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Catalyst: How Cryo-EM Shapes the Development of Next-Generation Batteries

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Cryo-EM Is Critical for Stabilizing Reactive and Sensitive Battery Materials

Despite the ubiquity of battery applications for portable electronics, electric vehicles, and grid storage in the past three decades, current chemistries are quickly approaching their theoretical limits. Future deployment of high-energy-density battery chemistries necessitates a fundamental understanding of their operation and failure mechanisms at the atomic scale. However, current understanding of existing batteries is limited to the macroscale and is still not adequate for continuously improving their performance. Most battery materials resist atomic-resolution studies by traditional transmission electron microscopy (TEM) because of their instability under the electron beam. In particular, metallic lithium (Li) anodes can enable battery chemistries with energy densities approaching that of gasoline[1] but quickly degrade under electron-beam irradiation.

This critical problem can be overcome by cryogenic electron microscopy (cryo-EM), which was recognized by the 2017 Nobel Prize in Chemistry for its profound impact on structural biology. Organic biomolecules are even more sensitive to electron beams than many battery materials, yet structural biologists can routinely image their structures with angstrom-level resolution by using cryo-EM.[2] Therefore, the challenge faced by battery scientists is to adopt these biological cryo-EM methods for battery materials.

Traditional plunge-freezing techniques used for biomolecules are incompatible with battery materials because they degrade quickly in air and moisture.[3] To overcome this problem, the Cui group at Stanford University recently developed a unique cryo-transfer method to deliver samples of Li metal from a battery into the TEM column without exposure to the ambient environment.[4] Thus, the cryo-transfer method successfully preserves the native state of the battery and enables high-resolution imaging at cryogenic temperatures. For the first time, the atomic structure of Li metal and its interface with the solid electrolyte interphase (SEI) was imaged, resolving decades of uncertainty in the battery field. This work also showed that cryogenic conditions could stabilize Li metal for chemical mapping by energy-filtered TEM and thus generate spatially resolved chemical distributions of elements within the SEI and Li metal.[4] Furthermore, the Stanford team discovered that two distinct SEI nanostructures result in starkly different battery performances. Using cryogenic scanning transmission electron microscopy (cryo-STEM) and cryo-EM, they correlated these nanostructures with battery function and revealed a new failure mechanism that has implications for future battery development.[5]

After the initial successful demonstration of cryo-EM,[4] the Meng group at the University of California, San Diego, and the Kourkoutis group at Cornell University used cryo-EM to further explore the operating mechanism of Li-metal batteries. The Meng group investigated the initial nucleation states of Li metal,[6] whereas the Kourkoutis group coupled cryo-STEM with cryogenic-focused ion beam (cryo-FIB) techniques to image the solid-liquid interface within batteries.[7] Both these works further illustrate the tremendous potential that cryo-EM has for battery research. Although existing cryo-EM studies have focused on the Li-metal anode, all aspects of a battery can be probed by this powerful technique (Figure 1).

Future Opportunities

Here, we outline important yet poorly understood aspects of (1) the cathode, (2) the anode, (3) their interfaces, and (4) the full battery. It is necessary to use cryo-EM to probe the atomic structure of these sensitive battery materials and interfaces. Such studies will provide detailed chemical and structural information spanning from the single-particle level (nanoscale) to the electrode and full-cell level (macroscale).

Cathodes: Sulfur, Li-Rich Layered Oxides, High-Nickel Oxides, and High-Voltage Materials

Sulfur is a high-energy cathode material that suffers from poor rechargeability

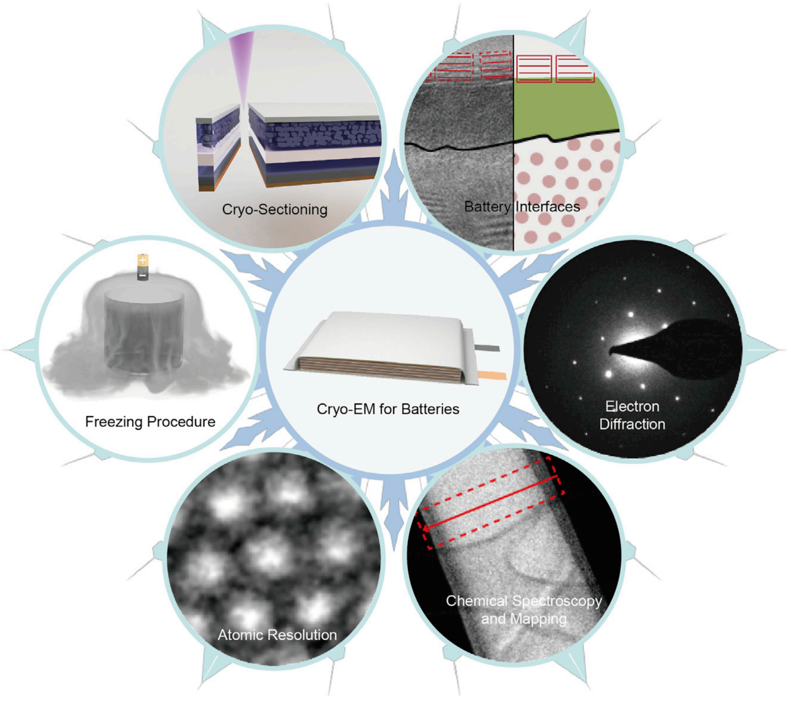

Figure 1. Cryo-EM Opportunities for Battery Research

Snowflake diagram illustrating the capabilities of cryo-EM for battery research. The outer branches highlight the various opportunities and challenges of cryo-EM battery studies, including sample preparation, resolution of atomic interfaces, and analytical chemistry and spectroscopy.

because of a phase transformation during charge and discharge. The atomic details of this process and its associated structure changes have not been observed as a result of sulfur's sensitivity to an electron beam. Cryo-EM can elucidate the atomic structure of the sulfur cathode at distinct electrochemical states, providing tremendous insight into its failure modes and facilitating future engineering solutions.

Many Li-rich layered oxides and high-voltage (>4.5 V) materials for energy-dense batteries are thought to lose capacity from an unstable oxygen redox. The implications of this proposed mechanism on the atomic and nano structure of the cathode particle can be probed with cryo-EM. Additionally, cryo-EM can investigate the possible dissolution of metal ions during battery operation, which is a proposed pathway for further capacity decay.

Anodes: Li Metal, Silicon, and Graphite

The performance of Li-metal batteries is strongly influenced by electrolyte chemistry and operating conditions. Cryo-EM can be used to correlate their morphology and atomic structure to such performance enhancements or deterioration. The crystallography of Li-metal growth during battery performance has implications for both efficiency and safety. Initial cryo-EM studies can later be coupled with cryo-tomography, which would enable reconstruction of the 3D structure.

Silicon (Si) and graphite are commercially relevant anode materials that would benefit from fundamental study. Huge volume expansion (~300%) of Si during battery operation results in large stresses that could prevent full utilization. Cryo-EM can study the atomic interface between crystalline Si and amorphous Li silicide to provide quantitative insight into the extent of lithiation. Graphite exfoliation within various electrolyte chemistries is a critical failure mode that can also be studied at the atomic scale by cryo-EM. The extent of electrolyte intercalation between the graphene layers can be quantified.

Interfaces

The performance and stability of a battery material are largely dictated by its interfaces. In particular, the SEI layer formed on the Li-metal anode has a distinct nanostructure depending on the electrolyte. Elucidating how these different SEI nanostructures form during cycling and the dependence on anode materials (i.e., Li metal, Si, Sn, or graphite), electrolytes and additives, and formation conditions (temperature, current density, etc.) will be important to guide engineering efforts for artificial SEI layers. 3D reconstruction can be used to later reveal the spatial distribution of SEI components and further inform its impact on battery performance.

High-voltage (>4.5 V) cathode materials oxidize the liquid electrolyte and form a cathode electrolyte interphase (CEI), the cathode analog of the anode SEI. Investigating this CEI nanostructure by cryo-EM will improve our understanding of how such high-voltage cathode materials degrade. The interface between the CEI layer and the high-voltage cathode material will also be an important feature that can be revealed by cryo-EM.

Full Battery

Perhaps the most challenging yet most exciting possibility is the potential to freeze an entire battery in the middle of its operation and directly observe the intersecting phenomena. For example, cross-contamination between the cathode and anode from mass loss can result in severe degradation mechanisms that currently are unknown. Oxygen and metal-ion loss from the cathode and gas generation from the anode can diffuse toward each other and cause instabilities. Freezing the battery at different points of operation will make it possible to stitch together a time series and acquire the 3D structure by cryo-tomography. This real-time, atomic-resolution imaging of the battery charging and discharging process would be unprecedented and result in numerous new discoveries that could accelerate the deployment of high-energy battery chemistries.

Challenges and Outlook

Cryo-EM consists of three major stages of operation: (1) sample preparation, (2) imaging conditions, and (3) data post-processing. Challenges must be overcome for all three stages in the pursuit of the opportunities we previously highlighted.

Sample Preparation

The freezing process is critical for sample preparation. Typically, biomolecules are frozen in their hydrated state within an aqueous film of less than 100 nm, which is thin enough to become vitrified quickly. However, even the thinnest batteries are hundreds of microns thick. Therefore, new procedures must be developed to ensure that the freezing process does not affect the chemistry or structure of the material. Furthermore, bulk samples must be thinned under cryogenic conditions. Although cryo-FIB is used extensively in structural biology, chemical analysis is rarely performed. Gallium implantation during cryo-FIB will amorphize the outer layer of the specimen and could influence local chemical compositions within the sample, although the extent of this effect is not known.[8] Thus, great care should be taken when performing analytical microscopy on battery materials to prevent spurious conclusions.

Imaging Conditions

Once the sample is successfully frozen, thinned, and transferred into the TEM column, the electron dose rate during imaging must be closely monitored. Although Li metal shows a surprising tolerance for high dose rates,[4] insulating materials such as sulfur and the liquid electrolyte have much lower melting points and are more likely to be damaged.[9] For such sensitive battery materials, a direct-detection electron-counting camera with a high quantum efficiency must be used to enable ultralow electron doses.

Data Post-processing

Additionally, the contrast in high resolution cryo-EM depends on the specimen thickness and defocus, making it difficult to directly interpret a single image without post-processing. For example, correcting the "contrast inversion" caused by the contrast transfer function of the objective lens would allow for a more interpretable image.[10]

Finally, most cryo-EM instruments are optimized for biology. Unfortunately, absent in many current cryo-EM configurations are analytical capabilities that are critical for battery research, including electron energy-loss spectroscopy, energy-dispersive spectroscopy, and aberration-corrected objective lenses. As the value of cryo-EM research for battery materials is recognized, expanded capabilities at cryo-EM facilities will become available.

In conclusion, we have highlighted several key areas of battery research in which cryo-EM can make a significant impact. Although several successful examples of its implementation have been demonstrated,[4–7] we have yet to reach the full potential of cryo-EM for battery research. Many exciting opportunities exist for scientific discovery, and we expect cryo-EM to reveal new insights for battery materials as it has for structural biology.

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