Applications of Cryogenic Electron Microscopy in Characterizing Electrochemical Materials and Interfaces

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Abstract. Cryogenic electron microscopy (cryo-EM) has emerged as a pivotal technology in materials science, particularly in characterizing electrochemical materials and interfaces. This paper delves into the recent advancements and applications of cryo-EM, underscoring its significance in understanding the intricate structures and mechanisms of materials sensitive to air and electron beams, such as lithium-ion battery electrodes. Cryo-EM's ability to capture materials in a near-natural state using vitreous ice and its compatibility with advanced imaging techniques like cryo-electron energy loss spectroscopy (cryo-EELS), cryo-electron tomography (cryo-ET), and cryo-focused ion beam (cryo-FIB) enhances our understanding of quantum and energy materials. This research will discuss the revolutionary impact of cryo-EM in areas like energy conservation and conversion, highlighting its role in visualizing sensitive materials and electrochemical reaction processes. This research addresses the need for comprehensive discussions on the characterization of quantum and energy materials through cryo-EM and related techniques, offering a thorough overview of recent advancements in this rapidly evolving field.

Keywords: Cryogenic electron microscopy; Electrochemical materials; Quantum material characterization; Energy storage; Advanced imaging techniques.

1. Introduction

Cryogenic electron microscopy (cryo-EM) has a wide range of uses in areas like biology and materials sciences. Glaeser et al. originally proposed the utilization of liquid nitrogen for direct freezing of samples (cryogenics) [1]. McDowell's group was possible to refine this freezing method by replacing liquid nitrogen with ethane [2]. Water is transferred from the samples into the vitreous ice via ethane, thus preventing the damage to the samples caused by crystallized ice. These investigations contributed to the development of cryo-EM, which combines TEM with cryogenic technology.

The algorithmic techniques and hardware infrastructure of cryo-EM technology have advanced along with computer science as well as other technological advancements. These discoveries have accelerated the advancement of 3D reconstruction and cryo-EM data processing technologies in particular. Cheng's team was the first to use a direct electron detector (DDD) to resolve the structure of a 20S proteasome at 3.4 Å, which was later regarded as a "resolution revolution" in cryo-EM technology [3]. Compared to traditional cameras, DDD cameras can directly detect electron signals, bypassing the electron-photon-electron transfer process typically used in charge-coupled devices. DDD cameras can broadcast hundreds of frames per second and scan electron signals rapidly. Sample jitter may be tracked by DDD cameras because of their quick reaction time. Therefore, the high-frequency signal can be restored via a post-corrective exercise, resulting in clearer images. There has also been significant development in data processing methods for cryo-EM.

Cryo-EM, with its vitreous ice state, can suppress radiation damage from electron beams or high temperatures and effectively maintain the inherent structure of sensitive nanomaterials. In recent years, cryo-EM technology has been applied by researchers in the chemical and materials science domains. There are three major benefits of cryo-EM. In cryo-EM, low-dose electron beam irradiation can evidently decrease irradiation damage to materials. Samples are frozen in liquid nitrogen and subsequently transferred at low temperatures, thereby prohibiting sample contact with air. Samples can be rapidly frozen, preserving their intermediate or physiological states, which can also be viewed as in situ observations of reaction processes. Because of these benefits, cryo-EM is a viable substitute technique for evaluating materials that are susceptible to air and electron beams. However, comprehensive discussions on the characterization of quantum and energy materials through cryo-EM together with associated techniques (encompassing cryo-electron energy loss spectroscopy (cryo-EELS), cryo-electron tomography (cryo-ET) as well as cryo-focused ion beam (cryo-FIB) are still scarce. As a result, this research gives an overview of the latest research advancements in this field.

2. Applications of Cryo-EM in the characterization of energy and quantum materials

Cryo-EM, including cryogenic TEM (cryo-TEM) and cryogenic SEM (cryo-SEM), has widespread applications in materials characterization. Samples can be chilled to liquid nitrogen temperature, or 77 K, in cryo-EM. Furthermore, the microstructure of water (solvent) samples that are susceptible to electron beams may be seen utilizing cryo-SEM. It is important to note that sample preparation, including cryogenic fixation, fracturing, cold storage transportation and coating (namely, carbon and sputtering gold), is essential prior to observation utilizing cryo-SEM. Rapid freezing and cold storage transportation technologies keep the ice in a vitreous state, avoiding ice crystal formation and ensuring in situ low-temperature observation. The application of cryo-EM facilitates the atomic-scale characterization of electrode materials and facilitates the investigation of battery production procedures, encompassing spectroscopy, chemical analysis, and sample preparation. Significant advancements have been made in studying the interfacial composition together with lithium state of lithium batteries using cryo-EM. Li et al. advanced cryo-EM further into the field of electrocatalysis, elucidating the specific function of metallic lithium and its SEI in ammonia electrosynthesis through experiments [4]. Contrary to traditional views, it was discovered that the SEI layer impedes nitrogen fixation, thus necessitating the destruction of the SEI layer to activate catalytic properties. Exploring lithium reactivity and SEI using cryo-TEM as part of a multi-scale approach revealed that proton donors (e.g., ethanol) control lithium's reactivity towards nitrogen fixation, presenting fresh ideas for developing electrochemical systems that will reduce the carbon footprint of fertilizer manufacturing in the future.

Hart and his research team utilized in situ cryo-TEM and electrical biasing techniques to investigate the relationship between charge density waves (CDW) and the insulator-to-metal transition (IMT) in the two-dimensional transition metal dichalcogenide 1T-TaS2 [5]. Electron diffraction data was gathered via employing electron microscope pixel array detector (EMPAD) at a frame rate of 2 milliseconds, they were able to study the changes in CDW. This study is important for designing electronic components on the basis of 2D quantum material. It proves the important effect of in situ cryo-TEM in combination with electrical polarization in the area of quantum materials studies. The capability to view and comprehend dynamic electronic properties in materials such as 1T-TaS2 at this fine scale is essential for the advancement of nanoelectronics and quantum computing technologies. This research highlights the promise of sophisticated microscopy in revealing the intricate behavior of materials down to the atomic scale. By developing a better insight into the CDW and IMT in 1T-TaS2, this work helps to utilize the distinctive characteristics of 2D materials for the creation of higher-efficiency, smaller electronic components.

3. Other applications based on cryo-EM

Additional techniques associated with cryo-EM, like cryo- focused ion beam (FIB), cryo-ET, cryo-EELS, and single-particle and micro-crystalline electron diffraction (micro-ED), have also been advanced and have contributed greatly to the material characterization.

3.1. Cryo-ET

The study of the 3D architecture of soft materials is at the heart of the cryo-EM discipline in the materials domain. By viewing quickly frozen in-situ examples at various tilt angles, the stability can be maintained close to the physiological condition and collected in series of 2D projected images. Those images are subsequently utilized to rebuild the 3D structure.

He and his group explored the structural and chemical characteristics of the SEI layer in charging batteries utilizing cryo-STEM and EDS tomography imaging techniques [6]. This research integrated low-temperature imaging with sophisticated reconstruction algorithms to retain the lightweight materials in the SEI and minimize sample damages in the electron tomography procedure. The outcomes indicate that the structural and chemical characteristics among SEI and silicon change with cell cycling. As shown in Figure 1, Mejia and colleagues focused on improving the temporal resolution of cryo-ET in capturing transient events within cells [7]. They also explored workflows for preparing transparent lamellae using polydimethylsiloxane (PDMS)-based microfluidics and plasma FIB. Cryo-ET can provide detailed views of large molecular structures in natural cellular environments, bridging the gap between high-resolution ectopic single-particle analysis and low-resolution in situ data.

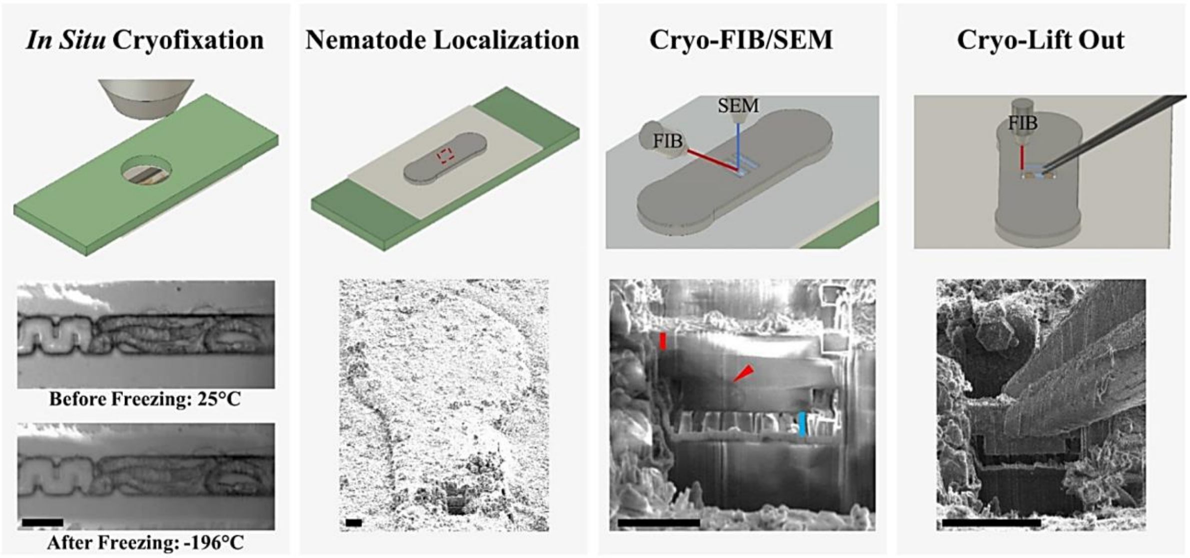

Figure 1. Bridging in situ microfluidic cryofixation and cryo-ET [7].

3.2. Cryo-FIB

Cryo-FIB employs an accelerated ion beam for surface observation of samples at low temperatures (i.e., liquid nitrogen temperature). Micro/nanoscale surface tomography may be characterized and surface atoms stripped utilizing a powerful ion beam. In order to minimize beam damage and contamination, Stephenson et al. suggested a novel experimental approach for assessing temperature- and beam-sensitive materials, in which the plasma FIB is fitted with a solid-state cooling step [8]. This scheme effectively suppresses surface oxidation of the sample.

Klie and colleagues researched the characteristics of layered transition metal carbides and nitrides (known as MXenes), which indicate potential uses in several domains, including energy storage [9]. MXenes exhibit tuneable plasmonic resonances in the visible and near-infrared regions, but their impact on nanophononics or plasmonic is not yet clear. The team used the cryogenic FIB/SEM capabilities of the ThermoFisher Helios 5CX, combined with EELS technology and in situ cooling experiments, to reveal the effects of different defects on local bonding, carrier concentration, and optical coupling. Particularly, under cryogenic STEM/EELS conditions, the CK edge exhibited rich near-edge fine structures. This study is significant for understanding and optimizing the plasmonic response of MXenes, providing new perspectives for future applications in energy storage and optoelectronics.

3.3. 4D STEM

In scanning transmission electron microscopy (STEM), 4D-STEM utilizes convergent electron beams to scan a sample in 2D real space. Concurrently, a pixelated detector records 2D momentum-space data at each scan point. Unlike traditional STEM, 4D-STEM does not rely on conventional detectors like bright-field (BF), differential phase contrast (DPC) or high-angle annular dark-field (HAADF), and it is not limited by scattering angles. It employs a pixelated direct electron detector to record the entire diffraction pattern. The subsequent analysis of this dataset is done using “virtual” detectors and algorithms, allowing for the extraction of comprehensive sample information.

Minor and colleagues employed 4D-STEM technology, utilizing fast direct electron detectors to capture large, multi-dimensional diffraction datasets. This method enabled one to map the intrinsic structural ordering of localized structures in "beam-sensitive" samples like semi-crystalline polymers [10]. Using this method, investigators can differentiate crystalline and amorphous phases in semi-crystalline polymers, allowing for the qualification and visualization of a wide range of ordering length scales in polymer morphology. The utilization of low-temperature 4D-STEM can provide deeper understanding of structure-function relations and efficiently represent the heterogeneous architecture of semi-crystalline polymers employed in energy-related industries. It is especially critical in the energy sector, since it is crucial to understand the complex relations among the microstructure of a material and its macroscopic behavior.

Cryogenic STEM has made significant progress in imaging with atomic level resolutions and atomic displacement measurements of CDW materials to picometer accuracy. Ni and his group have gathered a 4D-STEM dataset of EuAl4 at 93 K and performed in-depth analysis and data mining to identify local symmetries and symmetry breaking aided with simulations [11]. Visualization of the structural modulation is made possible by diffraction contrast utilizing reflections sensitive to the CDW. This sort of imaging permits the observation of longwave CDWs in actual space. Through the symmetry of the tissue diffraction pattern, periodic disruptions of symmetric components were found along the c-axis, consisting of two mirrors and inversion symmetry. This suggests that 4D-STEM with convergent beam electron diffraction (CBED) could offer elaborate and realistic spatial information about structural variations on larger length scales, maintaining the subsubunit cell resolution. This progress is important for the investigation of intricate materials at great detail, in particular for learning about the intricate interactions between structural elements at atomistic scales.

3.4. Electron Energy Loss Spectroscopy (EELS)

EELS is an analytical technology that collects physical and chemical data on surface atoms by utilizing the energy lost by incident electrons through inelastic scattering. This energy is lost by processes like nuclear level ionization of surface atomic electrons, valence electron excitation, collective valence electron oscillations and electronic oscillatory excitations. EELS focuses on the main energy loss procedures resulting from inelastic scattering and excludes signature excitations taking place as the atom moves back to the ground state. By combining EELS with EDS, investigators are able to gain chemical insights into a sample that could supplement or substitute for structural insights. This technology is especially relevant in the area of materials science to study the chemical constituents and electronic properties of materials at the nanoscale, and EELS offers valuable insights about the bonding, electronic states, and partial chemical settings of the atoms in samples, providing a valuable instrument for the characterization of a variety of materials ranging from complex oxides to nanostructured materials.

Plotkin-Swin and co-workers demonstrated the ability to use ultra-high energy resolution EELS at low temperatures [12]. Their research concerned a tri-layered MoS_2 sample encapsulated in hexagonal boron nitride. The exciton peak spectrum acquired from the identical area at ambient conditions and 100 K revealed remarkable modifications, consisting of an indistinguishable interlayer exciton signature and a 44 meV redshift. The shifts and variations in the exciton peak spectrum at various degrees of separation emphasize the strong integration of ultra-high energy resolution EELS with low-temperature sample cooling. The capability to examine this subtle variation at various temperatures offers an essential perspective for learning about the electronic and structural behavior of materials, particularly those with layered or 2D characteristics (e.g., MoS_2). This ability has shown to be helpful in understanding not just the basic characteristics of these materials, but the electronic and structural characteristics of the materials.

Kumar and his group determined the local temperature of an aluminum (Al) sample inside a cryogenic TEM fixture utilizing a monochromatic EELS [13]. A number of physical characteristics of quantum materials, for instance superconductivity or charge density waves, are highly related to temperature. Such characteristics are intimately connected with the variation of the strategy of the material at various temperatures. In their studies, the low-loss EELS of Al revealed a body plasma peak of approximately 15.23 eV at room temperature, moving to greater energies (blueshifted) as the temperature is reduced. The rate of movement of the bulk plasma peak for Al was observed to be around 0.54 meV/K. By the comparison of the experiment blue-shift with the theoretical blue-shift, the team discovered that a discrepancy of approximately 15-20 K occurred in the actual sample temperature versus that determined using thermocouples on the support. The research also examined the ways in which the thickness of the Al samples influenced the location of the bulk plasma peak as the temperatures changed. In addition, the study compares the outcome of temperature calibrations conducted with the plasma peak of Al and the exciton peak of MoS_2. Such comparisons offer novel insights and approaches for precisely measuring the low temperatures of quantum material samples. These inspirations are essential for understand and control physical properties in quantum material, particularly in areas of application where temperature is critical to the materials' performance.

Tiukalova and her group performed studies at LN2 concentrations of approximately 100 K with STEM and monochromatic EEL spectroscopy [14]. They used the highly spatial and energetic resolutions of those technique to investigate the atomic-scale reconfiguration and positioning of Moiré excitons. Their analyzed HAADF STEM images of the $hBN/WSe_2/WS_2$ superlattice indicate the existence of a distinct Moiré period of approximately 5 nm. The contextual subtraction of the interlayer exciton spectra of hBN/WSe_2 and hBN/WS_2 within 1.5-3.5 eV at the temperatures of liquid nitrogen explicitly displays four peaks that correspond to the A, B, C, and D excitons. These findings agree with the available data. This study is significant because it showcases the capability to view and analyze complex exciton architectures at low temperatures, essential for learning about the electronic and optical characteristics of layered systems. Accurate mapping of atomic-scale exciton signatures in such heterogeneous architectures offers valuable insight into the physics of 2D materials and its potential use in nanotechnology and materials science.

Susarla and his team of researchers have used a combined approach of sophisticated monochromators, directly electron detectors, and cryogenic scaffolds to visualize structural and electronic phase transformations together with the topological evolution of complicated structures [15]. Their work has especially concentrated on TMD layered architectures, particularly WS_2/WSe_2, in which they have been able to visualize complex localized electronic linkages associated with excitons or electron-hole pairs at particular locations in the Moiré pattern. The coupling of low-temperature STEM with low-loss EELS is a novel way to investigate emergent states in quantum materials. This technique enables studying the local electronic architecture and reactions of these layered material in detail, thus yielding an in-depth knowledge of the essential features that drive their behaviors. The evolution of techniques like ultracold scaffolds, electrically biased scaffolds and EELS-CL technology holds great promise for the future. These advances are promising to enhance the capability to explore and analyze nanoscale excitons at low temperatures, which paves the road to novel findings in the areas of nanomaterials and quantum physics. The promising implications of these research results span a wide prospect for application, ranging from electronics to photonics and energy storage technologies.

Electron beam damage in electron microscopy has emerged as a rising interest in the area of materials research as demand for characterizing novel electron beam sensitive compounds, like lithium-based compounds, has risen. A research study assessed the efficiency of quantitative approaches in 30 keV electron spectroscopy. It revealed that model-based quantitative approaches are preferred to the Egerton integral method [16], especially due to the existence of an overlap between Ti L3,2-edge and N K-edge. The quantization error of the Hartree-Slater partial cross section of the N K side is approximately 10%. In this investigation, two lithium-based compounds were detected at low temperatures (-160°C) with a 30 keV electron beam: lithium titanate (LTO) and lithium aluminum silicate ($LiAl(SiO_2)_2$). The clear background reveals the Li K, Ti L2,3 and O K edges of the LTO, and no obvious damage was observable after acquisition. Similar tests were conducted on lithium aluminum silicate films fabricated by FIB, and Li K, Al L2,3, and Si L2,3 edges were readily identified. The lithium signals were isolated as decomposition components with the use of non-negative matrix factorization (NMF). Intensity maps produced from the NMFs associated with the components of the Li signals provide insight into the distributions of Li in the minerals. This method offers a prospective approach to investigating and understanding the distribution and state of lithium in such compounds, essential for the discovery and optimization of lithium-based materials for a variety of applications, encompassing energy storage systems.

4. Conclusion

This research explored the transformative role of cryo-EM in analysing electrochemical materials and interfaces. The investigations revealed that cryo-EM, with its advanced imaging capabilities, is crucial for obtaining near-atomic resolutions of materials sensitive to air and electron beams. It demonstrated the application of cryo-EM in preserving the native state of materials through vitreous ice, enhancing our understanding of quantum and energy materials. Furthermore, the results underscored the efficacy of integrating cryo-EM with techniques like cryo-EELS, cryo-ET, and cryo-FIB, providing novel insights into the dynamics of electrochemical processes and material behaviours. This paper, therefore, not only highlights the advancements in cryo-EM technology but also opens new avenues for research in materials science, particularly in energy conservation and conversion.

Cryo-EM and its related technologies, like cryo-ET and cryo-FIB, are gaining importance in the materials science field. The benefits of cryogenic cryopreparation and low-dose radiation tactics enable cryo-EM to successfully acquire fine structures of temperature-sensitive and electron-beam materials, ranging from perovskites, COFs, MOFs, soft materials as well as battery electrodes. Besides those well-established approaches, the introduction of novel emerging technologies such as low-temperature FIB. Many materials are natural existing finite-size crystals, and therefore, characterizing these structures at the atomic level is quite achievable. Furthermore, 3D morphology and structural heterogeneity of soft materials may be effectively and promisingly characterized in situ using low-dose imaging and micro-electron diffraction (micro-ED). It is astounding how structural biologists have averaged data and seen interactions between residues to rebuild high-resolution 3D structures of biomolecules. It is envisioned that this method of three-dimensional reconstruction shows broad potential and could be extended to characterizing the structure of sensitive materials. Such advancements in cryo-EM techniques not only enhance our understanding of the complex structures of these materials but also pave the way for novel usage in a variety of fields, encompassing nanotechnology, energy storage, and pharmaceuticals. Moreover, cryo-EM might be employed to further enhance additional electrochemical materials with extraordinary electrochemical performance in order to better understand their remarkable features and reaction processes. This technique holds promise for synthesizing metastable structural materials that are unstable under the irradiation of electron beam. Consequently, cryo-EM has great promise for directly monitoring metastable phases and identifying atomic configurations, and even recording the evolution of defects in real time.

Cryo-EM's ability to preserve the original structure is critically important for researching the connection between lithium-ion batteries' actual structure and electrochemical performance. For instance, defect engineering (namely, vacancies and doping) is a useful tactic in lithium-ion batteries for creating unique nanostructures and improving electrochemical performance. Nevertheless, electron beam irradiation frequently causes these fault formations to become vulnerable. By utilizing cryo-EM in conjunction with related 3D reconstruction approaches, it is possible to maximally identify sensitive structures, particularly at interfaces, thus giving a new platform for further investigation of their relationships between structure and property.

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