

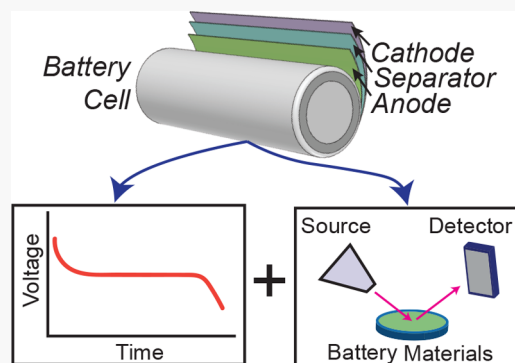
Understanding Transformations in Battery Materials Using in Situ and Operando Experiments: Progress and Outlook

Matthew G. Boebinger,[†] John A. Lewis,[†] Stephanie E. Sandoval,[†] and Matthew T. McDowell^{*,†,‡,§}

[†]School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, Georgia 30332, United States

[‡]George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 801 Ferst Drive, Atlanta, Georgia 30332, United States

ABSTRACT: Over the past decade, significant progress has been made toward understanding the intricate dynamics that underlie the operation of batteries. The development of in situ and operando experimental techniques has been critical for revealing how materials change, transform, and degrade within battery systems during charge and discharge. This Perspective first highlights recent successes in the use of in situ and operando experiments to understand dynamics in a variety of different battery materials, including alloy/conversion electrodes, intercalation electrodes, and alkali metal anodes. We then discuss four emerging focus areas in which in situ and operando experiments are expected to make an impact. These areas include solid-state batteries, improved data analytics, the linkage of dynamics across time and length scales, and understanding the atomic-scale evolution of interphases. We expect that continued progress in investigating the elaborate inner workings of battery systems across time and length scales will help to advance future battery technologies.



It is an exciting time for electrochemical energy storage, as recent years have seen substantial growth of energy storage markets due to the rise of electric vehicles and grid-scale applications. While the rechargeable Li-ion battery is at the forefront of many applications, a number of new materials and emerging battery systems could lead to batteries with higher energy, improved safety, and/or lower cost. These new technologies include replacement electrode materials with higher capacity for Li-ion batteries, as well as entirely new systems such as solid-state batteries. Such technologies hold great promise for future electrification and mitigation of greenhouse gas emissions.

An integral aspect of the continued improvement of Li-ion batteries and the development of new energy storage technologies has been the battery community's efforts over the past decade to create improved characterization techniques that have given us a more complete view of how batteries work. In particular, in situ and operando experiments, which probe reaction processes and dynamics as they occur, have provided key insights into the evolution of electrode materials, interphase formation, ionic transport, and other processes (Figure 1). A variety of in situ and operando characterization tools and methods have been developed for battery systems, and these have been used to probe reaction and degradation mechanisms in multiple classes of electrode materials at

different length scales.^{1–6} Such knowledge has been critical for designing Li-ion battery electrode materials with improved structural/chemical stability and cycle life.⁷ However, our understanding of the operational dynamics of emerging battery systems, such as batteries with alkali metal anodes and solid-state batteries, is still largely in a preliminary state. Further advances in experimentation and data analysis in the coming years are expected to dramatically improve our understanding of these emerging battery technologies while also guiding their development. This Perspective provides a brief overview of recent advances in understanding battery dynamics using in situ/operando experiments, and then it builds on this knowledge to motivate future areas in which further advances are needed to impact technologies.

Brief Overview of Recent Advances. Li-ion battery electrodes are made up of a mixture of active material particles, polymer binder, and electrically conductive nanoscale carbon. Liquid electrolyte is infiltrated within these porous electrodes, enabling ion transport throughout the composite mixture. Two electrodes are sandwiched with a polymer separator between them, and this layered structure is stacked or rolled

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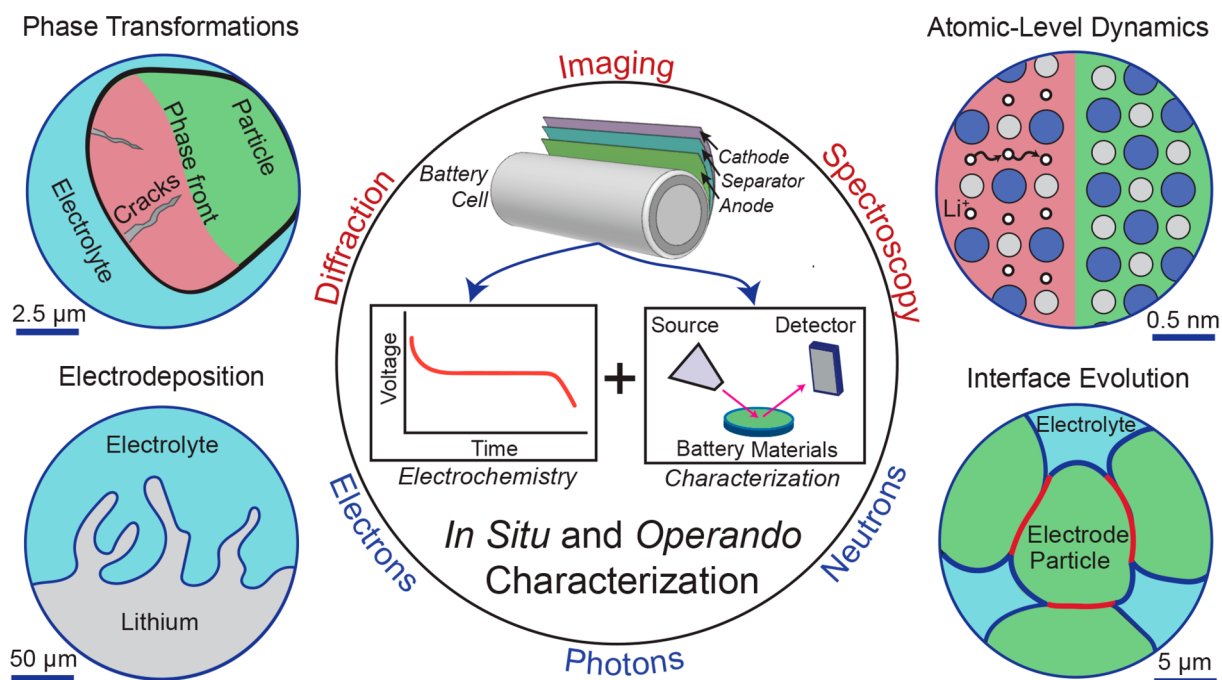


Figure 1. In situ and operando characterization of transformations in battery materials. Investigating the dynamic evolution of battery materials involves using various characterization techniques to probe the materials while causing electrochemical reactions to occur (central circle in figure). Phenomena of interest include phase transformations in active electrode materials (upper left), electrodeposition/stripping of metal anodes (lower left), atomic-level dynamics and lattice transformations (upper right), and interface evolution (lower right).

In situ and operando experiments, which probe reaction processes and dynamics as they occur, have provided key insights into the evolution of electrode materials, interphase formation, ionic transport, and other processes.

into a full battery cell. Emerging battery systems (such as solid-state batteries or alkali metal batteries) can have different components and architectures, such as pure metal anodes or completely solid composite electrodes with no liquid electrolyte. Dynamic processes, such as phase transformations, interfacial reactions, and mechanical degradation, occur across length scales within a battery cell (Figure 1). While electrochemical experiments provide important indirect information regarding these processes, the closed nature of the cell and the liquid electrolyte environment are not conducive for other types of characterization experiments to be carried out on batteries during operation. Ex situ or post-mortem experiments are commonly performed to characterize battery materials after electrochemical cycling, but much information is lost in this way because the materials are examined only at one point in time, and analysis is confounded because the materials themselves are often unstable in contact with air and moisture. Thus, significant efforts have been expended over the past decade to develop distinctive cell configurations and experimental techniques that enable the investigation of battery reaction mechanisms in situ or operando.^{1,3} In the battery literature, operando experiments usually refer to those that characterize a battery during electrochemical operation in a realistic cell, while in situ

techniques also investigate dynamics but either use different cell configurations or are not in real time (but still investigate some aspect of battery evolution). The variety of in situ and operando techniques that have been developed include transmission electron microscopy (TEM),^{8–10} X-ray imaging and spectroscopy,^{11–16} nuclear magnetic resonance (NMR),^{17,18} and surface-sensitive methods such as X-ray photoelectron spectroscopy (XPS),¹⁹ among others. These developments have produced a wealth of insights on the fundamental reaction mechanisms of different electrode materials for various battery systems across length and time scales. In this section, we discuss some of these insights, organized by the class of electrode material. We emphasize that this section is not a comprehensive review and thus omits important references; instead, it is meant to provide a basis for discussing future efforts.

High-Capacity Alloying and Conversion Electrode Materials. Materials that form alloys or other compounds when reacting with Li often exhibit very high specific Li storage capacities compared to conventional Li-ion battery electrode materials.²⁰ They could therefore replace electrode materials in Li-ion batteries to enable higher specific energy, and they can also be used in sodium- or potassium-based systems. However, the large volume changes (100–300%) during ion insertion–extraction within these materials cause significant challenges, including mechanical fracture of active particles and continuous growth of solid-electrolyte interphase (SEI) on the evolving surfaces of anode particles.²¹

In situ experiments have been critical for understanding phase transformations and morphological/structural changes within alloying and conversion battery materials (Figure 2a). In situ TEM has proven particularly useful in this regard. Open-cell in situ TEM methods (Figure 2a), first developed in 2010,⁸ have been used to reveal reaction mechanisms in

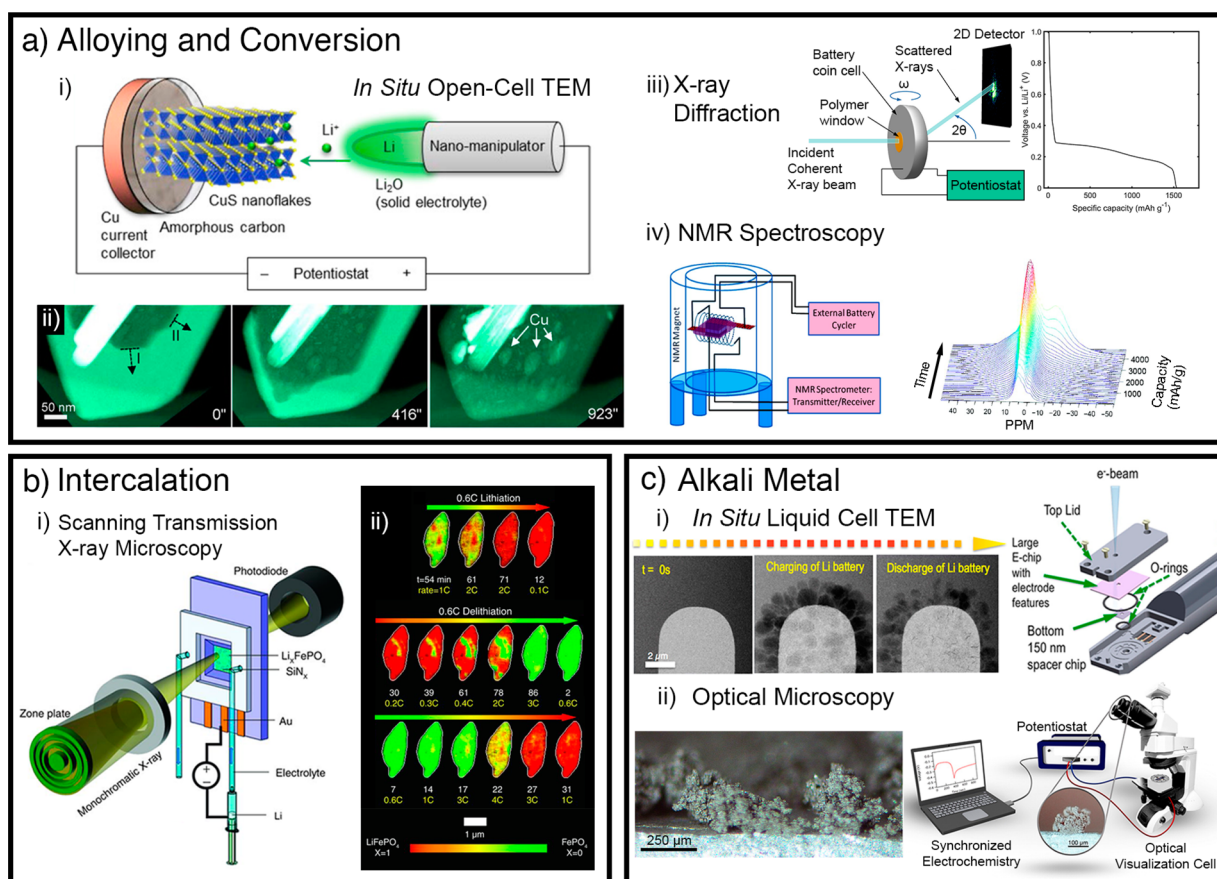


Figure 2. Highlights of in situ/operando experiments for investigating transformations in different classes of battery electrode materials. (a) Alloy and conversion materials: (i) schematic of an in situ open-cell TEM experimental setup to induce and visualize electrochemical reactions inside the TEM. (ii) Time-sequence of scanning TEM images during in situ lithiation of a CuS particle revealing reaction front progression and formation of Cu metal. Reproduced from ref 25. Copyright 2017 American Chemical Society. (iii) Operando synchrotron X-ray diffraction to reveal strain evolution in individual Ge active material particles during reaction with Li. Reproduced from ref 34. Copyright 2018 American Chemical Society. (iv) In situ ^7Li nuclear magnetic resonance (NMR) spectroscopy experiments to study the reaction of Si anodes with Li. Reproduced from ref 17. Copyright 2009 American Chemical Society. (b) Intercalation materials: (i) schematic of an operando liquid scanning transmission X-ray microscopy experiment using a LiFePO_4 working electrode. (ii) Transformation process during lithium insertion and extraction in a single LiFePO_4 particle, with color representing Li concentration (green, $x = 0$; red, $x = 1$). Reprinted with permission from ref 54. Copyright 2016 AAAS. (c) Alkali metals: (i) in situ liquid-cell TEM investigation of lithium deposition and dissolution within a liquid electrolyte. Reproduced from ref 9. Copyright 2015 American Chemical Society. (ii) A synchronized operando video microscopy setup used to visualize the growth of mossy lithium metal dendrites while tracking the corresponding voltage signatures. Reproduced from ref 63. Copyright 2016 American Chemical Society.

individual active nanostructures down to the atomic level.^{22–25} These experiments involve the use of a specialized TEM holder that allows for physical positioning and electrical biasing to controllably react active materials with alkali ions (usually in the solid state without a liquid electrolyte). While the reaction can be observed at high resolution outside of a liquid electrolyte, electrochemical signatures are more difficult to measure. Important findings from such experiments have included mechanisms and size-dependence of mechanical degradation in silicon anode materials,²⁶ complex phase evolution in conversion materials,^{24,27} and chemo-mechanical effects on reaction kinetics.²⁸ Liquid-cell TEM methods have also been used to probe similar reactions, which has resulted in lower resolution but improved electrochemical measurement.^{29,30}

At larger length scales, operando X-ray imaging has proven useful for revealing reaction mechanisms and mechanical degradation within collections of particles in the electrode architecture.^{12,31,32} In contrast to TEM, X-ray imaging can be

performed with real composite battery electrodes in electrochemical cells, allowing for operando studies.² In situ and operando X-ray diffraction and NMR have also been used to understand structural changes, atomic rearrangement, and strain evolution during charge and discharge (Figure 2a).^{17,33–35} In situ X-ray reflectivity has been useful for revealing subtle structural/morphological changes and SEI growth behavior in thin-film alloy anodes.³⁶ Scanning probe methods, including in situ atomic force microscopy (AFM), have been employed to directly measure volumetric changes in alloy materials.³⁷ Beyond alloy anodes and metal oxide or sulfide conversion electrodes, reaction mechanisms in elemental sulfur cathodes have also been investigated with these methods;¹⁵ the complex cascade of reactions exhibited by sulfur cathodes in liquid electrolytes has required significant effort to understand.

To conclude this section, we highlight the success of fundamental efforts dedicated to one specific material: silicon-based alloy anodes. Widespread research over the past decade

dedicated to understanding structural evolution and SEI growth on silicon active materials²¹ has coincided with commercial efforts to implement silicon–carbon composite anodes within Li-ion batteries for boosted capacity.³⁸ We posit that the body of work on fundamental reaction mechanisms has been an integral aspect that has driven this material forward to applications, as evidenced by the sophisticated active material designs that can accommodate structural and volumetric changes being commercially developed.³⁹

Intercalation Electrode Materials. “Intercalation” involves Li⁺ insertion into (and removal from) a crystal lattice that largely retains its structure during this process. Both the anode and cathode materials (graphite and Li-metal oxides) in commercial Li-ion batteries operate via the intercalation mechanism.⁴⁰ There has been a tremendous amount of work dedicated to developing new intercalation cathode materials with higher capacity or improved safety compared to the original LiCoO₂,^{41,42} as well as understanding redox mechanisms⁴³ and material stability during cycling.⁴⁴ In recent years, a variety of materials have received attention, including LiNi_xCo_yMn_zO₂ and related materials,^{45,46} as well as Li-rich layered transition metal oxides.⁴⁷ Both materials classes offer increased capacity and specific energy when used in Li-ion batteries. Challenges with these materials include near-surface structural instabilities during cycling,⁴⁵ as well as understanding reaction characteristics in Li-rich materials in which anions may undergo redox.⁴⁸

A variety of in situ and operando techniques have been developed and used to investigate reaction and cycling characteristics of intercalation materials, and a limited selection of recent studies is highlighted here. The structural and morphological changes in intercalation materials are generally much less substantial than alloy and conversion electrode materials, and this requires careful experimental design to detect subtle structural changes. In situ or operando X-ray diffraction is particularly useful and has been widely employed to understand phase transformations and to distinguish between single- and two-phase reactions during ion insertion/extraction.⁴⁹ The use of synchrotron X-rays can enable fast collection times for operando scattering experiments with high temporal resolution. Imaging of reaction processes has been carried out with a few different techniques. In situ TEM, using both solid-state and liquid cells, has been used to a limited extent to characterize structural and chemical changes in individual nanoscale particles during intercalation.^{29,50} With liquid-cell TEM, it is challenging to obtain atomic-level information while controlling electrochemistry because of the interaction of the beam with the liquid. Various synchrotron X-ray imaging techniques developed in recent years have proven to be quite useful for understanding reaction mechanisms in individual particles as well as particle ensembles. In situ coherent diffraction imaging, which uses hard coherent X-rays and utilizes three-dimensional diffraction data to reconstruct real-space images of individual crystallites,⁵¹ has been used to precisely track strain evolution and dislocation motion in individual transition metal oxide cathode particles within operating batteries.^{52,53} Other efforts have used soft X-ray imaging and spectroscopy with specialized operando cells to image localized oxidation state changes during charge–discharge in individual LiFePO₄ particles and collections of particles (Figure 2b).^{54,55} This work has revealed different phase transformation behavior at different current densities, as well as the impact of surface reaction rates on asymmetric transformation pathways during lithium insertion and removal.

Related spectroscopy on Li-rich layered transition metal oxides has shown evidence for anion redox,⁴³ and ptychographic soft X-ray tomography has been used to reconstruct the chemical heterogeneity of LiFePO₄ particles at 11 nm spatial resolution (this study uses ex situ techniques, with in situ experimentation requiring further development).⁵⁶ Other soft X-ray spectroscopy techniques and resonant inelastic X-ray scattering (RIXS) can also enable sensitive detection of transition metal/anion redox and surface chemistry,⁵⁷ and they are increasingly being used in in situ setups.⁵ Together, these powerful techniques provide a variety of chemical and structural insights down to the nanoscale, and these studies have been useful in improving our fundamental understanding of intercalation electrode dynamics.

Alkali Metal Anodes. Alkali metal anodes offer unmatched theoretical capacity and the potential for batteries with specific energy 30–50% higher than that of Li-ion cells.⁵⁸ The Li metal anode has received increased attention in recent years after decades of study and development.⁵⁹ The commercial implementation of Li in liquid-electrolyte batteries is challenging: nonuniform electrodeposition and stripping can result in inactive “dead” Li formation, which reduces Coulombic efficiency to unacceptable levels.^{60,61} Continuous SEI formation on the surface and Li corrosion are also issues,⁶² as is Li dendrite/filament formation,⁶³ which can be a safety hazard. In recent years, different electrolyte formulations and surface coatings have been developed to enable more uniform deposition and stripping,^{64–66} but fundamental challenges remain.

Characterizing the structural/morphological evolution of Li metal and its SEI during charge–discharge is a key aspect of engineering this material for next-generation battery systems. Because Li metal is notoriously sensitive to reaction with atmosphere and corrosion within the liquid electrolyte, conventional ex situ techniques provide limited information. Operando optical microscopy has provided important insights related to nucleation, growth, and dendrite formation during Li deposition and stripping (Figure 2c).^{63,67} To perform these experiments, electrochemical cells with optical viewing windows are used, and Li electrodeposition can be directly correlated to electrochemistry.⁶³ X-ray techniques, including phase-contrast imaging, have also been used to image Li electrodeposition at submicrometer length scales,^{68–70} which is challenging considering that the low atomic mass of Li results in weak X-ray interactions. In situ TEM experiments of Li deposition and stripping and SEI growth in liquid cells have also been carried out, revealing nanoscale growth processes and the formation of dead Li away from the current collector (Figure 2c).^{9,71} TEM liquid cells require very thin (~50–100 nm) liquid layers for e-beam transmission, however, and this creates a constricted environment for Li growth that is different than conventional batteries. Finally, in situ X-ray scattering has been used to investigate the nucleation behavior of nanoscale lithium crystallites during electrodeposition.⁷²

In addition to these in situ and operando experiments, specialized ex situ techniques have been specifically designed to stabilize Li metal during characterization. Recently, electron-beam-based imaging under cryogenic conditions has been shown to be useful for characterizing the atomic-scale structure of the SEI on Li,^{73,74} and cryo-TEM has revealed that different electrolyte compositions can cause either “mosaic” or layered SEI structures.⁷⁴ Cryo-focused ion beam (FIB) techniques were recently shown to be able to accurately characterize the

three-dimensional structure of electrodeposited lithium, whereas FIB at room temperature causes extensive morphological changes and the formation of Li–Ga alloys.⁷⁵ A recent report used titration gas chromatography to quantify the amount of inactive and electrically disconnected Li remaining after cycling in different electrolytes, and it revealed that the Coulombic efficiency is directly determined by the amount of inactive Li instead of the extent of SEI formation in all cases.⁷⁶ This important result points to the necessity of understanding and controlling Li morphology⁶⁵ as it evolves over hundreds of cycles in battery cells.

Emerging Opportunities and Challenges. As described in the previous section, the research community has made significant progress over the past decade toward understanding the intricate dynamics that underlie battery operation. In current Li-ion batteries and emerging battery systems, however, there is still much to learn and unravel. This is largely due to the electro-chemo-mechanical complexity of battery systems, and the fact that subtle changes in materials and at interfaces that occur over hundreds of cycles can play major roles in determining electrochemical behavior. In this section, we present a number of different research areas that we believe to be among the most important for advancing fundamental battery science and the resulting technologies.

Subtle changes in materials and at interfaces that occur over hundreds of cycles can play major roles in determining electrochemical behavior.

Characterizing Solid-State Batteries. Solid-state batteries (SSBs) have received increased attention in recent years because of their potential for improved safety and increased energy density compared to Li-ion batteries.⁷⁷ In SSBs, a solid-state electrolyte (either an inorganic or polymer material) is used to shuttle ions between the anode and cathode. The electrochemical interfaces in SSBs are thus between two solids, which is different than the solid/liquid interface in conventional battery systems. While seemingly a minor change, this difference has significant consequences for interfacial charge transfer, chemo-mechanical degradation, and integration of Li metal anodes, as highlighted in recent studies.^{78–83} Our level of understanding of the structure and dynamics at interfaces within SSBs is far behind that in conventional battery systems, and there is an urgent need for improved characterization to guide SSB engineering.

Our level of understanding of the structure and dynamics at interfaces within solid-state batteries is far behind that in conventional battery systems, and there is an urgent need for improved characterization to guide solid-state battery engineering.

The recent progress in SSB development has highlighted the difficulties of experimentally investigating the dynamic evolution of buried interfaces between solid phases. The interface itself makes up a small fraction of the volume within

the bulk of the materials, making bulk-sensitive techniques such as X-ray spectroscopy challenging to implement. Furthermore, many of the in situ and operando techniques already discussed were designed with conventional liquid-electrolyte batteries in mind, requiring entirely new methods and cell designs for solid-state batteries. While the lack of liquid electrolyte is potentially more compatible with high-vacuum techniques, in situ and operando investigation of SSBs is still in a nascent stage.

Understanding and controlling instabilities and the evolution of interfaces between solid-state electrolytes and electrode materials is a critical aspect of improving SSBs. A number of efforts have been dedicated to in situ investigation of reactions between Li metal anodes and various solid-state electrolytes. In situ TEM has revealed structural transformations and nano-scale reaction mechanisms between oxide solid-state electrolytes and Li,^{84–86} and in situ XPS has shed light on chemical changes at these interfaces.^{19,87} TEM experiments have not been as widespread as with other battery materials, however, and the sensitivity of many solid-state electrolyte materials to e-beam irradiation may be one reason for this. Furthermore, many previous experiments have investigated only a single interface, but it is possible to build a functioning full-cell SSB within the TEM, as has been demonstrated.⁸⁸ Future in situ experiments could use such cells with a variety of SSB chemistries to correlate evolution of interfaces and electrode materials to electrochemical signatures. Low-dose techniques will likely be critical for enabling such experiments.

In situ and operando methods for imaging structure and morphology of SSBs at longer length scales will be necessary to understand the origins of a variety of phenomena, including metal filament growth through solid-state electrolytes,^{89,90} chemo-mechanical degradation of solid-state composite electrodes,⁹¹ and the evolution of metal anode morphology. X-ray imaging promises to be an important technique to further our understanding of these phenomena, as it can provide spatial information from submicrometer to millimeter length scales. A few in situ X-ray imaging studies of SSBs have recently been published, focusing on mechanical degradation due to reaction of active materials and interfaces (Figure 3a).^{82,91} In situ optical imaging or SEM of SSB cells⁹⁰ could also lead to improved knowledge of electrode evolution and metal filament growth.

As a final note, this discussion of solid-state electrolyte materials highlights the importance of implementing improved methods for atomic-scale characterization of battery materials that are sensitive to interrogating irradiation. (S)TEM and related spectroscopies are invaluable for providing atomic-level structural and chemical information, but the combination of high ionic conductivity and low electronic conductivity of solid-state electrolyte materials makes them quite sensitive to e-beam damage. It is critical to control dose rate and accelerating voltage for such experiments, but other methods could also be useful to enable new types of in situ TEM experiments. For instance, developing a low-temperature TEM holder that also allows for positioning and biasing could allow for a thin SSB to be operated at higher temperature without beam exposure and then cooled to improve stability during imaging. Beyond SSB materials, we note that many other battery materials, including alkali metals, SEI films (formed both in liquid and solid electrolyte cells), and some cathode materials can also be sensitive to e-beam irradiation, which necessitates improved characterization techniques.

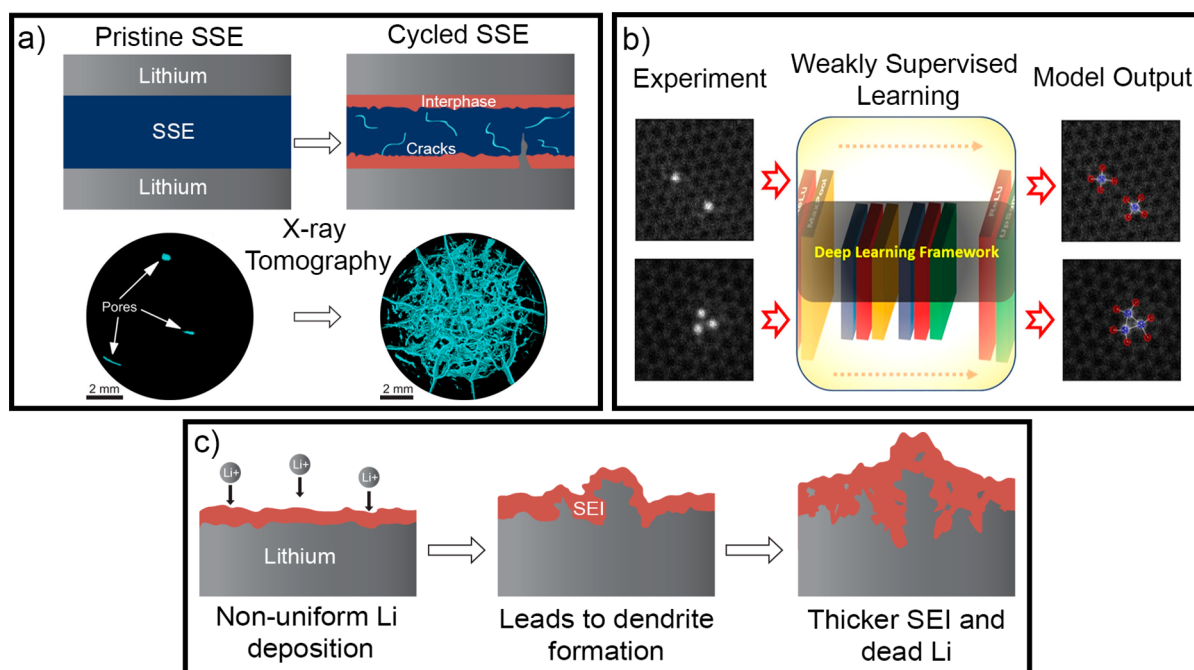


Figure 3. Emerging opportunities for in situ and operando experiments for next-generation energy storage systems. (a) Solid-state batteries offer technological promise, but characterizing buried solid-state interfaces is challenging. The schematic shows the evolution of a solid-state electrolyte (SSE) in a symmetric cell, in which the formation of an interphase region in contact with Li causes mechanical degradation. The reconstructed images below are from an in situ X-ray tomography study that revealed the formation of cracks (blue lines) during cycling. Reproduced from ref 82. Copyright 2019 American Chemical Society. (b) Improved data analytics has the potential to revolutionize the knowledge we can obtain from in situ/operando experiments. As an example, neural network analysis of STEM data is able to identify and classify individual defects in two-dimensional materials in an automated fashion. Reproduced from ref 97. Copyright 2017 American Chemical Society. (c) Improved understanding of the complex behavior of the SEI and how it affects the growth and cycling of alkali metals is critical for the development of metal anodes.

Improved Analytics for in Situ Experiments. The expansive and fast-growing intersection of energy materials research with artificial intelligence and machine learning methods promises innovative advances in the coming years.^{82,93} These methods could play an important part in in situ and operando investigations of battery materials and devices. We highlight two potential roles here.

Experiments designed to uncover the dynamic behavior of batteries often produce an enormous amount of data, whether they are real-space images, diffraction data, spectroscopic signatures, or other types of information. The large quantity arises because the data are usually continuously collected over the experiment, with a temporal resolution determined by the expected time scales for dynamics as well as by equipment limitations. Sometimes the dynamic phenomena of interest are obvious from the collected data, but more commonly, extracting important aspects of materials evolution from the collected data is a difficult task. Even deciding which part of the data is of interest, or the location to examine on a specific sample, can be challenging given the limited information available to the experimenter. Improved data analytics could therefore be a boon to the development of better in situ experiments. Intelligent analysis is needed to reduce the complexity of the full data set and to provide information regarding regions or events of interest, especially if such analysis can be performed in real time to guide the scientist during the experiment.⁹⁴ An example is principal component analysis,^{95,96} which can extract patterns from image data and could potentially be used in an “intelligent” fashion to actively guide decisions during in situ experiments. Such capabilities

would enable more precise in situ experimentation for transformative new discoveries.

Another exciting development that could significantly enhance in situ experimentation is the idea of combining recorded in situ data sets with other information, such as structures calculated with density functional theory or simulated images, to bolster and enhance the information that can be extracted from the data set.⁹⁷ This may be particularly useful for imaging techniques, such as electron, photon, or scanning probe-based microscopies, where the (potentially dynamic) structure of and defects within materials may be investigated.⁹⁸ Such techniques have been used in STEM imaging to provide atomic-level understanding of defect dynamics in two-dimensional materials.⁹⁷ In this case, a fully convolutional network was trained with simulated images of atomic lattices, and this network was then applied to experimental data sets to classify and identify more complex atomic-level defects that were not included in the original training set (Figure 3b). Combining known structural information with in situ data sets via deep-learning approaches could provide a pathway to provide more detailed and useful information than the raw data can provide alone, portending revolutionary advances in the characterization of energy materials.

Linking Dynamics across Time and Length Scales. A fundamental challenge in the study of rechargeable battery systems is the difference in the overall lifetime of a battery versus the time scale of dynamics usually measured with in situ or operando experiments. For instance, most studies focus on structural or chemical changes in materials during a single

charge–discharge cycle, while batteries are expected to last hundreds or even thousands of cycles. When trying to understand battery degradation, it is often difficult to relate observations from a single cycle to the progression of phenomena that eventually leads to battery failure over many cycles. To compound this challenge, battery degradation can sometimes be caused by “rare events,” or distinct phenomena that occur at a particular location in space or time within a battery cell. These rare events may not be closely related to the general transformations occurring in active materials during charge and discharge. An example is electrical shorting due to lithium filament growth through the electrolyte. Improved methodologies to link cell degradation mechanisms to internal evolution of materials across length and time scales are needed.

From this discussion, it is clear that cell degradation does not occur in precisely the same way even in supposedly identical batteries, and we need more knowledge of the internal evolution of batteries during cycling to understand these differences. However, most types of *in situ* and *operando* experiments do not produce a statistically representative picture of material evolution across different cells. Furthermore, many studies on new materials for battery systems often report “champion” cells without discussing or analyzing the range of cycling behavior that may have been measured from different cells. Although challenging, this situation calls for more careful statistical analysis of the electrochemical behavior of a larger number of battery cells before characterizing the internal materials, with the goal of establishing the average behavior and outliers. This knowledge can then inform design of experiments to uncover fundamental causes for these different behaviors. As a recent example, a study by Severson et al. collected a large quantity of data on cycling of commercial LiFePO₄ cells, and machine learning tools were used to reveal subtle features of early cycle voltage curves that tended to predict cycle life.⁹⁹ This approach indicates the promise of data-driven methods for performance prediction, and linking such knowledge to internal materials evolution will enable improved design of batteries.

Cell degradation does not occur in precisely the same way even in supposedly identical batteries, and we need more knowledge of the internal evolution of batteries during cycling to understand these differences.

In addition to these ideas, there is a trend toward “multimodal characterization” of energy materials, in which multiple *in situ* techniques are utilized either simultaneously or separately to investigate different aspects of the evolution of the system.¹⁰⁰ Imaging and spectroscopy data could be collected simultaneously, or alternatively, imaging with different probes (e.g., e-beam and X-ray) at different length scales is a possibility.⁵⁴ When multiple data sets are linked to the measured electrochemistry, a more complete picture of battery evolution can be obtained. While multimodal approaches offer the promise of more holistic understanding, they are often difficult to implement because of the different experimental and cell requirements of different techniques.

Interphases. The solid-electrolyte interphase (SEI) between an electrode material and the electrolyte is a distinct region

which forms and changes during cycling, with important consequences for Coulombic efficiency, battery lifetime, and safety. The study of interfaces and interphases has been a key area in the historical development of batteries, and its inclusion here is not meant to signify that it is an emerging topic (in contrast to the other discussed areas). Instead, despite the significant research attention devoted to understanding interphases within the battery community, there is still much that we do not know. In particular, understanding how the nanoscale structure of interphases evolves during cycling and how such evolution affects electrochemistry is a longstanding challenge. Generally, interphases have nanoscale dimensions, and they are usually composed of multiple materials combined within a composite structure.¹⁰¹ Interphases are often quite sensitive to atmospheric exposure and interrogating radiation, so conventional *ex situ* experiments are not particularly useful for probing their structure. As previously discussed, a few groups have applied cryo-electron microscopy methods borrowed from the biological sciences to stabilize SEI formed in liquid to determine atomic-scale structure,^{73,74} and new techniques are also being introduced to investigate interphases formed in solid-state batteries.^{84,85,87} Other methods, such as scanning probe techniques,¹⁰² Raman spectroscopy,¹⁰³ and *in situ* neutron reflectometry,¹⁰⁴ have also been used and will likely continue to be useful for probing the structure and chemistry of the SEI.

An important area that requires more attention is to understand how an interphase directs or controls morphology evolution in alkali metal electrodes in liquid electrolytes (Figure 3c). For instance, the morphology of deposited Li metal varies significantly in different liquid electrolytes and under different external conditions,^{66,105} and the SEI structure and thickness also vary. However, *ex situ* efforts cannot determine how the dynamic interplay between SEI growth and alkali metal growth determines final morphology, and controlling these features is key for attaining high-efficiency alkali metal anodes. The complexity of interphases is vast, with different interphase structures and properties expected when using the wide variety of different electrode and electrolyte materials in liquid- and solid-based batteries. Developing improved capabilities to understand the role of interphases in batteries will continue to be an essential aspect of battery research in the coming years.

This Perspective has provided an overview of recent progress and emerging opportunities related to the *in situ* and *operando* characterization of battery materials and systems. Experiments to uncover the dynamic behavior of batteries have played an important role in improving our understanding of energy storage systems. In turn, such knowledge is critical for guiding the development of better battery materials. Further efforts are needed to explore emerging battery systems, such as solid-state batteries and alkali metal anodes in liquid electrolytes. In addition, the development of improved data analytics tailored for the large data sets generated with *in situ/operando* experiments, as well as better methodologies and techniques to understand interactions across length and time scale within batteries, are expected to further advance our capabilities and knowledge. The future is bright for battery technology, and improved understanding of the elaborate inner workings of batteries has an important role to play in advancing the scientific foundation upon which these devices are built.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mattmcdowell@gatech.edu.

ORCID

Matthew T. McDowell: 0000-0001-5552-3456

Notes

The authors declare no competing financial interest.

Biographies

Matthew G. Boebinger is a doctoral researcher who is studying nanoscale reaction mechanisms in battery materials. He received his B.S. in mechanical engineering from Florida State University in 2015 and has previously worked at Oak Ridge National Laboratory under the Department of Energy's SCGSR Fellowship.

John (Jack) A. Lewis is a graduate student in the School of Materials Science and Engineering at Georgia Tech. He received his B.S. in Engineering Science from Trinity University in 2017, and his research is focused on understanding chemo-mechanical phenomena in solid-state batteries. He is supported by a NASA Space Technology Research Fellowship.

Stephanie E. Sandoval is a Ph.D. student in materials science and engineering at Georgia Tech. She received her B.S. in electrical engineering from the University of Arkansas in 2018 and has received several awards, including the NSF GRFP, the GEM Fellowship, and the Sloan Fellowship within the Minority Ph.D. program.

Matthew T. McDowell is an assistant professor at Georgia Tech with appointments in the Woodruff School of Mechanical Engineering and the School of Materials Science and Engineering. McDowell has 70 publications and has received numerous awards, including the Presidential Early Career Award for Scientists and Engineers (PECASE), Sloan Fellowship, NSF CAREER Award, and the NASA Early Career Faculty Award.

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