium-Ion Conductivity. *Matter* **2024**, 7 (2), 485–499.

(235) Deysher, G.; Oh, J. A. S.; Chen, Y. T.; Sayahpour, B.; Ham, S. Y.; Cheng, D.; Ridley, P.; Cronk, A.; Lin, S. W. H.; Qian, K.; Nguyen, L. H. B.; Jang, J.; Meng, Y. S. Design Principles for Enabling an Anode-Free Sodium All-Solid-State Battery. *Nat. Energy* **2024**, *9* (9), 1161–1172. (236) Singh, D. K.; Henss, A.; Mogwitz, B.; Gautam, A.; Horn, J.; Krauskopf, T.; Burkhardt, S.; Sann, J.; Richter, F. H.; Janek, J. Li6PSSCI Microstructure and Influence on Dendrite Growth in Solid-State Batteries with Lithium Metal Anode. *Cell Reports Phys. Sci.* **2022**, *3* (9), 101043.

(237) Wang, Y.; Hao, H.; Naik, K. G.; Vishnugopi, B. S.; Fincher, C. D.; Yan, Q.; Raj, V.; Celio, H.; Yang, G.; Fang, H.; Chiang, Y. M.; Perras, F. A.; Jena, P.; Watt, J.; Mukherjee, P. P.; Mitlin, D. Mechanical Milling Induced Microstructure Changes in Argyrodite LPSCl Solid-State Electrolyte Critically Affect Electrochemical Stability. *Adv. Energy Mater.* **2024**, *14* (23), 2304530.

(238) McConohy, G.; Xu, X.; Cui, T.; Barks, E.; Wang, S.; Kaeli, E.; Melamed, C.; Gu, X. W.; Chueh, W. C. Mechanical Regulation of Lithium Intrusion Probability in Garnet Solid Electrolytes. *Nat. Energy* **2023**, *8* (3), 241–250.

(239) Chen, Y. T.; Jang, J.; Oh, J. A. S.; Ham, S. Y.; Yang, H.; Lee, D. J.; Vicencio, M.; Lee, J. B.; Tan, D. H. S.; Chouchane, M.; Cronk, A.; Song, M. S.; Yin, Y.; Qian, J.; Chen, Z.; Meng, Y. S. Enabling Uniform and Accurate Control of Cycling Pressure for All-Solid-State Batteries. *Adv. Energy Mater.* **2024**, *14* (30), 2304327.

(240) Choi, S.; Jeon, M.; Ahn, J.; Jung, W. D.; Choi, S. M.; Kim, J. S.; Lim, J.; Jang, Y. J.; Jung, H. G.; Lee, J. H.; Sang, B. I.; Kim, H. Quantitative Analysis of Microstructures and Reaction Interfaces on Composite Cathodes in All-Solid-State Batteries Using a Three-Dimensional Reconstruction Technique. ACS Appl. Mater. Interfaces 2018, 10 (28), 23740–23747.

(241) Minnmann, P.; Schubert, J.; Kremer, S.; Rekers, R.; Burkhardt, S.; Ruess, R.; Bielefeld, A.; Richter, F. H.; Janek, J. Editors' Choice— Visualizing the Impact of the Composite Cathode Microstructure and Porosity on Solid-State Battery Performance. *J. Electrochem. Soc.* **2024**, *171* (6), 060514.

(242) Xiao, Y.; Wang, Y.; Bo, S. H.; Kim, J. C.; Miara, L. J.; Ceder, G. Understanding Interface Stability in Solid-State Batteries. *Nat. Rev. Mater.* **2020**, *5* (2), 105–126.

(243) Jang, J.; Chen, Y. T.; Deysher, G.; Cheng, D.; Ham, S. Y.; Cronk, A.; Ridley, P.; Yang, H.; Sayahpour, B.; Han, B.; Li, W.; Yao, W.; Wu, E. A.; Doux, J. M.; Nguyen, L. H. B.; Oh, J. A. S.; Tan, D. H. S.; Meng, Y. S. Enabling a Co-Free, High-Voltage LiNi0.5Mn1.5O4Cathode in All-Solid-State Batteries with a Halide Electrolyte. *ACS Energy Lett.* **2022**, *7* (8), 2531–2539.

(244) Walther, F.; Koerver, R.; Fuchs, T.; Ohno, S.; Sann, J.; Rohnke, M.; Zeier, W. G.; Janek, J. Visualization of the Interfacial Decomposition of Composite Cathodes in Argyrodite-Based All-Solid-State Batteries Using Time-of-Flight Secondary-Ion Mass Spectrometry. *Chem. Mater.* **2019**, *31* (10), 3745–3755.

(245) Goodwin, L. E.; Ziegler, M.; Till, P.; Nazer, N.; Adelhelm, P.; Zeier, W. G.; Richter, F. H.; Janek, J. Halide and Sulfide Electrolytes in Cathode Composites for Sodium All-Solid-State Batteries and Their Stability. *ACS Appl. Mater. Interfaces* **2024**, *16* (15), 19792–19805.

(246) Rosenbach, C.; Walther, F.; Ruhl, J.; Hartmann, M.; Hendriks, T. A.; Ohno, S.; Janek, J.; Zeier, W. G. Visualizing the Chemical Incompatibility of Halide and Sulfide-Based Electrolytes in Solid-State Batteries. *Adv. Energy Mater.* **2023**, *13* (6), 2203673.

(247) Walther, F.; Randau, S.; Schneider, Y.; Sann, J.; Rohnke, M.; Richter, F. H.; Zeier, W. G.; Janek, J. Influence of Carbon Additives on the Decomposition Pathways in Cathodes of Lithium Thiophosphate-Based All-Solid-State Batteries. *Chem. Mater.* **2020**, *32* (14), 6123– 6136.

(248) Deysher, G.; Chen, Y. T.; Sayahpour, B.; Lin, S. W. H.; Ham, S. Y.; Ridley, P.; Cronk, A.; Wu, E. A.; Tan, D. H. S.; Doux, J. M.; Oh, J. A. S.; Jang, J.; Nguyen, L. H. B.; Meng, Y. S. Evaluating Electrolyte-Anode Interface Stability in Sodium All-Solid-State Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14* (42), 47706–47715.

(249) Hatzell, K. B. Anode-Less or Anode-Free? ACS Energy Lett. 2023, 8 (11), 4775–4776.

(250) Cheng, E. J.; Sharafi, A.; Sakamoto, J. Intergranular Li Metal Propagation through Polycrystalline Li6.25Al0.25La3Zr2O12 Ceramic Electrolyte. *Electrochim. Acta* **2017**, *223*, 85–91.

(251) Kazyak, E.; Garcia-Mendez, R.; LePage, W. S.; Sharafi, A.; Davis, A. L.; Sanchez, A. J.; Chen, K. H.; Haslam, C.; Sakamoto, J.; Dasgupta, N. P. Li Penetration in Ceramic Solid Electrolytes: Operando Microscopy Analysis of Morphology, Propagation, and Reversibility. *Matter* **2020**, *2* (4), 1025–1048.

(252) Ham, S. Y.; Yang, H.; Nunez-cuacuas, O.; Tan, D. H. S.; Chen, Y. T.; Deysher, G.; Cronk, A.; Ridley, P.; Doux, J. M.; Wu, E. A.; Jang, J.; Meng, Y. S. Assessing the Critical Current Density of All-Solid-State Li Metal Symmetric and Full Cells. *Energy Storage Mater.* **2023**, *55*, 455– 462.

(253) Lewis, J. A.; Sandoval, S. E.; Liu, Y.; Nelson, D. L.; Yoon, S. G.; Wang, R.; Zhao, Y.; Tian, M.; Shevchenko, P.; Martínez-Pañeda, E.; McDowell, M. T. Accelerated Short Circuiting in Anode-Free Solid-State Batteries Driven by Local Lithium Depletion. *Adv. Energy Mater.* **2023**, *13* (12), 2204186.

(254) Lee, Y. G.; Fujiki, S.; Jung, C.; Suzuki, N.; Yashiro, N.; Omoda, R.; Ko, D. S.; Shiratsuchi, T.; Sugimoto, T.; Ryu, S.; Ku, J. H.; Watanabe, T.; Park, Y.; Aihara, Y.; Im, D.; Han, I. T. High-Energy Long-Cycling All-Solid-State Lithium Metal Batteries Enabled by Silver-Carbon Composite Anodes. *Nat. Energy* **2020**, *5* (4), 299–308.

(255) Hao, H.; Liu, Y.; Greene, S. M.; Yang, G.; Naik, K. G.; Vishnugopi, B. S.; Wang, Y.; Celio, H.; Dolocan, A.; Tsai, W. Y.; Fang, R.; Watt, J.; Mukherjee, P. P.; Siegel, D. J.; Mitlin, D. Tuned Reactivity at the Lithium Metal-Argyrodite Solid State Electrolyte Interphase. *Adv. Energy Mater.* **2023**, *13* (46), 2301338.

(256) Tan, D. H. S.; Chen, Y. T.; Yang, H.; Bao, W.; Sreenarayanan, B.; Doux, J. M.; Li, W.; Lu, B.; Ham, S. Y.; Sayahpour, B.; Scharf, J.; Wu, E. A.; Deysher, G.; Han, H. E.; Hah, H. J.; Jeong, H.; Lee, J. B.; Chen, Z.; Meng, Y. S. Carbon-Free High-Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes. *Science* (80-.). **2021**, 373 (6562), 1494–1499.

(257) Ham, S. Y.; Sebti, E.; Cronk, A.; Pennebaker, T.; Deysher, G.; Chen, Y. T.; Oh, J. A. S.; Lee, J. B.; Song, M. S.; Ridley, P.; Tan, D. H. S.; Clément, R. J.; Jang, J.; Meng, Y. S. Overcoming Low Initial Coulombic Efficiencies of Si Anodes through Prelithiation in All-Solid-State Batteries. *Nat. Commun.* **2024**, *15* (1), 1–9.

(258) Huo, H.; Jiang, M.; Bai, Y.; Ahmed, S.; Volz, K.; Hartmann, H.; Henss, A.; Singh, C. V.; Raabe, D.; Janek, J. Chemo-Mechanical Failure Mechanisms of the Silicon Anode in Solid-State Batteries. *Nat. Mater.* **2024**, 23 (4), 543–551.

(259) Liu, Y.; Wang, C.; Yoon, S. G.; Han, S. Y.; Lewis, J. A.; Prakash, D.; Klein, E. J.; Chen, T.; Kang, D. H.; Majumdar, D.; Gopalaswamy, R.; McDowell, M. T. Aluminum Foil Negative Electrodes with Multiphase Microstructure for All-Solid-State Li-Ion Batteries. *Nat. Commun.* **2023**, *14* (1), 1–10.

(260) Jeong, W. J.; Wang, C.; Yoon, S. G.; Liu, Y.; Chen, T.; McDowell, M. T. Electrochemical Behavior of Elemental Alloy Anodes in Solid-State Batteries. *ACS Energy Lett.* **2024**, *9* (6), 2554–2563.

(261) Parmenter, C. D.; Nizamudeen, Z. A. Cryo-FIB-Lift-out: Practically Impossible to Practical Reality. *J. Microsc.* **2021**, *281* (2), 157–174.

(262) Parmenter, C. D. J.; Fay, M. W.; Hartfield, C.; Eltaher, H. M. Making the Practically Impossible "Merely Difficult"—Cryogenic FIB Lift-out for "Damage Free" Soft Matter Imaging. *Microsc. Res. Technol.* **2016**, *79* (4), 298–303.

(263) Kuba, J.; Mitchels, J.; Hovorka, M.; Erdmann, P.; Berka, L.; Kirmse, R.; König, J.; De Bock, J.; Goetze, B.; Rigort, A. Advanced Cryo-Tomography Workflow Developments - Correlative Microscopy, Milling Automation and Cryo-Lift-Out. *J. Microsc.* **2021**, *281* (2), 112– 124.

(264) Douglas, J. O.; Conroy, M.; Giuliani, F.; Gault, B. In Situ Sputtering From the Micromanipulator to Enable Cryogenic Preparation of Specimens for Atom Probe Tomography by Focused-Ion Beam. *Microsc. Microanal.* **2023**, *29* (3), 1009–1017. (265) Moriarty, M.; Blackwood, J. Method for Preparing Samples for Imaging, December 16, 2014.

(266) Woods, E. V.; Singh, M. P.; Kim, S. H.; Schwarz, T. M.; Douglas, J. O.; El-Zoka, A. A.; Giulani, F.; Gault, B. A Versatile and Reproducible Cryo-Sample Preparation Methodology for Atom Probe Studies. *Microsc. Microanal.* **2023**, 29 (6), 1992–2003.

(267) Schiøtz, O. H.; Kaiser, C. J. O.; Klumpe, S.; Morado, D. R.; Poege, M.; Schneider, J.; Beck, F.; Klebl, D. P.; Thompson, C.; Plitzko, J. M. Serial Lift-Out: Sampling the Molecular Anatomy of Whole Organisms. *Nat. Methods* **2024**, *21* (9), 1684–1692.

(268) Zhou, S.; Liu, K.; Ying, Y.; Chen, L.; Meng, G.; Zheng, Q.; Sun, S. G.; Liao, H. G. Perspective of Operando/in Situ Scanning Electron Microscope in Rechargeable Batteries. *Curr. Opin. Electrochem.* **2023**, *41*, 101374.

(269) Wu, J.; Fenech, M.; Webster, R. F.; Tilley, R. D.; Sharma, N. Electron Microscopy and Its Role in Advanced Lithium-Ion Battery Research. *Sustain. Energy Fuels* **2019**, *3* (7), 1623–1646.

(270) Klvač, O.; Kazda, T. Review of In-Situ and Ex-Situ Techniques for Characterization of Li-Ion Batteries. In *Proceedings II of the 29st Conference STUDENT EEICT 2023: Selected papers*; Brno University of Technology, 2023; pp 207–211. DOI: 10.13164/EEICT.2023.207.

(271) Zhou, X.; Li, T.; Cui, Y.; Meyerson, M. L.; Weeks, J. A.; Mullins, C. B.; Jin, Y.; Shin, H.; Liu, Y.; Zhu, L. Blade-Type Reaction Front in Micrometer-Sized Germanium Particles during Lithiation. *ACS Appl. Mater. Interfaces* **2020**, *12* (42), 47574–47579.

(272) Klvac, O.; Kazda, T.; Cech, O.; Fam, Y.; Novak, L. Electrochemical Cell Preparation on MEMS Chip Surface Inside Scanning Electron Microscope. *ECS Trans.* **2021**, *105* (1), 655–663. (273) Strelcov, E.; Cothren, J.; Leonard, D.; Borisevich, A. Y.;

Kolmakov, A. In Situ SEM Study of Lithium Intercalation in Individual V2O5 Nanowires. *Nanoscale* 2015, 7 (7), 3022–3027.

(274) Zhao, J.; Zhao, C.; Zhu, J.; Liu, X.; Yao, J.; Wang, B.; Dai, Q.; Wang, Z.; Chen, J.; Jia, P.; Li, Y.; Harris, S. J.; Yang, Y.; Tang, Y.; Zhang, L.; Ding, F.; Huang, J. Size-Dependent Chemomechanical Failure of Sulfide Solid Electrolyte Particles during Electrochemical Reaction with Lithium. *Nano Lett.* **2022**, *22* (1), 411–418.

(275) Novak, L.; Glajc, P.; Klvac, O. Battery in Situ Electrical Testing in FIB-SEM. *Microsc. Microanal.* **2022**, *28* (S1), 834–835.

(276) Neelisetty, K. K.; Stetina, J.; Vondruška, J.; Trenz, M.; Kazda, T.; Hrouzek, M.; Wandrol, P. Transfer of Lithium Foil under Inert Conditions Using CleanConnect Inert Gas Transfer System. *Microsc. Microanal.* **2021**, *27* (S1), 2508–2509.

(277) Mele, L.; Konings, S.; Dona, P.; Evertz, F.; Mitterbauer, C.; Faber, P.; Schampers, R.; Jinschek, J. R. A MEMS-Based Heating Holder for the Direct Imaging of Simultaneous in-Situ Heating and Biasing Experiments in Scanning/Transmission Electron Microscopes. *Microsc. Res. Technol.* **2016**, *79* (4), 239–250.

(278) Chen, D.; Indris, S.; Schulz, M.; Gamer, B.; Mönig, R. In Situ Scanning Electron Microscopy on Lithium-Ion Battery Electrodes Using an Ionic Liquid. *J. Power Sources* **2011**, *196* (15), 6382–6387.

(279) Nagao, M.; Hayashi, A.; Tatsumisago, M.; Kanetsuku, T.; Tsuda, T.; Kuwabata, S. In Situ SEM Study of a Lithium Deposition and Dissolution Mechanism in a Bulk-Type Solid-State Cell with a Li2S-P2S5 Solid Electrolyte. *Phys. Chem. Chem. Phys.* **2013**, *15* (42), 18600– 18606.

(280) Sagane, F.; Shimokawa, R.; Sano, H.; Sakaebe, H.; Iriyama, Y. In-Situ Scanning Electron Microscopy Observations of Li Plating and Stripping Reactions at the Lithium Phosphorus Oxynitride Glass Electrolyte/Cu Interface. J. Power Sources **2013**, 225, 245–250.

(281) Krauskopf, T.; Dippel, R.; Hartmann, H.; Peppler, K.; Mogwitz, B.; Richter, F. H.; Zeier, W. G.; Janek, J. Lithium-Metal Growth Kinetics on LLZO Garnet-Type Solid Electrolytes. *Joule* **2019**, *3* (8), 2030–2049.

(282) Tsuda, T.; Kanetsuku, T.; Sano, T.; Oshima, Y.; Ui, K.; Yamagata, M.; Ishikawa, M.; Kuwabata, S. In Situ SEM Observation of the Si Negative Electrode Reaction in an Ionic-Liquid-Based Lithium-Ion Secondary Battery. *Microscopy* **2015**, *64* (3), 159–168.

(283) Chen, C. Y.; Sano, T.; Tsuda, T.; Ui, K.; Oshima, Y.; Yamagata, M.; Ishikawa, M.; Haruta, M.; Doi, T.; Inaba, M.; Kuwabata, S. In Situ

Scanning Electron Microscopy of Silicon Anode Reactions in Lithium-Ion Batteries during Charge/Discharge Processes. *Sci. Rep.* **2016**, *6* (1), 1–9.

(284) Cui, C.; Yang, H.; Zeng, C.; Gui, S.; Liang, J.; Xiao, P.; Wang, S.; Huang, G.; Hu, M.; Zhai, T.; Li, H. Unlocking the in Situ Li Plating Dynamics and Evolution Mediated by Diverse Metallic Substrates in All-Solid-State Batteries. *Sci. Adv.* **2022**, *8* (43), 2000.

(285) Rong, G.; Zhang, X.; Zhao, W.; Qiu, Y.; Liu, M.; Ye, F.; Xu, Y.; Chen, J.; Hou, Y.; Li, W.; Duan, W.; Zhang, Y. Liquid-Phase Electrochemical Scanning Electron Microscopy for In Situ Investigation of Lithium Dendrite Growth and Dissolution. *Adv. Mater.* **2017**, *29* (13), 1606187.

(286) Orsini, F.; Du Pasquier, A.; Beaudoin, B.; Tarascon, J. M.; Trentin, M.; Langenhuizen, N.; De Beer, E.; Notten, P. In Situ Scanning Electron Microscopy (SEM) Observation of Interfaces within Plastic Lithium Batteries. *J. Power Sources* **1998**, *76* (1), 19–29.

(287) Kaboli, S.; Demers, H.; Paolella, A.; Darwiche, A.; Dontigny, M.; Clément, D.; Guerfi, A.; Trudeau, M. L.; Goodenough, J. B.; Zaghib, K. Behavior of Solid Electrolyte in Li-Polymer Battery with NMC Cathode via in-Situ Scanning Electron Microscopy. *Nano Lett.* **2020**, *20* (3), 1607–1613.

(288) Marceau, H.; Kim, C. S.; Paolella, A.; Ladouceur, S.; Lagacé, M.; Chaker, M.; Vijh, A.; Guerfi, A.; Julien, C. M.; Mauger, A.; Armand, M.; Hovington, P.; Zaghib, K. In Operando Scanning Electron Microscopy and Ultraviolet-Visible Spectroscopy Studies of Lithium/Sulfur Cells Using All Solid-State Polymer Electrolyte. *J. Power Sources* **2016**, *319*, 247–254.

(289) Hovington, P.; Dontigny, M.; Guerfi, A.; Trottier, J.; Lagacé, M.; Mauger, A.; Julien, C. M.; Zaghib, K. In Situ Scanning Electron Microscope Study and Microstructural Evolution of Nano Silicon Anode for High Energy Li-Ion Batteries. *J. Power Sources* **2014**, *248*, 457–464.

(290) Shi, H.; Liu, X.; Wu, R.; Zheng, Y.; Li, Y.; Cheng, X.; Pfleging, W.; Zhang, Y. In Situ SEM Observation of Structured Si/C Anodes Reactions in an Ionic-Liquid-Based Lithium-Ion Battery. *Appl. Sci.* **2019**, *9* (5), 956.

(291) Kaboli, S.; Noel, P.; Clément, D.; Demers, H.; Paolella, A.; Bouchard, P.; Trudeau, M. L.; Goodenough, J. B.; Zaghib, K. On High-Temperature Evolution of Passivation Layer in Li-10 Wt% Mg Alloy via in Situ SEM-EBSD. *Sci. Adv.* **2020**, *6* (50), DOI: 10.1126/sciadv.abd5708.

(292) Tang, C.-Y.; Dillon, S. J. In Situ Scanning Electron Microscopy Characterization of the Mechanism for Li Dendrite Growth. *J. Electrochem. Soc.* **2016**, *163* (8), A1660–A1665.

(293) Motoyama, M.; Ejiri, M.; Iriyama, Y. Modeling the Nucleation and Growth of Li at Metal Current Collector/LiPON Interfaces. J. Electrochem. Soc. 2015, 162 (13), A7067–A7071.

(294) Kundrat, V.; Bukvisova, K.; Novak, L.; Prucha, L.; Houben, L.; Zalesak, J.; Vukusic, A.; Holec, D.; Tenne, R.; Pinkas, J. W18O49 Nanowhiskers Decorating SiO2 Nanofibers: Lessons from In Situ SEM/TEM Growth to Large Scale Synthesis and Fundamental Structural Understanding. *Cryst. Growth Des.* **2024**, *24* (1), 378–390. (295) Danilatos, G. D. Foundations of Environmental Scanning Electron Microscopy. *Adv. Electron. Electron Phys.* **1988**, *71* (C), 109– 250.

(296) Novak, L.; Wandrol, P.; Vesseur, E. J. R. Microreactor for Clean and Controlled In-Situ SEM Imaging of CVD Processes. *Microsc. Microanal.* **2020**, *26* (S2), 1144–1145.

(297) Wu, B.; Yi, R.; Xu, Y.; Gao, P.; Bi, Y.; Novák, L.; Liu, Z.; Hu, E.; Wang, N.; Rijssenbeek, J.; Venkatachalam, S.; Wu, J.; Liu, D.; Cao, X.; Xiao, J. Unusual Li<sub>2</sub>O sublimation promotes single-crystal growth and sintering. *Nat. Energy* **2025**, DOI: 10.1038/s41560-025-01738-4.

(298) Kundrát, V.; Novák, L.; Bukvišová, K.; Zálešák, J.; Kolíbalová, E.; Rosentsveig, R.; Sreedhara, M.; Shalom, H.; Yadgarov, L.; Zak, A.; Kolíbal, M.; Tenne, R. Mechanism of WS2 Nanotube Formation Revealed by in Situ/Ex Situ Imaging. *ACS Nano* **2024**, *18* (19), 12284–12294.

(299) Burnett, T. L.; McDonald, S. A.; Gholinia, A.; Geurts, R.; Janus, M.; Slater, T.; Haigh, S. J.; Ornek, C.; Almuaili, F.; Engelberg, D. L.;

Thompson, G. E.; Withers, P. J. Correlative Tomography. Sci. Rep. 2014, 4 (1), 1-6.

(300) Rutherford, D.; Kolářová, K.; Čech, J.; Haušild, P.; Kuliček, J.; Ukraintsev, E.; Stehlík, Š.; Dao, R.; Neuman, J.; Rezek, B. Correlative Atomic Force Microscopy and Scanning Electron Microscopy of Bacteria-Diamond-Metal Nanocomposites. *Ultramicroscopy* **2024**, *258*, 113909.

(301) Lallo, J.; Nunney, T. S.; Mack, P.; Simpson, R.; Oppong-Mensah, H. Correlative Surface Analysis: Combining XPS, Electron Microscopy, and Other Spectroscopies. *Microsc. Microanal.* **2023**, 29 (Supplement 1), 789–789.

(302) Beatty, K. E.; López, C. S. Characteristics of Genetic Tags for Correlative Light and Electron Microscopy. *Curr. Opin. Chem. Biol.* **2023**, *76*, 102369.

(303) Mazal, H.; Wieser, F. F.; Sandoghdar, V. Insights into Protein Structure Using Cryogenic Light Microscopy. *Biochem. Soc. Trans.* **2023**, 51 (6), 2041–2059.

(304) Scharf, J.; Chouchane, M.; Finegan, D. P.; Lu, B.; Redquest, C.; Kim, M.-c.; Yao, W.; Franco, A. A.; Gostovic, D.; Liu, Z.; Riccio, M.; Zelenka, F.; Doux, J. M.; Meng, Y. S. Bridging Nano- and Microscale X-Ray Tomography for Battery Research by Leveraging Artificial Intelligence. *Nat. Nanotechnol.* **2022**, *17* (5), 446–459.

(305) Daemi, S. R.; Tan, C.; Volkenandt, T.; Cooper, S. J.; Palacios-Padros, A.; Cookson, J.; Brett, D. J. L.; Shearing, P. R. Visualizing the Carbon Binder Phase of Battery Electrodes in Three Dimensions. *ACS Appl. Energy Mater.* **2018**, *1* (8), 3702–3710.

(306) Lou, S.; Yu, Z.; Liu, Q.; Wang, H.; Chen, M.; Wang, J. Multi-Scale Imaging of Solid-State Battery Interfaces: From Atomic Scale to Macroscopic Scale. *Chem.* **2020**, *6* (9), 2199–2218.

(307) Ryu, H. H.; Lim, H. W.; Kang, G. C.; Park, N. Y.; Sun, Y. K. Long-Lasting Ni-Rich NCMA Cathodes via Simultaneous Microstructural Refinement and Surface Modification. *ACS Energy Lett.* **2023**, 8 (3), 1354–1361.

(308) Lombardo, T.; Duquesnoy, M.; El-Bouysidy, H.; Årén, F.; Gallo-Bueno, A.; Jørgensen, P. B.; Bhowmik, A.; Demortière, A.; Ayerbe, E.; Alcaide, F.; Reynaud, M.; Carrasco, J.; Grimaud, A.; Zhang, C.; Vegge, T.; Johansson, P.; Franco, A. A. Artificial Intelligence Applied to Battery Research: Hype or Reality? *Chem. Rev.* **2022**, *122* (12), 10899–10969.

(309) Osenberg, M.; Hilger, A.; Neumann, M.; Wagner, A.; Bohn, N.; Binder, J. R.; Schmidt, V.; Banhart, J.; Manke, I. Classification of FIB/ SEM-Tomography Images for Highly Porous Multiphase Materials Using Random Forest Classifiers. *J. Power Sources* **2023**, *570*, 233030. (310) Furat, O.; Finegan, D. P.; Diercks, D.; Usseglio-Viretta, F.; Smith, K.; Schmidt, V. Mapping the Architecture of Single Lithium Ion Electrode Particles in 3D, Using Electron Backscatter Diffraction and Machine Learning Segmentation. *J. Power Sources* **2021**, 483, 229148.

(311) Yang, Y.; Li, N.; Wang, B.; Li, N.; Gao, K.; Liang, Y.; Wei, Y.;
Yang, L.; Song, W. L.; Chen, H. Microstructure Evolution of Lithium-Ion Battery Electrodes at Different States of Charge: Deep Learning-Based Segmentation. *Electrochem. commun.* 2022, 136, 107224.

(312) Hu, E.; Choo, H. H.; Zhang, W.; Sumboja, A.; Anggraningrum, I. T.; Syahrial, A. Z.; Zhu, Q.; Xu, J.; Loh, X. J.; Pan, H.; Chen, J.; Yan, Q. Integrating Machine Learning and Characterization in Battery Research: Toward Cognitive Digital Twins with Physics and Knowledge. *Adv. Funct. Mater.* **2025**, 2422601.

(313) Kim, S.; Lee, H.; Lim, J.; Park, J.; Lee, Y. M. Digital Twin Battery Modeling and Simulations: A New Analysis and Design Tool for Rechargeable Batteries. *ACS Energy Lett.* **2024**, *9*, 5225–5239.

(314) Song, J.; Lim, S. H.; Kim, K. G.; Umirov, N.; Lee, H.; Dzakpasu, C. B.; Lim, J.; Nam, J.; Park, J.; Lee, J. N.; Munakata, H.; Kanamura, K.; Kim, S. S.; Lee, Y. M. Digital-Twin-Driven Diagnostics of Crack Propagation in a Single LiNi0.7Mn0.15Co0.15O2 Secondary Particle during Lithium Intercalation. *Adv. Energy Mater.* **2023**, *13* (23), 2204328.

(315) Oh, J.; Yeom, J.; Madika, B.; Kim, K. M.; Liow, C. H.; Agar, J. C.; Hong, S. Composition and State Prediction of Lithium-Ion Cathode via Convolutional Neural Network Trained on Scanning Electron Microscopy Images. *npj Comput. Mater.* **2024**, *10* (1), 1–9.